JOURNAL

OF

THE CHEMICAL SOCIETY.

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Vol. XLIV.

1883. ABSTRACTS.

LONDON:
J. VAN VOORST, 1, PATERNOSTER ROW.
1883.

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Spectrum of Carbon. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **33**, 403—410).—The results obtained by the authors in their spectroscopic investigations on the reversals of the lines of metallic vapours (Abstr., 1882, 254—256) have shown the importance of an accurate knowledge of the ultra-violet spectra, for the lines of short wave-length are, as a rule, the more readily reversed.

Ångström and Thalén have mapped the line-spectrum of carbon in the visible part, and shown it to consist of 11 lines, of which the single line in the yellow, followed by a triplet in the green and a strong line in the blue, recall the spectrum of magnesium. Photographs were taken of the spark of a large induction coil between poles of purified graphite in air, carbonic anhydride, hydrogen, and coal-gas; the wave-lengths were determined by a Rutherford diffraction grating, having 17,296 lines to the inch, and found to be for the principal lines 2296·5, 2478·3, 2509, 2511·9, 2836·3, and 2837·2. When the spark was taken in air, the photographs showed, besides the carbon lines above, the six cyanogen flutings in the blue, and those between K and L and near N, but this practically disappeared when carbonic anhydride was substituted for air.

The spectrum of Swan's incandescent lamps was examined and found to be continuous until the thread gave way, when the characteristic green flutings of carbonic oxide appeared; in some cases a sort of flame appeared at the positive electrode when the current was not quite intense enough to rupture the thread. The spectrum of the rarefied atmosphere within the envelope of the lamp revealed the presence of carbonic oxide. By interposing different flames between the incandescent lamp and the slit of the spectroscope, a comparison could be made of the probable temperature of the flames and filament, and from the experiments it is inferred that the emissive power of the carbon thread for light of the refrangibility of the D lines is approximately balanced by that of sodium at the temperature of the flame of cyanogen burning in air, but is sensibly less than that of sodium at the temperature of a jet of coal-gas or hydrogen, in oxygen. It is thus probable that the temperature of the incandescent thread is not far different from that conveyed to sodium by the cyanogen flame burning in air. V. H. V.

Disappearance of some Spectral Lines, and the Variations of Metallic Spectra due to Mixed Vapours. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **33**, 428—434).—The most commonly received theory of spectral lines is that the motions of the luminiferous ether producing them are not due to any translated motion of the molecules, but rather to vibrations within the molecules themselves; whilst the mutual action of the molecules, although it may give rise to irregular vibrations producing the lines, affects the regular vibrations only by converting a part of the motions of translation into internal vibrations. According to this theory, the spectral lines will be limited to a certain number of fundamental lines, and others harmonically related to them. Variations of temperature, by altering the rapidity and violence of the mutual action of the molecules, will alter the intensity of the vibrations, but not their periods, unless the molecule is disintegrated, which would give rise to new molecules with new fundamental periods of vibration.

With a view of subjecting this theory to an adequate test, the authors have made a minute examination of the spectrum of magnesium under various conditions, and have failed to detect the formation of such new molecules (*vide* Abstr., 1882, 254—256). The authors have extended these experiments by the observation of the spectrum emitted by a block of magnesia rendered incandescent by an oxyhydrogen jet. In the visible part of the spectrum, no discontinuity was observable, and the photographs of the ultra-violet region showed a continuous spectrum, on which only one line, λ 2852, comes out, sometimes bright, sometimes reversed; this line is the strongest line of burning magnesium and of the arc spectrum. This observation offers corroborative evidence of the theoretical view that alterations in temperature cannot stop any fundamental vibrations of the molecule.

But the question arises how far the presence of a mixture of molecules of different elements affects their respective vibrations; this condition was obtained in the authors' observation of the spectrum of the arc in crucibles, as well as in the solar atmosphere. Thus the authors have observed the effect of hydrogen in producing the reversal of chromium and iron lines, and the effects of a mixture of metallic vapours in developing bright lines. These effects are the more frequent in the case of metals which produce a large number of lines, such as nickel and titanium. A large quantity of nickel may be introduced into a crucible of magnesia through which the arc of a Siemens dynamo-machine is passing without the lines of nickel being developed, but on the introduction of iron and chromium into the crucible, the nickel lines come out with great brilliance. A similar result was obtained in the case of titanium. In some cases, when a fragment of a metal is dropped into the crucible, brilliant lines, hitherto unrecorded, reveal themselves, and it is difficult to establish without further examination whether these lines belong to the newly introduced metal or to those previously put in.

Figures are given in the paper to illustrate these phenomena.

A line λ 4923, which occurs so often in the chromosphere, and is generally attributed to iron, is so near to lines which come out in the crucibles that the authors doubt whether it can be absolutely identified with the iron line. Similarly a line, λ 4921·3, which comes out on the addition of chromium and titanum, is probably identical with a line observed by Young in the chromosphere, but which up to the present has been attributed to sulphur. The authors in conclusion draw attention to the large amount of work necessary before any of the solar lines can be considered not to be due to terrestrial elements, and they deprecate any hasty generalisation based upon the present state of knowledge. V. H. V.

Action of Light on Silver Bromide. By D. TOMMASI (*Bull. Soc. Chim.* [2], **37**, 291—293).—Thirty grams freshly prepared silver bromide were exposed in water to the action of sunlight for three months. At the end of this time, it had become brown, and had lost 2·3 per cent. of bromine. The author concludes that the change is a case of dissociation rather than decomposition.* Under the influence of the sun's rays, the bromide undergoes partial decomposition to an extent which depends on the surface exposed, the time of insolation, and the intensity of the light. A small quantity is transformed into Ag_2Br, which, on prolonged exposure, decomposes into silver and bromine. The brown silver bromide consequently contains variable proportions of argentic bromide, AgBr, argentous bromide, Ag_2Br, and metallic silver. C. H. B.

Sources of Error in Polarising. (Preliminary Communication.) By A. HÖLZER (*Ber.*, **15**, 1932—1938).—The author has undertaken the investigation of the causes of discrepancy so frequently found in different observations of the specific rotatory power of the same body by different experimenters. Starting with colourless sugar solutions of definite strength, he added small quantities of known colouring matters, such as picric acid, and noted the effect of the latter on the specific rotatory power of the solution, as determined by Mitscherlich's apparatus with day and lamp light, and by Laurent's apparatus with sodium light. His experiments show that when compound light is employed, the specific rotatory power is increased or diminished according to the colouring matter added, the error in some cases amounting to as much as 4°, or to 20—24 per cent. of the rotation. On the contrary, with Laurent's apparatus and monochromatic sodium light, only small and inconsiderable differences were found to result from the introduction of colouring substances. From these results, the author also explains the discrepancies in the relation of

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* According to the author, decomposition differs from dissociation, in that the former takes place in a very short time.

$[\alpha]_D : [\alpha]_j$. According to Mongolfier, $[\alpha]_D : [\alpha]_j = 1 : 1{\cdot}129$. According to Weiss, $[\alpha]_D : [\alpha]_j = 1 : 1{\cdot}034$. According to author $[\alpha]_D : [\alpha]_j = 1 : 1{\cdot}03239$ when a lamp is used, and $1 : 1{\cdot}16010$ when daylight is employed. Differences were also observed with clear and clouded skies. A. K. M.

Method of Determining the Ohm. By J. JOUBERT (*Compt. rend.*, **94**, 1519—1521).—The paper contains a mathematical investigation of a method of measuring electrical resistances, which is capable of easy practical application under conditions whereby the measures and calculations may be made with great exactness. R. R.

Oscillations of the Plane of Polarisation by Electric Discharges. By E. BICHAT and R. BLONDLOT (*Compt. rend.*, **94**, 1590—1592).—The experiments described in this paper show that electric discharges from a Leyden jar are capable of making the plane of polarisation *oscillate* about its normal position. The electric and the optical phenomena are simultaneous, or at all events the interval between them is less than the $\frac{1}{30000}$ part of a second. R. R.

Zinc-carbon Couples in Electrolysis. By D. TOMMASI (*Compt. rend.*, **94**, 1709).—Two zinc-platinum couples with dilute sulphuric acid fail to decompose a solution of potassium sulphate, but when carbon is substituted for the platinum, the decomposition is effected. This result cannot be due to metallic substances contained in the carbon, as these would diminish rather than increase the difference of potential at the electrodes. On the other hand, E. Becquerel observed in 1856 that the substitution of pure carbon for platinum in the couple with dilute sulphuric acid diminished the electromotive force. But it has since been found that in cells with two couples the substitution of carbon for platinum may either leave the electromotive force unchanged or, in some cases, may much increase it. The author has found that in order to obtain good results with carbon, that substance must contain in its pores some gas, like carbonic anhydride, which may retard or prevent the polarisation of the cells. It is possible that the absorption of certain gases by the carbon may cause the increased energy of the couple, but there is no experimental proof of this.
R. R.

The Reaction Current of the Electric Arc. By JAMIN and G. MANEUVRIER (*Compt. rend.*, **94**, 1615—1619).—The currents from the Gramme dynamo-electric machine are absolutely equal, so that they neither decompose water nor affect a tangent galvanometer interposed in the circuit. When one or more electric lamps are in the circuit this equality is still unaltered, provided the two carbons are alike, similarly arranged, and equally heated. If the carbons are unequal in size, then that current of the machine prevails which passes from the larger to the smaller carbon, *i.e.*, from the less heated to the more heated. Between a large mass of carbon or a mass of metal, on the one hand, and a carbon point on the other, the phenomenon attains a maximum: the intensity of the differential current under such conditions was found to be equal to the following numbers of Bunsen cells: with iron, 3·2; with retort-coke, 5·0; with copper, 50·6; with mercury, 103·7. As the resistance of the arc was found to be independent of the direction of the current, the latter cannot be the cause of the differential current. The carbon-mercury burner in fact changes the action of the machine, for one set of currents is abolished, or at least greatly weakened, and the other set is formed by successive currents of greater intensity and duration. An electric arc lamp introduced into such a circuit acts in the same way as if it were worked with a battery current, that is, there is greater heat at the positive pole and transference of matter to the negative pole. The machine, moreover, before incapable of decomposing water, now acts as energetically as a pile of 100 Bunsen elements; similarly other chemical actions, the magnetisation of soft iron, the reduction of metals, &c., can be effected by it as by a machine with constant currents. Those magneto-electric machines which give alternating currents can be used only for the production of light, and the attempt to make them available for chemical work by rectifying their currents by means of a commutator, has failed. It is now seen that this commutator may be replaced by one or more arcs formed between mercury and a charcoal point, if the economic conditions of that transformation should be favourable.

R. R.

Movement of Gas in "Vacuum Discharges." By W. Spottiswoode and J. F. Moulton (*Proc. Roy. Soc.*, **33**, 453—455).—In the course of preparation of vacuum tubes, the authors observed that after the exhaustion had been carried to a certain degree, the passage of a strong current increased the pressure, probably from an expulsion of gas from the terminals themselves. On the other hand, after the tube had been taken off the pump and sealed, the passage of a current seemed to decrease the pressure. Again some completed tubes showed a decreased pressure after prolonged passage of a strong current, others an increased pressure, but among both classes tubes were found which recovered their original pressure after the cessation of the discharge. The authors examined more carefully a tube, the exhaustion of which was near the phosphorescent state, and whose terminals were metallic cones. In its normal condition, it showed three or four large striæ with a dark space around the negative terminal; but on passing the discharge the dark space increased, the striæ became feebler, while the green phosphorescence began to show itself, and the discharge manifested the signs of reduced pressure. On reversing the current, the phenomena were reversed, and the feature of the discharge corresponded to an increase of pressure.

The authors explain these phenomena by supposing that the effect of the discharge is to drive occluded gas out of one terminal into the other; and on reversing the discharge, the operation is reversed and the occluded contents of one terminal are thrown along the tube to be occluded at the other. These phenomena appear to have an important bearing on the mechanism of the discharge, and the authors are examining at which terminal the gas is occluded or ejected.

V. H. V.

Apparatus for the Determination of Specific Heats by Cooling. By J. VIOLLE (*Compt. rend.*, **94**, 1510—1512).—A thin glass bottle is employed having a narrow neck and double envelope, the spaces between the outer and inner shell being exhausted. The surface of the interior shell therefore being contained in a vacuum, the conditions of cooling are always the same. An agitator and a thermometer pass through the neck of the bottle, the former supplying the means of equalising the temperature throughout the mass of the contained liquid. With this apparatus the method by cooling may be used for the determination of the specific heats. The outer surface of the inner envelope may be silvered to render the radiation slower. R. R.

Specific Heats of Small Quantities of Substances. By THOULET and LAGARDE (*Compt. rend.*, **94**, 1512—1514).—The authors make use of thermo-electric indications of the rise in temperature of a small quantity of liquid into which is dropped 0·1 to 0·5 gram of the heated substance, the specific heat of which is to be found. The test determinations quoted show remarkable accuracy. R. R.

Specific Heat of Gaseous Acetic Acid. By BERTHELOT and OGIER (*Bull. Soc. Chim.* [2], **38**, 60—64).—It is well known that the vapour-density of acetic acid varies with the temperature, and the change is generally supposed to be due to a greater complexity of the molecule at the lower temperature, although a variation in the intermolecular action is possible, in which case an increase of kinetic energy would not necessarily correspond with an increase of volume.

The authors have made a series of determinations of the specific molecular heat of gaseous acetic acid with the following results:—

Temperature.	Total heat.	Specific molecular heat.
110—140°	1000°	90·1°
140—180	3050	76·2
180—220	2280	57·0
220—260	1530	38·2
260—300	1140	28·5

The specific molecular heat decreases rapidly with the temperature, and at about 300° reaches a minimum which is approximately equal to the number 27·21 required by theory. From the results of these numbers a general rule for the molecular heat of gaseous acetic acid $\frac{dQ}{\delta t} = 150{\cdot}3 - {\cdot}467t$. The authors remark that the sums of the heats absorbed by the change of state of vaporisation of acetic acid, 9·905, is approximately equal to those of vapour of water (9·65), and alcohol (9·8), substances which acquire at once their theoretical vapour-density. This seems to show that the work done is equal in the three cases, and that the abnormal vapour-density of acetic acid is a purely physical phenomenon, and not due to a change of molecular complexity. V. H. V.

The Constituent of the Atmosphere which Absorbs Radiant Heat. By S. A. Hill (*Proc. Roy. Soc.*, **33**, 435—436).—By a comparison of actinometric observations made at Dehra and Mussooree, the author has shown in a former communication (Abstr., 1882, 566), that water-vapour in the atmosphere is the principal absorbent of radiant heat; in the present paper the relative absorbtive powers are calculated from the data of the observations.

Starting with Pouillet's formula $r = \mathrm{R}p^e$ in which e represents the atmospheric thickness, and p the fraction of total radiation which would penetrate through an atmosphere of unit thickness; p may be separated into two factors, α and β, representing the diathermacy of dry air and water-vapour respectively.

The masses of dry air and vapour will be approximately proportional to the barometric pressure p and the vapour-tension f; and the length of an oblique ray through any atmospheric stratum is proportional to sec z. So the above formula may be written $\log r = \log \mathrm{R} + b \sec z \log \alpha + f \sec z \log \beta$.

The data of these observations give, by the use of this formula, the following results:—

	α.	β.	$1-\alpha$.	$1-\beta$.
1st set	0·99856	0·76030	0·00144	0·2397
2nd „	0·99853	0·69536	0·00145	0·30464

The absorption due to dry air of one-inch pressure is invariable and equals 0·1445 per cent. of the total radiation, while that due to water-vapour of the same pressure varies from 24—30 per cent., and possibly between wider limits; in the two cases above = 27·217 per cent. Since the quantities of air (Q) and water-vapour (Q_1) in a vertical column of sectional area are in the ratio $\frac{\mathrm{Q}}{\mathrm{Q}_1} = \frac{b}{f} \times \frac{\sigma}{\sigma_1} \times \frac{\mathrm{C}}{\mathrm{C}_1}$, where C and C_1 are constants of logarithmic formulæ for vertical distribution, the absorptive powers for equal masses of the two gases will be in the ratio $\frac{0·1445}{27·217} \times \frac{5}{8} \times \frac{26,106}{66,218} = \frac{1}{764·4}$. Water-vapour at the dates of observation, 12th and 14th November, 1879, had 764·4 times the absorptive power of air for the sun's radiant heat. V. H. V.

Law of Freezing of Aqueous Solutions of Carbon Compounds. By F. M. Raoult (*Compt. rend.*, **94**, 1517—1519).—Operating with 1 gram of substance in 1 litre of water, the author has found that the lowering of the freezing point is subject to the following law: the product of the molecular weight of the substance into the lowering of the freezing point, produced by 1 gram of the substance, is nearly constant. It may therefore be affirmed that the molecules of different organic substances dissolved in the same quantity of water lower the freezing point to the same extent.

R. R.

Nascent Hydrogen. By D. Tommasi (*Bull. Soc. Chim.* [2], **38**, 148—152).—The author has examined the question whether the peculiar reducing properties of hydrogen at the moment of liberation from its compounds are due to an allotropic modification of hydrogen, or to a difference of thermic conditions. Among the cases investigated were the reduction of the halogen salts of silver, chlorates and perchlorates, ferric chloride, nitrates, and chloral. It was found that silver chloride is not reduced by sodium amalgam and acidulated water, although it is immediately reduced when an electric current is passed through acidulated water in which the salt is suspended.

Again, a saturated solution of potassium chlorate is not reduced by zinc and sulphuric acid, but is reduced by sodium amalgam and sulphuric acid; or again, potassium perchlorate is unaltered by most reducing agents which give off hydrogen, but is immediately reduced by sodium hyposulphite.

Examples such as these show that the properties of so-called nascent hydrogen are not due to any allotropic modification, for if this were the case, the same result would be obtained, whatever the reagents used for the production of the hydrogen: these differences, therefore, can be attributed only to differences of thermic conditions, *i.e.*, the heat developed, which obtain in the several reactions. This view is confirmed by the combination of sulphur with hydrogen; for it is well known that hydrogen at the moment of its liberation readily combines with sulphur at ordinary temperatures, but to make hydrogen combine directly with sulphur it is necessary to pass the gas over melted sulphur. In these reactions, sulphur and hydrogen require a certain amount of heat to effect their combination; in the first case this heat is furnished by a chemical reaction, but in the second case from an external source. V. H. V.

Reciprocal Displacement of the Halogens. By BERTHELOT (*Compt. rend.*, **94**, 1619—1625).—The well-known displacement of bromine by chlorine in haloïd salts, has by recent experiments been shown to be to a certain extent capable of inversion in presence of a large excess of bromine, and to a small extent the inverse action occurs even with equal equivalents. These results have induced the author of this paper to repeat the experiment under definite thermochemical conditions, and he has thus been led to the discovery of certain hitherto unknown intermediate compounds which intervene in these inverse actions. Such are the metallic perbromides and chlorobromides, and the chloride of bromine. The heats of formation and the dissociation of these secondary compounds explain all the phenomena. The inverse substitution is least with potassium chloride, greater with barium chloride, and most marked with silver chloride. The whole of the facts are shown to be in accordance with the provisions of thermo-chemistry, the data of which are adduced in the paper. R. R.

Perchloric Acid. By BERTHELOT (*Bull. Soc. Chim.* [2], **37**, 381—385).—The author in continuation of his researches on the oxyacids of chlorine has made a thermo-chemical investigation of perchloric acid. The acid, $HClO_4$, may be obtained in the crystalline form by subjecting the liquid acid containing a trace of water to a freezing mixture, and decanting off the mother-liquor; the crystals when purified melt at 15°. This acid dissolved in 100 times its weight of water at 19°, disengages + 20·3 cal., a number which exceeds the heat of solution of other monohydroxyl acids. This phenomenon explains the great difference in chemical properties between the anhydrous and the dilute acid, for the latter is unaffected by every known reducing agent, whilst the former ignites hydriodic acid and sodium iodide, and attacks arsenious acid with great energy.

The following determinations of the heat of neutralisation of the acid are recorded:—

1 eq. in 6 litres.		1 eq. in 6 litres.			cal.
$HClO_4$	+	$\frac{1}{2}Na_2O$	disengages	+	14·25
„	+	Na_2O	„	+	0·07
„	+	$\frac{1}{2}BaO$	„	+	14·47
„	+	BaO	„	+	0·08
„	+	NH_3	„	+	12·90
„	+	$2NH_3$	„		nil.

For the heats of solution of the perchlorates, the following values were obtained:—

$KClO_4$	absorbs	−12·1	$Ba(ClO_4)_2$	absorbs	−1·8
$NaClO_4$	„	− 3·5	NH_4ClO_4	„	−0·6

For the heat of formation of the acid, the author in conjunction with Vieille has found—

$Cl + O_4 + K = KClO_4$ (solid) disengages + 112·5 cal.

From this number and the preceding data, the values below are deduced—

$Cl + O_4 + H = HClO_4$ (liquid) disengages + 19·1 cal.
$Cl_2 + O_7 + H_2O = 2HClO_4$ (dilute) „ + 78·70 „
$Cl + O_4 + K = KClO_4$ (dissolved) „ + 100·4 „
$Cl + O_4 + Na = NaClO_4$ (solid) „ + 100·2 „
(dissolved) 96·7
$Cl + O_4 + H_4 + N = NH_4ClO_4$ (solid) „ + 79·7 cal.

Hence for the heats of decomposition of the acid and its salts—

$HClO_4$ (liquid) $= HCl$ (gas) $+ O_4$ disengages + 2·9 cal.
$2HClO_4$ (liquid) $= Cl_2 + O_7 + H_2O$ (gas) „ + 19·8 H_2O (liq.) = 29·8 cal.
HCl_4O_4 (dilute) $= HCl$ (dilute) $+ O_4$ „ nil.
$2HClO_4$ (dilute) $= Cl_2$ (gas) $+ O_7 + H_2O$ „ − 9·8 cal.
$KClO_4$ (solid) $= KCl$ (solid) $+ O_4$ „ − 7·5 „
$NaClO_4$ (solid) $= NaCl$ (solid) $+ O_4$ „ − 3·0 „
$Ba(ClO_4)_2$ (solid) $= BaCl_2$ (solid) $+ 2O_4$ „ − 2·2 „

These numbers explain the difference in stability between the concentrated and dilute acid, and the readiness with which the concentrated acid decomposes. The change of the perchlorate into the chloride absorbs heat, whilst the reverse is the case with the chlorates; the conversion of potassium chlorate into the perchlorate is consequently an exothermic reaction, for $4KClO_3 = 3KClO_4 + KCl$, would disengage + 63 cal. at ordinary temperature. According to calculation, the decomposition of ammonium perchlorate should be explosive, for NH_4ClO_4 (solid) $= Cl + O_2 + N + 2H_2O$ (liquid) disengages + 58·3 cal.; and this is verified by experiment, for ammonium perchlorate when heated at first melts, and then the liquid mass becomes incandescent, assuming the spheroidal form, and finally decomposes with production of yellowish flame. V. H. V.

Berthollet's Laws and the Combinations of Mercuric Oxide with Acids. By Berthelot (*Compt. rend.*, **94**, 1672—1678).—An equivalent of mercuric oxide disengages heat in combining with the under-named acids as follows:—

Acetic acid	+ 4·6 cal.
Oxalic acid	+ 7·1 ,,
Hydrochloric acid	+ 11·7 ,,
Hydrocyanic acid	+ 17·0 ,,

Hence the principles of thermo-chemistry indicate that oxalic acid should decompose mercuric acetate; hydrochloric acid should decompose both mercuric acetate and oxalate; and hydrocyanic acid should decompose mercuric acetate, oxalate, or chloride. On the other hand, Berthollet's laws indicate that acetic acid and hydrochloric acid severally combined with mercuric oxide should be displaced by oxalic acid, because mercuric oxalate is insoluble. In the former case, the thermo-chemical laws and those of Berthollet agree in their previsions and are in accordance with experiment. In the latter case, the facts are that mercuric chloride is not precipitated by oxalic acid, and the absence of any disengagement of heat shows that this is not due to the formation of any preponderating double salt; and again, mercuric oxalate is entirely dissolved by hydrochloric acid, the disengaged heat corresponding with the difference of the heats of neutralisation. That is, the facts entirely conform to thermo-chemical laws, and are in direct opposition to those of Berthollet.

The contrast between the precipitation of mercuric oxalate from the acetate, conformably to Berthollet's laws, and the re-solution of the precipitate by hydrochloric acid, contrary to the same laws, may be shown in a single experiment by first adding oxalic acid to a solution of the acetate, when 4·4 cal. of heat is developed, and then adding hydrochloric acid, when there is a further development of heat amounting to 3·0 cal.

Similarly, oxalic acid fails to precipitate mercuric cyanide, whilst hydrocyanic acid dissolves the oxalate, with development of the amount of heat indicated by thermo-chemical theory.

Reactions analogous to the above are obtained by acting on mercuric salts with potassium salts instead of with the acids. The general interpretation of the phenomena is the same, but double salts intervene in the reactions. R. R.

Double Salts Formed by Fusion. By BERTHELOT and ILOSVAY (*Compt. rend.*, **94**, 1487—1493, and 1551—1557).—These papers have reference to the thermic phenomena attending the formation and decomposition of double salts. The anhydrous double salts are divisible into two classes, viz., salts of the one class are permanent at ordinary temperatures, and are formed even in the cold with disengagement of heat; whilst those of the other class prepared by fusion subsist only temporarily at ordinary temperatures, and gradually revert in a longer or shorter period to the state of simple salts, the transformation being attended with development of heat. The heat of formation of double salts (F_T) can scarcely ever be directly measured, but is inferred from the thermic effects obtained by dissolving, under identical circumstances, the double salt, and each of its components, and again by mixing the two latter solutions. T being the temperature at which the salt is formed by fusion, and t that at which it is dissolved, C, C_1, and C_2 the several molecular specific heats, and ϕ, ϕ_1, and ϕ_2 the heats of fusion, we have—

$$F_T = F_t + (C_1 + C_2 - C)(T - t) + \phi_1 + \phi_2 - \phi.$$

Tables of the numerical values of the quantities concerned in numerous determinations are given in the papers, and they furnish also a number of important deductions which throw a new light on the properties of many double salts. R. R.

Decompositions of Salts by Fused Substances. By A. DITTE (*Compt. rend.*, **94**, 1592—1595).—The results obtained by treating calcium phosphates with sodium chloride or with potassium chloride in fusion, show that the decomposition of the phosphates takes place in the same way as the decomposition of salts by water or other liquids at ordinary temperatures, and that it is governed by similar laws of equilibrium.

These properties are also observed in analogous compounds containing arsenic and vanadium, and in salts other than those of lime. R. R.

Mutual Solution of Liquids. By W. ALEXEJEFF (*Bull. Soc. Chim.* [2], **38**, 145—148).—The author remarks at the outset that the phenomenon of mutual solution is not so simple as the hypothesis of Dossios supposes, for the mutual solubility does not in every case increase with the temperature, but sometimes decreases until a certain limit is reached, which the author denominates the *minimum of solubility*.

Phenol and water in contact form two layers, of which the upper is a solution of water in phenol, the lower a solution of phenol in water, but the mutual solubility increases at a temperature of 68°, until a homogeneous liquid is formed; a similar phenomenon occurs with mixtures of aniline and water.

From numerous experiments, the author concludes that liquids which dissolve one another appreciably at ordinary temperatures mix entirely at temperatures considerably below their absolute boiling points; so that there is no essential difference between the laws of mutual solubility of liquids and solids, a conclusion which is confirmed by the following experiments:—Sealed tubes containing water and salicylic acid in various proportions were heated to 100°, and allowed to cool slowly; no trace of turbidity appeared until a temperature of 91° was reached, when the contents separated into two layers; this shows that within certain limits of temperature there is a reciprocal solution of water and liquid salicylic acid, for at 100° water dissolves only 8 per cent. of salicylic acid. These experiments seem to point to a physical isomerism existing between solutions of solid and liquid salicylic acid, the calorific capacities of which the author proposes to examine.

V. H. V.

Velocity of Explosion of a Mixture of Carbonic Oxide and Oxygen with Varying Quantities of Aqueous Vapour. By H. B. DIXON (*Chem. News*, **46**, 151—152).—The velocities of explosion were measured by observing the pressure registered in a mercurial gauge attached to the endiometer in which the gases were fired. The gauge (1 mm. bore) was **U**-shaped, and contained air in the closed limb. Near the bend, two bulbs were blown to act as reservoirs, so that the mercury could be lowered in the eudiometer without the air escaping from the closed limb. The index employed was carried up and left at the highest point reached by the mercury.

In the experiments the same mass of carbonic oxide and oxygen was exploded each time at nearly constant temperature and volume; therefore the heat evolved in each explosion and the cooling surface being the same, a quicker explosion would bring the gases to a higher average temperature than a slower one, and would consequently cause a sharper push on the mercury column. From a series of experiments in which the tension of aqueous vapour varied from a mere trace to 40 mm. of mercury, it would appear that the larger the quantity of water the quicker the combustion. D. A. L.

Influence of Aqueous Vapour on the Explosion of Carbonic Oxide and Oxygen. By H. B. DIXON (*Chem. News*, **46**, 151).—It is a known fact that the addition of a minute quantity of aqueous vapour to a non-explosive mixture of dry carbonic oxide and oxygen causes explosive combination when the spark is passed. This phenomenon has been thus explained:—The carbonic oxide does not combine directly with oxygen at a high temperature, but it decomposes the water, combining with its oxygen to form carbonic anhydride; the liberated hydrogen immediately unites with more oxygen to re-form water, which undergoes the same changes until all the oxygen is transferred to the carbonic oxide; therefore a comparatively small quantity of water would suffice to convert a large quantity of carbonic oxide, inasmuch as that quantity would remain unaltered. This hypothesis is now confirmed by the author's experiments, and may be illustrated at the lecture table in the following manner:—

A glass tube 2 feet long, closed at one end, and provided with platinum wires, is bent so that the shorter arm makes an angle of 60° with the longer arm. The tube is heated and filled with mercury heated to 130° C. The mixture of gases is then passed up into the longer arm and some dry phosphoric anhydride introduced, care being taken that none of it comes in contact with the platinum. After a few hours, strong sparks from a Leyden jar or Holtz machine or coil may be passed through the gaseous mixture without causing ignition. Sometimes, however, when a coil is used and the platinum wires become red hot, explosion ensues. This, the author suggests, is probably due to the presence of occluded hydrogen in the platinum, which is given off on heating, and forms steam with the oxygen present.

In another experiment, a tube open at both ends and bent thus, W, is employed; the open ends are short, and the platinum wires are in the highest bend; the tube is filled with hot mercury, a dry mixture of 5 volumes of air and 2 volumes of carbonic oxide is introduced, and some phosphoric anhydride passed up one arm. After a short time, the spark may be passed through the gases without causing an explosion. Some water is now introduced into the other arm and the spark passed immediately; the gases ignite in the wet arm only.

D. A. L.

Specific Volumes of Liquids. By W. Lossen (*Annalen*, **214**, 81—137).—After referring to the researches of Buff (*Ann.*, Suppl., **4**, 129), Thorpe (this Journal, Trans., 1880, 141 and 327), Ramsay, *ibid.*, 1879, 463; 1881, 49, 63 and 66), Schröder (*Ber.*, **13**, 1561), and Kopp on specific volumes, the author points out that the specific volumes of acids of the acetic series follow Kopp's law. The specific volumes of the alcohols (with the exception of methyl alcohol) are lower than the calculated values, and this difference increases with the molecular weight. The specific volumes of the aldehydes are generally lower than the calculated values. The difference between the specific volume of an aldehyde and the corresponding alcohol is nearly constant, viz., 5·2—5·9; but the difference between the specific volume of an aldehyde and the corresponding acid increases with the molecular weight.

Univalent elements appear to have the same value in different compounds. This is not the case with regard to multivalent atoms.

W. C. W.

Specific Volumes of Allyl and Propyl Compounds. By A. Zander (*Annalen*, **214**, 138—193).—The author has determined the specific volumes of the following substances at 0° and at their respective boiling points:—

	B. p.	Sp. gr. at 0°.	Sp. gr. at boiling point.	Vol. at b. p. compared with vol. at 0° as unity.	Sp. vol.
Allyl alcohol	96·5°	0·8724	0·7830	1·11453	73·9
Allyl chloride........	46·0	0·9610	0·9002	1·06747	84·7
Allyl bromide........	70·5	1·4593	1·3333	1·09417	90·5
Allyl iodide	102·7	1·8696	1·6601	1·12602	100·9
Allyl ether	94·3	0·8223	0·7217	1·14097	135·5
Diallyl...............	59·5	0·7074	0·6508	1·08681	125·7
Diallylaniline........	244·0	0·9680	0·7667	1·26045	225·2
Triallylamine	155·5	0·8206	0·6826	1·20229	200·3
Propyl alcohol	97·4	0·8177	0·7369	1·10956	81·2

	B. p.	Sp. gr. at 0°.	Sp. gr. at boiling point.	Vol. at b. p. compared with vol. at 0° as unity.	Sp. vol.
Isopropyl alcohol	82·8°	0·7996	0·7231	1·10565	82·8
Propyl chloride	46·5	0·9123	0·8536	1·06876	91·7
Isopropyl chloride	36·5	0·8825	0·8326	1·05699	94·0
Propyl bromide	71·0	1·3835	1·2639	1·09465	97·0
Isopropyl bromide	60·0	1·3397	1·2368	1·08312	99·2
Propyl iodide	102·5	—	1·5867	—	106·8
Isopropyl iodide	89·0	—	1·5650	—	108·3
Propyl ether	90·7	0·7633	0·6743	1·13220	150·9
Isopropyl ether	68·8	0·7435	0·6715	1·10733	151·6
Dipropyl	69·0	0·6753	0·6129	1·10171	140·0
Di-isopropyl	58·0	0·6829	0·6286	1·08636	136·5
Di-propylaniline	245·4	0·9240	0·7267	1·27156	243·1
Di-isopropylaniline	221·0	0·9338	0·7504	1·24466	235·4
Tripropylaniline	156·5	0·7699	0·6426	1·19830	222·1
Acetone	56·3	0·8125	0·7489	1·08505	77·3
Propionic acid	140·7	1·0199	0·8657	1·17811	85·3
Propylene bromide	141·7	1·9617	1·6944	1·15783	118·9
Trimethylene bromide	165·0	2·0060	1·7101	1·17300	117·8
Propylene glycol	188·5	1·0527	0·8899	1·18289	85·2
Trimethylene glycol	214·0	1·0625	0·9028	1·17701	84·0

The above table shows that—(1) Normal propyl and isopropyl compounds do not possess identical specific volumes. (2) The specific volumes of allyl compounds are higher than the values calculated from the observed specific volumes of the corresponding normal propyl compounds. W. C. W.

Inorganic Chemistry.

On the Supposed Compound NH_2. By Combes (*Compt. rend.*, 94, 1717).—Reference is made to a communication from Maumené (*Compt. rend.*, 1882), in which he claims to have produced a new substance, NH_2, by the reaction of potassium permanganate on ammonium oxalate. As the existence of NH_2 or rather of N_2H_4, is theoretically probable, the author has repeated the experiments, with the following results:—The carbonate mentioned by Maumené, treated with hydrochloric acid and platinum chloride, gives a crystalline precipitate identical in form with ammonium platinochloride, and containing 1·9 per cent. of hydrogen ($NH_4Cl,PtCl_4$ = 1·8 per cent. H), whilst Maumené obtained only 1·35. The aqueous solution of the supposed new body, saturated with hydrochloric acid, yields crystals identical in form with ammonium chloride, and this is confirmed by the analytical results. The reaction, therefore, yields only ammonia and carbonic acid. R. R.

Silicon. By P. Schützenberger and A. Colson (*Compt. rend.*, **94**, 1710—1713).—Platinum foil, heated to a reddish-white heat amidst a mass of lamp-black, is found to contain silicon, which must have been carried through the lamp-black from the crucible. Other experiments detailed in the paper show that the silicon reaches the platinum in the vaporous form, and that nitrogen, and probably also oxygen, play a part in the transference of the silicon, as well as in the formation of the carbo-silicic compounds which the authors have previously described.

R. R.

Compounds of Silicon with Sulphur. By P. Sabatier (*Bull. Soc. Chim.* [2], **38**, 153—154).—When dry hydrogen sulphide is passed over crystalline silicon at a red heat, a violent reaction occurs, and at the cooled part of the tube a ring of a reddish substance is obtained, in which fine white needles of silicon disulphide, SiS_2, are found. Beyond the ring, the tube is covered with an orange-yellow powder, which is given off in fumes during the course of the reaction. The yellow and brown substances seem to be identical with those obtained by Colson (*vide* following Abstract). The latter has a variable composition, and is probably a mixture of the disulphide with amorphous silicon or a subsulphide; on treatment with water, it gives off hydrogen sulphide and leaves a brown residue. In the tube, there is always present a deposit of crystalline silicon, which the author explains by supposing the formation at the high temperature of a volatile subsulphide, which at the lower temperature is decomposed into disulphide and silicon. The yellow substance seems to consist for the greater part of the disulphide contaminated with a certain quantity of the subsulphide, to which the author attributes a probable formula Si_3S_4.

V. H. V.

Combination of Tetratomic Elements. By A. Colson (*Bull. Soc. Chim.* [2], **38**, 56—60, and *Compt. rend.*, **94**, 1526—1528).—If a current of ethylene or hydrogen saturated with benzene is passed over silicon contained in a porcelain tube surrounded by a clay jacketing tube which is heated in a reverberatory furnace, a carbosilicide of the formula $SiCO_2$ is obtained; the necessary oxygen is derived from the silica of the tube. This compound is a whitish powder, and is unattacked by acids, chlorine, or oxygen at a red heat. It is decomposed by fused potash, or a mixture of litharge and lead chromate. On substituting carbonic anhydride for ethylene, a compound of the formula Si_2C_3O is formed, with liberation of carbonic oxide. The author explains the fact that an oxygen-containing compound like carbonic anhydride yields a less oxygenated product than ethylene, by supposing a simultaneous loss of oxygen of the silica and carbonic anhydride, analogous to the simultaneous loss of hydrogen when benzene and methane are passed through a red-hot tube. On heating pulverised silicon in a carbon crucible surrounded by a titaniferous (carbon and rutile) jacket, and heated to a white heat, a compound of formula $Si_2C_3O_2$ was obtained.

If vapour of carbon bisulphide is passed over silicon at a white heat, two compounds are formed, the one a yellow volatile compound of the formula SiS, the other a yellowish substance of probable composition SiSO. Both these substances are decomposed by water or dilute alkalis, with evolution of hydrogen. If the contents of the tube are further heated with a boiling solution of potash to remove the excess of silicon and its sulphur compounds, and then digested for some time with warm hydrofluoric acid, a greenish powder of the composition Si_4C_4S is obtained: when heated in a current of oxygen this does not alter in weight, but is converted into an oxygenated compound, $Si_4C_4O_2$.

The author draws attention to the fact that the analogy of sulphur and oxygen does not hold good at high temperatures, for CO_2 yields $Si_4C_4O_2$, but CS_2 yields SiS and Si_4C_4S. V. H. V.

Extraction of Selenium from a Waste Product. By P. KIENLEN (*Bull. Soc. Chim.* [2], **37**, 440—443).—The selenious anhydride produced by the combustion of seleniferous pyrites is reduced by sulphurous anhydride in the Glover tower to the state of selenium, which partly dissolves in the acid, partly remains in suspension. At a works where pyrites from Sain Bel, near Lyons, are used, the amount of selenium present in the acid is often sufficient to impart to it a distinct blood-red tint.

The amount of selenium in the sulphuric acid may be estimated by diluting a considerable quantity of the acid with three times its bulk of water, and leaving it in a warm place for a long time. The clear liquid is then decanted or siphoned off, the selenium collected on a weighed filter, washed, and dried at 100°. Glover tower acid of sp. gr. 1·606 was found to contain 28·3 mgrms. of selenium per litre, or 17·6 mgrms. per 1000 grams, whilst chamber acid of sp. gr. 1·532 contained 34·2 mgrms. per litre, or 22·3 mgrms. per 1000 grams.

When the sulphuric acid containing selenium is used for the manufacture of salt-cake, the selenium volatilises along with the hydrochloric acid, and is deposited in the first condensers, sometimes in such quantity that it imparts a red fluorescence to the acid. It is the deposit in these condensers which constitutes the new source of selenium. This deposit forms a brick-red mud, which becomes black on drying. When dried at 100° it contains from 41 to 45 per cent. of selenium. The selenium is estimated by suspending 20 grams of the dried mud in water in a flask with a long neck, adding soda to feeble alkaline reaction, and then adding bromine drop by drop with continual agitation. After some time the liquid is filtered, the filtrate mixed with the washings, boiled with a little hydrochloric acid, and the selenium precipitated by sulphurous acid.

In order to extract selenium from the deposit, it is suspended in water, and treated with a current of chlorine in large Woolf's bottles. The selenium is converted into tetrachloride, and this is decomposed by the water, yielding selenious acid, which is partially oxidised to selenic acid. As soon as the brick-red tint in the first vessel has disappeared, the vessel is removed, and the second vessel put in its place, another vessel containing fresh mud being put on at the end. The dark-coloured liquid thus obtained contains selenious, selenic, and hydrochloric acids. It is filtered through cloth, and boiled with excess of hydrochloric acid, which reduces the selenic acid to selenious acid, then diluted to its original volume, and the selenium precipitated by adding sodium hydrogen sulphite until the liquid smells strongly of sulphurous anhydride. The selenium is deposited in large red flakes, which agglomerate to a pitchy mass with a bronze lustre. The liquid is boiled by passing in steam, when the precipitate rapidly agglomerates and contracts, forming a spongy steel-grey mass, which is then washed, dried, fused in a clay muffle, and cooled under water or in glass moulds. By this method large quantities of selenium can be easily and rapidly obtained in a state of considerable purity.

C. H. B.

Boiling Point of Selenium. By L. Troost (*Compt. rend.*, **94**, 1508—1510).—The author finds that the boiling point of selenium under 760 mm. pressure is 665°, and he suggests the use of boiling selenium as a means of maintaining a constant temperature for the determination of vapour-densities, &c. R. R.

Coefficient of Expansion of Sodium Sulphate Solutions. By W. W. J. Nicol (*Ber.*, **15**, 1931—1932).—On the assumption that in sodium sulphate solutions the salt is in the anhydrous condition above 33—34°, and hydrated below this temperature, the author thought it probable that a solution of this salt would show a suddenly increased or diminished coefficient of expansion at about this temperature. He has examined solutions of different strengths between 20° and 40°, and has found that the coefficient of expansion gradually increases with rise of temperature up to 34—36°, when it suddenly diminishes. It increases again with further rise of temperature.

A. K. M.

"Chloride of Lime" and "Chloride of Lithia." By K. Kraut (*Annalen*, **214**, 254—360).—When chlorine is passed over moist lithia, a mixture of lithium chloride and hypochlorite is produced, but half of the lithia present takes no part in the reaction—

$$4LiOH + 2Cl = LiOCl + LiCl + H_2O + 2LiOH.$$

When exposed to the action of carbonic acid, the hypochlorite is decomposed, and the hypochlorous acid which is set free acts on the chloride, and chlorine is evolved. A similar reaction takes place when a mixture of basic calcium chloride and calcium hypochlorite is submitted to the action of carbonic acid.

As it would not be possible for a monad metal, such as lithium, to form a compound having a composition analogous to $ClCaOCl$, the author concludes that Odling's formula for bleaching powder is incorrect. W. C. W.

Calcium Hypoiodite. By G. Lunge and R. Schoch (*Ber.*, **15**, 1883—1888).—The hypoiodites are generally stated to be highly unstable compounds, of which, however, little is known, as they have not been isolated.

By the action of iodine on lime suspended in water (several hours being allowed to complete the reaction), the authors have obtained a colourless solution, which has an odour of iodoform, and gives the following reactions:—Addition of acid produces immediate separation of iodine; solution of starch gives no coloration; hydrogen peroxide in acid solution produces turbidity and abundant evolution of oxygen; cobaltous nitrate gives a green-coloured precipitate; coal-tar colours are not affected, whilst cochineal, logwood, litmus, &c., are bleached. From these results, and more especially from the bleaching power of the solution, the authors conclude that by the action of iodine on lime at the ordinary temperature the compound $CaOI_2 = Ca(OI)_2 + CaI_2$ is produced, besides calcium iodide and iodate. From quantitative experiments on the bleaching power of this *iodide of lime*, they show that it is much more stable than the alkaline hypoiodites are generally supposed to be. It decomposes slowly in the dark, more rapidly when exposed to sunlight, and by boiling for many hours is decomposed only to the extent of one-half. A. K. M.

Didymium. By P. T. Clève (*Compt. rend.*, **94**, 1528—1530).—The author has for several years suspected the presence of a new element accompanying didymium, and he has recently by fractional precipitation and decomposition separated a portion, the spectrum of which, besides the known lines of didymium and lanthanum, gave new lines, and amongst these a very strong one of wave-length = 4333·5. This line was previously observed by Thalén in 1868, in a mixture of lanthanum and didymium, but was absent from the spectra of samples of lanthanum and of didymium prepared by the author in 1874.

The atomic weight of the first fraction precipitated by potassium sulphate was 146; that of the last fraction, 142. Without naming the new element, the author proposes to designate it by the symbol $Di\beta'$.

The author intends to continue his researches on didymium.

R. R.

Didymium. By B. Brauner (*Compt. rend.*, **94**, 1718—1719).—In this paper the author does not claim priority over Clève (preceding Abstract), but merely asserts that his observations are independent, and were announced in the *Anzeiger der Acad. Wissenschaft in Wien* of 6th October, 1881, and 9th June, 1882. He found that lanthanum sulphate may by repeated crystallisations be divided into two fractions, the more basic having an atomic weight = 138·3, and the less basic = 140·2. By repeatedly treating didymium free from oxide of lanthanum with ammonium nitrate, the author obtained an earth having the atomic weight of 140·6, the atomic weight of the remaining didymium being 142·5; but by repeated precipitations a product was obtained with an atomic weight of 146·6. In the spark spectra of the different fractions, rays were found belonging to none of the known cerite metals. These phenomena are doubtless due to the fourth element designated $Di\beta$ by Clève. The author succeeded in separating another earth of a higher atomic weight than 145·4. Ordinary didymium appears to be a mixture of at least three elements. One is true didymium (Di = 145·4); another (the $Di\beta$ of Clève) is a more basic metal, and has an atomic weight of about 141; the third, of a higher atomic weight, is less basic than didymium. R. R.

Explosive Alloys of Zinc with Certain Platinum Metals. By H. SAINTE-CLAIRE DEVILLE and H. DEBRAY (*Compt. rend.*, **94**, 1557—1560).—Oxide of iridium is projected into fused zinc, the mass is kept in fusion for six hours, and the cooled ingot treated with hydrochloric acid to remove the excess of zinc, &c. When the graphite-like residue, washed and dried at 100°, is heated to 300° it instantly takes fire, almost explosively, giving off fumes of zinc and of osmic acid. This deflagration occurs also in a vacuum, but naturally, without production of zinc oxide or of osmic acid. At 300°, there is therefore a change of state attended by great development of heat, which in the air occasions combustion. This phenomenon is so marked that by its means 1 or 2 per cent. of iridium may be detected in platinum. Ruthenium and rhodium produce similar effects.

R. R.

Action of Aluminium on Cupric Chloride. By D. TOMMASI (*Bull. Soc. Chim.* [2], **37**, 443—445).—Aluminium acts rapidly, even at ordinary temperatures, on a solution of cupric chloride, with liberation of hydrogen and copper, and formation of an aluminium oxychloride, the composition of which depends on the concentration of the copper solution. With a 31·25 per cent. solution of cupric chloride, the aluminium oxychloride had the composition $2Al_2H_6O_6,3Al_2Cl_6$, and with a 7·81 per cent. solution, the composition $Al_2H_6O_6,4Al_2Cl_6$. These oxychlorides are easily decomposed and will not crystallise: They are not true compounds, but variable mixtures of aluminium chloride and oxychloride. The action of metallic aluminium on these oxychlorides yields as a final product the compound

$$Al_2Cl_6,6Al_2H_6O_6 + 12H_2O.$$

To obtain this compound, a 31·25 per cent. solution of cupric chloride is treated with aluminium until all the copper is precipitated; the liquid is filtered, the filtrate heated, and aluminium added in successive small quantities until it ceases to dissolve, water being added from time to time to make up for loss by evaporation. The clear liquid is then evaporated to a syrup, and finally dried at 40—50°. In this way the oxychloride is obtained in white flakes resembling those of potassium boro-tartrate. A solution of this oxychloride, like that of ferric oxychloride, is precipitated by sulphuric acid and by certain salts, such as the sulphates of sodium, ammonium, potassium, magnesium, zinc, copper, and iron; but it is not precipitated, even on boiling, by the chlorides of potassium, ammonium, sodium, copper, or barium, by potassium iodide, potassium bromide, ammonium nitrate, or potassium nitrate. The aluminium hydroxide thrown down is but slightly soluble in sulphuric acid, and appears to be an isomeric modification, probably the modification δ, described by the author (*Compt. rend.*, 1880).

C. H. B.

Stability of Cupric Hydroxide. By D. TOMMASI (*Bull. Soc. Chim.* [2], **37**, 197—202).—Cupric hydroxide, perfectly free from oxide, can be obtained only by using very dilute solutions of copper sulphate and sodium hydroxide, the precipitation being effected at 0°. The author has determined the influence of the presence of various salts on the dehydration of the cupric hydroxide. In contact with distilled water at 6—8°, cupric hydroxide undergoes sensible dehydration after 120 hours. A sensible amount of dehydration takes place in 24 hours in presence of sodium hydroxide, and is greater the more dilute the soda solution. It is most marked with a 0·2 per cent. solution, but with a 10 per cent. solution the hydroxide remains blue, even after 48 hours; it becomes black, however, after 96 hours. In presence of sodium acetate, carbonate, or sulphate, dehydration takes place more slowly, and, in presence of calcium chloride, sugar, manganese sulphate, or potassium chlorate, no dehydration is perceptible, even after a long time. Haloïd salts of the alkalis appear to form small quantities of oxyhaloïd copper compounds. The presence of small quantities of certain substances altogether prevents the dehydration of the copper hydroxide; the presence of 0·3 per cent. manganese sulphate, for example, prevents dehydration, even at 100°.

Cupric hydroxide added to a solution of nickel sulphate is converted into an apple-green precipitate which contains both copper and nickel, probably in the form of a double basic sulphate. No copper passes into solution. When the hydroxide is added to a solution of lead nitrate, the copper displaces a portion of the lead, which is precipitated as hydroxide, whilst the copper passes into solution.

The influence of different salts on the temperature of dehydration is shown by the following table:—

Salt.	Strength of solution.	Temperature of dehydration.
Na_2CO_3	5 per cent.	50°
KCl	10 ,,	71
NaHO	10 ,,	74
H_2O	—	77
$NaC_2H_3O_2$	10 ,,	78
Na_2SO_4	10 ,,	79
NaHO	1 ,,	83
NaHO	0·5 ,,	84
KBr	10 ,,	85
$KClO_3$	—	85
KI	10 ,,	86
$CaCl_2$	10 ,,	No dehydration, even at 100°.
$MnSO_4$	10 ,,	
Sugar	10 ,,	

C. H. B.

Transformations of Cuprosocupric Sulphites. By A. Étard (*Compt. rend.*, **94**, 1475—1477).—The formula for the precipitate, obtained by the addition of an insufficient quantity of sulphurous acid or sodium hydrogen sulphite to a solution of cupric acetate, was given by Péan as $SO_3Cu_2,SO_3Cu,5H_2O$. The author's analyses of this salt lead him to assign to it the composition $S_8O_{27}Cu''_{10}(Cu_2) + 26H_2O$, with the following rational formula:—

$$S_8O_{32}Cu'_2,Cu''_2,Cu''_8(H_8)H_2 + 21H_2O,$$

after a type already adopted by him, and he proposes to call the substance *acid cuproso-cupric octosulphite.*

By the action of sulphurous acid, the above salt is transformed into Chevreul's salt, $SO_3Cu_2SO_3.2H_2O$, and by the action of sodium hydrogen sulphite into a yellow salt already described by the author as *acid octosulphite of cuprosum, cupricum, and sodium* (*ibid.*, **94**, 1422). The reaction is represented thus :—

$$S_8O_{32}Cu'_2Cu''_2Cu''_8(H_8)H_2,21H_2O + S_8O_{24}Na_8H_8 = S_2O_8H_8 +$$
$$8H_2O + S_8O_{32}Cu'_2Cu''_2Cu''_8(Na_8)H_2,S_6O_{24}H_{24},5H_2O.$$

R. R.

Separation of Gallium. By L. de Boisbaudran (*Compt. rend.*, **94**, 1439—1442; 1625—1629).—*Separation from Glucinum.*—The gallium is precipitated by potassium ferrocyanide from a solution containing hydrochloric acid in large excess, or it may be thrown down along with arsenious sulphide.

Separation from Cerium, Lanthanum, Didymium, Samarium, Yttrium, Holmium, and Thulium.—These earths may be precipitated by potassium hydroxide in considerable excess at the boiling temperature, and the gallium separated from the alkaline solution by means of cupric hydroxide or by addition of ammonia and long boiling after previous neutralisation with hydrochloric acid. Gallium may also be separated from the above-named metals by precipitating it with potassium ferrocyanide from solutions containing excess of hydrochloric acid. Gallium is carried down when arsenious acid is precipitated by hydrogen sulphide.

Separation from Iron.—This is effected by a boiling solution of potassium hydroxide, but as the iron oxide carries down with it a little gallium, it must be re-dissolved and re-precipitated four or five times. When the quantity of iron present is relatively large, it is preferable to reduce the ferric salt with metallic copper, add a small excess of cuprous oxide, and, after repeating this operation three or four times, to pass hydrogen sulphide through the last strongly acid hydrochloric acid solution. The remainder of the iron is then eliminated by two or three treatments with boiling potassium hydroxide.

Separation from Thorium.—The methods with potassium hydroxide, with potassium ferrocyanide, and with arsenious sulphide are all applicable in this case.

Separation from Zirconium.—This may be effected either by boiling with potassium hydroxide or by arsenious sulphide, but not by potassium ferrocyanide, because the latter precipitates very acid and dilute solutions of zirconium.

Separation from Manganese.—For this nine processes are given. That by potassium hydroxide is applicable, but it must be several times repeated, and has no advantages in the presence of much manganese. Barium carbonate or calcium carbonate separates gallium in the cold after some hours, leaving manganous chloride in solution. Very good separations may be obtained by arsenious sulphide, also by cupric hydroxide used hot. The reaction with potassium ferrocyanide may be used, but with special modifications, of which a long and detailed account is given in the paper.

Separation from Zinc.—The method with copper hydroxide completely separates gallium from zinc. Barium or calcium carbonate precipitates gallium, but considerable quantities of zinc are carried down with it. R. R.

Action of Ammonium Sulphide on Stannous Sulphide. By H. BAUBIGNY (*Compt. rend.*, **94**, 1473—1475).—Stannous sulphide is quite insoluble in pure normal ammonium sulphide. If air has access, however, the oxygen decomposes the ammonium sulphide with formation of sulphur; this unites with a portion of the stannous sulphide and transforms it into stannic sulphide which is soluble in the liquid. Sulphide of ammonium or of the alkaline metals is employed in analysis to dissolve and separate stannous sulphide, but these reagents act as solvents only when they contain sulphur in excess, and are without action when reduced to the state of normal sulphides. This source of uncertainty would be avoided if the ammonium sulphide used in analysis were always fully sulphurised by previously dissolving in it a sufficient quantity of sulphur. R. R.

Chromic Acid and Chromates. By M. PRUDHOMME and F. BINDER (*Bull. Soc. Chim.* [2], **37**, 194—196).—When barium chloride is added to a solution of potassium dichromate, normal barium chromate is precipitated, and potassium chloride and chromic acid remain in solution, thus: $K_2Cr_2O_7 + BaCl_2 = BaCrO_4 + 2KCl + CrO_3$. This reaction furnishes additional evidence in favour of the view that potassium dichromate is a molecular combination of the normal chromate with an easily displaceable molecule of chromic anhydride, a view also supported by the fact that many dichromates (NH_4, K, Ca, &c.), can be prepared by the direct action of chromic anhydride on a molecule of the corresponding normal chromate. By treating dichromates with alkalis, alkaline earths, or the corresponding carbonates, double chromates are frequently formed. Zinc, aluminium, cupric, and chromic hydroxides, when heated with potassium dichromate, form normal potassium chromate and a chromate of the particular base. In this way, certain chromates, *e.g.*, $ZnCrO_4$, can be prepared, which were formerly obtained only by the action of chromic acid on the carbonate or oxide. This method of preparation explains the formation of chromium chromate when potassium dichromate is treated with hydrogen sulphide or sodium thiosulphate. Chromic hydroxide is first formed, and is then acted on by the excess of dichromate. When a strong solution of potassium dichromate is added to a solution of sodium hydrogen sulphite of 30° B., a green solution is obtained, which rapidly solidifies, owing to the formation of green chromic oxide. If the dichromate is in excess, brown chromium chromate is formed. C. H. B.

Chromous Sulphate. By H. MOISSAN (*Bull. Soc. Chim.* [2], **37**, 296—298).—The greater part of this paper has already appeared in the *Compt. rend.* (Abstr., 1881, p. 684). Chromous sulphate does not decompose water at 100°. 12·35 grams of the salt dissolve in 100 c.c. of water at 0°, but it is only slightly soluble in alcohol. With potassium or sodium hydroxide, a solution of chromous sulphate gives a black precipitate, insoluble in excess; with ammonia, a black precipitate, soluble in excess, forming a blue solution; with alkaline carbonates, a reddish precipitate; with potassium chromate, a maroon precipitate; cupric salts, a brick-red precipitate; ammonium molybdate, a dark maroon precipitate; gold chloride, a deposit of metallic gold; hydrogen sulphide, no precipitate; alkaline hydrosulphides, a black precipitate.

When moist chromous carbonate or acetate is treated with a large excess of concentrated sulphuric acid, the hydrate $CrSO_4 + 3H_2O$ is obtained in white crystals, more stable when exposed to air than the hydrate $CrSO_4 + 7H_2O$. In contact with a small quantity of water, it passes into the normal hydrate $CrSO_4 + 7H_2O$. C. H. B.

New Class of Borotungstates. By D. Klein (*Bull. Soc. Chim.* [2], **37**, 202—208).—The disodium salt previously described (*Bull. Soc. Chim.*, **35**, 14) may be a boroduodecitungstate, or a boroquatuordecitungstate, or a boroquindecitungstate. The analytical results agree equally well with all three formulæ.

The *barium salt* is obtained in white crystals by adding a boiling saturated solution of barium chloride in excess to a warm saturated solution of the sodium salt. If the mixed solutions are allowed to boil, the small quantity of hydrochloric acid which is set free precipitates tungstic acid. Too frequent crystallisation from water also decomposes the salt, probably with separation of metatungstic acid and formation of a basic salt. The addition of a few drops of hydrochloric acid appears to prevent this decomposition. The amount of water of crystallisation in the salt appears to be very variable, and the salt is in all probability efflorescent. When dried at 160°, the composition of the salt agrees more closely with the formula $14WO_3,B_2O_3,3BaO,5H_2O$ than with $15WO_3,B_2O_3,3BaO,5H_2O$.

The *potassium salt* is obtained in slender needles, closely resembling dipotassium tungstoborate, by decomposing the barium salt with potassium sulphate. It has the composition $14WO_3,B_2O_3,3K_2O,H_2O + 21H_2O$.

The *silver salt* is obtained by adding silver sulphate to a solution of the barium salt. It is a white crystalline powder, almost insoluble in cold, and very slightly soluble in hot water. It cannot be completely dried without partial decomposition, but appears to have the composition $14WO_3,B_2O_3,3Ag_2O,H_2O + 7H_2O$.

When a limited quantity of barium chloride is added to the solution which yields the sodium salt on acidification, and the precipitate filtered off, the filtrate deposits small granular crystals, very slightly soluble in cold, more soluble in hot water. They have the composition $14WO_3,B_2O_3,(3\frac{1}{2}BaO,1\frac{1}{2}Na_2O),6H_2O+29H_2O$. This complicated double salt resembles the double paratungstates obtained by Marignac. The corresponding strontium compound, $14WO_3,B_2O_3,(3\frac{1}{2}SrO.1\frac{1}{2}Na_2O),6H_2O + 29H_2O$, is obtained in a similar manner by mixing saturated solutions of strontium chloride and the sodium salt. All these salts form a new group of *boroquatuordecitungstates*. The barium-sodium and strontium-sodium compounds are possibly not true double salts, but molecular combinations of the two salts. The author was unable to obtain the tetrapotassium or pentapotassium salts. When potassium carbonate is added to tripotassium boroquatuordecitungstate, potassium tungstoborate and a precipitate of potassium paratungstate are formed. C. H. B.

Change which Ferric Hydrate undergoes after a Time. By D. Tommasi and G. Pellizzari (*Bull. Soc. Chim.* [2], **37**, 196—197).—Ferric hydrate kept under water for a year loses its gelatinous structure, and changes in colour from brown to yellowish-red. About 30 per cent. passes into a modification insoluble in dilute acids, and about 0·3 per cent. is converted into a soluble modification identical with Graham's colloïdal hydrate. The change is very slightly, if at all, affected by light. C. H. B.

Ferric Hydrates. By D. Tommasi (*Bull. Soc. Chim.* [2], **38**, 152—153).—The author separates the ferric hydrates into two isomeric classes, the α or red series, and the β or yellow series, the main points of difference between which are given in the table below:—

Red or α-series.	*Yellow or β-series.*
Obtained by precipitating a ferric salt with alkalis.	Obtained by oxidation of ferrous hydrate, ferroso-ferric hydrate, or ferrous carbonate.
α-$Fe_2O_3,2H_2O$ begins to be dehydrated at 50°.	β-$Fe_2O_3,2H_2O$ begins to be dehydrated at 105°.
α-Fe_2O_3,H_2O dehydrated at 92°.	β-Fe_2O_3,H_2O dehydrated at 150°.
α-Fe_2O_3 is brown.	β-Fe_2O_3 is red or yellowish-red.
Sp. gr. of $Fe_2O_3 = 5·11$.	Sp. gr. of $Fe_2O_3 = 3·95$.
The hydrates dissolve in dilute acids.	The hydrates are sparingly soluble in concentrated acids.
The hydrates are dehydrated on boiling with water.	The hydrates, even on long boiling, retain a molecule of water, which can easily be removed by a concentrated solution of calcium chloride.

The hydrates of the α-series may not only be distinguished, but separated from the hydrates of the β-series; for the former are soluble in ferric chloride and are reprecipitated by the addition of sodium sulphate or sulphuric acid, whereas the latter are quite insoluble in the same reagent. V. H. V.

Action of Hydrogen Sulphide on Solutions of Normal Nickel Sulphate. By H. Baubigny (*Compt. rend.*, **94**, 1473—1475).—The experiments described in this paper show that the precipitation of nickel from a solution of the normal sulphate by hydrogen sulphide depends on the tension of the gas. The quantity of sulphide thrown down in a given time is greater as the liquid is richer in hydrogen sulphide, and the effect of heating at 100° in closed vessels is that the same limits of precipitation are obtained in a few hours which at the ordinary temperature would require as many weeks.

The precipitation of the nickel is complete when the solution does not contain more than 1 gram of sulphate in the litre.

The limit of precipitation does not depend entirely on the degree of acidity acquired by the liquid, but varies according to other circumstances.

The action of heat on a solution of neutral nickel sulphate in the presence of hydrogen sulphate furnishes an exact method of separating nickel from manganese, aluminium, &c., whose salts are not decomposed by hydrogen sulphide, but not from iron. R. R.

Action of Hydrogen Sulphide on Nickel Sulphate in Acetic Acid Solution. By H. Baubigny (*Compt. rend.*, **94**, 1715—1717).—The action of hydrogen sulphide on nickel sulphate in solution is retarded or entirely prevented if a sufficient quantity of acetic acid is added in proportion to the quantity of nickel salt present. At the temperature of 100°, however, and in a closed vessel, acetic acid has no power to retard the action of hydrogen sulphide on dissolved nickel sulphate, the reaction taking place as with an aqueous solution of the neutral sulphate. R. R.

Action of Heat on an Acid Solution of Nickel Sulphate in Presence of Hydrogen Sulphide. By H. Baubigny (*Compt. rend.*, **94**, 1595—1598).—The experiments detailed in this paper lead to the conclusions that—

1. In acid solutions of nickel sulphate, as in neutral solutions, when the ratio of the weights of the acid and the metal remains constant, the precipitation of the nickel by hydrogen sulphide is more complete as the solution is more dilute.

2. Whatever the ratio of the volumes of gas and of liquid, the amount of nickel precipitated increases with the time. R. R.

Cobalt Sulphate. By G. Vortmann (*Ber.*, **15**, 1888—1889).—On adding concentrated sulphuric acid to an aqueous solution of a cobalt salt, and then evaporating, cobalt sulphate containing 1 mol. of water of crystallisation is produced. The same compound is also formed on treating purpureocobaltic chloride with a small quantity of water and strong sulphuric acid until dissolved, and then heating to 220°. It forms a crystalline peach-coloured powder, sparingly soluble in cold water, being less soluble than the anhydrous salt. A low red heat is required to drive off the water. In contact with moist air, it absorbs water very slowly. A. K. M.

Cobaltamine Compounds. (Part III.) By G. Vortmann (*Ber.*, **15**, 1890—1903).—*Octamine Compounds.*—Instead of preparing these compounds from the carbonate, as described in his first paper (*Ber.*, **10**, 154), the author heats the decamine-purpureo chloride for some time on a water-bath with dilute ammonia and solid ammonium carbonate. On evaporating the solution it assumes the dark cherry-red colour of the octamine carbonate. If any luteo-chloride should be present, it will separate out on cooling, and can be filtered off. *Octamine-roseocobaltic chloride*, $Co_2(NH_3)_8(2H_2O)Cl_6 + 4H_2O$, generally crystallises (as previously shown by the author) with 2 mols. H_2O, but by adding concentrated hydrochloric acid to the cold solution above-mentioned, it is obtained with $4H_2O$. With mercuric chloride, the compound $Co_2(NH_3)_8(2H_2O)Cl_6,6HgCl_2 + 3H_2O$ is precipitated of a pale-red colour. Heated to 100° it loses $3H_2O$. Octamine-purpureocobaltic chloride also forms a double salt with mercuric chloride; this when treated with concentrated hydrochloric acid and evaporated on a water-bath yields greyish-violet crystals of $Co_2(NH_3)_8Cl_6,3HgCl_2 + H_2O$, but on further concentration, green crystals of the praseo double salt, $Co_2(NH_3)_8Cl_6,HgCl_2$, are obtained. This compound is sparingly soluble in cold water; hot water converts it into octamine-purpureocobaltic chloride. On adding praseocobaltic chlornitrate to acidulated mercuric chloride solution, a green precipitate of

$$Co_2(NH_3)_8Cl_6,2HgCl_2$$

is produced. Octamine-cobaltic nitrate, prepared by adding nitric acid to a solution of the corresponding carbonate, forms a crystalline precipitate of the formula $Co_2(NH_3)_8(NO_3)_6 2H_2O$. It has also been obtained with 1 and with 6 mols. H_2O, also anhydrous. *Octamine-cobaltic chromate*, $Co_2(NH_3)_8(2H_2O)(CrO_4)_3 + 2H_2O$, is prepared by the action of potassium dichromate on the octamine-purpureo chloride, sulphate, or nitrate, and may be purified by crystallisation from a weak acetic acid solution: it forms bronze-coloured plates. If normal potassium chromate is employed, the compound obtained is olive-green, and contains 8 mols. H_2O. Solutions of both compounds in strong acetic acid when evaporated yield an orange-red body of the formula $Co_2(NH_3)_8(2H_2O)(CrO_4)_2,Cr_2O_7 + H_2O$. A platinochloride has been prepared, but its formula is not established. The acid carbonate, to which the author previously gave the formula $Co_2O_3(NH_3)_8,4CO_2 + 2H_2O$, contains $3H_2O$, 2 mols. of which are driven off at 100°. *Praseocobaltic chlornitrate*, $CO_2(NH_3)_8(NO_3)_2Cl_4 + 2H_2O$, is precipitated on adding dilute nitric acid or potassium nitrate solution to solution of praseocobaltic chloride. With potassium dichromate the latter gives a yellowish-green precipitate of the chlorochromate, $Co_2(NH_3)_8(Cr_2O_7)Cl_4 + H_2O$.

Hexamine Compounds.—To an ammoniacal solution of octamine-cobaltic chloride, ammonium carbonate is added, and the solution evaporated to dryness. On redissolving and repeating the same treatment, the residue consists of cobalt hydroxide and hexaminecobaltic carbonate, and from this other hexamine salts are obtained by the action of acids. Hexamine-cobaltic chloride is a green compound, of the formula $Co_2(NH_3)_6Cl_6 + 2H_2O$. It dissolves in cold water to a bluish-violet solution, which changes to violet-red on warming; from this solution concentrated hydrochloric acid precipitates octamine-purpureocobaltic chloride. Hexamine-cobaltic sulphate was obtained as an oil, which after frequent treatment with alcohol gradually became crystalline. It forms a red powder, easily soluble in water. Its formula is $Co_2(NH_3)_6(SO_4)_3 + 6H_2O$. The nitrate, $Co_2(NH_3)_6(NO_3)_6 + 8H_2O$, is a dark cherry-red deliquescent body. The carbonate, $Co_2(NH_3)_6(OH)_2(CO_3)_2 + 3H_2O$, is formed in preparing the octamine-carbonate, and is precipitated by alcohol as an oil, which after repeated solution, precipitation, and treatment with alcohol, becomes crystalline.

Heptamine Compounds.—The author has in a previous paper given a method for the preparation of melanocobaltic chloride. In order to confirm the formula which he gave for Rose's "black salt,"

$$Co_2(NH_3)_6(NH_2Cl)Cl_4,$$

he has prepared other derivatives, which he finds to be of analogous composition. *Melanocobaltic chlorochromate,*

$$Co_2(NH_3)_6(NH_2Cl)Cl_2,Cr_2O_7 + H_2O,$$

by precipitating the melanochloride with potassium dichromate. With platinum chloride, the melanochloride gives a brownish-black precipitate of $Co_2(NH_3)_6(NH_2Cl)Cl_4,PtCl_4$. On heating melanocobaltic chloride solution, it becomes red; with platinum chloride this red solution gives a reddish-brown precipitate, which (air-dried) has the formula $Co_2(NH_3)_6(NH_2Cl)Cl_2(OH)_2,PtCl_4$. With mercuric chloride, pale-red needles of $Co_2(NH_3)_6(NH_2Cl)Cl_2(OH)_2,3HgCl_2 + H_2O$, are precipitated. With picric acid, melanocobaltic chloride gives a brown precipitate, which explodes violently on heating. A. K. M.

Electrolysis of Ammonium Carbamate and Carbonate with Alternating Currents and Platinum Electrodes. By B. GERDES (*J. pr. Chem.* [2], **26**, 257—276).—Drechsel has observed (*J. pr. Chem.* [2], **22**, 476) that on electrolysing solutions of ammonium carbamate and carbonate with alternating currents, the platinum electrodes become strongly corroded, with formation of soluble and insoluble platinum bases, of urea, and of an oily substance soluble in ammonia. The author has isolated and studied the platinum bases referred to. He used platinum electrodes two inches by one inch, a battery of 4—6 Grove's cells, and alternated the current about 10 times in each second, the duration of each experiment being 10—12 hours, and the solution being kept cool. After that time a thick yellowish or white precipitate had formed, the solution being colourless, and the electrodes much attacked.

Besides ammonium nitrite and nitrate, urea, and a fatty substance, the filtrate was found to contain a soluble platinum salt thrown down as a blue or green precipitate by hydrochloric acid, and crystallising in needles. It was not, however, obtained in quantity sufficient to allow of detailed investigation.

The white precipitate contains most of the platinum dissolved off the electrodes. It is a carbonate insoluble in cold water, but on heating dissolves sparingly, forming an alkaline solution. After having been dried over sulphuric acid, it does not lose weight at 110°, but at higher temperatures it first becomes yellow and then suddenly decomposes, with evolution of ammonia and water, leaving metallic platinum in a very fine state of division. Its composition corresponds well with the formula $PtN_6H_{10}C_2O_6$. The carbonate dissolves in dilute soda, and is precipitated without alteration from its solution by carbonic anhydride. When dissolved in hydrochloric acid and precipitated by sodium carbonate in sufficiently dilute solutions small well formed octohedrons separate.

The *chloride*, $Pt(NH_3)_6Cl_4$, is easily obtained in small rhombohedrons or in needles; it dissolves readily in hot water, and with gold or platinum chloride gives precipitates resembling ammonium platinochloride. The *nitrate*, $Pt(NH_3)_6(NO_3)_4$, is readily soluble in water, and crystallises in needles. The *sulphate* is practically insoluble in water, even calcium sulphate solution giving an immediate precipitate with solutions of the soluble salts. It could only be obtained in the amorphous condition. Other compounds have been prepared, but have not been analysed. Chromates produce a yellow, hydrofluosilicic acid a white precipitate. The free base has not yet been isolated in a state of purity.

If during the action of the electric current the solution of carbonate or carbamate is not artificially cooled, the temperature of the fluid rises to 40—50°, and no precipitate of the carbonate just described is obtained, but on cooling, long prismatic highly refractive crystals separate from the solution. These likewise consist of a carbonate, $Pt_2N_7C_4O_{14}H_{27}$. Their solution gives with nitric acid a colourless precipitate, which gradually changes into bright blue octohedrons of *platodiammonium nitrate*, $Pt(NH_3)_4(NO_3)_2$.

The author believes the formation of the several platinum bases to take place as follows:—Electrolysis at first takes place in the ordinary manner, $(NH_4)_2CO_3$, splitting up into $2NH_4$ and CO_3, the former combining in the nascent state with the negative electrode, forming $PtH_2(NH_3)_2$. The current alternating, the negative pole becomes positive, and CO_3 is added to the compound formed, yielding $H_2 + Pt\left\{\begin{matrix}NH_3O\\NH_3O\end{matrix}\right.{>}CO$, that is to say, *platosammonium carbonate*, which salt directly combines with NH_3, yielding *platodiammonium carbonate*, $Pt\left\{\begin{matrix}NH_3,NH_3O\\NH_3,NH_3O\end{matrix}\right.{>}CO$. To the latter, on further alternation of current, $2NH_4$ are added, giving $\begin{matrix}HNH_3\\HNH_3\end{matrix}{>}Pt{<}\begin{matrix}NH_3.NH_3O\\NH_3.NH_3O\end{matrix}{>}CO$, from which in a similar manner the insoluble carbonate—

$$CO{<}\begin{matrix}NH_3\\NH_3\end{matrix}{>}Pt{<}\begin{matrix}NH_3.NH_3O\\NH_3.NH_3O\end{matrix}{>}CO \text{ is formed.}$$

O. H.

Ammonioplatinum Diammonium Compounds. By E. DRECHSEL (*J. pr. Chem.* [2], **26**, 277—281).—In an appendix to the previous paper, the author points out the striking similarity of the reactions of the platinum base described by Gerdes with those of barium compounds, the solutions being precipitated by sodium carbonate, potassium dichromate, sodium phosphate, sulphuric acid, calcium sulphate, hydrofluosilicic acid, and alkaline oxalates, hyposulphates and ferrocyanides. By the reagents named in fact the platinum compound cannot be distinguished from baryta. Hydric sulphide and ammonium sulphide produce precipitates only after some time. The ammonioplatinum diammonium compounds stand therefore in the same relation to the alkaline earths as ammonium does to the alkalis. O. H.

Mineralogical Chemistry.

Metallic Iron accompanying Native Gold in Montgomery Co., Virginia, and in Burke Co., N. Carolina. By W. T. Page (*Chem. News*, **46**, 205).—The grains of iron removed by a magnet from gold, obtained by alluvial washing in the bed of Brush Creek, have a sp. gr. 7·20, and consist of—

Fe.	Cu.	S.	Quartz.
97·12	0·04	1·47	0·82 = 99·45.

C, P, Ni, Co, Sn, and Mn absent. This iron is shown not to be derived from tools employed by workers, but is a case of the occurrence of native iron with gold. Similar specimens from Carolina had a sp. gr. = 7·57, and consisted of—

Fe.	Co.	Sn.	Quartz.
99·77	trace	trace (?)	0·25 = 100·02.

E. W. P.

Chemical Composition of Minerals of the Cryolite-group. By J. Brandl (*Jahrb. f. Min.*, 1882, **2**, Ref., 201—203).

	a.	*b.*	*c*1.	*c*2.	*c*3.
Al........	13·01	13·606	13·04	13·00	13·26
Ca........	—	18·83	17·22	17·21	17·22
Mg	—	—	0·39	0·20	—
Na	32·41	11·73	10·02	10·49	10·43
F	54·29	55·69	50·65	50·62	50·61
H_2O	—	—	8·48	8·33	8·42
	99·71	99·856	99·80	99·85	99·94

	d.	*e*1.	*e*2.	*f.*
Al..........	22·14	17·66	17·64	23·37
Ca..........	1·53	—	—	16·19
Mg	3·56	—	—	0·11
Na	5·50	24·97	25·00	0·33
F	57·12	57·30	57·30	35·01
H_2O	10·00	—	—	12·41
	99·85	99·93	99·94	87·42
Loss reckoned as oxygen				12·58
				100·00

a. Cryolite, representing the formula $AlF_3 + 3NaF$. *b.* Pachnolite, $AlF_3 + CaF_2 + NaF$. Pachnolite contains no water, and thus differs from thomsenolite. *c* 1, 2, and 3, are analyses of thomsenolite, agreeing with the formula $AlF_3 + CaF_2 + NaF + H_2O$. *d.* Ralstonite, $4AlF_3 + 3Na\,(MgCa)F + 3H_2O$. *e* 1, 2, are analyses of chiolite from

Miask. They represent the formula $3AlF_3 + 5NaF$. *f* is an analysis of prosopite from Altenberg in Saxony. It proves that this mineral is free from silicon. Supposing that the oxygen is combined with aluminium, so that the aluminium is partly combined with fluorine and partly with oxygen, the analysis gives the following results:—

Ca.	Mg.	Na.	Al.	Al_2O_3.	F.	H_2O.
16·19	0·11	0·33	9·22	26·55	35·01	12·41

Taking for granted that fluorine and hydroxyl can replace each other, the formula for prosopite should be $Ca(Mg,Na)Al_2(F,OH)_2$. This mineral does not yield up its water at 260°. B. H. B.

Some Artificial Products from Cryolite. By NOELLNER (*Jahrb. f. Min.*, 1882, **2**, Ref., 200—201).—In order to determine, experimentally, if the minerals crystallised out in the cavities of cryolite have originated from the action of salt solutions, the author digested for three months at 100° about 12 grams finely powdered cryolite with a saturated solution of barium chloride. Saturated solutions of strontium nitrate, calcium chloride, and magnesium chloride, were also employed. Cryolite was also treated with the same solutions for six days in closed tubes at a temperature of 180—190°. The products thus obtained were then dried and analysed, giving the following results:—

Material. (Cryolite = $Al_2Na_6F_{12}$.	Products of the reaction. *a.* At 180° after 6 days.	*b.* At 100° after 3 months.
1. Cryolite + $BaCl_2$....	$Al_4Ba_4Na_4F_{24}$	$Al_4Ba_5Na_2F_{24} + H_2O$
2. Cryolite + SrN_2O_6..	$Al_4Sr_4Na_4F_{24}$	$Al_4Sr_5Na_2F_{24} + 4H_2O$
3. Cryolite + $CaCl_2$....	$Al_4Ca_4Na_4F_{24}$	$Al_4Ca_5Na_2F_{24} + 4H_2O$
4. Cryolite + $MgCl_2$...	$Al_4Mg_4Na_4F_{24}$	$Al_4Mg_5Na_2F_{24} + 4H_2O$

The product No. 3*a* was further treated with $MgCl_2$ at 180° for six days, and the product had the composition $Al_8Ca_4Mg_5Na_6F_{48} + 8H_2O$. In the same way the product No. 4*a* was heated at 180° for six days with $CaCl_2$, and yielded a body of the composition $Al_8Mg_7Ca_2Na_6F_{48} + 8H_2O$.

From these experiments the author deduces:—(1), that cryolite is decomposed by solutions of salts of the alkaline earths; (2), that the alkaline earths displace the sodium which goes into solution; (3), that the degree of change effected is dependent on the time, the temperature, and the proportion of the salt in the solution; (4), that the perfect displacement of the sodium did not occur, but that it would probably be effected after the lapse of sufficient time. (5.) That the substituted calcium or magnesium can be partially replaced by magnesium or calcium. (6.) That in all these reactions water is taken up; the amount being dependent on the nature of the incoming elements. (7.) That the products obtained artificially closely resemble the natural minerals crystallised out in the cavities of cryolite, and that the theory of their formation by the same chemical process is highly probable. B. H. B.

The Pyrolusite Mines of Bölet. By T. NORDSTRÖM (*Jahrb. f. Min.*, 1882, **2**, Ref., 195).—At Bölet, in Sweden, pyrolusite occurs in sufficient quantity to be worked. The veins and pockets are found at the contact of finely granular gneiss and mica-slates with granitic gneiss, which is a variety of Örebro granite. The cavities were first filled with mica and chlorite, which was then partially replaced by pyrolusite. The latter is, in places, accompanied by heavy spar, calcspar, quartz, felspar, vanadinite, fluorspar, and calcspar coloured black by fine needles of pyrolusite. B. H. B.

Artificial Production of Witherite, Strontianite, and Calcite. By L. BOURGEOIS (*Bull. Soc. Chim.* [2], **37**, 447—448).—If small quantities of precipitated barium, strontium, or calcium carbonate are thrown into a fused mixture of potassium and sodium chlorides in equivalent proportions, no carbonic anhydride is given off, but the carbonates assume a distinct crystalline form, identical in each case with that of the corresponding mineral. Barium carbonate forms hexagonal plates, sometimes elongated in a direction parallel with the faces of the prism. Strontium carbonate forms elongated prisms, and calcium carbonate usually forms agglomerations of crystals resembling snow crystals. C. H. B.

Mineralogical Notes. By A. BRUN (*Jahrb. f. Min.*, 1882, **2**, Ref., 198).—(*a.*) *Stypticite from Chili.*—The empirical formula of this salt, $Fe_2O_3,2SO_3 + 10H_2O$, should be $H_4Fe_2S_2O_{11} + 8Aq$, as the water is given up at 80—180°, with the exception of the last 8 per cent., which is only driven off at a dull red heat together with the sulphuric acid. On dissolving it in boiling water, brown basic iron sulphate is precipitated.

(*b.*) *Dolomite from Teruel in Spain.*—This is shown by the microscope to be composed of grey and brown zones; the latter being coloured by numerous opaque granules (magnetic iron ore). The analysis gave 2·63 per cent. FeO, and traces of MnO.

(*c.*) *Minerals of the Miage Glacier, M. Blanc.*—In the moraine of the "Glacier de Miage," crystals of quartz have been found, on which only $R(10\bar{1}\bar{1})$ is developed, without $-R(01\bar{1}\bar{1})$. The author also found galena, albite (complicated crystals), orthoclase (simple combinations), various micas, chlorite, asbestos, and small crystals of beryl. B. H. B.

Chalcomenite, a New Mineral Species (Selenite of Copper). By DES CLOIZEAUX and DAMOUR (*Jahrb. f. Min.*, 1882, **2**, Ref., 204).—For some time the existence has been known of selenium-lead, selenium-silver-copper-lead, and selenium-copper-lead ores at the Cerro de Cachenta, about 50 miles south-west of Mendoza in the Argentine Republic. Accompanying these ores, Des Cloiseaux found some very small crystals of a violet-blue colour, which he called chalcomenite. The system of this new mineral is monoclinic; the axes have the proportion $a : b : c = 0·722187 : 1 : 0·246037$. $\beta = 89° 9'$. Chalcomenite has the formula $CuSeO_3 + 2H_2O$; and is therefore a representative of a group, the selenious acid salts, up to the present time unknown in nature. When heated in a tube closed at one end, the mineral gives up first water, which is acid, then selenious acid, and finally melts to a brown mass. Heated on charcoal before the blowpipe, it melts to a black slag, gives off selenium vapours, and colours the flame dark blue. In a bead of microcosmic salt, it is quickly dissolved, and gives a greenish-blue glass, which becomes red in the reducing flame, especially after the addition of tin. The mineral is soluble in the ordinary acids. A drop of the solution in sulphuric acid, placed on a bright plate of copper, gives a black stain which cannot be removed by washing, and the mineral can thus be distinguished from the phosphates and arsenates of copper. Its sp. gr. is 3·76. The analysis gave the following result:—

SeO.	CuO.	H_2O.	Total.
48·12	35·40	15·30	98·82

At the request of Des Cloizeaux, Friedel and Sarasin prepared chalcomenite artificially. They employed for the purpose a neutral solution of potassium selenide, and to this they added copper sulphate, when a white amorphous precipitate was formed, which became converted into a blue crystalline powder. Seen under the microscope this was found to be a mass of small rectangular pyramids, which might be rhombic or monoclinic. The analysis gave results corresponding with the formula of chalcomenite. B. H. B.

Fergusonite from Brindletown, Burke Co., N. Carolina. By W. H. Seamon (*Chem. News*, **46**, 205).—The crystals are small, of tetragonal habit, reddish-brown, and give a yellow-brown streak. Lustre between vitreous and resinous, brittle, fracture conchoidal. Hardness = 6. Sp. gr. 5·6.

Nb_2O_5.	Ta_2O_5.	WO_3,SnO_2.	UrO_2.	Y_2O_3, &c.	Ce_2O_3.	Di_2O_3,La_2O_3.
43·78	4·08	0·76	5·81	37·21	0·66	3·49

FeO.	CaO.	H_2O.
1·81	0·65	1·62

Counting the water as basic, the above figures lead to the orthoniobate formula $M'''NbO_4$. E. W. P.

Analysis of a Niobate which has been improperly called Euxenite from Mitchell Co., N. Carolina. By W. H. Seamom (*Chem. News*, **46**, 205).—This mineral, formerly described by J. L. Smith, in no way agrees with the mineral of that name from Norway; it is reddish-brown in colour, with lustre between resinous and adamantine. Hardness = 5·5. Sp. gr. 4·33. Freed from mica and crust the mineral contains:—

Nb_2O_5.	WO_3SnO_2.	UrO_2.	Y_2O_3.	Ce_2O_3.	$Di_2O_3La_2O_3$.	FeO.	CaO.	H_2O.
47·09	0·40	15·15	13·46	1·40	4·00	7·09	1·53	9·55

but very little of any oxide of the erbium or ytterbium class could be detected by the spectroscope; the orthoniobate formula is therefore $M''_3Nb_2O_8$, in which about one-eighth of the hydrogen of the water is basic, the actual distribution of the elements being $(\frac{23}{30}M' + \frac{21}{30}M'' + \frac{25}{30}M''' + \frac{10}{30}M'''')Nb_2O_8$; euxenite, besides containing much titanic oxide, is a metaniobate. E. W. P.

Rutile, as a Product of the Decomposition of Titanite. By P. MANN (*Jahrb. f. Min.*, 1882, **2**, Briefw., 200—201).—In some foyaites from the Serro de Monchique, the titanite (sphene) was completely decomposed, and the author found in the decomposed mass numerous bright yellow crystals which, by the help of the microscope, he proved to consist of rutile.

The lime had probably been extracted by the action of water and converted into carbonate of lime, whilst the titanic acid, mixed perhaps with some amorphous silica, formed the decomposed crust.

B. H. B.

Artificial Production of a Crystallised Hydrated Silicate. By A. DE SCHULTEN (*Bull. Soc. Chim.* [2], **37**, 449—457).—When lime-water is added to a concentrated solution of potassium silicate until a slight precipitate is formed, and the mixture is then heated in sealed tubes at 180—200° for 24 hours, the gelatinous mass which forms on cooling encloses a small quantity of some substance crystallised in prismatic needles. If the tube is heated for several days with occasional agitation, the gelatinous matter gradually disappears, and the quantity of the crystals increases. By repeated levigation, the plates of silica can be removed, and the prismatic crystals are then obtained, mixed only with a small quantity of hexagonal plates: the quantity of hexagonal plates increases, and that of the needles diminishes if the lime-water is added in too small quantity; if, however, too much lime-water is added, no crystals are formed at all. The prismatic crystals are white, have a nacreous lustre, melt before the blowpipe, and are decomposed by hydrochloric acid with separation of gelatinous silica which retains the form of the original crystals. They have the composition:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	
64·2	0·7	14·7	3·3	2·2	14·5	= 99·6,

which corresponds with the formula $(K_2,Na_2,Ca)O,3SiO_2,2H_2O$, the ratios between K_2O,Na_2O and CaO being 1 : 2 : 10. The soda is derived from the glass tubes, and the presence of alumina is due to the presence of the hexagonal plates, which probably consist of *levyne*, formed by the action of potassium silicate on the aluminous glass. When dried in a water-bath, the crystals lose 4 to 5 per cent. of water. No natural zeolite has the composition of these artificial crystals. Okenite consists of calcium silicate, and contains SiO_2, 56·60; CaO, 26·42; H_2O, 16·98.

Examined by polarised light, between crossed nicols, the crystals exhibit brilliant colours which are extinguished longitudinally. The greatest axis of elasticity corresponds with the direction of elongation.

If sodium silicate is used instead of potassium silicate, a compound is obtained which has a very similar composition. C. H. B.

Artificial Analcime. By A. de Schulten (*Bull. Soc. Chim.* [2], **37**, 448—449).—When solutions of sodium silicate and sodium aluminate are mixed in such proportions that the silica and the alumina are in the same ratio as in analcime, a suitable quantity of lime-water added, and the liquid heated in a closed copper tube at 180° for 18 hours, crystals are obtained which have a composition identical with that of natural analcime. The lime-water simply facilitates crystallisation. If it is not added, isolated crystals are rarely obtained; the crystals separate out in spherical aggregations with rough surfaces. The crystals are sometimes cubical trapezohedrons, sometimes hexahedrons. Apparently the trapezohedrons are formed when the solutions are concentrated and strongly alkaline, and the hexahedrons under the reverse conditions. Unlike the artificial analcime obtained in glass tubes (Abstr., 1881, p. 25), the crystals have no action on polarised light, even when a quartz plate cut parallel with the axis is interposed. The optical properties of natural analcime are similar to those of crystals of the quadratic system; the optical properties of the artificial variety previously obtained (*loc. cit.*) are those of the hexagonal system. The optical behaviour of the new crystals is identical with that of crystals of the cubic system. It is evident therefore, that the axes of elasticity of the crystals of analcime undergo slight changes sufficient to modify their optical properties, but not sufficient to alter the external forms of the crystals from those of the cubic system. C. H. B.

Rutile in Phlogopite. By Sandberger (*Jahrb. f. Min.*, 1882, **2**, Briefw., 192—193).—The author received a crystal of phlogopite, about a pound in weight, from Ontario, in Canada. In it he discovered, by means of a lens, numerous colourless crystalline needles, which he proved by analysis to consist of pure titanic acid. This is, without doubt, the best material to illustrate the separating out of titanic acid from a decomposing mica. B. H. B.

Analysis of beautifully Crystallised Albite from Amelia Co. By R. N. Musgrave (*Chem. News*, **46**, 204).—This mineral occurs in masses of clear colourless flattened crystals, having a hardness = 6; sp. gr. = 2·605; and a composition of—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.
68·44	19·35	11·67	0·43 = 99·89.

E. W. P.

Euclase from the Alps. By F. Becke (*Jahrb. f. Min.*, 1882, **2**, Ref., 209).—Small pale yellow crystals, which proved to be euclase, have been found in the Alps, together with pericline. The crystals were about 0·5 mm. long. The following combination is tolerably general: $\infty\breve{P}\infty$, $\infty\breve{P}2$, $\infty\bar{P}20$, $2\breve{P}\infty$, ∞P, $3\breve{P}\infty$, $-P$. The accompanying minerals are pericline and ankerite as the oldest, also rock crystal in long prisms. The euclase appears to have been formed at the same time as the rock crystal, as do also little globules of helminth.

B. H. B.

Occurrence of Minerals at Jordansmühl, in Silesia. By B. SCHUBERT (*Jahrb. f. Min.*, 1882, **2**, Ref., 193—195).—This paper describes the following minerals and rocks found in the serpentine bed at Jordansmühl.

Prehnite occurs partly in crystals, partly in crystalline aggregates. It is rose-red, orange-yellow, or greenish, rarely colourless. The following faces occur: $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $0P$, ∞P, $\bar{P}\infty$, $\frac{3}{4}\bar{P}\infty$, $\frac{3}{8}\bar{P}\infty$, $\frac{1}{2}\bar{P}\infty$, P, $\frac{1}{4}P$. The analysis yielded :—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.
44·12	26·00	0·61	25·26	traces	4·90

approximating to the prehnite formula $H_4Ca_4Al_4Si_6O_{24} = \left\{\begin{array}{l} H_4SiO_4 \\ 2Ca_2SiO_4. \\ Al_4Si_3O_{12} \end{array}\right.$

White garnet, for which the formula is calculated to be $Ca_3Al_2Si_3O_{12}$.

Chromium garnet forms an emerald-green coating over prehnite.

Garnet rock, of a white colour, has the following composition :—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	H_2O.	Total.
38·91	24·29	0·70	37·07	0·45	101·42

From this the formula of the lime-alumina-garnet may be calculated. A second piece of rock gave—

SiO_2.	Al_2O_3.	CaO.	MgO.	H_2O.	Total.
43·94	21·79	34·19	1·54	0·60	102·06

From this is calculated the formula $Ca_3Al_2Si_3O_{12} + SiO_2$.

By the help of the microscope, the rock was proved to consist of lime-alumina-garnet and quartz. A third rock of a dirty pink colour gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
36·84	31·53	2·78	25·53	1·92	2·51	101·11

It contained diaspore, and probably some quartz.

Vesuvian, characterised by its fine blood-red colour and the combination of the forms ∞P, $\infty P\infty$, P, $P\infty$, $0P$. It occurs in drusy cavities of the white garnet rock; the analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
37·51	21·24	0·69	35·45	2·11	2·77	99·77

Diaspore occurs in compact garnet; analysis gave—

Al_2O_3.	H_2O.
82·66	17·44

Natrolite, in drusy cavities of the garnet rock in radiated aggregates, in the combination ∞P, P.

Manganese-ore.—Pseudomorphs, apparently pyrolusite after calcite, consisting of

MnO_2.	MnO.	SiO_2.	H_2O.	Fe_2O_3.	MgO.	Total.
62·92	4·80	8·00	18·79	2·77	4·41	101·69

Quartz Rock.—This rock was rich in quartz, of a rose-red colour, and occurred in great beds. It gave on analysis:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	H_2O.	MgO.	Total.
69·48	19·21	0·34	10·29	0·34	trace	99·66

It probably consists of a mixture of quartz and a lime felspar.

Opal, of a bright green colour, gave on analysis:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
81·43	4·11	1·04	0·83	8·06	4·65	0·80	100·92

Serpentine, containing magnetic iron ore, gave on analysis:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	H_2O.	Total.
42·21	9·59	1·40	34·88	13·28	101·36

B. H. B.

Waltherite from Joachimsthal. By C. Bertrand (*Jahrb. f. Min.*, 1882, **2**, Ref., 195—197).—Vogl described, under the name of waltherite, a mineral from Joachimsthal, occurring in thin prisms of a brown and green colour. This is now proved to consist of two distinct minerals. The *brown fibrous mineral* cleaves easily. It is rhombic; $\infty P = 116°$. The cleavage is in the direction of $0P$, ∞P, and $\infty P\breve{\infty}$.

The *green mineral*, on the other hand, is not so distinctly fibrous, and does not cleave so easily as the brown. The system could not be determined, on account of the smallness of the crystals.

B. H. B.

The Granites on the Banks of the Saône. By F. Gonnard (*Jahrb. f. Min.*, 1882, **2**, Ref., 199).—During the construction of a water reservoir near Lyons, a bed of pegmatite was laid bare, in which the following accessory minerals were found:—

(1.) Garnet. Almandine, combinations ∞O, $2O2$ of 15—20 mm. diameter. The smaller crystals were partly opaque and partly translucent, of a fine red colour, and simple ($2O2$).

(2.) Small columnar crystals of black tourmaline.

(3.) Pinite. Only one crystal was found, 10 mm. long and 4½ mm. diameter, enclosed in the quartz of the pegmatite.

(4.) A mineral belonging to the Cordierite group, very similar to the chlorophyllite of Haddam.

(5.) A yellowish-grey mica, of silky lustre, and easily scratched with the nail; it appears to be related to sericite. B. H. B.

Chemical Composition of Various Layers of a Lava Current from Etna. By L. Ricciardi (*Compt. rend.*, **94**, 1657—1659).—The results given in this paper go to prove that samples of lava taken from one current at various depths on the same vertical plane differ only in the greater or lesser quantity of protoxide and peroxide of iron they contain, the quantity of the latter being greater where the parts have been in contact with aqueous vapour or the atmosphere. The lavas belonging to one and the same eruption, however, if collected at different points, may differ in their chemical and mineralogical composition. R. R.

Lithological Determination of the Meteorite of Estherville, Emmet Co., Iowa (10th May, 1879). By S. MEUNIER (*Compt. rend.*, **94**, 1659—1661).—The Emmet meteorite belongs to the type designated *logronite* by the author in 1870. The chief minerals it contains are *olivine*, *bronzite*, *peckhamite* (Lawrence Smith), *pyrrhotine*, *schreibersite*, *ferric oxide*, and *nickeliferous iron*. R. R.

Supposed Meteorite found in Augusta Co., Virginia. By W. H. SEAMON (*Chem. News*, **46**, 204).—The mass of metallic iron, which weighed 1·25 kilos., and was covered with a crust 13 mm. deep, was at first supposed to be a meteorite, but the analyses show that it is not so.

Fe.	Mn.	C.	S.	P.	SiO_2.	Al_2O_3.	CaO.	O and loss.
90·45	0·10	0·19	0·15	0·37	4·18	0·49	2·16	1·91

Sp. gr. = 5·76; Ni and Co absent; SiO_2 soluble in sodium carbonate. Widmanstatt figures not produced by treatment with acids.

E. W. P.

Organic Chemistry.

Action of Ozone on Hydrocarbons. By L. MAQUENNE (*Bull. Soc. Chim.* [2], **37**, 298—300).—Coal-gas, purified by being passed through sulphuric acid and potash, is oxidised by ozone, with formation of formic acid, together with small quantities of methaldehyde and a substance which reduces cupropotassic tartrate, probably methylenitan. A small quantity of an amber liquid, which sometimes explodes violently, is also formed; it is possibly either oxybenzene or a nitrogen compound. Nitrogen tetroxide also combines readily with hydrocarbons. A sensible quantity of nitrobenzene is quickly formed when benzene mixed with sulphuric acid is exposed to the action of ozonised air. Pure methane is not affected by ozone, but if a mixture of methane and oxygen is subjected to the silent discharge, formic acid and methaldehyde are formed. These results confirm Berthelot's view of the experiments of MM. Thénard (*Compt. rend.*, 1873). The products obtained by the action of the silent discharge on a mixture of carbonic anhydride and methane are undoubtedly formed by the oxidation of the latter, and the sugar produced is methylenitan, $C_7H_{14}O_6$. The same substance is formed by the action of hydrogen on carbonic oxide.

These facts possibly explain the formation of carbohydrates in plants. Methane may occupy an intermediate position between the carbohydrates and the mixture $CO + H_2$, produced in the chlorophyll cells under the influence of light; by simple oxidation, it yields methylene oxides and sugars; by polymerisation analogous to that which takes place under the influence of the silent discharge, it yields the complex hydrocarbons and various products so common in the vegetable kingdom. C. H. B.

Dissociation of Trichloromethyl Sulphochloride. By E. NOELTING (*Bull. Soc. Chim.* [2], **37**, 392—394).—*Trichloromethyl sulphochloride*, $CCl_3.SO_2Cl$, was heated in sealed tubes for eight or ten hours at a temperature between 170° and 200°. At 170° some unaltered compound remains, but at 200° it is completely decomposed into sulphurous anhydride, carbon tetrachloride, carbon oxychloride, and thionyl chloride, thus: $CCl_3.SO_2Cl = CCl_4 + SO_2$ and $CCl_3.SO_2Cl = COCl_2 + SOCl_2$. C. H. B.

Action of Cupric Hydroxide on Sugars. By J. HABERMANN and M. HÖNIG (*Monatsh. Chem.*, **3**, 651—667).—By the action of cupric hydroxide in neutral solution on cane-sugar, inverted sugar, grape-sugar, and fruit-sugar, there were obtained in each case carbonic anhydride, formic acid, glycollic acid, and a mixture of acids whose uncrystallisable calcium salts gave an amount of calcium intermediate between that required for erythroglucic and glyceric acids. In the experiments made in alkaline solution (with baryta-water) the same products were observed, but were obtained in shorter time and in increased amount: in one experiment, in which a solution of grape-sugar was heated with soda and copper hydroxide, gluconic acid was obtained. Although the products were the same with each of these sugars, there were great differences in the course of the reactions. In the case of cane-sugar, the reduction commenced only after some hours' boiling, apparently not until the sugar had been inverted. With inverted sugar, reduction of the copper oxide commenced shortly after the boiling point was reached. With grape-sugar in neutral solution the reduction was rather slow, whilst in alkaline solution it started with the introduction of the copper oxide into the warm liquid. With fruit-sugar the reduction was much quicker than with grape-sugar.

In conclusion, the authors give reasons for doubting the accuracy of the statements of Reichardt (*Annalen*, **127**, 297), that gum and gummic acid, and of Claus (*ibid.*, **147**, 114), that tartronic acid are amongst the products of the oxidation of sugar with copper oxide. A. J. G.

Conversion of Maltose into Glucose. By S. J. PHILLIPPS (*Bied. Centr.*, 1882, 710).—Maltose yields glucose under the influence of ferments; artificial gastric juice produces no change. Maltose appears in the intestinal canal after feeding with starchy matters. Maltose appears in the urine if it has been previously injected into a vein; subcutaneous injection of maltose results in the conversion of a portion of it into glucose. After feeding with starch, the blood of the mesenteries contains glucose only. E. W. P.

Manufacture of Starch-sugar. By F. SOXHLET and A. BEHR (*Bied. Centr.*, 1882, 698; compare Abstr., 1882, 1274).—From concentrated grape-syrup at 30—35°, Behr has obtained crystallised anhydrous grape-sugar by the introduction of a crystal of the same. The sweetness of grape- as compared with that of cane-sugar is $1 : 1\frac{2}{3}$. E. W. P.

Action of Ammonia on Propaldehyde. By A. WAAGE (*Monatsh. Chem.*, **3**, 693—695).—By the action of ammonia gas on propaldehyde, cooled by a mixture of ice and salt, a small quantity of a solid product, C_3H_6O,NH_3, and an oil were obtained. The oil appears to be a mixture, and on exposure to an atmosphere containing carbonic acid, long colourless tabular crystals separate, of the formula $C_{15}H_{29}N_3$ (m. p. 74°), soluble in ether and alcohol, but insoluble in water. What part the carbonic acid plays in the formation of these crystals could not be ascertained.

By heating the crude product of this reaction for some days at 200° in sealed tubes, a dark-brown liquid is obtained; and when this is distilled, and the fraction 170—210° dissolved in hydrochloric acid, separated from resinous and oily matters, and distilled with potash, a colourless base, $C_9H_{13}N$, is obtained, boiling at 193—195° (corr.), probably parvoline. A. J. G.

γ-Diethylbutyrolactone. By A. EMMERT and R. FRIEDRICH (*Ber.*, **15**, 1851—1852).—From succinic chloride and zinc-ethyl, Wischin (*Annalen*, **143**, 262) obtained ethylene diethyl diketone, which decomposed on distillation. On repeating his experiments, a body of acid reaction was obtained which boiled at 230—235° without decomposition, and on analysis gave numbers corresponding with a mixture of nearly equal parts of γ-diethylbutyrolactone and γ-diethyloxybutyric acid. The latter was converted into the lactone by standing over solid potassium carbonate; the liquid then boiled at 228—233°. The barium and calcium salts were prepared, both soluble in alcohol and in water.

On attempting to convert the acid into lactone by means of phosphoric anhydride, a hydrocarbon $(C_8H_{11})_n$ distilled over at 270°. J. K. C.

Bees' Wax. By E. ZATZEK (*Monatsh. Chem.*, **3**, 677—679).—Schalfeef has stated (this Journal, 1877, i, 454) that Brodie's cerotic acid is in reality a mixture of acids, into which it may be resolved by fractional precipitation with lead acetate. The author has repeated these experiments, but entirely fails to confirm Schalfeef's results. The first fraction which, according to Schalfeef, should contain an acid $C_{34}H_{68}O_2$, gave numbers perfectly agreeing with those required for cerotic acid ($C_{27}H_{54}O_2$). A. J. G.

Action of Thiacetic Acid on Ethyl Thiocyanate. By M. CHANLAROFF (*Ber.*, **15**, 1987—1989).—On heating these substances together for 10—15 minutes, they combine, forming *ethylic acetyldithiocarbamate*, $CS(SEt).NH\overline{Ac}$; it crystallises in brilliant yellow needles, melting at 122—123°, and is readily soluble in alcohol, ether, and hot water. On being heated, it decomposes into its original constituents. When boiled with baryta-water, it yields mercaptan and barium thiocyanate and acetate; with dilute hydrochloric acid, it gives ethylic dithiocarbamate, mercaptan, carbon oxysulphide, acetic acid, and ammonium chloride. A. J. G.

Azaurolic Acids. By V. MEYER and E. J. CONSTAM (*Annalen*, **214**, 328—353).—The ethylnitrolic acid used in the preparation of ethylazaurolic acid is best obtained by the following process:—6 c.c. nitroethane are brought into a vessel containing small pieces of ice, 15 c.c. of potash solution (= 6·7 grams KOH) are added, and the mixture is shaken until the nitroethane is dissolved. The liquid, having been transferred to a beaker containing ice, is mixed with 15 c.c. of sodium nitrite solution (15 c.c. = 8 grams $NaNO_2$). Dilute sulphuric acid is now added until the red colour of the mixture changes to pale yellow, when the solution is rendered alkaline by the addition of potash. The liquid is three times alternately acidified and made alkaline. It is finally acidified with sulphuric acid, and three times extracted with one-sixth of its volume of ether. The nitrolic acid is deposited on evaporating the ether.

In order to prepare *ethylazaurolic acid*, 45 grams of 5 per cent. sodium amalgam are added to 2 grams of ethylnitrolic acid, suspended in 10 c.c. of water. The vessel in which the operation is conducted is surrounded by ice and salt, so as to keep the temperature about zero. The alkaline liquid is separated from the metallic mercury and acidified with dilute sulphuric acid, whereupon ethylazaurolic acid is deposited in needle-shaped crystals, which are purified by recrystallisation from boiling alcohol. The pure acid forms orange-coloured prisms, sparingly soluble in water and in ether. It melts at 142° with detonation, forming leucazone, nitrous oxide, and water. On oxidation with chromic acid mixture, it is converted into acetic and carbonic acids. An ammoniacal solution of ethylazaurolic acid gives a brown precipitate with silver nitrate, and yellow precipitates with lead and zinc salts. Ethylazaurolic acid is decomposed by warm dilute hydrochloric acid into ethylleucazone and hydroxylamine: to separate these bodies, the hydrochlorides are converted into sulphates by treatment with silver sulphate, and on adding a large quantity of alcohol to a cold concentrated aqueous solution of the sulphates, hydroxylamine sulphate is precipitated, and on evaporating the alcoholic filtrate, ethylleucazone sulphate is deposited in colourless prisms, melting at 161·5°. By double decomposition with baryta-water, the sulphate is converted into the free base $C_4H_7N_3O$, which crystallises in white needles, melting at 158°, and soluble in alcohol and in water. The aqueous solution gives a reddish-brown coloration with ferric chloride. The barium salt, $(C_4H_6N_3O)_2Ba$, is a colourless hygroscopic powder. On the addition of silver nitrate to a solution of leucazone, leucazone silver nitrate, $C_4H_7N_3O,AgNO_3$, is deposited as a white crystalline precipitate. Ethylleucazone is also produced by the action of strong ammonia or of sodium amalgam on ethyl azaurolic acid. The constitution of azaurolic acid may perhaps be represented by CMe(NO)⁚N.NH.CMe(NOH), or more probably by the formula CHMe(NO).N⁚N.CHMe.NO.

Propylazaurolic acid, $C_3H_6N_2O$, prepared from propylnitrolic acid, forms pink crystals, soluble in ether and in alcohol. It melts at 127·5° to a colourless liquid, which does not solidify on cooling.

Methylazaurolic acid has not yet been obtained in the pure state.

W. C. W.

Acetoacetic Acids. By M. Ceresole (*Ber.*, **15**, 1871—1878).—These acids were isolated by saponification with potash, and treatment with sulphuric acid. The ethyl salt of the acid required is shaken up with a slight excess of a 2½ per cent. aqueous solution of potash until the ether is dissolved. The mixture is then left for 24 hours in the cold, acidified with sulphuric acid, and shaken with ether. The ethereal solution is carefully evaporated and the mixture of the new acid and unchanged salt treated with barium carbonate and water, the acid going into solution as barium salt, whilst the unaltered ethyl salt is removed by ether. The free acid is obtained from the barium salt by treatment with sulphuric acid, shaking with ether, evaporating the ethereal solution, and drying over sulphuric acid.

Acetoacetic Acid.—The free acid is a hygroscopic and very acid liquid, miscible with water in all proportions, and decomposing rapidly below 100° into carbonic anhydride and acetone. The silver and copper salts are less stable than the barium salt, which is very deliquescent, but stable in dilute solutions; on evaporation, it undergoes partial decomposition into acetone, barium carbonate, and carbonic acid; on boiling its aqueous solution, it was found that 1 molecule of carbonic anhydride was given off for each molecule of barium carbonate thrown down. The dried barium salt was analysed volumetrically with satisfactory results, the admixed barium carbonate being estimated and allowed for. By dry distillation, it yields barium carbonate and acetone.

Monomethylacetoacetic acid, prepared in the same way as acetoacetic acid, is a viscid liquid of similar properties. On boiling, it decomposes into carbonic anhydride and ethyl methyl ketone. The barium salt is very soluble, and gives no precipitate with silver nitrate; by dry distillation it yields ethyl methyl ketone. Nitrous acid converts the acid into nitrosomethyl acetone, melting at 74°.

Dimethylacetoacetic acid, dried over sulphuric acid, forms colourless crystals of agreeably acid smell, which are however undergoing continual decomposition, and deliquesce at once in the air. The barium salt can also be obtained crystalline, and possesses similar properties to those of the other two acids. On dry distillation, it yields the corresponding ketone.

Benzylacetoacetic acid is an acid and aromatic oil, sparingly soluble in water, and easily decomposable. Its barium salt is soluble, but not deliquescent, and yields benzyl acetone on dry distillation. Concentrated solutions give a precipitate with silver nitrate. With nitrous acid, nitrosobenzyl-acetone was obtained in white needles melting at

80—81°. The barium salts of all the acetoacetic acids give violet or brown colorations with ferric chloride.

The above acids were obtained from the corresponding ethyl salts by saponification, without any separation of ketone or acid. Their most prominent characteristic is their instability, and in this they agree with other ketone acids in which the carbonyl and carboxyl groups are only separated by one methylene or substituted methylene. Where, however, separation is effected by several methylene groups or by an aromatic residue, the ketone acids appear to be stable, as in the case of lævulic or benzoylbenzoic acids. J. K. C.

Formation of Saccharin and Lactic Acid from Sugars. By L. Cuisinier and H. Kiliani (*Bied. Centr.*, 1882, 703—705).—If maltose is treated with lime, a solution is obtained which after concentration yields coloured crystals of the composition $C_{12}H_{20}O_{10}CaO + H_2O$ (14·07 per cent. CaO). This salt has been termed maltate of lime, and is soluble in 100 parts hot water; from it, oxalic acid separates "maltic" acid, $C_6H_{10}O_5$, which melts at 95° and resembles saccharin; a 10 per cent. solution of the crystals has a dextrorotatory power of $[\alpha]_D = +63°$, which is reduced by dilute acids, but raised to $+73·5°$ by concentrated acetic acid. Maltic acid is readily soluble in water, glycerol, methyl, and ethyl alcohol, reduces alkaline copper solutions, and does not ferment. The salts are lævorotatory, and so is the free acid when first separated, but after being kept, and more rapidly when heated with an acid, it changes into a dextrorotatory modification; it is therefore analogous to saccharin, and the name *maltosaccharin* is proposed for it, in contradistinction to glucosaccharin.

Maltate of lime has also been obtained from lactose. In another communication, it is stated that glucose loses its rotatory power when in contact with alkalis in the cold, but not its reducing action on copper solutions; in the presence of alkalis, oxygen is absorbed from the air.

Kiliani prepares lactic acid from inverted sugar by the following process: 500 grams of cane-sugar are heated for three hours at 50° in a stoppered flask with 250 c.c. water and 10 of acid (3 parts H_2SO_4 with 4 parts H_2O); after cooling, 400 c.c. of soda solution (1 NaHO in 1 H_2O) are added in small portions, the whole being kept cool, but afterwards the mixture is to be heated to 70° until it only colours Fehling's solution green, then sulphuric acid is added in quantity equivalent to the soda present, and the freed lactic acid is separated by 93 per cent. alcohol, and converted into the zinc salt. Saccharin is also formed at the same time; it is converted by silver oxide and water into glycollic acid, together with a small quantity of formic and acetic acids. E. W. P.

γ-Hydroxybutyric Acid. By J. Frühling (*Monatsh. Chem.*, 3, 696—704).—Trimethylene glycol (100 parts) was heated with hydrobromic acid (70 parts) at 100° for five hours. The resulting *trimethylene bromhydrin*, $CH_2Br.CH_2.CH_2.OH$, forms a colourless liquid distilling between 98° and 112° under a pressure of 185° mm. Its sp. gr. at 20° is 1·5374. On treatment with potassium cyanide, it gives the corresponding cyanhydrin, which by the action of moderately concentrated hydrochloric acid or of potash is converted into *γ-hydroxybutyric acid*, thus completely confirming Saytzeff's formula,

$$CH_2(OH).CH_2.COOH,$$

for this acid. A. J. G.

Purification of Carbon Bisulphide. By E. Obach (*J. pr. Chem.* [2], **26**, 281—307).—The author finds that potassium permanganate is without action on pure carbon bisulphide or on the odorous impurities present in the commercial article, hydric sulphide excepted. Under the influence of daylight the pure bisulphide however yields some sulphuretted hydrogen, which is oxidised by permanganate, free sulphur passing into solution. In the case of impure bisulphide, treatment with permanganate causes a rise in the amount of dissolved solid matters, chiefly sulphur.

Effectual purification is obtained by first filtering the bisulphide through a dry paper filter to separate water and dirt, distilling from calcined lime, treatment of the distillate with about 5 grams per litre of dry powdered permanganate, then with metallic mercury until all free sulphur has combined, and lastly with mercuric sulphate. The bisulphide is then redistilled from calcium chloride, and must be kept in the dark. O. H.

Physical Properties of Carbon Oxysulphide. By Ilosvay (*Bull. Soc. Chim.* [2], **37**, 294—296).—Carbon oxysulphide can be freed from carbon bisulphide by passing the gas over a column of wood charcoal. The mean coefficient of expansion of the gas between 0° and 100° at constant volume is 0·0037317; at constant pressure, 0·0037908. The pressure necessary to liquefy the gas at different temperatures is given in the following table. The critical point is 105°.

Temperature :	0°	3·8°	10·7°	12·0°	17·0°	39·8°	41·2°	63·0°	69·0°	74·6°	85·0°.
Press. in atmos. :	12·5	15·0	17·5	19·6	21·5	44·0	45·0	59·0	65·0	74·0	80.

Liquid carbon oxysulphide is colourless, mobile, and highly refractive. It dissolves sulphur, and mixes with alcohol or ether, but not with water or glycerol. If the pressure is suddenly released, solid flakes are deposited, and persist for some time. These experiments show that the physical and chemical properties of carbon oxysulphide are intermediate between those of carbon bisulphide and carbon dioxide, and also afford further evidence that the coefficient of expansion of an easily liquefiable gas is greater than that of a gas difficult to liquefy.

Carbon oxysulphide, mixed however with mercaptan, carbon dioxide, hydrogen sulphide, &c., can be obtained by the action of sulphuric acid on potassium ethyl-thiocarbonate, CO_2SKEt.

C. H. B.

Dibromosuccinic Acid and Diamidosuccinic Acid. By A. Claus (*Ber.*, **15**, 1844—1851).—In the preparation of diethyl dibromosuccinate by Kekulé's method, after separation of the ethereal salt by adding water and evaporating the solution, a crystalline substance is left, which is the monoethylic salt of dibromo-succinic acid (m. p. 275°). Potassium and sodium ethyl-dibromosuccinates were formed by mixing alcoholic solutions of the alkalis with the acid, as crystalline groups, easily soluble in water: the silver salt is a white crystalline precipitate. With ammonia, the ammonium salt of dibromosuccinamic acid is obtained, but an attempt to isolate the acid failed. *Methyldibromosuccinic acid* is prepared in the same way as the ethyl compound. Its sodium and ethyl salts (m. p. 62·5°) were obtained in the usual way.

When ethyl dibromosuccinate is treated with sodium and ethyl bromide, only diethyl and black products are obtained; if, however, the sodium is replaced by zinc, the ethyl bromide is not attacked, and distils over unchanged, while one or two atoms of zinc enter into combination with the acid, without removing the bromine, and syrupy liquids are formed containing varying percentages of zinc. Heated with ethyl bromide in sealed tubes at above 150°, fumaric acid and zinc bromide are the chief products.

According to Lehrfeld, the amide of ethyl imidosuccinate is formed by the action of ammonia gas on an alcoholic solution of ethyl dibromosuccinate. The author, however, on repeating the experiment could obtain nothing beyond ethyl diamidosuccinate. Lindner, by treating free dibromosuccinic acid with ammonia, claims to have prepared the diamido-acid, which he states is insoluble in water, alcohol, and ether. This body the author was also unable to prepare, and he is of the opinion that Lindner worked with impure materials, and that the body he describes was perhaps produced from the glass of the sealed tube.

As regards bromamidosuccinic acid, traces of the diamido-acid are always formed, whether excess of ammonia or of dibromosuccinic acid be present. The pure acid can only be obtained by fractional precipitation of the silver salt, the middle fractions consisting of pure silver bromamidosuccinate. J. K. C.

Geometrical Formulæ of Maleic and Fumaric Acids deduced from their Products of Oxidation. By J. A. Le Bel (*Bull. Soc. Chim.* [2], **37**, 300—302).—By oxidation, fumaric acid yields racemic acid, and maleic acid yields mesotartaric acid. The only supposition which agrees with these and other known properties of the two acids is that the four hydrogen-atoms are in the same plane as the carbon-atoms and form a rectangle. In maleic acid, the rectangle is symmetrical about a plane perpendicular to the rectangle and bisecting it. The COOH-groups are at opposite ends of one side of the rectangle, and the H-atoms at opposite ends of the other side. In fumaric acid, the rectangle is symmetrical about its central point, the COOH-groups being one at each end of one diagonal, and the H-atoms one at each end of the other diagonal. It follows from these structures that maleic acid can yield only mesotartaric acid, whilst fumaric acid can yield only racemic acid. C. H. B.

Ethylic Methenyltricarboxylate and Ethylic Acetomalonate.

By M. CONRAD and M. GUTHZEIT (*Annalen*, **214**, 31—38).—*Ethylic methenyltricarboxylate*, $CH(COOEt)_3$, prepared by warming a mixture of ethyl chlorocarbonate, benzene, and ethyl sodium malonate, crystallises in needles or prisms which melt at 29°, and boil at 253°. Its sp. gr. at 19° is 1·10 compared with water at 15°. The crystals are soluble in ether and alcohol. On saponification, it yields malonic acid. Methenyltricarboxylic acid could not be isolated.

Ethylic acetomalonate described by Ehrlich (*Ber.*, **7**, 892) decomposes on saponification, forming alcohol, acetone, carbonic and acetic acids.

W. C. W.

Ethylic Ethenyltricarboxylate. By C. A. BISCHOFF (*Annalen*, **214**, 38—44).—The preparation of the ethylic salt of ethenyltricarboxylic acid has been described by Full (*Ber.*, **14**, 752). This compound is a colourless liquid (b. p. 278°) soluble in alcohol and ether. Its sp. gr. at 17° is 1·1089 compared with water at 15°. It is readily saponified by a solution of soda, and on decomposing the sodium salt, *ethenyltricarboxylic acid*, $COOH.CH_2.CH(COOH)_2$ is obtained in prismatic crystals soluble in alcohol, ether, and water.

The acid melts at 159°, decomposing into carbonic and succinic acids. Barium tri-ethenylcarboxylate crystallises in white prisms sparingly soluble in hot water. The zinc salt contains 2 mols. H_2O. It is less soluble in hot than in cold water.

W. C. W.

Ethylic Monochlorethenyltricarboxylate. By C. A. BISCHOFF (*Annalen*, **214**, 44—53).—When a current of chlorine is passed through warm ethylic ethenyltricarboxylate, the monochlorinated derivative,

$$CCl(COOEt).CH_2.COOEt,$$

is produced. This substance is purified by distillation under reduced pressure. It boils at 205—215° under 160 mm. pressure. Continued boiling with dilute hydrochloric acid splits up the ethereal salt into carbonic and fumaric acids. On saponification with an aqueous solution of potash, it yields malic acid (m. p. 130—135°), which appears to be identical with the malic acid which Loydl (*ibid.*, **192**, 80) obtained from fumaric acid. Treatment with alcoholic potash converts ethylic monochlorethenyltricarboxylate into ethoxyethenyltricarboxylic acid.

W. C. W.

Ethereal Salts of Propenyltricarboxylic Acid. By C. A. BISCHOFF (*Annalen*, **214**, 53—58).—*Ethylic propenyltricarboxylate*, $CHMe(COOEt).CH(COOEt)_2$, prepared by the action of ethyl α-bromopropionate on an alcoholic solution of the sodium compound of ethyl malonate, is a colourless oil (b. p. 270°) miscible with alcohol and ether. Its sp. gr. at 16° is 1·092. *Diethylic monomethyl propenyltricarboxylate*, $COOEt.CH(COOEt).CHMe.COOMe$, is obtained when methylic α-chloropropionate is substituted for ethyl bromopropionate in the above reaction. This liquid boils at 267°. It is soluble in alcohol and ether. Its sp. gr. is 1·079 at 15° compared with water at 4°. *Propenyltricarboxylic acid* melts at 146°, splitting up into carbonic and pyrotartaric acids and alcohol. The barium salt, $Ba_3(C_6H_5O_6)_2$ is sparingly soluble in water.

W. C. W.

Ethylic Propyl- and Isopropyl-ethenyltricarboxylates. By G. Waltz (*Annalen*, **214**, 58—61).—*Ethylic propylethenyltricarboxylate*, $CPr(COOEt)_2.CH_2.COOEt$, prepared by the action of sodium ethylate and propyl iodide on ethylic ethenyltricarboxylate, is a colourless oil miscible with ether and alcohol. It boils at 280° with partial decomposition. Its sp. gr. at 13° = 1·052. The free acid,

$$CPr(COOH)_2.CH_2.COOH,$$

forms lustrous needles (m. p. 148°) soluble in water, ether, and alcohol. A solution of ammonium propylethenyltricarboxylate gives a crystalline precipitate with barium, silver, and lead salts. Zinc, calcium, iron, and copper are precipitated from hot solutions. The acid begins to decompose at its melting point, yielding carbonic, propylsuccinic, and traces of butyric acids.

Propylsuccinic acid, $CHPr(COOH).CH_2.COOH$, melts at 91°. The neutral solution gives a white crystalline precipitate with silver and lead salts.

Ethylic isopropylethenyltricarboxylate was not obtained in a state of purity. The impure compound decomposes at 180° forming isopropylsuccinic acid (m. p. 114°). W. C. W.

Ethylic Isallylenetetracarboxylate. By C. A. Bischoff (*Annalen*, **214**, 61—67).—The preparation and properties of isallylenetetracarboxylic acid, $(COOH.CH_2)_2C(COOH)_2$, and of its ethyl salt have already been described by the author (Abstr., 1881, 156). The following salts were prepared:—$C_7H_4Ag_4O_8$, somewhat soluble in hot water: $C_7H_4Pb_2O_8 + H_2O$ and $C_7H_{10}Zn_2O_8$ are crystalline salts. The *tricarballyllic acid*, obtained by heating isallylenetetracarboxylic acid, is identical with the acid described by Miehle (*Annalen*, **190**, 325). W. C. W.

Tetrethylic Acetylenetetracarboxylate. By M. Conrad and C. A. Bischoff (*Annalen*, **214**, 68—72).—The ethereal salt,

$$(COOEt)_2CH.CH(COOEt)_2,$$

formed by the action of ethyl monochloromalonate on ethyl sodium malonate, crystallises in needles (m. p. 76°) soluble in alcohol, ether, and benzene. It boils at 305° with partial decomposition. When heated with hydrochloric acid or with alkalis, it splits up into alcohol, carbonic and ethenyltricarboxylic acids. W. C. W.

Diethylic Acetylenetetracarboxylate. By M. Guthzeit (*Annalen*, **214**, 72—75).—When an alcoholic solution of tetrethylic acetylenetetracarboxylate is treated with potash at 0°, the diethyl salt,

$$COOEt.CH(COOH).CH(COOH).COOEt + \tfrac{1}{2}H_2O,$$

is deposited. This substance forms deliquescent plates soluble in alcohol and ether. It melts at 132° with decomposition, and at 180° it splits up into carbonic and succinic anhydrides and ethyl succinate. W. C. W.

Tetrethylic Dicarbontetracarboxylate. By M. Conrad and M. Guthzeit (*Annalen*, **214**, 76—80).—Tetrethylic dicarbontetracarboxylate, $(COOEt)_2C : C(COOEt)_2$, prepared by warming an alcoholic solution of sodium ethylate with ethyl chloromalonate, crystallises in monoclinic plates soluble in ether and in boiling alcohol. It melts at 58° and boils at 325—328° with partial decomposition. On saponifying it with potash solution, the potassium salt, $C_6H_2O_8K_2$, is obtained in monoclinic prisms. The lead, zinc, and calcium ($C_6O_8Ca_2 + 7H_2O$) salts are crystalline; the silver salt, $Ag_4C_6O_8$, explodes when heated. The free acid is an unstable compound. It decomposes below 100°.

W. C. W.

Action of Potassium Nitrite on Mucobromic Acid. By H. B. Hill and C. R. Sanger (*Ber.*, **15**, 1906—1910).—The reaction took place in alcoholic solution; on gently warming it, carbonic anhydride was given off, and a reddish-yellow potassium salt, $K_2C_3HN_3O_7$, separated out in small flat needles. This salt is easily soluble in cold water, sparingly in dilute alcohol. When dry, it explodes on warming or when struck, also on moistening it with concentrated mineral acids. It is decomposed by water at 40°, but can be crystallised unchanged from dilute potash. When heated with strong potash, a new and very unstable compound is obtained, the composition of which has not yet been determined. By the action of bromine on $K_2C_3HN_3O_7$ suspended in carbon bisulphide, the compound $C_3HBr_3N_2O_5$ was produced. It crystallises like ammonium chloride, and is easily soluble in carbon bisulphide, sparingly in cold chloroform. On heating $K_2C_3HN_3O_7$ with water or dilute alcohol to 40—60°, an evolution of carbonic anhydride, hydrocyanic acid, and nitrous acid takes place, and, on evaporating the solution, crystals of the composition $KC_3H_2NO_4,H_2O$ were obtained which lost their water over sulphuric acid. This salt explodes on heating. It is easily soluble in water, sparingly in alcohol.

From sodium nitrite and mucobromic acid, the corresponding sodium salt, $Na_2C_3HN_3O_7$, could not be obtained, but, on heating the solution to 40—60°, the compound $NaC_3H_2NO_4,H_2O$ was formed and crystallised out on cooling. The calcium salt, $Ca(C_3H_2NO_4)_2,4H_2O$, crystallises in sparingly soluble prisms. Salts of barium, lead, copper, and silver have also been prepared. Attempts to prepare the free acid have as yet been unsuccessful.

The action of potassium nitrite on ethyl mucobromate was found to differ from its action on the free acid, a compound of the formula $KC_6H_6NO_6$ being formed. A. K. M.

Alkylthiosulphuric Acids. By W. Spring and E. Legros (*Ber.*, **15**, 1938—1940).—The sodium salts of ethyl- and methyl-thiosulphuric acids, prepared by digesting equivalent quantities of the alcoholic iodides with sodium thiosulphate, have already been described (*Ber.*, **7**, 646 and 1162; also *Ber.*, **15**, 946). The authors have continued their experiments, and have succeeded in preparing sodium salts of propyl-, primary isobutyl-, and amyl-thiosulphuric acids. All three crystallise well, and are soluble in water and in alcohol. When decomposed, they yield disulphides of the radicles, sodium sulphate and sulphurous anhydride. Attempts to make alkylthiosulphates containing other radicles have been unsuccessful. With allyl and isopropyl iodides, the authors obtained allyl and isopropyl bisulphides, together with sodium sulphate and sulphurous acid. Chloroform, ethylidene dichloride, and some other similarly constituted bodies also yielded negative results.

The conclusions drawn by the authors are that the only alkylthiosulphates which can exist are those in which the alkyl-group is primary and saturated, and that they are the more easily formed the simpler the organic radicle. It also seems that compounds do not exist in which more than one S_2O_3Na group is joined to one carbon-atom.

Propyl bisulphide, $(C_3H_7)_2S_2$ (normal and iso-), butyl bisulphide, $(C_4H_9)_2S_2$, and amyl bisulphide, $(C_5H_{11})_2S_2$, which were obtained in course of the research, are liquids having the characteristic odour and other properties belonging to this class of compounds.

A. K. M.

Action of Phosphorus Pentachloride on Acid Amides. Part II. By O. Wallach (*Annalen*, **214**, 193—327).—*Action of Phosphorus Pentachloride on the Amides of Monobasic Acids in which one Hydrogen-atom of the* NH_2 *group has been replaced by a Hydrocarbon Radicle.*—The imidochloride, $CMeCl\colon NC_6H_4Me$, obtained by the action of phosphorus pentachloride on acetoparatoluidide, and the amines derived from this compound, have already been described (this Journal, 1877, i, 91). Analogous products can be prepared from acetorthotoluide. On carefully heating the imidochloride obtained in this way, a base, $C_{18}H_{19}ClN_2$ (m. p. 52°), is formed. *Orthotolylacetamidine*, $NHC_7H_7.CMe\colon NC_7H_7$, melts at 69°; the corresponding para-compound melts at 120°, and the mixed orthopara-amidine melts at 142°. The imidochloride of benzoylbenzyl sulphamide, $CPhCl\colon NSO_2Ph$ (Abstr., 1878, 669) melts at 80°, and at a higher temperature decomposes into benzonitrile and benzenesulphonic chloride, instead of yielding a new base. By the action of aniline on the chloride, *phenylsulphophenyl benzamidine*, $NHPh.CPh\colon NSO_2Ph$, is produced. This amidine crystallises in plates (m. p. 139°), soluble in alcohol and benzene. On distillation it decomposes into diphenylamine, benzonitrile, and phenyl sulphide.

Tolylsulphophenylbenzamidine, $C_6H_4Me.NH.CPh\colon NSO_2Ph$, forms monoclinic crystals (m. p. 145°), soluble in alcohol and benzene. On distillation, tolylphenylamine is produced.

Benzenesulphodiphenylamine, $PhSO_2.NPh_2$, prepared by heating a mixture of benzene sulphochloride and diphenylamine at 200°, crystallises in silky needles (m. p. 124°), soluble in alcohol, ether, and benzene. *Benzene sulphanilide*, $PhSO_2.NHPh$, forms octahedra, which melt at 102°. It is completely decomposed by heating at 220° with lead dioxide.

The products of the action of phosphorus pentachloride on mono- and tri-chloracetanilide, and on mono-, di-, and tri-chloracetethylamide, have been previously described by Kamenski (Abstr., 1880. 547).

The amidine, $C_4H_3O.C(NHEt)\colon NEt$, prepared by distilling ethylamine pyromucamide, $C_4H_3O.CONHEt$, with phosphorus pentachloride (Abstr., 1881, 714), boils at 240°. It forms a crystalline platinochloride. When phosphorus pentachloride and formanilide are brought together, carbonic oxide and hydrochloric acid are evolved, leaving a mixture of phosphorus oxychloride and diphenyl-formamidine, $NHPh.CH\vdots NPh$, melting at 137°.

II. *Action of Phosphorus Pentachloride on those Amides of Monobasic Acids in which the Hydrogen of the* NH_2*-group has been completely replaced by Hydrocarbon Radicles.*—No new bases were obtained by treating acetodiethylamide, $MeCONEt_2$ (b. p. 185°) or diphenyl benzamide, $PhCONPh_2$ (m. p. 176°) with phosphorus pentachloride. *Diphenylacetamide*, $MeCONPh_2$ (m. p. 101°), yields a base which was not obtained in a state of purity. From *acetomethylanilide*,

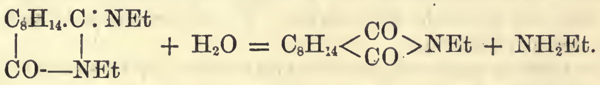
$$MeCONMePh,$$

a base is derived which probably has the composition $C_{17}H_{17}ClN_2$. Acetopiperidide when treated with phosphorus pentachloride yields the chloride $CMeCl_2.NC_5H_{10}$. The following reaction takes place when phosphorus pentachloride acts on diethylformamide :—

$$HCONEt_2 + PCl_5 = POCl_3 + CHCl_2.NEt_2, \text{ and}$$
$$2CHCl_2.NEt_2 = C_{10}H_{19}CN_2 + 3HCl.$$

III. *Action of Phosphorus Pentachloride on the Amides of Dibasic Acids.*—*Camphorethylimidethylimidine*, $C_{14}H_{24}N_2O$, prepared by heating ethylamine camphorate with phosphorus pentachloride (Abstr., 1881, 284), is decomposed by hydrochloric acid at 200° into ethylamine hydrochloride and camphoric ethylimide.

This decomposition may be represented by—



$$\begin{array}{l} C_8H_{14}.C\vdots NEt \\ \;\;|\qquad\;\; | \\ CO—NEt \end{array} + H_2O = C_8H_{14}{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}NEt + NH_2Et.$$

Camphor ethylimidethylimidine can be prepared synthetically by treating the product of the action of phosphoric chloride on camphor ethylimide with ethylamine (Abstr., 1881, 285).

IV. *Action of Phosphorus Pentachloride on the Amides of Oxalic Acid.*—An account of the substituted oxamides and formamides has been previously published (*Ber.*, **14**, 735—751; this Journal, Abstr., 1881, 717). Chloroxalethyline and many of its derivatives have also been described (Abstr., 1880, 546—547). By the action of bromine on a solution of chloroxalethyline in chloroform, *chloroxalethyline hydrobromide*, $C_6H_9ClN_2,HBr$, and *dibromide*, $C_6H_9ClN_2,Br_2$, are produced. The crystals of the hydrobromide are colourless; those of the dibromide have a deep red colour. A mixture of *bromochloroxalethyline hydrobromide*, $C_6H_8ClBrN_2,HBr$, and *bromochloroxalethyline dibromide*, $C_6H_8ClBrN_2,Br_2$, is formed when bromine acts on a solution of chloroxalethyline dibromide in chloroform. Bromochloroxalethyline dibromide crystallises in red needles or prisms melting at 113°. It is soluble in alcohol and ether, and sparingly soluble in chloroform. The hydrobromide forms bright red monoclinic prisms (m. p. 133°), which dissolve freely in chloroform. Both the hydrobromide and the dibromide are decomposed by hot water, yielding *bromochloroxalethyline*, $C_6H_8BrClN_2$. From this solution, the free base is obtained by adding an alkali to the solution, and extracting the mixture with chloroform. On evaporating the extract, the base remains as an oily liquid, which slowly solidifies to a crystalline mass. The *hydrochloride*,

$$C_6H_8BrClN_2,HCl,$$

and the nitrate form prisms containing water of crystallisation. The *platinochloride*, $(C_6H_8BrClN_2,HCl)_2,PtCl_4$, and the *silver salt*,

$$(C_6H_8BrClN_2)_2,AgNO_3,$$

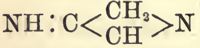
can be recrystallised from alcohol.

Chloroxalethyline is decomposed by dilute sulphuric acid at 240°, with formation of ammonia and ethylamine. On oxidation with chromic acid, ethyloxamide, oxalic and (probably) ethyloxamic acids are produced. When a mixture of chloroxalethyline and lime is distilled, pyrroline, ammonium chloride, and *para-oxalmethyline*, $C_4H_6N_2$, are formed. This base crystallises in silky needles, melting at 136°.

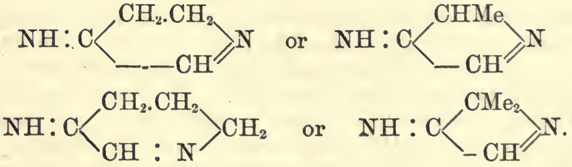
Dioxalethyline, $C_{12}H_{18}N_4$, prepared by the action of sodium on chloroxalethyline, is an oily liquid which boils above 300°. On distillation with lime, oxalethyline yields pyrroline, hydrocyanic acid, paraoxalmethyline, and ammonium chloride. When oxalethyline is heated with dilute sulphuric acid at 240°, it yields ethylamine, and on oxidation with potassium permanganate it splits up into ammonia, acetic and oxalic acids.

The derivatives of oxalmethyline and propyline have been previously described (Abstr., 1881, 572).

Chloroxalamyline, $C_{12}H_{21}ClN_2$, prepared by the action of phosphoric chloride on di-amyloxamide (m. p. 128°), is a liquid boiling at 267—270°. It is not miscible with water. The hydrochloride and platinochloride are crystalline.

Oxalmethyline has been shown to be identical with *methyl-glyoxaline*,  $NH\colon C\Big<{CH_2 \atop CH}\Big>N$ (Abstr., 1882, 821), but oxalethyline and oxalpropyline are not identical with propyl- and amyl-glyoxalines.

The constitutional formulæ of these two oxalines is either—

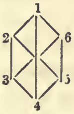


W. C. W.

Mannitine, a New Alkaloïd obtained from Mannitol. By S. Scichilone and A. Denaro (*Gazzetta*, **12**, 416—424).—This base, $C_6H_8N_2$, is formed by distilling mannite with ammonium chloride, the reaction, which takes place according to the equation, $C_6H_8(OH)_6 + 2(NH_3,HCl) = 2HCl + 6H_2O + C_6H_8N_2$, being analogous to that of sal-ammoniac on ethyl alcohol, by which Berthelot obtained ethylamine (*Ann. Chim. Phys.* [3], **38**, 63), and to that of the same salt on glycerol, by which Étard obtained glycoline, $C_{10}H_{10}N_2$

(Abstr., 1881, 708). The distillate is a red-brown liquid, having a strong but pleasant odour, and containing a few drops of oil, the quantity of which is increased on adding strong potash-ley; and on agitating the liquid several times with ether, separating the ethereal solution by a tap-funnel, and distilling it, the mannitine remains in the form of a brown strong-smelling oil soluble in hydrochloric acid, and precipitated therefrom by potash. It was purified by converting it into hydrochloride, and decomposing that salt with potash, and then gave by analysis 66·77 per cent. C, 6·32 H, and 25·84 N, agreeing nearly with the formula $C_6H_8N_2$, which requires 66·67 C, 7·40 H, and 25·93 N. Its vapour-density, determined by V. Meyer's method, is 3·82 (air = 1), the formula requiring 3·74. Mannitine boils without alteration at 170° (bar. 760 mm.). It dissolves in alcohol, in ether, and to a perceptible amount in water; it has a very bitter taste, and exhibits the following reactions: with *sodium phosphomolybdate*, immediate orange-yellow precipitate, soluble in ammonia; with *potassio-mercuric iodide*, reddish-yellow amorphous precipitate; with *iodised potassium iodide*, reddish-yellow, insoluble in dilute hydrochloric acid; with *mercuric iodide*, flesh-coloured precipitate soluble in ammonium chloride; with *Fröhde's reagent*, indistinct yellow coloration; with *auric chloride*, black precipitate. H. W.

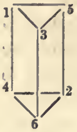
Benzene Formulæ. By A. LADENBURG (*Ber.*, **15**, 1782—1783).—According to Claus, the best expression of the atomic relationship in benzene is shown by the appended figure.



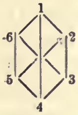
Claus meets the objection raised by the author, that when the atomic linking only is taken into consideration, the combinations 1 : 2, 1 : 4, and 1 : 6, are equal, by quoting another of his statements, that the geometrical relationships of a formula must represent corresponding relative attractions of the atoms, and that therefore 1 : 4, as representing a diagonal, cannot be equal to 1 : 2, which expresses a side. To this the author replies that such an assumption necessitates the hypothesis that one of the combining affinities of the carbon-atom is different from the rest. As such a hypothesis is opposed to all known facts, he considers the above graphic formula untenable.

J. K. C.

Benzene Formulæ. By R. MEYER (*Ber.*, **15**, 1823—1828).—The so-called "diagonal" formula, defended by Claus, has been represented by the author as only allowing the possibility of two isomeric bisubstitution products: this statement being denied by Claus, the author proceeds to explain his reasons. In the prism formula, the positions represented by the two kinds of sides, differ from one another in other respects than in their functions as sides of triangles or quadrilaterals. For example, the two carbon-atoms 1 and 3, besides being in direct combination, are also bound indirectly through 5, whilst 1 and 4 are indirectly bound by two atoms, 3 and 6 or 5 and 2.



In other words, the difference of the positions (1, 3) and (1, 4) is not a geometrical one only, but expresses also a difference in the atomic linking. On the other hand, in the diagonal formula—



the indirect communication between (1, 2) is exactly the same as between (1, 4), for instance, (1, 6, 3, 2) and (1, 6, 3, 4), &c.

To this Claus answers that the diagonal linkings have a different value from the ordinary or side bonds, but this assumption the author regards as arbitrary and as introducing a new definition into the science. The objection to the prism formula, that it does not express the well-known tendency of ortho-compounds to form " inner anhydrides," becomes groundless, when it is recollected that a similar objection was raised against the formulæ of quinones.

Claus considers that it is more than probable that the formula of naphthalene is unsymmetrical, as it would be if represented by the diagonal formula. If such were the case, however, there would exist four isomeric mono-derivatives, whilst as yet only two have been discovered. Molecules like those of benzene and naphthalene, which possess such an extraordinary degree of stability, must exhibit a very stable equilibrium in the position of the various component atoms, and this would be best attained by a symmetrical structure.

J. K. C.

Isodurene, Isodurylic Acids, and the Third Trimethylbenzene. By O. JACOBSEN (*Ber.*, **15**, 1853—1858).—Isodurene is obtained by the action of methyl chloride and aluminium chloride on mesitylene (b. p. 195°). Dibromisodurene (m. p. 209°) is formed from this by treating it with excess of bromine in presence of iodine: it crystallises from hot alcohol in long needles. The dinitro-compound crystallises from the same solvent in colourless prisms melting at 156°. The sulphonic acid was obtained in fine plates, and its barium and sodium salts prepared: the corresponding amide (m. p. 118°) may be obtained in thin needles from its aqueous solution, by the usual method. By fusing sodium isodurenesulphonate with potash, isodurenol is obtained as a crystalline mass melting at 108°.

Isodurylic Acids.—Isodurene is boiled for some time with dilute nitric acid, and after removal of the nitro-compounds the liquid is steam-distilled. From the mixture of the three acids, the α-acid may be separated as crystalline barium salt, the other two acids being left in the uncrystallisable mother-liquor: in its properties it agrees with Bielefeldt's description. The remaining acids are precipitated by hydrochloric acid, and separated by crystallisation from petroleum. The less soluble, termed β-isodurylic acid, is obtained in hard shining prisms, melting at 151°: its calcium salt crystallises from water in a mass consisting of fine needles. On evaporating the petroleum solution, γ-isodurylic acid (m. p. 84—85°) is left behind in crystalline crusts, and may be purified from adhering β-acid by taking advantage of the greater solubility of its calcium salt. It is precipitated from the latter in flakes, and crystallises from alcohol and water in needles. The barium and potassium salts are uncrystallisable.

By the oxidation of isodurenesulphonamide with potassium permanganate, sulphaminisodurylic acids are formed, corresponding to the above β- and γ-acids.

The three isodurylic acids were distilled with lime in order to ascertain their constitution. α-Isodurylic acid yields the third trimethylbenzene called by the author *hemellithene:* it is therefore represented as $C_6H_2Me_3COOH$ [COOH : Me : Me : Me = 1 : 3 : 4 : 5]. From the β-acid [COOH : Me : Me : Me = 1 : 2 : 4 : 6] pure mesitylene was obtained, and pseudocumene from the γ-acid, [COOH : Me : Me : Me = 1 : 3 : 5 : 6]. Hemellithene, $C_6H_3Me_3$ [Me : Me : Me = 1 : 2 : 3], was obtained pure from its sulphamide by heating it with hydrochloric acid at 200°. It boils at 168—170°. Tribromhemellithene crystallises from alcohol in fine needles, melting at 245°. *Hemellithenesulphonic acid* crystallises well in six-sided plates, and its amide in short transparent prisms, melting at 196°. Coal-tar cumene does not contain hemellithene. J. K. C.

Action of Aluminium Chloride on the Monohalogen Derivatives of Benzene. By O. v. Dumreicher (*Ber.*, **15**, 1866—1870).—Chlorobenzene is not acted on even when boiled for several days with aluminium chloride; with bromobenzene, however, a lively reaction sets in above 100°, hydrochloric and hydrobromic acids are evolved in large quantities, and after eight or ten hours a black mass is formed. When this is steam-distilled, and the oil fractioned, pure benzene, and two dibromobenzenes, para and liquid, together with unaltered bromobenzene, are obtained, the benzene and dibromobenzene being formed in equal molecular weights.

Iodobenzene reacts with aluminium chloride at 80°, the liquid becoming violet from separation of iodine. No hydriodic acid is given off, the products of the reaction being benzene and diiodobenzene, with large quantities of iodine. The benzene formed is very large in comparison with the diiodobenzene, and the latter consists chiefly of the para-compound. It appears that the hydriodic acid formed decomposes at once with iodobenzene into free iodine and benzene.

The author explains the action of aluminium chloride on bromobenzene by the following equations:—

(1.) $Al_2Cl_6 + C_6H_5Br = BrCl + Al_2Cl_5.C_6H_5$.
(2.) $C_6H_5Br + BrCl = C_6H_4Br_2 + HCl$.
(3.) $Al_2Cl_5(C_6H_5) + HCl = Al_2Cl_6 + C_6H_6$. J. K. C.

Metatoluidine. By A. EHRLICH (*Ber.*, **15**, 2009—2012).—The greater portion of this paper describes improvements in the details of the methods for the preparation of metatoluidine proposed by Beilstein and Kuhlberg and by O. Widman.

Metatoluylglycocine is obtained as a non-crystalline mass by the action of 2 mols. metatoluidine in ethereal solution on 1 mol. monochloracetic acid. The *copper salt*, $(C_9H_{10}NO_2)_2Cu,2H_2O$, forms brilliant grass-green plates. *Ethylmetatoluylglycocine*, $CH_2(NH.C_7H_7).COOEt$ (ethyl metatoluylamidoacetate), is obtained by the action of metatoluidine on ethyl chloracetate; it crystallises in flat plates melting at 68°, and is readily soluble in alcohol and ether, but only sparingly in hot water. By the action of ammonia in alcoholic solution, it is converted into the amide of toluylglycocine crystallising in long spear-shaped needles. A. J. G.

Rosaniline-derivatives. By E. NOELTING (*Bull. Soc. Chim.* [2], **37**, 390—392).—The introduction of the NO_2-group into the halogen-derivatives of the hydrocarbons of the benzene series renders the halogen more easily displaceable. Ammonia, for example, has no action on monochlorobenzene, but yields dinitraniline by its action on monochlorodinitrobenzene. The chloro-derivatives of the benzene series are without action on rosaniline, but the chloronitro-derivatives form substitution-products which give various shades of brown and maroon. The author has obtained such compounds by acting on rosaniline with [1 : 2 : 4] chlorodinitrobenzene chlorotrinitrobenzene, and a mixture of chloronitronaphthalenes obtained by treating monochloronaphthalene with a mixture of nitric and sulphuric acids.

1 mol. rosaniline is heated with 1 mol. of the chloronitro-derivative, *e.g.*, chlorodinitrobenzene, and some glacial acetic acid in an oil-bath at 180—200° for five or six hours. When cold, the product is extracted with very dilute acid to remove unaltered rosaniline, then dried and treated with benzene to remove excess of the chloride and resinous compounds. The residue consists of the hydrochloride of the new base, mixed with carbonaceous products. The hydrochloride and the sulphate are insoluble in water, but soluble in alcohol; the acetate is soluble both in water and in alcohol. The hydrochloride is extracted from the residue by means of alcohol, and the solution mixed with sodium hydroxide, which precipitates the base in the form of a paste. The base is dissolved in dilute acetic acid, and can then be used for dyeing. On silk, it yields a very fast violet garnet colour, approaching maroon. The dried base forms an amorphous black powder; the salts are green, with metallic lustre, but are not crystalline.

The new colouring matter formed from chlorodinitrobenzene is in all probability dinitrophenyl-rosaniline formed in accordance with the equation $C_{20}H_{19}N_3,H_2O + C_6H_3Cl(NO_2)_2 = C_{20}H_{18}N_3.C_6H_3(NO_2)_2,HCl + H_2O$. Attempts to introduce two or three dinitrophenyl-groups were unsuccessful. Any excess of chlorodinitrobenzene always remained unaltered. No satisfactory results were obtained by heating neutral or alkaline alcoholic solutions in sealed tubes. It is worthy of note that the introduction of two nitroxyl-groups changes the colour of monophenylrosaniline from violet to maroon.

Phenylrosaniline is converted into a sulphonic acid by the action of strong sulphuric acid. Dinitrophenylrosaniline is carbonised without formation of sulphonic acid. The sulphonic acid may, however, be obtained by the action of chlorosulphonic acid SO_3HCl. It forms salts which yield colours very similar to those of the original base.

Nitronaphthylrosaniline has a much more violet colour than the nitrophenyl-derivative. C. H. B.

Azylines. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **3**, 705—714).—The authors apply the term *azylines* to a series of bases obtained by the action of nitric oxide on tertiary amines, and in which the tetravalent-group $>N-N<$ is contained in union with benzene nuclei. At present, tertiary azylines of the aromatic series alone have been obtained. These compounds are crystalline, and of red colour; dissolve in hydrochloric acid to fine purple liquids, and in acetic acid to green solutions, from which they are reprecipitated in the amorphous form on adding water. They yield crystalline compounds with the chlorides of platinum, iron, gold, &c. The picrates are crystalline and sparingly soluble. When heated with alcoholic iodides at 100°, the azylines form ammonium compounds. With nitrous acid, nitroso-compounds are formed; as these give Liebermann's colour-reaction with phenol and sulphuric acid, the tertiary nature of the compounds is rendered highly probable. If treated with stannous chloride or with hydriodic acid and phosphorus, the azylines yield unstable hydro-compounds, from which crystalline platinochlorides can be prepared.

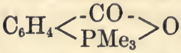
Dimethylanilineazyline, $NMe_2.C_6H_3\colon N.N\colon C_6H_3.NMe_2$ (m. p. 266°), has been already described (Abstr., 1881, 161, the formula, $C_9H_{12}N_2$, there ascribed to it being due to an error in analysis). Its formation is represented by the equation $2C_8H_{11}N + 2NO = 2H_2O + C_{16}H_{18}N_4$. On oxidation, it yields oxalic acid and carbonic anhydride. The *picrate* is obtained as an alcoholate, $C_{16}H_{18}N_4,C_6H_3(NO_2)_3O + C_2H_6O$, in brilliant leaf-green needles.

Diethylanilineazyline, $C_{20}H_{26}N_4$ (m. p. 170°), forms red needles soluble in chloroform and hot alcohol, sparingly soluble in cold alcohol. The *picrate*, $C_{20}H_{26}N_4.2[C_6H_3(NO_2)_3O]$, crystallises in yellow needles.

Dipropylanilineazyline, $C_{24}H_{34}N_4$, crystallises in red tables of the rhombic system, melting at 90°. The crystals were measured by Scrauf, and gave axial relations $a : b : c = 1 : 0{\cdot}629 : 0{\cdot}913$. The most important faces are $\bar{1}01 : 100 : 110 : 001$.

Dibutylanilineazyline, $C_{28}H_{42}N_4$, crystallises in needles melting at 158°.

Diamylanilineazyline, $C_{32}H_{54}N_4$ (m. p. 115°), forms red spear-shaped crystals, soluble in hot alcohol. It dissolves in concentrated hydrochloric acid, but is decomposed on boiling. A. J. G.

Trimethylphosphobenzobetaïne. By A. Michaelis and L. Czimatis (*Ber.*, **15**, 2018—2020).—Trimethylphosphobenzobetaïne is obtained as chloride by the oxidation of paratolyltrimethylphosphonium chloride with potassium permanganate at a temperature of 55°. The *chloride* forms short, thick, brilliant, colourless prisms of the formula $C_6H_4(COOH),PMe_3Cl$; it is insoluble in ether, soluble in hot alcohol, and very soluble in water. It is decomposed by heat. The *platinochloride* is obtained as a light yellow crystalline precipitate. The free *betaïne*,  $C_6H_4<\substack{-CO-\\PMe_3}>O,3H_2O$, is obtained by neutralisation of a solution of the chloride; it crystallises in rhombohedrons, and effloresces readily. It does not give salts with bases, but with acids it gives well characterised compounds. The acetate crystallises in slender needles of nacreous lustre, the nitrate in needles. With excess of dilute sulphuric acid, it gives an acid salt also crystallising in needles. On heating the chloride with potash, it is decomposed according to the equation—

$$C_6H_4(COOH).PMe_3Cl + KOH = C_6H_5.COOH + PMe_3O + KCl.$$

By the action of potassium permanganate, on the addition-product of ethylene bromide and dimethyltolylphosphine, a compound,

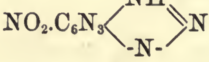
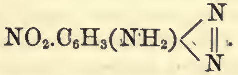
$$C_6H_4(COOH).PMe_2O,$$

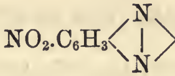
is obtained; it crystallises in colourless prisms of faint acid taste, melts at 243°, and can be sublimed with but little decomposition.

A. J. G.

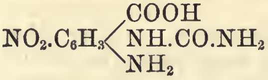
Formation and Decomposition of Acetanilide. By L. MEYER (*Ber.*, **15**, 1977—1978).—With regard to the formation of acetanilide, the results obtained at 130° by Steudel in the author's laboratory agree with those of Menschutkin; at 155° a complete reaction never takes place, but in the reverse reaction an important difference occurs. According to Menschutkin, the incompleteness of the reaction is due to the resulting water reacting on the acetanilide and partially decomposing it; but on heating acetanilide with water at 130° for some time, no trace of an acid reaction could be obtained, so that the incompleteness of the reaction cannot be due to that cause.

A. J. G.

Constitution of the Azimido-compounds. By P. GRIESS (*Ber.*, **15**, 1878—1882).—Under the above definition, the author includes those bodies which have so far been obtained only by the action of nitrous acid on aromatic orthodiamido-compounds, the first of which was prepared by Hofmann from orthodiamidonitrobenzene. Amongst others, two have been obtained by the author from β- and γ-diamidobenzoic acids. Two different views of the constitution of these bodies have been proposed, the one by Kekulé, and the other by Ladenburg. According to the former, Hofmann's compound would be represented by  $NO_2.C_6N_3<\substack{NH\\-N-}>N$, while Ladenburg assigns the formula  $NO_2.C_6H_3(NH_2)<\substack{N\\\|\\N}$.

The author's investigations, however, lead him to represent the above compound thus:  $NO_2.C_6H_3\Big\langle\begin{matrix}N\\|\\N\end{matrix}\Big\rangle NH$, and he bases his view on the following facts:—

β- and δ-nitrouramido-benzoic acids,



$$NO_2.C_6H_3\left\langle\begin{matrix}COOH\\NH.CO.NH_2\\NH_2\end{matrix}\right.$$

	β.	δ.
COOH	(1)	(1)
$NH.CO.NH_2$	(3)	(4)
NH_2	(4)	(3)

when heated to boiling with concentrated potash-solution, are both converted into β-azimidobenzoic acid with formation of ammonia and carbonic anhydride.

According to Kekulé's view, two isomeric acids would be formed; whilst, if Ladenburg's view were correct, the production of an azimidobenzoic acid would in this case be impossible.

When the above β- and δ-acids are treated with tin and dilute hydrochloric acid, they are converted into the corresponding diamido-acids, which by nitrous acid are converted into the same azimido-uramidobenzoic acid, a fact which only admits of explanation when the formula proposed by the author is employed.

In the same manner, γ-nitrouramidobenzoic acid can be converted into azimido-compounds; the α- and ε-acids, however, react in a totally different way. J. K. C.

Mixed Aromatic Tertiary Phosphines. By L. Czimatis (*Ber.*, **15**, 2014—2018).—These compounds were prepared from the homologues of phosphenyl chloride by the action of the zinc alkyls.

Paradimethyltolylphosphine, $C_6H_4Me.PMe_2$, is a colourless liquid of disagreeable odour; it boils at 210°, and does not solidify at — 10°; it has basic properties, and dissolves in acids; the chloride yields a yellow flocculent precipitate with platinum chloride. It does not oxidise on exposure to air, but is converted by mercuric oxide into *dimethyltolylphosphine oxide*, $C_6H_4Me.PMeO$, forming a thick oily liquid. With mercuric chloride, this yields the double salt,

$$C_6H_4Me.PMe_2O,HgCl_2,H_2O,$$

crystallising in slender silky needles, melting at 156°. Methyl iodide unites violently with dimethyltolylphosphine, yielding the phosphonium iodide, $C_6H_4Me.PMe_3I$; it crystallises in colourless needles melting at 255°, readily soluble in water and hot alcohol, sparingly in cold alcohol, insoluble in ether. With mercuric chloride it gives an unstable double salt crystallising in needles. The *hydroxide* is obtained by the action of silver oxide and water as a strongly basic deliquescent mass; on treatment with hydrochloric acid and platinum chloride, the platinochloride, $(C_6H_4Me.PMe_3Cl)_2,PtCl_4$, is obtained in orange-yellow plates melting at 230°. *Trimethyltolylphosphonium periodide*,

$$C_6H_4Me.PMe_3I_3,$$

obtained by the action of iodine on the iodide, crystallises in steel-blue rhombs, soluble in alcohol, and sparingly in benzene and ether. Dimethyltolylphosphine combines with benzyl chloride to an uncrystalline mass; the platinochloride, $(C_6H_4Me.PMe_2.ClC_7H_7)_2,PtCl_4$, melts at 226°.

Paradiethyltolylphosphine, $C_6H_4Me.PEt_2$, boils at 240°, and resembles the preceding compound. The methiodide crystallises in colourless needles melting at 137°; the platinochloride in clear yellow plates.

Dimethylxylylphosphine, $C_6H_3Me_2.PMe_2$, is a colourless liquid boiling at 230°.

Diethylxylylphosphine, $C_6H_3Me_2.PEt_2$, is a thickish liquid of faint colour, boiling at 260°. The methiodide (m. p. 90°), and ethiodide (m. p. 136°), form white crystalline powders, readily soluble in water and hot alcohol, insoluble in ether. Methyldiethylphosphonium platinochloride crystallises in cadmium-yellow rhombic plates, melting at 202°.

A comparison of the boiling points of the phosphines shows a rise of 20° for the entry of a methyl-group into the aromatic nucleus, whilst the difference of boiling points of the members of the series is 30°.

	B. p.		B. p.	Diff.
$C_6H_5.PMe_2$	190°	$C_6H_4Me.PMe_2$	210°	20°
$C_6H_5.PEt_2$	220	$C_6H_4Me.PEt_2$	240	20

	B. p.	Diff.
$C_6H_3Me_2.PMe_2$	230°	20°
$C_6H_3Me_2.PEt_2$............	260	20

Dimethylphenylphosphine and carbon bisulphide, when mixed in ethereal solution, give a compound of the formula $C_6H_5.PMe_2,CS_2$, crystallising in glistening red scales, soluble in carbon bisulphide, insoluble in ether. It melts in open tubes, with dissociation, at 97°; in closed tubes at 101°. It has basic properties, is dissolved by dilute acids, and reprecipitated by soda. The platinochloride,

$$(C_6H_5.PMe_2,HCl,CS_2)_2,PtCl_4,$$

is obtained as an amorphous pale yellow precipitate; on exposure to air, it loses carbon bisulphide, and is converted into dimethylphosphonium platinochloride. When the original compound is treated with dry hydrochloric acid or methyl iodide, it is decomposed, carbon bisulphide being eliminated and phosphonium compounds formed. Water decomposes the compound slowly at ordinary temperatures; rapidly on heating.

Dimethyltolylphosphine unites with carbon bisulphide, forming clear red plates of the formula $C_6H_4MePMe_2,CS_2$, melting at 110° in an open tube, at 116° in closed tubes. It closely resembles the preceding compound; the platinochloride, however, is more stable when exposed to the air.

Dimethylxylylphosphine and carbon bisulphide form the compound $C_6H_3Me_2.PMe_2,CS_2$; it crystallises in clear red plates, and melts at 115° in open, and at 121° in closed tubes.

Diethylphenylphosphine unites slowly with carbon bisulphide, forming a red crystalline product which could not be obtained in a state of sufficient purity for analysis. A. J. G.

Action of Potassium Carbonate on the Chlorides of Benzyl and Benzylene. By J. MEUNIER (*Bull. Soc. Chim.* [2], **38**, 159—

160). — By heating ethylene bromide with an aqueous solution of potassium carbonate, Zeller and Hüfner have obtained glycol directly (this Journal, 1876, ii, 64); the author has studied an analogous reaction with benzyl and benzylene chlorides. In the case of benzyl chloride the corresponding or benzylic alcohol was obtained, but with benzylene chloride benzaldehyde was formed, the yield being two-thirds of that required by theory. V. H. V.

Isobutyl- and Amyl-phenols. By A. Liebmann (*Ber.*, **15**, 1990—1992).—Isobutylphenyl ethyl oxide boils at 241—242° uncorr. (not 234—236°, as given in the author's previous communications, Abstr., 1882, 171, 727). By treatment with nitric acid, it yields the *nitro*-ether as an oil volatile with water vapour, boiling with decomposition at about 300°, and yielding the *amido*-ether on reduction. *Amylphenyl ethyl oxide* boils at 259—261°, and yields mononitro- and amido-compounds like the above. A. J. G.

Nitro-derivatives of the Cresols. By E. Nölting and E. v. Salis (*Ber.*, **15**, 1858—1865).—*Dinitro-paracresol.*—The ethylic ether of this body is prepared by treating the silver salt suspended in alcohol with ethyl bromide or iodide; it melts at 73°. The corresponding diamido-salt, of which only the hydrochloride was prepared, shows the characteristic reactions of metadiamides.

Dinitro-orthocresol, $C_6H_2Me(NO_2)_2.OH$ [$NO_2 : NO_2 = 4 : 6$], agrees in all its properties with that obtained by Picard from saffron substitute. The ethylic ether melts at 46°. The barium salt crystallises in shining yellow needles, easily soluble in hot water. The hydrochloride of the diamido-compound decomposes in the air, and must be evaporated in a stream of sulphuretted hydrogen.

Trinitro-cresol, obtained from coal-tar cresol, is identical with that prepared from meta-cresol: it separates from water in slender yellowish-white needles melting at 106°. Like picric acid, it forms molecular compounds with hydrocarbons. Its composition is represented by the formula—

$$[NO_2 : OH : NO_2 : Me : NO_2 = 1 : 2 : 3 : 4 : 5].$$

The ethyl ether is easily converted into trinitro-toluidine by treatment with ammonia; no separation of a nitro-group occurs as would be the case if two of these groups were in the ortho-position to each other. The ethylic ether may be prepared by treating the silver salt with ethyl bromide, and forms thick white needles, melting at 72°.

Trinitro-metatoluidine forms small crystals melting at 126°, very soluble in alcohol and ether, and having weak acid characteristics. Heated with alkaline solutions, it is convered into trinitro-cresol.

J. K. C.

Fusion of Orcinol and Gallic Acid with Soda. By L. Barth and J. Schreder (*Monatsh. Chem.*, **3**, 645—650). — Orcinol, when fused with sodium hydroxide, yields resorcinol (15—16 per cent.), phloroglucol (about 1·5 per cent.), pyrocatechol (1—1·5 per cent.), and a new body, $C_{13}H_{12}O_4$ (about 5 per cent.). This latter is, in all probability, *tetrahydroxydiphenlymethane*, $CH_2[C_6H_3(OH)_2]_2$, it forms long, satiny, snow-white needles, readily soluble in alcohol and ether;

it commences to decompose at 260°. It gives no coloration with ferric chloride. In this reaction, it would appear that the methyl-group is first oxidised, and then split off, so that resorcinol is formed, which by further oxidation yields phloroglucol: a very large proportion of the orcinol however is completely oxidised. The substance, $C_{13}H_{12}O_4$, is an intermediate product, and the catechol is due to a secondary reaction. In accordance with this view, when the heating is continued further, little but phloroglucol is obtained.

By the action of fused soda on gallic acid, phloroglucol is formed in small quantity (0·6—0·8 per cent.) in addition to pyrogallol and hexhydroxydiphenyl (Abstr., 1879, 926).

Catechol is acted on by soda at a high temperature only, and is then completely oxidised. Quinol also is but slowly attacked by soda; the products of the reaction have not yet been obtained in the pure state. A. J. G.

Methylarbutin. By H. SCHIFF (*Ber.*, **15**, 1841—1844).—This body has already been prepared by Michael from methylquinol and acetochlorhydrose; it was thought advisable to prepare it by another method, and to compare the substances obtained. Equal volumes of methyl alcohol solutions of methyl iodide and potassium hydroxide, were gradually added to a solution of arbutin in the same medium, the mixture being boiled after each addition: after concentration and cooling, the methylarbutin which separated was purified by repeated crystallisation from water; it was found to differ in two points from Michael's preparation: it melted at 175—176° (168—169° Michael), and contained 1 mol. H_2O instead of half a molecule. Mixed with arbutin (m. p. 187°) it melted at a much lower temperature. From concentrated solutions containing potassium iodide it can be recrystallised free from water. It is soluble in water especially when hot, and in alcohol, but only sparingly in ether. Commercial arbutin contains about 30 per cent. methylarbutin, identical with that obtained by the author. Whether the latter is the same as that prepared by Michael is still open to question. J. K. C.

Di-isobutylquinol. By S. SCHUBERT (*Monatsh. Chem.*, **3**, 680—687).—Di-isobutylquinol (*paradi-isobutoxybenzene*), $C_6H_4(C_4H_9O)_2$, is prepared by heating together quinol, potassium isobutyl sulphate, and potassium hydroxide, in sealed tubes, for 4—5 hours at 150°. It forms a colourless leafy crystalline mass of fatty lustre, is insoluble in water, more soluble in benzene and light petroleum, readily soluble in alcohol and in hot glacial acetic acid. It boils at about 262°. By the action of chlorine, it yields chloranil, *dichlorodi-isobutylquinol*, crystallising in colourless rhombic plates, and *tetrachlorodi-isobutylquinol*, forming long, colourless, interlaced needles, of silky lustre. The only bromine-derivative obtained was *dibromodi-isobutylquinol*, crystallising in colourless quadratic plates. *Tetranitrodi-isobutylquinol* crystallises in long thin needles, sparingly soluble in water, readily soluble in alcohol, ether, and hot glacial acetic acid. A. J. G.

Compounds of Benzo- and Tolu-quinol with Amines and of Quinone with Nitranilines. By A. HEBERAND (*Ber.*, **15**, 1973—

1976).—Occasionally, in the preparation of quinonedianilide, a compound of quinol and aniline, $C_6H_4(OH)_2,(C_6H_5NH_2)_2$, is found in the mother-liquor. It forms large micaeous plates, melting at 89—90°, and is readily soluble in hot water and in alcohol. In aqueous solution, it is readily oxidised to quinonedianilide. It is decomposed when boiled with benzene, and quinol crystallises out, but the same substance can be prepared by boiling quinol and aniline in aqueous solution. The corresponding paratoluidine compound, $C_6H_4(OH)_2,(C_7H_7.NH_2)_2$ (m. p. 95—98°), prepared directly from quinol, resembles the aniline compound. Orthotoluidine and naphthylamine compounds could not be obtained in the pure state.

Attempts were made to prepare similar compounds with phenol, resorcinol, and pyrogallol, but without success. With toluquinol, an aniline compound, crystallising in white needles, melting at 82—85°, and a paratoluidine compound, crystallising in nacreous plates, melting at 90°, were obtained.

Quinone and Paranitraniline.—On mixing hot alcoholic solutions of these bodies and cooling, large dark-red crystals (m. p. 115—120°) separate, which by heating or by boiling with water are resolved into their constituents. The composition of this substance varied in different preparations from—

$$C_6H_4O,C_6H_4(NO_2)NH_2, \text{ to } 2C_6H_4O_2,3(NO_2.C_6H_4.NH_2).$$

In acetic acid solution, or by long boiling with alcohol, the course of the reaction is different, quinonedinitranilide being formed in small brown needles, together with a substance of acid nature, crystallising in red-violet plates, melting at 183°.

Quinone and Orthonitraniline.—Solutions of these substances, when mixed, yield large red crystals melting at 94—97°; with excess of nitraniline, a new body of the formula $C_6H_4O_2,2(NO_2.C_6H_2.NH_2)$, is obtained. When boiled with glacial acetic acid, it yielded the corresponding dinitranilide, crystallising in brownish-red needles. Metanitraniline and quinone yield nothing but *quinonedimetanitranilide*, forming yellowish-brown needles.

With orthonitraniline toluquinone gives an addition-product (m. p. 37°) resembling those already described. A. J. G.

Compounds of Vanillin with Pyrogallol and with Phloroglucinol. By C. ETTI (*Monatsh. Chem.*, **3**, 637—644).—Singer has recently shown (Abstr., 1882, 1122) that the deep red coloration imparted to pine wood by phloroglucol in presence of hydrochloric acid, is due to a compound formed with the vanillin which is present in the wood. The author has further investigated this compound, and also the analogous one of pyrogallol with vanillin.

Pyrogallovanillein, $C_{20}H_{18}O_8$, is prepared by mixing vanillin and pyrogallol with alcohol and an excess of concentrated hydrochloric acid; it forms colourless crystals destitute of odour, insoluble in water, sparingly soluble in ether, readily soluble in strong alcohol. By long standing over sulphuric acid, or by drying at 110°, 2 mols. of the substance lose 1 mol. of water, yielding the body $C_{40}H_{30}O_{15}$. When crystallised from solutions containing free hydrochloric acid, pyrogallovanilleïn is obtained in fine violet-blue crystals, which contain however, a trace of hydrochloric acid.

Phloroglucinolvanilleïn, prepared in a manner similar to the above, forms yellowish-white crystals, and behaves towards solvents like pyrogallovanilleïn. It loses water more readily with formation of the brownish-red compound, $C_{40}H_{34}O_{15}$. Crystallised from hydrochloric acid solutions, the characteristic fiery-red compound is obtained, but as in the previous case the amount of chlorine contained is too small to estimate. The formation of these vanilleïns is expressed by the equation—

$$COH.C_6H_3(OH).OMe + 2C_6H_3(OH)_3 = CH[C_6H_2(OH)_3]_2.C_6H_3(OH).OMe + H_2O,$$

and they must be regarded as derivatives of triphenylmethane.

On rubbing together resorcinol with vanillin and hydrochloric acid, a deep bluish-violet coloration is produced; but the colour vanishes after a time; the addition of water causes the precipitation of a white crystalline powder. A. J. G.

Action of Acetic Chloride on Benzaldehyde in presence of Zinc-dust. By C. PAAL (*Ber.*, **15**, 1818—1820).—When acetic chloride is dropped into an ethereal solution of benzaldehyde in which zinc-dust is suspended, a violent reaction takes place; zinc chloride is formed, and the ethereal solution, after being washed with water and evaporated, deposits a yellow crystalline mass from which alcohol extracts a substance crystallising in white needles of the formula $C_9H_8O_2$, melting at 125—128°. Heated with amorphous phosphorus and hydriodic acid, it yields dibenzyl, and, when distilled with zinc-dust, it gives rise to stilbene: these decompositions, however, throw no light on its constitution. A reaction similar to the above occurs when ethaldehyde is treated with acetic chloride. J. K. C.

Orthamidobenzaldehyde. By S. GABRIEL (*Ber.*, **15**, 2004—2006).—The author has already shown, in conjunction with R. Meyer (Abstr., 1882, 188), that nitrosomethylorthonitrobenzene yields orthonitrobenzaldehyde on oxidation, and (Abstr., 1882, 1070) that the corresponding meta-compounds give similar results; as this appears to be a general reaction for nitrosomethyl compounds, he has applied it to nitrosomethylorthamidobenzene. The oxidation was effected by a slightly insufficient quantity of ferric chloride; during the reaction, some salicylic aldehyde distils. The contents of the retort are made alkaline and distilled, when *orthamidobenzaldehyde* is obtained as an oil, solidifying to a crystalline mass on cooling; it melts at the temperature of the hand. In an exsiccator over sulphuric acid, it appears to decompose, the walls being covered with a crystalline deposit, whilst the other (greater) part of the substance is converted into a yellow body not melting at 100°. A. J. G.

Action of Benzoic Anhydride on Epichlorhydrin. By P. VAN ROMBURGH (*Rec. Trav. Chim.*, I, 46—52).*—When these two bodies

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* Recueil des Travaux Chimiques des Pays-Bas: par W. A. van Dorp, A. P. N. Franchimont, S. Hoogewerff, E. Mulder, et A. C. Oudemans, Jr. Leide. 1882.

in molecular proportion are heated together in sealed tubes at about 190° for seven to ten hours, and the product is left at rest for some time, the whole concretes to a mass of small crystals soaked in a thick liquid. By solution in ether and spontaneous evaporation, colourless crystals (m. p. 70°) are obtained containing a small quantity of chlorine, and by recrystallising these from alcohol crystals are formed free from chlorine, and melting at 74°. These crystals have the composition $C_{12}H_{10}O_3$, or rather $C_{24}H_{20}O_6$, and are resolved by saponification with alcoholic potash into benzoic acid and glycerol. The compound is therefore tribenzoïcin, formed according to the equation

$$CH_2 \colon CHO.CH_2Cl + 2\overline{Bz}_2O = \overline{Bz}Cl + O\overline{Bz}.CH(CH_2.O\overline{Bz})_2;$$

Epichlorhydrin. Tribenzoïcin..

and, as thus prepared, it is identical in its properties with that which is obtained by heating glycerol with benzoic acid or benzoic anhydride. Its formation in the manner above described is accompanied by that of a liquid, which the author regards as probably consisting of a mixture of mono- and di-benzoïcin. H. W.

Action of Benzoic Anhydride on Monochloracetone and on Pyruvyl Benzoate. By P. van Romburgh (*Rec. Trav. Chim.*, **1**, 53—54).—Monochloracetone and benzoic anhydride, heated together for three hours in a sealed tube at 180°, formed a black solid substance containing benzoic acid, and having a faint odour of benzoic chloride.

By heating monochloracetone with potassium benzoate in alcoholic solution for 12 hours, then filtering and expelling the alcohol by evaporation, a liquid is obtained which, when distilled at 245° under a pressure of 380 mm., yields a yellow distillate solidifying when surrounded by ice; and on pressing the solid mass between bibulous paper to remove oily products, then dissolving it in ether and evaporating, pyruvyl benzoate, $C_{10}H_{10}O_3 = COMe.CH_2.O\overline{Bz}$, is obtained in splendid colourless crystals which melt at the heat of the hand (25°) and have a density of 1·143 at 25°. Their alcoholic solution has no action on polarised light. Pyruvyl benzoate, like monochloracetone, reduces potassio-cupric sulphate, even at ordinary temperatures. Heated with benzoic anhydride in a sealed tube at 180°, it gradually blackens and yields a sublimate of benzoic acid. H. W.

Synthesis of Cumic Acid. By R. Meyer and E. Müller (*Ber.*, **15**, 1903—1906).—The authors have repeated their synthesis of cumic acid (*Ber.*, **15**, 496) on a larger scale with the view of examining the cause of discrepancy between the melting point (110°) of their synthesised acid and that (116°) of ordinary cumic acid. The cumene was prepared by the action of isopropyl bromide on benzene in the presence of aluminium bromide, then converted into parabromocumene, and this, after careful purification, was submitted to the action of sodium and moist carbonic anhydride. The acid obtained in this way differed from that previously prepared in having the correct melting point (116—117°), and it agreed in all respects with ordinary cumic acid. Since both the para-propylbenzoic acids have now been made synthetically by similar reactions, there can be no further doubt of their constitution—cumic acid containing the isopropyl group, and its isomeride, normal propyl.

An attempt to prepare propylbenzoic acid by the action of sodium amalgam on para-propylbenzene and chlorocarbonic ether did not yield very definite results, for although a small quantity of propylbenzoic acid appeared to be formed, the chief product of the reaction was a new body of the formula $Hg(C_6H_4.C_3H_7)_2$ [$Hg : C_3H_7 = 1 : 4$] (m. p. 109°).
A. K. M.

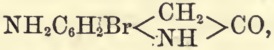
Phenylacetic Acid. By S. Gabriel (*Ber.*, **15**, 1992—2003).—By the action of fuming nitric acid on bromacetamidobenzyl cyanide (m. p. 127—129°), *acetamidobromonitrobenzyl cyanide*,

$$C_6H_2(CH_2.CN)(NO_2)(NH\overline{Ac})Br = [1 : 3 : 4 : 5],$$

is obtained in slender pale-yellow needles melting at 190—191°, and sparingly soluble in cold water, more readily in alcohol and glacial acetic acid. When boiled with hydrochloric acid, it yields *amidobromonitrophenylacetic acid*, $C_6H_2(NO_2)(NH_2)Br(CH_2.COOH) = [3 : 4 : 5 : 1]$, crystallising in long golden-yellow needles melting at 191—192°, and sparingly soluble in cold water, readily in hot alcohol, moderately soluble in chloroform and benzene. By reduction with tin and hydrochloric acid, it is reduced to the *diamido-acid*,

$$C_6H_2Br(NH_2)_2.CH_2.COOH.$$

This forms groups of long colourless needles, which darken at 190° and melt with intumescence to a black mass at 195—200°. The results of the reduction show that the nitro-group must have entered the benzene nucleus at the 3-position, as in the case of the other possibilities [2 or 6], an inner anhydride, bromamido-oxindole,



$$NH_2C_6H_2Br{<}\genfrac{}{}{0pt}{}{CH_2}{NH}{>}CO,$$

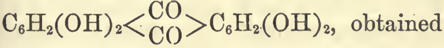
would be produced on reduction.

Metanitroparamidophenylacetic acid (m. p. 143·5—144·5°) gives on reduction the diamido-acid, $C_6H_3(NH_2)(NH_2)(CH_2.COOH) = [3 : 4 : 1]$, crystallising with 1 mol. H_2O in short hard compact forms showing numerous faces, sparingly soluble in hot alcohol.

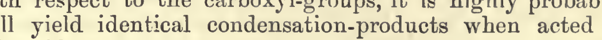
By the action of amyl nitrite and hydrochloric acid on the above metanitro-acid (m. p. 191—192°), a large yield of a substance giving diazo-reactions was obtained, but no formula could be deduced from its analysis, the fact that it contains chlorine and bromine in no simple ratio to one another pointing to a mixture of substances. On gently heating it with alcohol, a crystalline mass is obtained which, on being mixed with soda and distilled with steam, gives an oil solidifying after a time to a mass of crystals insoluble in soda, whilst the residue in the retort, after acidification and renewed distillation with steam, yields colourless crystals (m. p. 108—109°) soluble in water. The results of analysis showed these to be a mixture of dihalogen nitrosomethylbenzenes, $C_6H_3X_2.CH_2NO$ ($X_2 = Cl_2$ or Br_2 or $BrCl$). The crystals insoluble in soda first obtained (broad flat needles melting at 65—65·5°) gave results agreeing with a mixture of dihalogen benzaldehyde, and on oxidation yielded a mixture of dihalogen cinnamic acids.
A. J. G.

Action of Sulphuric Acid on Protocatechuic Acid. By E. Noelting and R. Bourchart (*Bull. Soc. Chim.* [2], **37**, 394—397).—1 gram protocatechuic acid is heated with 2 grams of benzoic acid and 50 grams of sulphuric acid of 66° B. at 140—145° for eight hours, and the product is poured into water, which throws down a deep brown flocculent precipitate; this is collected, dissolved in dilute soda solution, and precipitated by hydrochloric acid, this treatment being repeated several times. The clear brown flocculent substance thus obtained produces with mordants almost the same shades as alizarin, but is distinguished from the latter by the reddish-brown colour of its alkaline solution and by its absorption-spectrum. The yield is very small, whatever the proportion of sulphuric acid, the time of heating, and the temperature. The benzoic acid appears to play no part in the reaction, for, when protocatechuic acid is heated alone at 140—145° with 20—25 times its weight of sulphuric acid, the same product is obtained, although in this case also the yield is very small.

The substance thus formed yields an orange-yellow alcoholic solution, which becomes violet with a yellowish fluorescence on addition of potash. After some time, the compound is precipitated in red flocks. *Alcoholic lead acetate* throws down a flocculent brown precipitate: *calcium chloride* and *barium chloride* produce a violet fluorescence in the yellow solution, and after some time a precipitate is formed; *ferric chloride* gives a blackish-brown, *ammonia* a violet-brown, and *alum* a reddish precipitate. Its solution in dilute ammonia is brownish-red, approaching violet. In this solution calcium and barium chlorides produce a brown, lead acetate a reddish-brown, and absolute alcohol a violet-brown precipitate. Its solution in dilute potash gives, with absolute alcohol, a reddish precipitate, with alum a reddish-lake, and with ferric chloride a blackish-green lake. The substance is dissolved by strong sulphuric acid, with formation of a brownish-violet solution which, when poured into water, yields a yellow solution and a slight precipitate. It also dissolves in glacial acetic acid, forming an orange solution. It cannot be sublimed without decomposition.



The properties of this substance agree with those of *rufiopine*, $C_6H_2(OH)_2{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6H_2(OH)_2$, obtained by Anderson (*Annalen*, **98**, 51) by the action of concentrated sulphuric acid on opianic acid at 180°, and described by Liebermann and Chonjnacki (*Annalen*, **162**, 321). By analogy from the behaviour of other hydroxyl-derivatives of benzoic acid, protocatechuic acid ought to form a colouring matter according to the equation



$$2C_6H_3(OH)_2COOH = C_6H_2(OH)_2{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6H_2(OH)_2.$$

This reaction is more complicated in the case of opianic acid; but since in both compounds the hydroxyl-groups occupy the same positions with respect to the carboxyl-groups, it is highly probable that they will yield identical condensation-products when acted on by sulphuric acid. C. H. B.

Oxidation-products of Carbon obtained by Electrolysis. By A. Millot (*Bull. Soc. Chim.* [2], **37**, 337—339).—The gas-carbon electrodes (Abstr., 1880, 482) are much more rapidly attacked in alkaline solutions than in pure or acidulated water. The dark solution obtained by the electrolysis of a 5 per cent. solution of ammonia with gas-carbon electrodes becomes acid on evaporation. It contains ammonium nitrate and an acid which may be isolated by evaporating almost to dryness, heating the precipitated black matter with alcohol, and evaporating the alcoholic solution, when crystals of the ammonium salt of the acid, mixed with ammonium nitrate, separate out. The crystals are dissolved in water and mixed with lead nitrate which produces a crystalline precipitate. This precipitate is suspended in water, treated with hydrogen sulphide, the solution filtered from lead sulphide and evaporated, when the acid separates out in needles. Its composition will be determined when a sufficient quantity has been obtained.

The black matter precipitated by the addition of an acid to the solution obtained by the electrolysis of a 2 per cent. solution of potassium hydroxide has the composition O 37·72; C, 58·65; H, 3·27; N, 0·56. The whole of the nitrogen was evidently not removed from the carbon electrodes, although the latter were treated with chlorine for 150 hours. The black substance is soluble in boiling water even after being dried at 100°, but is precipitated by ebullition in contact with air. It is insoluble in alcohol, ether, benzene, and chloroform. When an aqueous solution of the black substance is treated with a current of air, it absorbs a considerable quantity of nitrogen, which however is again partially removed by continued passage of the air, the substance at the same time being oxidised and destroyed. C. H. B.

Caffeic Acid from Cuprea Bark. By G. Körner (*Pharm. J. Trans.* [3], **13**, 246). — The bark employed differs from ordinary cinchona bark, in that its aqueous solution becomes reddish-violet on the addition of potash, and, moreover, it yields caffeic acid when employed for the manufacture of sulphate of quinine; the caffeic acid is found in the mother-liquors as quinine caffeate. The author has obtained the acid from the bark by the following process, the yield being about 0·5 per cent.:—The powdered bark is first extracted with ether and then thoroughly with boiling alcohol. The latter extract is evaporated to dryness and the residue treated with 2½ times its weight of boiling water and its own weight of potash; the whole is then boiled for three hours, supersaturated with dilute sulphuric acid, filtered hot, and extracted with ether. This extract is concentrated until crystals form. The crystals are well washed with small quantities of ether, and are purified by boiling with animal charcoal and recrystallising. They form brilliant hard yellowish tables, with 4·8 per cent. water of crystallisation. From acetic acid they separate in crusts of opaque nodules, which decompose without melting at 212°, and have the formula $C_9H_8O_4 + \frac{1}{2}H_2O$, and they give the characteristic reactions of caffeic acid. Dimethylcaffeic acid and methylic dimethylcaffeate were prepared from the acid and identified.

The presence of this acid furnishes an additional proof of the relationship existing between the coffee and cinchona plants.

D. A. L.

Dibromonaphthalene from β-Naphthol. By F. Canzoneri (*Gazzetta*, **12**, 424—431).—When 10 g. of the monobromonaphthol which A. J. Smith obtained by the action of bromine on naphthol (this Journal, 1879, Trans., 789) is mixed in a retort with 15 g. phosphorus tribromide, no action takes place in the cold; but on gradually heating the mixture to a temperature above its melting point, an action commences, attended with rapid evolution of hydrogen bromide. This, however, ceases in a few minutes, and if the mixture be then gradually heated, the action recommences less energetically, the contents of the retort at the same time distilling over. This distillation, if carried on to a red heat, yields:—(1) A quantity of unaltered phosphorous bromide; (2) an oil having a faint yellow colour; (3) a thick yellow oil, solidifying in the neck of the receiver. In the retort there remains a considerable quantity of charcoal.

The second fraction, which constitutes by far the larger fraction of the product, solidifies either at once or after renewed distillation (at about 300°) to a mass of hard transparent crystals melting at 67—68°. The substance thus obtained is a dibromonaphthalene, $C_{10}H_6Br_2$, and when recrystallised from a small quantity of alcohol, forms large monoclinic prisms, cleaving easily parallel to the base 0P, less easily parallel to ∞P. It is but slightly refractive, and exhibits only a faint coloration in polarised light.

This dibromonaphthalene does not dissolve in nitric acid of sp. gr. 1·40, but fuming nitric acid dissolves it, especially if the mixture be gently heated and immediately afterwards cooled. On subsequently adding water, a yellow disagreeably-smelling oil separates, which soon solidifies, and is best purified by dissolving it in a small quantity of alcohol and precipitating with water, whereupon it separates in yellowish-white flocks, apparently made up of slender needles. These crystals, after drying, melted at 100—105°, and gave by analysis 47·50 per cent. bromine, the formula $C_{10}H_6Br_2(NO_2)$ requiring 48·34. The substance is probably a new nitrodibromonaphthalene isomeric with that (m. p. 116·5°) which Jolin obtained (*Bull. Soc. Chim.* [2], **28**, 515) by the action of nitric acid on the β-dibromonaphthalene, which melts at 81°.

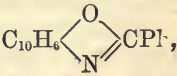
The third portion of the above-mentioned distillate, the quantity of which was relatively very small, consisted of opaque yellow scales impregnated with a yellow oil difficult to separate; but by crystallisation from dilute acetic acid and afterwards from alcohol, the substance was obtained in white silvery scales, melting at 55—60°, and giving by analysis numbers agreeing nearly with the formula of *monobromonaphthalene*, $C_{10}H_7Br$. As only two such compounds are possible, and one of them (α) is liquid, the compound obtained in the manner just described must be the β-modification which was obtained by Liebermann and Palm (*Annalen*, **183**, 267) from β-naphthylamine, and described as crystallising in laminæ, having the same appearance, but melting at 68°; the difference in the melting points perhaps arising from the circumstance that the author's determinations were made with a very small quantity of material. The formation of this monobromonaphthalene may perhaps be ascribed either to the action of the phosphorous bromide on small quantities of β-naphthol contained in the bromonaphthol, or to decomposition of the dibromonaphthalene at the high temperature of the reaction.

From the perfect agreement in melting point between the dibromonaphthalene above described and that recently isolated by Guareschi (Abstr., 1882, 734), from Glaser's impure product (melting at 76°), the author infers the identity of the bodies obtained in these several ways, and thence deduces the constitutional formula of the dibromonaphthalene in question. This body in fact, having been obtained by Glaser from α-bromonaphthalene, must have one of its bromine-atoms in the α-position, but since it is also producible from monobrom-β-naphthol, it must have the other in the β-position, and consequently must be an α-β-dibromonaphthalene. Now of the ten possible dibromonaphthalenes, four only have the α-β-structure, viz.: [1 : 2], [1 : 3], [1, 2′], [1 : 3′]. Moreover, A. J. Smith (*loc. cit.*), by oxidising monobrom-β-naphthol with permanganate, obtained phthalic acid or anhydride, and thence inferred that in this brom-β-naphthol the hydroxyl- and the bromine-atom must be found in the same benzene-ring. The same conclusion may be extended to the dibromonaphthalene derived therefrom: consequently, the two bromine-atoms of this latter cannot be in the positions 1 : 2′ or 1 : 3′, and must therefore have the position 1 : 2 or 1 : 3. Now, Meldola in a recent memoir (*Ber.*, **12**, 1962) describes a dibromonaphthalene melting at 64°—obtained by the action of nitrous acid on dibromonaphthylamine—to which he assigns the formula [1 : 3]; and since there appears to be no reason for supposing that this product is identical with the above-described dibromonaphthalene melting at 67—68°, the author infers that the latter must be represented by the formula [1 : 2].

Appendix.—The author has likewise obtained an acetyl-derivative and a nitroso-derivative of bromo-β-naphthol. The former is a dense faintly yellow liquid, decomposed by distillation under ordinary pressures, but passing over undecomposed at about 215° under a pressure of 20 mm. By bromine in acetic acid solution, it is converted into a brominated derivative, which is resinified by boiling with potash.

The nitroso-derivative separates from solution in ether in unstable green crystals, melting at 61—65°. H. W.

Action of Chloroform on Naphthalene in presence of Aluminium Chloride. By M. Hönig and F. Berger (*Monatsh. Chem.*, **3**, 668—672).—This reaction has been already investigated by Schwartz (Abstr., 1881, 912), who could not obtain any definite products from it. A pitch-like mass is obtained, from which solvents fail to extract any well-characterised substance. The crude product is dissolved in benzene, filtered, the benzene distilled off, and the residue after being heated at 230° for some time to remove unaltered naphthalene, is distilled in a vacuum. The distillation begins far above 360°, and was carried on to redness. By a long series of crystallisations, a substance was obtained from the distillate, forming plates of a pale yellow colour (m. p. 189—190°, uncorr.), whose formula would appear to be a multiple of $C_{14}H_{10}$ ($C_{42}H_{30}$?). It is possible that this hydrocarbon may be identical with Zeidler's synanthrene (*Annalen*, **191**, 298). Two substances, melting respectively at 170—175° and at 215°, were also obtained and are being investigated. A. J. G.

Constitution of Nitronaphthols. By R. WORMS (*Ber.*, **15**, 1813—1818).—Two nitronaphthols from α-naphthol are known: in one the nitro-group occupies the para- or α-position; in the other one of the β-positions, but it is not known which. An anhydro-base from α-naphthol is also known, but the corresponding nitro-compound has not been isolated, and it appeared interesting to compare it with the other known nitro-α-naphthols. For this purpose benz-α-naphthalide was converted in small quantities into the corresponding nitro-compounds. On cooling, the para-compound crystallises out, and the filtered liquid is thrown into water to precipitate the ortho-compound. It crystallises from alcohol in yellow needles, melting at 174°. On boiling it with potash and adding an acid, orthonitro-α-naphthol is obtained in yellow crystals, melting at 128°. It is identical with the β-nitro-α-naphthol obtained by Liebermann and Dittler (*Annalen*, **183**, 228). That the nitro-group occupies the ortho-position with respect to the hydroxyl is shown by the fact that the corresponding nitrosonaphthol is easily converted into an anhydro-base. To this end, β-nitroso-α-naphthol benzoate was first prepared by treating the corresponding sodium-nitrosonaphthol with benzoic chloride in the cold. The benzoate (m. p. 162°), purified by crystallisation from chloroform, is treated with tin and hydrochloric acid, when a violent reaction sets in, and the anhydro-base, benzenyl-β-amido-α-naphthol,  $C_{10}H_6\langle{}^{O}_{N}\rangle CPh$, is obtained in small needles (m. p. 122°), which may be purified by sublimation.

It appeared also of interest to ascertain whether an anhydro-base could be produced from the α-nitroso-β-naphthol of Stenhouse and Groves (*Annalen*, **189**, 153), in which the nitroso-group and the hydroxyl have been shown to stand relatively in the ortho-position. The same process was used as above, the sodium salt and then the benzoate (m. p. 114°) being first prepared, and the latter reduced with tin and hydrochloric acid. Benzenyl-α-amido-β-naphthol was thus obtained in colourless prisms melting at 120°, and soluble in water and alcohol; it may be purified by sublimation.

The formation of anhydro-bases in the naphthalene series seems thus to be a property of the ortho-position. It is also noteworthy that orthonitro-α-naphthol can be separated by steam from the solid para-compound, just in the same way as in the case of the two nitrophenols.
J. K. C.

Indophenol. By M. A. PABST (*Bull. Soc. Chim.* [2], **38**, 160—162).—Meldola, and Koechlin and Witt have obtained colouring matters by the action of nitrosodimethyl- or nitrosodiethyl-aniline on phenols or naphthols. One of these substances, indophenol, is manufactured by the oxidation of sodium α-naphthol and amidomethylaniline with potassium dichromate or sodium hypochlorite. It gives a blue dye on reduction, like indigo, and can be fixed on fabrics by stannous oxide. It is more stable than indigo to light and soap, and is less costly, but is destroyed by concentrated mineral acids. The colour varies from a violet to a greenish-blue, according to the particular phenol employed.

Koechlin, by the action of nitrosodimethylaniline on tannin, gallic acid, and the catechins, obtained a violet dye, *gallocyanine;* it forms beautiful crystalline salts, and can be fixed on cotton by chromium sesquioxide.

These colouring matters are prepared in France by Durand and Huguenin, and it seems probable that from their cheapness and stability they will replace alizarin for violet, and indigo for blue tints. V. H. V.

α-Naphthaquinone-ethylanilide. By L. Elsbach (*Ber.*, **15**, 1810—1813).—Two parts of α-naphthaquinone are heated in a flask with five parts of glacial acetic acid and three parts ethylaniline; the reaction proceeds by itself when the mixture has begun to boil. On cooling, the mass is extracted with alcohol, and by repeated crystallisations the pure α-naphthaquinone-ethylanilide,

$$(\beta)\ \mathrm{NEtPh.C_{10}H_5{:}O_2}\ (\alpha),$$

is obtained in dark violet needles, melting at 155°. When boiled with strong caustic soda, it is converted into a reduction product and a resinous mass. It is a feeble base, and combines readily with acids to form salts, which are easily decomposed.

During its formation by the above reaction, a yellowish-green bye-product is formed, which amounts to one-fifth of the yield. After boiling it with alcohol and ether, it was analysed, and found to contain no nitrogen, numbers being obtained corresponding with the formula $C_{20}H_{10}O_4$. It is soluble only in fuming nitric acid. Zinc and hydrochloric acid reduce it, forming a green fluorescent solution. In all probability, therefore, it appears to be the α-product corresponding with the β-dinaphthadiquinone discovered by Stenhouse and Groves.
J. K. C.

Derivatives of Styrolene. By A. Bernthsen and F. Bender (*Ber.*, **15**, 1982—1986).—In addition to the method already described (Abstr., 1882, 201), paramidostyrolene, $C_6H_4(NH_2)C_2H_3$, can be prepared by heating paranitrocinnamic acid in a paraffin-bath until the mass is in quiet fusion. The melting point is difficult to determine; softening occurs at 76°, complete fusion at 81°.

Parahydroxystyrolene appears to be obtained in small quantity by distilling barium paracoumarate mixed with sand, and forms a nearly colourless oil, of phenol-like odour, sparingly soluble in water. The solution is precipitated by bromine.

Styrolene unites directly with hydrobromic acid, yielding a *bromethylbenzene.* This is a pale-yellow liquid, of odour resembling that of benzyl chloride, sp. gr. 1·3108 at 23°. When heated, it is decomposed into hydrobromic acid and styrolene. It is probable that it has the constitution $CH_2Ph.CH_2Br$. A. J. G.

Methylanthraquinone and some of its Derivatives. By E. Börnstein (*Ber.*, **15**, 1820—1823).—The substance bearing this name, and sold commercially, was examined for the purpose of identification. After repeated crystallisations from alcohol, it melted at 175—176°, and gave on analysis numbers corresponding with the formula of methylanthraquinone. Reduced with zinc and ammonia, and boiled with xylene, greenish-yellow crystals of methylanthracene were obtained and analysed. After repeated crystallisation, it melted at 203°. By oxidation with chromic acid, anthraquinonecarboxylic acid was formed, and a dibrominated product was also prepared, melting at 148°. Attempts to prepare a definite methylhydroanthranol have hitherto been unsuccessful. J. K. C.

New Nitro- and Amido-anthraquinones, and New Method of Preparing Erythroxyanthraquinone. By H. Roemer (*Ber.*, **15**, 1786—1794).—Nitro- and amido-anthraquinones have been obtained by Böttger and Petersen (*Ber.*, **6**, 16), and an isomeric amido-compound by von Perger (*Ber.*, **12**, 1566). Other experimenters have failed to obtain a nitro-compound by Böttger and Petersen's method, and have recommended another, viz., to treat dibromanthracene with fuming nitric acid. The author was also forced to have recourse to this process, but on repeating his experiments could obtain no product of settled composition. Another method was therefore tried, and with success. Anthraquinone dissolved in sulphuric acid was treated with the requisite quantity of nitric acid; crystals were formed, and after two days the whole was poured into a large quantity of water. The white precipitate thus obtained could be separated into three bodies by crystallisation from alcohol. The body of medium solubility attracted attention at once by the beauty and size of its crystals.

The following method was found to give the largest yield:—10 grams of anthraquinone dissolved in sulphuric acid were treated with 4·5 grams of nitric acid (sp. gr. 1·48), and left for two days. The crude product after being washed with water was extracted with ether, the extract distilled until crystals began to form, and after cooling, the filtered liquid was found to contain the body most soluble in alcohol, whilst the crystals contained the wished-for product, purifiable by recrystallisation. For larger quantities, the crude product can be simply extracted by repeated small quantities of hot alcohol: after the second extraction the body is obtained almost pure. The pure product on analysis gave numbers closely agreeing with the formula for nitranthraquinone. That it is not a mixture of anthraquinone and its dinitro-compound is proved by its behaviour with ammonium sulphide, the latter converting it into a body soluble in cold strong hydrochloric acid, in which anthraquinone is insoluble, even after treatment with ammonium sulphide.

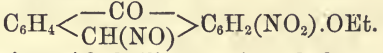
Nitranthraquinone sublimes in yellow crystals (m. p. 220°), insoluble in water, sparingly soluble in alcohol, ether, and glacial acetic acid, and crystallising therefrom in brilliant prismatic needles, but more soluble (with yellow colour) in benzene, chloroform, and concentrated sulphuric acid. Its solution in the latter becomes red when heated, and on being thrown into water gives a reddish-violet precipitate, which yields a purple solution in alcohol, showing two dark bands. It thus exhibits decided differences from the body described by Böttger and Petersen, which become more striking when the amido-compound is examined.

Orthamidoanthraquinone is easily obtained in a pure state by dissolving the above nitro-compound in alcohol, precipitating with water, and adding an alkaline solution of stannous oxide. A clear green solution is at once obtained, which after twelve hours' standing becomes reddish-yellow, and deposits the amido-compound in beautiful red needles, purified by washing with water. Analysis shows them to consist of amidoanthraquinone (m. p. 241°). It sublimes without charring in deep-red needles, insoluble in water, but giving reddish-yellow solutions with alcohol, ether, benzene, chloroform, glacial acetic, sulphuric, and hydrochloric acids. From its hot saturated solution in the last, the hydrochloride separates out on cooling in white needles. Its acetyl-compound is obtained by boiling it with acetic anhydride and sodium acetate, and may be separated by adding water. It crystallises from alcohol in orange-red needles melting at 202°, or 39° lower than Perger's acetyl-compound, exactly the same difference being observed between the two amidoanthraquinones. Perger's description and results were also confirmed by the author, and as his amidoanthraquinone is a meta-compound, it seemed probable that the bodies obtained by the author belonged to the ortho-series, an assumption which was confirmed by their conversion into erythro-oxyanthraquinone in the following way:—The amidoanthraquinone was dissolved in glacial acetic acid, a little concentrated sulphuric acid added, and then potassium nitrite until the solution had become yellow. After standing a short time water was added, the mixture boiled until yellow flakes separated, increasing in quantity as the acetic acid evaporated. Crystallisation from alcohol then yields at once orange-yellow feathery crystals melting at 191°, and agreeing in every other characteristic with erythroxyanthraquinone. The nitro- and amido-anthraquinones obtained by the author belong therefore to the ortho-series. J. K. C.

Action of Concentrated Sulphuric Acid on Dinitroanthraquinone. By C. LIEBERMANN and A. HAGEN (*Ber.*, **15**, 1801—1806).—By the action of hot concentrated sulphuric acid on dinitroanthraquinone, a dye-stuff is formed (*Ber.*, **3**, 905), which has not received a thorough investigation. To obtain it, the anthraquinone is heated with 15 times its weight of sulphuric acid at 200°, and the cooled mixture poured into water. A brown precipitate is thrown down, dissolving in alkalis with violet colour; after being thrown down again by hydrochloric acid, it is purified by boiling with baryta-water, in which it partly dissolves. The substance is again precipitated by acid from the solution, washed, and transferred in the pasty condition into cold baryta-water. After standing, the filtered liquid is again treated with acid, the precipitate washed, and crystallised repeatedly from alcohol. On analysis, numbers were obtained corresponding with the formula $C_{28}H_{18}N_2O_7$.

On heating it with hydrochloric acid, a colouring matter is obtained free from nitrogen. With nitrous acid, however, it splits up into erythroxyanthraquinone and purpuroxanthin. It appears therefore probable that the dye-stuff in question consists of a mixture of the amides of these two bodies. The action of sulphuric acid on dinitroanthraquinones is first an oxidation, sulphurous and phthalic acids being formed: the sulphurous acid then reduces the nitro-groups, forming amides, and this part of the process can be greatly accelerated by introducing sulphurous anhydride or zinc. The amido-groups are then partially attacked by sulphuric acid and converted into hydroxyls. A complicated mixture of substances is thus formed, of which the substance investigated by the authors forms but a small part. J. K. C.

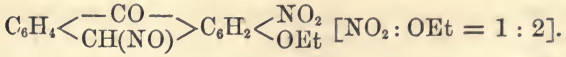
Derivatives of Anthrol Salts. By C. Liebermann and A. Hagen (*Ber.*, **15**, 1794—1800).—In a former communication (*Ber.*, **15**, 1427), the authors have given the name of ethyl dinitroanthrolate to the body obtained by the action of nitric acid on ethyl anthrolate. Further experiments have, however, shown that this view is not correct, both its reduction and oxidation products pointing to another formula. Boiled with glacial acetic acid, tin, and hydrochloric acid, ethyl monamidoanthrolate is formed, and the other half of the nitrogen is found in solution as ammonia. One only, therefore, of the nitro-groups possesses the ordinary characteristics of aromatic nitro-groups, and the other is in reality a nitroso-group. The body in question is therefore termed by the authors the nitroso-anthrone of ethyl mononitroanthrolate,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{\text{—CO—}}{\text{CH(NO)}}{>}C_6H_2(NO_2).OEt.$$

By oxidation with boiling acetic and chromic acids, the corresponding nitroxyanthraquinone ethylate is obtained in colourless needles melting at 243°; and this when boiled with glacial acetic acid and granulated tin until the solution becomes red, yields amidoxyanthraquinone ethylate in red crystals melting at 182°. Contrary to the author's expectation, the ethyl-group in the above compounds could not be eliminated by boiling with alkalis or acids, or with alcoholic potash: by fusion with potash, they are, however, decomposed in a more complicated way. The reactions of the hydroxyanthraquinone salts were therefore studied in order to throw light on this curious behaviour. Ethyl anthrolate was oxidised in acetic acid with excess of chromic acid, hydroxyanthraquinone ethylate being formed (m. p. 135°), very soluble in alcohol. This is also proof against all alkaline solutions, and is only gradually attacked by fused potash and converted into alizarin. The ethyl ether of anthraflavol was also found to exhibit this stability, which appears to be characteristic of the hydroxyanthraquinones. A decomposing agent was, however, found in hot concentrated sulphuric acid. On heating a solution of the ether in this acid to 200°, it turns brown, and on cooling and adding water, hydroxyanthraquinone is thrown down (m. p. 301°). A similar reaction takes place with the ethers of anthraflavol. Amidoanthraquinone ethylate was therefore treated in the same way, and was found to be converted into alizarinamide, easily recognised by its reactions.

The constitutional formula of the nitroso-anthrone of ethyl nitroanthrolate is therefore—



$$C_6H_4<\genfrac{}{}{0pt}{}{-CO-}{CH(NO)}>C_6H_2<\genfrac{}{}{0pt}{}{NO_2}{OEt}\ [NO_2 : OEt = 1 : 2].$$

J. K. C.

Dihydroxyanthracene from α-Anthraquinonedisulphonic Acid (Flavol). By G. SCHÜLER (*Ber.*, **15**, 1807—1810).—Commercial sodium α-anthraquinonedisulphonate was reduced with zinc-dust and ammonia to obtain the sodium salt of flavanthracenedisulphonic acid, which forms yellowish-grey crystals, dissolving in water with intense blue fluorescence. The thallium and barium salts are white and crystalline, those of silver and lead are yellowish precipitates. *Sodium anthrosulphonate*, $C_{14}H_8(OH).SO_3Na$, is obtained by fusing the corresponding disulphonate with potash until the mass has become thin: when cold, it is treated with acid filtered and alcohol added; the precipitated salt is recrystallised from water, to which it communicates a greenish fluorescence; precipitates are formed with the heavy and earth metals.

Flavol, $C_{14}H_8(OH)_2$, is formed when the fusion with potash is continued until the mass becomes intensely black, and gives off a tarry odour. By decomposing the product with acid, and repeatedly recrystallising the insoluble portion from alcohol, flavol is obtained as a bright yellow crystalline powder (m. p. 260—270°), soluble in alkalis with yellow colour and very fine green fluorescence. Diacetylflavol, prepared in the usual way, crystallises in white plates, melting at 254—255°. The diethylic ether, obtained by saturating an alcoholic solution of flavol with hydrochloric acid, melts at 229° after being purified by crystallisation from glacial acetic acid.

Flavol differs from the other known dihydroxyanthracenes in the strong fluorescence of its alkaline solutions and in the higher melting points of its salts. J. K. C.

Soluble Alizarin Blue. By H. BRUNCK and C. GRAEBE (*Ber.*, **15**, 1783—1786).—Alizarin blue being but sparingly soluble, and therefore difficult to fix on the fibre, has not been as extensively applied as was to be expected from its otherwise valuable properties. In order to convert it into a more soluble form, experiments were made by Brunck, ending in the issue of a patent, from which the method of obtaining the soluble blue may be briefly extracted as follows:—Alizarin blue in a fine state of division, and in the form of a paste containing 10—12 per cent. blue, is stirred up with 25—30 per cent. of a solution of sodium hydrogen sulphite (sp. gr. 1·25), and the mixture left for 8—10 days. It is then filtered, unchanged blue being left behind, and the soluble blue separated from the filtrate in reddish-brown crystals by addition of common salt, or evaporation at a low temperature. The dry powder can be heated to 150° without undergoing change, but its aqueous solution begins to decompose at 60°, and on boiling, the blue separates out. In the cold a solution of chromic acetate produces no change, but at 60—70°, the blue chromium lake is thrown down. This fact is made use of in printing; the soluble blue and chromic acetate mixed with starch are printed on the fabric, and the latter steamed for 10 or 20 minutes and then washed.

After making due allowance for the sodium chloride present, an analysis of the commercial article gave numbers corresponding with the formula $C_{17}H_9NO_4 + 2HNaSO_3$.

Neither alizarin nor the purpurins possess the property of combining with alkaline bisulphites; quinoline, however, forms very soluble crystalline compounds, whose aqueous solutions decompose in the same way as those of soluble alizarin blue. It appears therefore probable that the capacity for combining with bisulphites rests in both cases with the nitrogen-group. J. K. C.

Hydrocarbons of the Formula $(C_5H_8)_n$. By W. A. Tilden (*Chem. News*, **46**, 120—121).—The author has already suggested (Trans., 1878, 85—88) that the liquid terpenes and citrenes ($C_{10}H_{16}$) are not correctly represented as dihydrides of cymene. He now finds that the hydrocarbons of the formula C_5H_8 appear to supply important evidence in connection with this question. The author has further examined isoprene, the most interesting of these hydrocarbons, and observes that it boils at 35° (not 38°), has the vapour-density for C_5H_8, that it forms a tetrabromide, $C_5H_8Br_4$, an oily yellowish liquid which cannot be distilled without decomposition, and remains liquid at −18°, and moreover he confirms Bourchardat's statement that when heated for some time at 280° it forms di-isoprene, $C_{10}H_{16}$ (b. p. 174—176°), apparently identical with terpilene from turpentine, yielding the same hydrochloride, and being converted by the action of dilute acids into terpin, $C_{10}H_{22}O_3$, having the same crystalline form as the terpin from turpentine. It likewise resembles turpentine in its behaviour with sulphuric acid. Hence it seemed to the author that isoprene might be obtained by depolymerising turpentine. When turpentine is passed through a red-hot iron tube, among the other products a substance is found (b. p. about 37°, vap.-den. 35°, C_5H_8 requires 34°), having the same composition and some of the properties of isoprene. A litre of turpentine yields about 20 c.c. of the fraction (37—40°). Reboul's valerylene from amylene dibromide, and Hofmann's piperylene (Abstr., 1881, 571), are both isomerides of isoprene. Valerylene differs from piperylene by not forming a tetrabromide and from isoprene by forming a ketone when digested with mercuric bromide and water; isoprene is unaffected. Theoretically there are eight compounds of the formula C_5H_8, all open chains; of these, three are acetylenes, forming copper and silver derivatives, thus differing from the above isomerides. As valerylene is easily converted into a ketone, it would probably be correctly represented as a dimethylallene, either $CHMe : C : CHMe$ or $CMe_2 : C : CH_2$; and as isoprene does not undergo this change the author is inclined to regard it as β-methyl-crotonylene,—

$$CH_2 : CMe.CH : CH_2.$$

It would be difficult to explain how such a substance could be polymerised into a methylpropylbenzene, therefore the author is of opinion that terpene may be more correctly represented either by the formula $CH_2 : CH.CMe : CH.CH : CHPr^{\beta}$ or thus:—

$$CH_2 : CPr^{\beta}.CH : CH.CMe : CH_2.$$

He also feels disposed to look on isoprene as the first term of a series somewhat analogous to the olefines, C_5H_8, $C_{10}H_{16}$, $C_{15}H_{24}$, &c. Colophene from turpentine, seems to be a saturated hydrocarbon of this form. The absorption spectrum of isoprene at the ultra-red end has, according to Abney, the characteristics of that of an aromatic body. At the other end, according to Hartley, it resembles that of australene, the main constituent of common turpentine.

D. A. L.

Note.—Bourchardat has described two bromides of isoprene (*Compt. rend.*, **89**, 1117—1120: this Journal, Abstr., 1880, 323).—D. A. L.

Essence of Sandal Wood. By P. Chapoteaut (*Bull. Soc. Chim.* [2], **37**, 303—305).—Essence of sandal wood, obtaining by distilling the wood with water, is a somewhat thick liquid of sp. gr. 0·945 at 15°, and boiling between 300° and 340°. It consists almost entirely of two oxygenated bodies, the more abundant of which is $C_{15}H_{24}O$ (b. p. 300°); and the other, $C_{15}H_{26}O$ (b. p. 310°). When treated with phosphoric anhydride essence of sandal wood yields two hydrocarbons, $C_{15}H_{22}$ (b. p. 248°), and $C_{15}H_{24}$ (b. p. 260°). Oil of cedar, when purified from oxygen compounds, has the composition $C_{15}H_{22}$, and boils at the same temperature as the hydrocarbon from essence of sandal wood. The two products are probably identical. The hydrocarbon, $C_{15}H_{24}$, is either isomeric or identical with oil of copaiba.

When slowly distilled, essence of sandal wood yields products boiling below 250° and above 350°, together with water and hydrogen, but the decomposition is not complete. If the essence is heated in sealed tubes at 310°, it splits up in accordance with the equations $4C_{15}H_{24}O = C_{20}H_{30}O + C_{40}H_{62}O_3 + 2H_2$, and $C_{40}H_{62}O_3 = C_{40}H_{60}O_2 + H_2O$. The compound, $C_{20}H_{30}O$, boils at 240°, and when treated with phosphoric anhydride yields a cymene boiling at 175—180°. The product, $C_{40}H_{62}O_3$, is a thick liquid, boiling at about 340°, and the third body, $C_{40}H_{60}O_2$ boils at 350°, and has the consistence of honey. The essence, $C_{15}H_{26}O$, apparently splits up in a similar manner.

When heated at 150° under pressure for seven or eight hours with half its weight of glacial acetic acid, essence of sandal wood yields two products, $C_{30}H_{46}O$ (b. p. 280—285°), formed from $2C_{15}H_{24}O$ by loss of H_2O, and $C_{17}H_{28}O_2$ (b. p. 298°), the acetate derived from the body $C_{15}H_{26}O$. With hydrochloric acid at 125°, essence of sandal wood yields a hydrochloride boiling at about 275°, but the reaction is more complex than with acetic acid. The compound, $C_{15}H_{26}O$, has therefore the properties of an alcohol; the compound $C_{17}H_{24}O$ has the properties of an aldehyde, and is probably the aldehyde of $C_{15}H_{26}O$.

C. H. B.

Synthesis of Salicin and of Anhydrosalicylic Glucoside. By A. Michael (*Ber.*, **15**, 1922—1925).—By the action of sodium amalgam on helicin obtained from salicin, Lisenko succeeded in reforming the latter body. The author has repeated this with artificial helicin prepared by the action of acetochlorhydrose on potassium salicylate, and has obtained salicin identical in properties with natural salicin.

In an attempt to make the glucoside of salicylic acid, the action of acetochlorhydrose (2 mols.) on disodium salicylate (1 mol.) in alcoholic solution was tried. The sodium chloride, which separated out after several days, was filtered off, and by the spontaneous evaporation of the filtrate, a body of the formula $C_{26}H_{30}O_{15}$ was obtained, crystallising in needles. A portion of the same substance also separated with the sodium chloride. This new compound melted at 184—185°; it is almost insoluble in water and cold alcohol, moderately soluble in hot alcohol. It is insoluble in cold ammonia, but dissolves gradually in cold soda. Boiling it with alkalis or acids decomposes it into salicylic acid and dextrose. When heated with acetic anhydride and sodium acetate, it forms an acetyl-derivative, $C_{26}H_{22}O_{15}\overline{Ac}_8$, melting at 110—111°. A. K. M.

Santonous and Isosantonous Acids. By C. CANNIZZARO and G. CARNELUTTI (*Gazzetta*, **12**, 393—416).—I. SANTONOUS ACID, $C_{15}H_{20}O_3$.—This acid, containing 2 atoms of hydrogen more than santonic acid, is prepared by heating santonin in a reflux apparatus with hydriodic acid (b. p. 127°) and amorphous phosphorus. On filtering the resulting liquid through asbestos, and digesting the solid mass on the filter with cold aqueous sodium carbonate, the santonous acid dissolves, and on acidifying with hydrochloric acid and leaving the liquid to cool, separates in needle-shaped crystals, which may be purified by repeating this treatment several times, and finally crystallising from ether. The acid thus purified crystallises in white needles, melts at 178—179°, and resolidifies on cooling. Under a barometric pressure of 5 mm., it distils unaltered at 200—260°; under ordinary pressure, it is partly decomposed by distillation. It is very soluble in absolute alcohol and in ether, slightly in cold water, and crystallises from a boiling aqueous solution on cooling. Its solutions are optically dextrogyrate, a character by which it is most readily distinguished from isosantonous acid, which is optically inactive. It dissolves at the ordinary temperature in aqueous solutions of the alkaline carbonates, and of the earthy-alkaline hydroxides. Its alkali salts are very soluble in water and in alcohol, slightly also in a mixture of alcohol and ether.—The *sodium salt*, $C_{15}H_{19}NaO_3$, crystallises in very small needles; the *silver salt*, obtained by precipitation, blackens very quickly even in the dark.—The *barium salt*, $Ba(C_{15}H_{19}O_3)_2$, is soluble in water, and on evaporation in a vacuum separates in efflorescent crystals; on the other hand a cold saturated aqueous solution when heated deposits a salt which is not efflorescent, although it contains water of crystallisation; it is also much more soluble than the salt deposited at higher temperatures.

Ethyl santonite, $C_{17}H_{24}O_3 = C_{15}H_{19}O_3.C_2H_5$, prepared in the usual way, and purified by repeated crystallisation from ether, forms white crystals, soluble in alcohol and ether, melting at 116—117°. Its solutions are dextrogyrate.—*Methyl santonite*, prepared in like manner, is white, very soluble in ether, and melts at 81—84°.—*Ethylic sodium-santonite*, $C_{15}H_{18}NaO_3.Et$, obtained by boiling under pressure a solution of ethyl santonite in absolute ether with sodium, separates as a white powder, and is instantly resolved by cold water into ethyl santonite and sodium hydroxide.—*Ethylic benzoyl-santonite*, $C_{24}H_{28}O_3 = C_{15}H_{18}\overline{Bz}O_3Et$, formed by heating ethyl santonite with benzoyl chloride in a reflux apparatus, is a white crystalline body, very soluble in ether, melting at 78°. By boiling with alcoholic potash it is resolved into benzoic and santonous acids.—*Ethylic ethylsantonite*, $C_{19}H_{28}O_3 = C_{15}H_{18}EtO_3.Et$, obtained by heating ethylic sodium-santonite with ethyl iodide under pressure, crystallises in long needles, melts at 31—32°, dissolves in alcohol, and very easily in ether.—*Ethyl-santonous acid*, $C_{17}H_{24}O_3 = C_{15}H_{19}(C_2H_5)O_3$, obtained by boiling ethylic ethylsantonite with alcoholic potash, crystallises in long slender needles, melts between 115·5° and 116°, and exhibits strong acid properties. It is reconverted into the ethylic ether by passing hydrogen chloride through its alcoholic solution. The preceding facts show that santonous acid contains, in addition to acid hydroxyl-groups, an alcoholic or phenolic hydroxyl.

ISOSANTONOUS ACID, $C_{15}H_{20}O_3$.—When a mixture of santonous acid (1 pt.) and barium hydroxide (3 pts.) is heated to a temperature above the melting point of lead, a fused yellowish mass is obtained; and on exhausting this mass with hot water, and passing carbonic anhydride into the filtered solution, barium carbonate is precipitated together with a phenol; and on again filtering and treating the filtrate with hydrochloric acid, isosantonous acid is precipitated in larger or smaller quantity, according to the time for which the heating with baryta has been prolonged. The acid is purified by dissolving it in alcohol, precipitating with hot water, pressing the precipitate between cloth, and washing with water, till the liquid passes through clear. This treatment is repeated several times, and the product finally crystallised from ether. Isosantonous acid crystallises in laminæ, different in appearance from those of santonous acid, melts at 153—155°, and resolidifies on cooling. It distils unaltered at 150—160° under a pressure of 4 mm.; under ordinary pressure, it partly distils, partly decomposes like santonous acid. It is soluble in alcohol and in ether, very sparingly in cold water, and separates from a boiling aqueous solution as it cools in shining plates. The solutions are optically inactive.

Isosantonous acid is a strong acid, and is easily etherified. The *ethylic ether*, $C_{17}H_{24}O_3$, prepared by passing hydrogen chloride through the alcoholic solution of the acid, forms white crystals melting at 125°. In this ether, as in ethyl santonite, an atom of hydrogen may be replaced by benzoyl, sodium, or potassium, or by ethyl, whereby a series of derivatives is obtained isomeric with the corresponding santonites, but differing therefrom in melting point and other characters, especially by the absence of rotatory power.

The following table exhibits a comparative view of the melting points of the two isomeric acids and their ethereal derivatives:—

Santonous acid, 178°.	$C_{15}H_{20}O_3$	Isosantonous acid, 154°.
Ethylic santonite, 117°.	$C_{15}H_{19}O_3.Et$	Ethylic isosantonite, 125°.
Ethylic benzoylsantonite, 78°.	$C_{15}H_{18}\overline{Bz}O_3.Et$	Ethylic benzoylisosantonite, 91°.
Ethylic ethylsantonite, 31°.	$C_{15}H_{18}EtO_3.Et$	Ethylic ethylisosantonite, 54°.
Ethylsantonous acid, 116°.	$C_{15}H_{18}EtO_3.H$	Ethylisosantonous acid, 143°.

These two isomeric acids further yield the same products of decomposition, viz., dimethyl-naphthol and dimethyl-naphthalene.

DIMETHYL-NAPHTHOL, $C_{12}H_{12}O = C_{10}H_7Me_2.OH$.—This is the phenol obtained, as already observed, together with isosantonous acid, by heating santonous acid with barium hydroxide. It is also formed, together with dimethyl-naphthalene, by distilling santonous acid with zinc-powder, and may be separated by agitating the distillate with potash-ley, and extracting with ether the portion not dissolved by the alkali. The impure phenol, prepared in either way, may be purified by dissolving it in alcohol, precipitating with hot water, washing the precipitate on a cloth filter, and repeating this treatment till the product presents a homogeneous appearance. Dimethyl-naphthol thus purified crystallises in shining needles, melts without alteration at 135—136°, sublimes under ordinary pressure at 100°, and may be boiled and distilled under reduced pressure. It is very soluble in ether, soluble also in alcohol, very sparingly soluble in cold water, and separates on cooling from its solution in boiling water in very small needles. It dissolves in aqueous baryta, soda, and potash, and is precipitated by excess of the latter in a crystalline form.

Methylic dimethylnaphtholate, prepared by heating the phenol under pressure with methyl alcohol and methyl iodide, crystallises in hard white prisms, melts at 68°, is volatile, and dissolves in ethyl alcohol, methyl alcohol, and more abundantly in ether.—The *ethylic ether* is a viscid liquid, the solution of which in chloroform gives with bromine a crystalline product which melts at 90°.

Acetyl-dimethylnaphthol, $C_{14}H_{14}O_2 = C_{12}H_{11}.\overline{Ac}O$, prepared by boiling the phenol with fused sodium acetate and excess of acetic anhydride, crystallises after purification in white scales melting at 77—78°.

Dimethyl-naphthol, oxidised in acetic acid solution with chromic acid, yields yellowish rhombic plates, and a very small quantity of white, apparently rhomboïdal prisms, both of which melt between 104° and 105°. The yellow crystals gave by analysis numbers agreeing nearly with the formula $C_{12}H_{12}O_2$.—This substance when treated with potash blackens without dissolving. Heated with hydriodic acid and red phosphorus, it is reconverted into dimethylnaphthol.

DIMETHYL-NAPHTHALENE, $C_{12}H_{12} = C_{10}H_6Me_2$ may be prepared by heating dimethyl-naphthol with 10 parts of zinc-powder, and passing the resulting vapour through a column of the same powder heated to low redness, whereupon a yellow liquid distils over, from which potash dissolves out unaltered dimethyl-naphthol. The whole is then distilled with steam, and the watery distillate, holding an oil in suspension, is mixed with potash and shaken with ether, which dissolves out the dimethyl-naphthalene, together with a small quantity of naphthalene. The ether having been evaporated off, the remaining oil is boiled several times with sodium in a reflux apparatus till the globules of the metal remain bright, and is then distilled in a Sprengel vacuum at the heat of a salt-bath. By careful fractionation in this manner, it is possible to separate small quantities of naphthalene, but the removal of the last traces is very difficult.

Dimethyl-naphthalene purified in this manner as completely as possible, boils at 262—264° under a pressure of 751 mm., has a density of 1·0283 at 0°, and 1·10199 at 12°, and a vapour-density = 77·8° (H. = 1), the calculated density being 78. It unites with picric acid, forming a very characteristic compound, which may be obtained by mixing the two bodies in hot concentrated alcoholic solution, and crystallises on cooling in long orange-yellow needles melting at 139°. Dimethyl-naphthalene also forms a characteristic tribromo-derivative, $C_{12}H_9Br_3$, which crystallises in white needles melting at 228°.

The dimethyl-naphthalene obtained as above from dimethyl-naphthol, may also be prepared by the action of methyl iodide on Glaser's dibromonaphthalene melting at 81° (*Annalen*, **135**, 49); and finally, together with the above-mentioned dimethyl-naphthol, and a small quantity of xylene, by distilling santonous acid over zinc-powder in an atmosphere of hydrogen.

Santonin, $C_{15}H_{18}O_3$ (from wormseed), distilled with zinc-powder in a stream of hydrogen, yields the same dimethyl-naphthalene, together with propylene and a dimethyl-naphthol, apparently identical with that which is obtained by the decomposition of santonous acid. The authors have not been able to confirm the statement of Saint-Martin (*Compt. rend.*, **75**, 1120), according to which santonin distilled with zinc-powder yields a compound, which he calls santonal, partly liquid, partly crystalline, and having the composition $C_{30}H_{18}O_2$. H. W.

Psoromic Acid, a New Acid extracted from Psoroma crassum. By G. SPICA (*Gazzetta*, **12**, 431—435).—This lichen grows in a few localities in Sicily, and the small quantity with which the author's experiments were made was gathered near Dahlia, province of Caltanisetta. By exhaustion with ether in a percolator, it yielded a yellow substance (A) crystallising in needles from the ether on cooling, and a brown residue (B), which remained in considerable quantity on distilling off the solvent.

The crystallised body is soluble in warm alcohol, ether, chloroform, and acetic acid, and recrystallises from these solvents more or less on cooling, but benzene, unless employed in large excess, dissolves only a part of it, leaving a nearly white crystalline residue. The constituent soluble in benzene was purified by repeated crystallisation from that liquid; the insoluble portion by crystallisation from alcohol and repeated washing with cold alcohol.

The yellow substance crystallised from benzene is usnic acid, $C_{18}H_{18}O_8$, melting at 195—197°, and yielding a sodium salt,

$$C_{18}H_{17}NaO_8,2H_2O,$$

which crystallises from warm water in stellate groups of needles.

The white substance only slightly soluble in benzene crystallises from alcohol in silky needles, dissolves in the solvents above mentioned, and to a slight amount in water, to which it imparts a faint acid reaction. It dissolves also in alkalis and alkaline carbonates, and in sulphuric, nitric, and hydrochloric acids, melts with decomposition at 263—264°, and begins to sublime, but resolidifies at a high temperature, about 215°. Dried at 100° it gave by analysis 60·23—60·29 per cent. carbon, and 3·71—3·97 hydrogen, leading to the formula $C_{20}H_{14}O_9$, which requires 60·30 carbon and 3·51 hydrogen. Its silver salt, obtained by precipitation, forms white flocks, which alter on exposure to light. The analysis of this salt leads to the formula $C_{20}H_{15}AgO_{10}$, showing that the corresponding acid (*psoromic acid*) has the composition $C_{20}H_{16}O_{10}$, and that the compound $C_{20}H_{14}O_9$ extracted from the lichen as above described, is not the acid but the anhydride. The acid itself has not been obtained in the free state.

Psoromic anhydride boiled with aniline is converted into a crystalline yellow substance, which when further heated does not melt, but decomposes, yielding a carbonaceous residue, and a liquid having a characteristic acetic odour, probably psoromic anilide. The anhydride heated with water in sealed tubes at 240°, yields a yellow-brown liquid and a brown residue, which, as well as the residue left on evaporating the solution, exhibits the characters of an acid, and gives with ferric chloride a dark green coloration, not produced by psoromic acid.

The brown residue B, left on evaporating the ether used for the extraction, yields to benzene a small quantity of a resinous substance, together with psoromic acid.

The lichen, after exhaustion with ether, yields to boiling alcohol a substance having the characters of a wax. This the author reserves for further examination. H. W.

Laws of Variation of the Specific Rotatory Power of Alkaloïds under the Influence of Acids. By A. C. OUDEMANS, Jun. (*Rec. Trav. Chim.*, 1, 18—40).—The author records and tabulates a large number of observations relating to the influence of acids, organic and inorganic, on the mon-acid bases quinamine and conquinamine, and on the biacid bases quinine, quinidine, cinchonine, and cinchonidine, both in aqueous and in alcoholic solution,—and deduces from these observations the following general conclusions :—

1. The specific rotatory power of the mon-acid bases, as manifested in the aqueous solutions of their normal salts, is the same for all the salts, and is independent of the chemical character of the acid with which the base is united. Small differences occasionally observed are due to partial and unequal decomposition of these salts under the influence of water, and to the varying influence of the degree of concentration on the different salts.

2. As long as the normal salt is not decomposed by water, this specific rotatory power coincides with the maximum value, the small differences sometimes observed arising from partial decomposition.

3. Biacid bases form two series of salts, in each of which series the base exhibits a distinct specific rotatory power, the value of which is usually much smaller in the basic than in the normal salts.

4. The real specific rotatory power of the biacid bases in the form of *normal salts* and in aqueous solution is probably the same for all the salts, and independent of the chemical nature of the acid with which the base is combined; but in consequence of partial decomposition and of the unequal influence of concentration on the various salts, the specific rotatory power cannot show itself with its true value.

6. The real specific rotatory power of the biacid bases in the form of

basic salts is probably the same for all the salts, the differences between the observed values being due to partial decomposition, and for the most part to the unequal influence of concentration on the different salts. H. W.

Action of Nascent Hydrogen on Pyrroline. By G. L. Ciamician and M. Dennstedt (*Ber.*, **15**, 1831—1832).—An acetic acid solution of pyrroline is heated with zinc-dust for some days, the excess of pyrrol distilled off with steam, the zinc removed by sulphuretted hydrogen, and the acetic replaced by hydrochloric acid. The solution is then treated with potash and steam-distilled, the distillate treated with hydrochloric acid and evaporated to dryness on a water-bath, redissolved, and steam-distilled with potash. The first portions of the distillate richest in the base are mixed with solid potash, whereby the base is separated as an oil, and, after drying over fresh potash is again distilled. It boils at 90—91°, and is a colourless liquid having a strongly alkaline reaction and ammoniacal odour; it is very soluble in water, from which it is not easily separated. The platinochloride alone was analysed, as the free base could not be obtained in a sufficiently dry state. The former is a yellow precipitate almost insoluble in cold water. Analysis of this compound leads to the formula C_4H_7N for the free base. J. K. C.

Synthesis of Pyridine Derivatives from Ethyl Acetoacetate and Aldehydammonia. By A. Hantzsch (*Annalen*, **215**, 1—82).—*Diethyl hydrocollidinedicarboxylate*, $C_5Me_3(COOEt)_2H_2N$, is prepared by warming a mixture of 52 grams of ethyl acetoacetate and 13·5 grams of aldehydammonia for five minutes, and then adding an equal bulk of dilute hydrochloric acid to the mixture. After extracting the crude product with dilute hydrochloric acid and with water, it is recrystallised from boiling alcohol. Diethyl hydrocollidinecarboxylate crystallises in monoclinic or triclinic plates or needles (m. p. 131°) freely soluble in chloroform and hot alcohol. It begins to boil at 315°, but rapidly decomposes at this temperature. This ethereal salt resists the action of aqueous solutions of potash, but is completely decomposed by alcoholic potash. By the action of warm fuming hydrochloric acid, it is split up, yielding acetone, ethyl chloride, ammonium chloride, and aldehyde, $C_{14}H_{21}O_4N + 3H_2O + 3HCl = 2CO_2 + 2C_2H_5Cl + 2C_3H_6O + C_2H_4O + NH_4Cl$.

Ethyl dibromhydrocollidinedicarboxylate dibromide,

$$C_8H_7Br_2(COOEt)_2H_2N,Br_2,$$

formed by the action of bromine diluted with carbon bisulphide on the previously-mentioned ethylic salt, crystallises in thick prisms (m. p. 88°) of a yellow colour. The substance dissolves freely in hot alcohol. By the action of strong nitric acid, it is converted into *ethyl dibromocollidinedicarboxylate dibromide*, $C_8H_7Br_2(COOEt)_2NBr_2$, which crystallises in white needles (m. p. 102°) soluble in ether and in alcohol.

When chlorine is passed into a solution of ethyl hydrocollidinecarboxylate in chloroform, the hepta-derivative, $C_8H_4Cl_5(COOEt)_2Cl_2N$, is produced. This substance crystallises in needles (m. p. 150°) sparingly soluble in hot alcohol.

Ethyl collidinedicarboxylate, $C_5NMe_3(COOEt)_2$, is best prepared by the action of nitrous acid on a mixture of equal weights of alcohol and ethyl hydrocollidinedicarboxylate. When the reaction is complete, the excess of alcohol is removed by evaporation, and a dilute solution of sodium carbonate is added to the residue, which causes the ethyl collidinedicarboxylate to separate out in the form of a heavy oil boiling at 310°. This ethylic salt has the sp. gr. 1·087 at 15°. It combines readily with acids. The *hydrochloride*, $C_{14}H_9O_4N,HCl$, is deliquescent. The *platinochloride*, $(C_{14}H_{19}O_4N)_2H_2,PtCl_6$, forms pink-coloured triclinic plates melting at 184°, insoluble in alcohol and ether, but soluble in water. The *nitrate* crystallises in vitreous needles which melt at 92° and decompose at 122°. The *hydriodide* crystallises in plates, soluble in water and in hot alcohol. It melts at 170° with decomposition. By the action of an alcoholic solution of iodine, this salt is converted into the triodide, $C_{14}H_{19}O_2NHI,I_3$. The *methiodide*, $C_{14}H_{19}O_4N,MeI$, crystallises in white needles soluble in alcohol and water. Although it is precipitated from its aqueous solution by soda, it has a strongly acid reaction. The crystals melt at 138° and decompose at 160°. Ethyl collidinedicarboxylate is not attacked by strong hydrochloric acid or by ammonia at 150°, but it is easily saponified by alcoholic potash. From the potassium salt, lead collidinedicarboxylate and the free acid can be prepared. *Collidinedicarboxylic acid*, $C_5NMe_3(COOH)_2$, forms needle-shaped crystals, sparingly soluble in alcohol, ether, and cold water. The salts which this acid forms with the alkalis and alkaline earths are very soluble in water and do not crystallise well; $C_8H_9N(COO)_2Ba + 3H_2O$ is more soluble in water than the calcium salt $C_8H_9N(COO)_2Ca + H_2O$, which crystallises in needles. The silver salt, $C_8H_9N(COOAg)_2$, is an amorphous body insoluble in water. The pale-green precipitate, obtained by the addition of potassium collidinedicarboxylate to a solution of copper sulphate, has the composition $2C_8H_9N(CO)_2O + 3CuO + 11H_2O$. On boiling the mixture a pale-blue salt is produced which has the composition $C_8H_9N(CO)_2O + 3CuO$.

The hydrochloride of collidinedicarboxylic acid, $C_{10}H_{11}O_4NHCl + 2H_2O$, and the platinochloride, $(C_{10}H_{11}O_4N)_2,H_2PtCl_6$, are crystalline. On heating potassium collidinedicarboxylate with lime, *β-collidine*, or β-trimethylpyridine, $C_5NMe_3H_2$, is obtained. The following table shows the most marked points of difference between α- and β-collidine :—

	α-Collidine. B. p. 178°, sp. gr. 0·953.	β-Collidine. B. p. 171°, sp. gr. 0·917 at 15°.
Solubility	Very slightly soluble in water.	More soluble in cold than hot water.
Exposure to air	No change.	Turns brown.
$C_8H_{11}N,HAuCl_4$	Does not melt under water.	Melts under water; the dry salt melts at 112°.
The addition of CrO_3 gives	Red oil.	Red crystalline precipitate of $(C_8H_{11}N)_2H_2Cr_2O_7$.
Mn, Co, and Fe salts	No precipitate.	Slow precipitation of hydroxides.
$AgNO_3$	No precipitate.	White crystalline precipitate soluble in hot water.

An ethereal solution of ethyl hydrocollidinedicarboxylate absorbs hydrochloric acid gas, forming ethyl collidinedicarboxylate and other products. Dilute hydrochloric acid decomposes ethyl dihydrocollidinedicarboxylate at 100°, yielding ethyl chloride, carbonic anhydride, and *ethyl dihydrocollidinemonocarboxylate*, $C_8H_{11}NH.COOEt$, as a colourless oil. On treating the alcoholic solution of this ethylic salt with nitrous acid, it yelds *ethyl collidinemonocarboxylate*,

$$C_5NHMe_3,COOEt.$$

The platinochloride, $(C_{11}H_{15}O_2N)_2,H_2PtCl_6$, crystallises in prisms melting at 194°, soluble in water. By the action of dilute hydrochloric acid on ethyl dihydrocollidinedicarboxylate at 125°, a mixture of dihydrocollidine, tetrahydrodicollidine, a ketone, $C_8H_{12}O$, and another body of the composition $C_8H_{14}O_2$, is obtained. On distilling the crude product in a current of steam, the two bases are found in the residue.

Dihydrocollidine, $C_8H_{13}N$, is a strongly alkaline liquid, boiling at 175—180°, and having a penetrating odour. It dissolves in cold water, but is reprecipitated on heating the solution. The *platinochloride*, $(C_8H_{13}N)_2,H_2PtCl_6$, and the hydriodide, $C_8H_{13}N,HI$, are crystalline. Dihydrocollidine readily precipitates the hydroxides of magnesium, iron, manganese, and nickel from solutions of their salts, and forms a crystalline compound with methyl iodide. It is not oxidised by nitrous acid. *Tetrahydrodicollidine*, $C_{16}H_{26}N_2$, boils at 255—260°. The *hydriodide*, $C_{16}H_{26}N_2,HI$, is very soluble in water and alcohol. The *platinochloride*, $C_{16}H_{26}N_2,H_2PtCl_6$, crystallises with difficulty.

The *ketone*, $C_8H_{12}O$, is a mobile liquid having a pleasant odour and boiling at 208°. It combines directly with bromine to form the tetrabromide $C_8H_{12}Br_4O$, an oily liquid. By the action of bromine on this compound a crystalline substance is obtained of the composition $C_8H_8Br_4O$ or $C_8H_6Br_4O$, melting at 138°.

Oxidation-products of Collidinedicarboxylic Acid.—Potassium collidinedicarboxylate is converted into the lutidinedicarboxylate by boiling it with the theoretical amount of potassium permanganate solution for two hours. From the potassium salt, the lead salt and the free acid are prepared. *Lutidinetricarboxylic acid*, $C_{10}H_9O_6N + 2H_2O$, resembles collidinedicarboxylic acid. It crystallises in rhombohedrons, which lose their water of crystallisation at 120° and melt at 212° with decomposition. The neutral potassium salt of this acid is deliquescent; the ammonia salt is very soluble in water: $(C_{10}H_6O_6N)_2Ba_3 + 8H_2O$ forms hygroscopic needles; $(C_{10}H_6O_6N)_2Ca_3 + 8H_2O$ is gelatinous; $(C_{10}H_6O_6N)_2Mg_3 + 10H_2O$ is also amorphous and freely soluble. $C_{10}H_6O_6NAg_3$ and the lead and mercurous salts are insoluble or sparingly soluble. *Lutidine*, $C_5Me_2H_3N$, obtained by heating a mixture of potassium lutidinetricarboxylate and lime, boils at 154°.

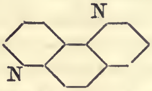
By the prolonged action of potassium permanganate on potassium collidinedicarboxylate, the potassium salts of picolinetetracarboxylic acid and pyridinepentacarboxylic acid are produced. To obtain picolinetetracarboxylic acid, strong nitric acid is added to a solution of the crude potassium salt, which precipitates an acid salt of the composition $C_5NMe(COOH)_2(COOK)_2 + 4H_2O$. The concentrated solution of this salt is decomposed by strong sulphuric acid, and the free acid extracted with ether. Pyridinepentacarboxylic acid is obtained by a similar process. *Picolinetetracarboxylic acid*, $C_5NMe(COOH)_4 + 2H_2O$, crystallises in prisms which lose their water of crystallisation at 120°, and melt with decomposition at 199°. The acid dissolves freely in water. Its salts do not crystallise well. The dipotassium salt forms large rhombic plates; the mono-potassium salt, $C_5NMe(COOH)_3.COOK + 2H_2O$, crystallises in needles. $C_5NMe(C_2O_4Ca)_2 + 4H_2O$ is sparingly soluble. Picoline, C_5NMeH_4, boils at 135°.

Pyridinepentacarboxylic acid, $C_5N(COOH)_5 + 2H_2O$, dissolves freely in water, forming a strongly acid solution. The crystals lose their water of crystallisation at 120°, and decompose without melting at 220°. It is a powerful acid, resembling oxalic acid in its property of forming acid and double salts. The following pyridinepentacarboxylates were prepared:—$C_{10}H_4O_{10}NK + 3$ or $2H_2O$, shining needles. $C_{10}H_3O_{10}NK_2 + 4$ or $3\frac{1}{2}H_2O$, cubes. $C_5N(COOK)_5$, crystalline powder, freely soluble in water. $(C_{10}O_{10}N)_2Ba_5 + 11H_2O$ is deposited as a crystalline powder when barium chloride is added to the free acid. $(C_{10}O_{10}N)_2Ca_5 + 12H_2O$, sparingly soluble non-crystalline powder. $C_{10}O_{10}NH_3Ca + \frac{1}{2}H_2O$, sparingly soluble crystalline powder. $C_{16}O_{10}NCa_2.NH_4 + 5H_2O$ is deposited as an amorphous precipitate when pyridinepentacarboxylic acid is added to an ammoniacal solution of calcium chloride. The ammonium in this salt can be replaced by potassium or sodium. Acid potassium oxalate also forms a double salt with potassium pyridinepentacarboxylate, viz., $C_{10}O_{10}NH_4K + C_2O_4HK + 5H_2O$. Pyridine, C_5H_5N, obtained by the action of lime on potassium pyridinepentacarboxylate, boils at 120°. W. C. W.

Dipyridyl Derivatives. By Z. H. SKRAUP and G. VORTMANN (*Monatsh. Chem.*, **3**, 570—602).—In this paper, the authors show that the reaction which takes place in the synthesis of quinoline, hitherto applied only to mono-substituted derivatives of benzene and phenol (Abstr., 1881, 919; also this vol., p. 89), may be extended to the diamidobenzenes, and in particular they describe the results obtained by heating a mixture of *m*-diamido- and *m*-dinitro-benzene with sulphuric acid and glycerol. The diamidobenzene—which was employed in the form of stannochloride—was prepared by the action of tin and hydrochloric acid on *m*-nitraniline; and the solution obtained by treating this stannochloride with glycerol and sulphuric acid—after being freed from separated resin and rendered alkaline—was shaken up with alcoholic ether. The ethereal liquid was then exhausted with hydrochloric acid; the solution of the new base thus obtained was evaporated; and the hydrochloride which crystallised out from it after addition of alcohol was converted by potassium dichromate into a sparingly soluble chromate (foreign matters being at the same time destroyed by oxidation); this chromate, heated with ammonia, yielded the base in the form of a hydrate, which when left over sulphuric acid, or more quickly when heated at 100°, gave off its water, leaving the anhydrous base, which was purified by distillation.

The base thus obtained is regarded by the authors, for reasons to be explained further on, as formed by the attachment of two pyridine-rings to a benzene-ring, in the manner represented by the right-hand figure below, and may be called phenanthroline, from the analogy of its structure to that of phenanthrene.


Phenanthrene.



Phenanthroline.

Pure phenanthroline forms a white crystalline mass made up of four-sided plates. It has a faint odour when cold, becoming stronger on heating, and resembling that of naphthaquinoline. It melts at 78—78·5°, remains liquid for some time after cooling, but then solidifies instantaneously on being touched with a solid body. It is somewhat hygroscopic, the clear crystals when exposed to the air becoming covered with a white opaque coating, and ultimately falling to powder. When the fused substance is covered with a very thin film of water and rubbed with a glass rod, it is completely converted into the hydrate, which is thus obtained as a perfectly dry mass. Phenanthroline is nearly insoluble in cold, more easily soluble in boiling water, dissolves in all proportions in alcohol, but is nearly insoluble in ether, benzene, and light petroleum; dilute acids dissolve it readily. The aqueous solution is nearly neutral when cold, but has a distinct alkaline reaction at the boiling heat. The pure base may be distilled without decomposition, and boils at a temperature much above 360°. It volatilises to a slight extent with the vapour of water. The hydrated compound, $C_{12}H_8N_2,2H_2O$, crystallises in long soft needles, which do not effloresce on exposure to the air, but give off their water over sulphuric acid, and melt in a capillary tube at 65·5°.

Phenanthroline in most of its salts appears as a mon-acid base, and it is only with a great excess of acid and very strong solutions that normal salts can be obtained in which it is bi-acid. The basic *hydrochloride*, $C_{12}H_8N_2,HCl + H_2O$, separates from alcoholic solution, even in presence of excess of acid, in long white prisms, easily soluble in water, sparingly in alcohol. The normal salt, $C_{12}H_8N_2,2HCl + 2H_2O$, separates in small prisms on cooling from a warm solution of the base in a small quantity of strong hydrochloric acid. It is very unstable, and is decomposed by water. The *platinochloride*, $C_{12}H_8N_2,H_2PtCl_4 + H_2O$, forms small reddish-yellow prisms, sparingly soluble in alcohol. The *chromate*, $(C_{12}H_8N_2)_2Cr_2O_7$, forms golden-yellow needles, slightly soluble in cold water. The *picrate*, $C_{12}H_8N_2,C_6H_2(NO_2)_3.OH$, crystallises in light-yellow prisms, very silghtly soluble in alcohol, melting at 238—240°. The *sulphate* is sparingly soluble in alcohol; the *tartrate* both in alcohol and in water.

A *methiodide*, $C_{12}H_8N_2,MeI + H_2O$, obtained by heating phenanthroline at 100° with methyl alcohol and excess of methyl iodide, crystallises in broad prisms, dissolves easily in water, sparingly in alcohol, and gives off its water of crystallisation with great facility. Its aqueous solution turns red on addition of potash-lye, and deposits a non-solidifying oil.

BROMIDES.—On adding bromine to a hot concentrated alcoholic solution of phenanthroline, an *octobromide*, $C_{12}H_8N_2,Br_8$, separates in red crystals melting at 176—178°. The *dibromide*, $C_{12}H_8N_2,Br_2$, separates on adding bromine-water to an aqueous solution of phenanthroline hydrochloride, as a light yellow crystalline precipitate melting at 149°; heated for a short time with a small quantity of alcohol, it is converted into dark-red crystals which have the composition $(C_{12}H_8N_2)_2Br_3$, or $C_{12}H_8N_2,Br_2 + C_{12}H_8N_2,HBr$, melting at 178°, and giving off bromine when heated with water. By prolonged boiling with alcohol, the dibromide is converted first into orange-red slender needles, then into thick yellow prisms, and finally into nearly colourless needles, consisting of phenanthroline hydrobromide, $C_{12}H_8N_2,HBr + \frac{1}{2}H_2O$, melting at 278—280°. When, on the other hand, phenanthroline is heated at 120—130° with excess of bromine and water, it yields a brownish-yellow bromine-compound, which dissolves in glacial acetic acid, and separates therefrom in non-crystalline crusts, and appears to be a mixture of $C_{12}H_6Br_2N_2$ and $C_{12}H_5Br_3N_2$.

HYDRIDES.—By reduction with tin and hydrochloric acid, phenanthroline is converted into an amorphous compound purifiable by distillation, and probably consisting of a mixture of tetra- and octo-hydride of phenanthroline, $C_{12}H_8N_2,H_4$ and $C_{12}H_8N_2,H_8$.

Dipyridyl-carboxylic Acids.—Phenanthroline is readily oxidised by potassium permanganate in very dilute solution (5 : 1000), yielding as chief product—together with a small quantity of quinolinic or pyridine-dicarboxylic acid—an acid, $C_{12}H_8N_2O_4$, or $C_{10}H_6N_2(COOH)_2$, called phenanthrolinic or dipyridyl-dicarboxylic acid, which may be isolated by nearly neutralising the concentrated filtrate with nitric acid, adding the calculated quantity of silver nitrate, and precipitating the resulting silver salt of phenanthrolinic acid by further cautious addition of nitric acid. This silver salt decomposed by hydrogen sulphide, yields the phenanthrolinic acid in large triclinic tablets, having the axes $a : b : c = 0{\cdot}5909 : 1 : 0{\cdot}9773$, and exhibiting the faces $\infty P\breve{\infty}$, $0P$, $\infty P'_{|}$, $\infty{}'_{|}P$, P', $'P$, $_{|}P$, $P_{|}$. They contain crystal-water, have a slightly acid taste, dissolve sparingly in cold, more freely in boiling water, easily in alcohol, very sparingly in ether and in benzene. They give off their water at 100°, melt with evolution of carbonic anhydride at 217°, give a blood-red to yellow-red coloration with ferrous sulphate, a yellowish gradually crystallising precipitate with ferric chloride and sodium carbonate, no precipitate with bromine-water.

Phenanthrolinic acid forms salts both with bases and with acids. The *normal potassium salt* is extremely deliquescent, and remains on evaporating its aqueous solution, as a vitreous mass, which becomes crystalline when left in contact with alcohol. The *acid potassium salt*, $C_{12}H_7N_2O_4K,1\frac{1}{2}H_2O$, may be crystallised in like manner. The *calcium salt*, $C_{12}H_6N_2O_4Ca,3H_2O$, forms transparent shimmering laminæ; the *barium salt*, $C_{12}H_6N_2O_4Ba,1\frac{1}{2}H_2O$, very sparingly soluble granules; the *copper salt*, $C_{12}H_6N_2O_4Cu,3H_2O$, nearly insoluble greenish-blue granules; the *normal silver salt* forms microscopic laminæ; the *acid silver salt*, $C_{12}H_7N_2O_4Ag,4H_2O$, is a precipitate composed of stellate groups of needles. The *hydrochloride*, $C_{12}H_8N_2O_4,2HCl$, prepared with strong hydrochloric acid, forms transparent prisms. The *platinochloride*, $(C_{12}H_8N_2O_4,HCl)_2,PtCl_4 + 6H_2O$, separates gradually in large thick yellow prisms, and the mother-liquor when left to evaporate yields the salt $C_{12}H_8N_2O_4,H_2PtCl_6$ in orange-red tablets.

Dipyridyl-monocarboxylic acid,

$$C_{11}H_8N_2O_2 = C_{10}H_7N_2(COOH),$$

is obtained by heating phenanthrolinic acid to its melting point, and crystallises in delicate white needles containing $2H_2O$, which they give off at 100°. The dehydrated acid cakes together at 179°, melts at 182·5—184°, solidifying to a vitreous mass on cooling, and is but slightly decomposed by distillation. It dissolves with difficulty in cold water and alcohol, easily with the aid of heat; gives no coloration with ferrous sulphate, yellow-brown with ferric chloride; a light-blue crystalline precipitate with cupric acetate, and with silver nitrate a white precipitate soluble in excess of the acid and of the precipitant; with bromine-water a cinnabar-red precipitate. The *calcium salt*, $(C_{11}H_7N_2O_2)_2Ca,2H_2O$, forms long shining easily soluble needles, which give off their water at 220°; the *silver salt*, $C_{11}H_7N_2O_2Ag,\frac{1}{2}H_2O$, is a dense precipitate, which becomes crystalline on standing.

A dipyridyl, $C_{10}H_8N_2$, is obtained by distilling calcium dipyridylmonocarboxylate with quicklime, and passes over as a colourless oil, boiling at 149·5°. Its *picrate*, $C_{10}H_8N_2,C_6H_2(NO_2)_3.OH$, forms small dull-yellow needles, slightly soluble in cold water, melting at 149·5°; and its *platinochloride*, $C_{10}H_8N_2,H_2PtCl_6 + \frac{1}{2}H_2O$, is a light-yellow precipitate, very slightly soluble in water and in hydrochloric acid. This dipyridyl, which differs distinctly from Anderson's dipyridine, and from the isodipyridine of Cahours and Étard, is related to pyridine in the same manner that diphenyl is related to benzene. The formation of dipyridyl-dicarboxylic acid has led the authors to assign to phenanthroline the constitutional formula above given (p. 86), analogous to that of phenanthrene. H. W.

Quinoline from Cinchonine. By O. de Coninck (*Bull. Soc.*

Chim. [2], **37**, 208—209; see this vol., 414).—The hydrochloric acid solution of the fraction of crude quinoline boiling between 226—231° is repeatedly treated with ether, which removes a small quantity of a neutral compound having a strong odour, and boiling at about 220°. The purified base is then distilled. It is at first colourless, but darkens somewhat rapidly, even when protected from air and light; sp. gr. at 0° = 1·1055; at 11·5, 1·0965; b. p. 236—237° at 775 mm. The quinoline obtained by adding potash to crystallised quinoline tartrate, also boils at 236—237° under the same pressure. Quinoline obtained by synthesis boils at 228° (Skraup and Koenigs), or 232° (Baeyer and others). Quinoline hydrochloride forms white deliquescent crystals, which emit an odour of quinoline, and melt at 93—94° to a colourless liquid. The hydrochloride is very soluble in warm, slightly less soluble in cold water, soluble in all proportions in absolute alcohol and chloroform, only slightly soluble in cold, but very soluble in hot ether or benzene. C. H. B.

The Quinoline of Coal-tar and of the Cinchona Alkaloïds, and its Oxidation by Potassium Permanganate. By S. Hoogewerff and W. A. v. Dorp (*Rec. Trav. Chim.*, **1**, 1—17 and 107—131). —After a historical sketch of the discussion as to the identity or isomerism of the bases C_9H_7N, obtained from the cinchona alkaloïds (quinoline), and from coal-tar (leucoline), the authors describe the methods which they adopted for purifying the bases obtained from these two sources, and give as the mean results of their analyses of both bases C = 83·58 per cent., H = 5·8. The boiling points found were for quinoline 238·25° to 239·25°, and for leucoline 239·25° to 240·25° (thermometer wholly in vapour). Moreover, both yield the same hydrate, $2C_9H_7N,3H_2O$, platinochloride,

$$(C_9H_7N)_2,H_2PtCl_6 + 2H_2O,$$

dichromate, $(C_9H_7N)_2H_2Cr_2O_7$, and argentonitrate. By oxidation with potassium permanganate in alkaline solution, both bases yield, as principal products, carbonic anhydride and quinoleic acid, $C_7H_5NO_4$, according to the equation $C_9H_7N + O_9 = C_7H_5NO_4 + 2CO_2 + H_2O$, together with very small quantities of oxalic acid and ammonia. The identity of the bases from the two sources may therefore be regarded as established, and the name "leucoline" may be dropped.

The quinoleic acid may be separated from the products by neutralising with nitric acid, removing the crystals of potassium nitrate which separate on concentration, then precipitating with calcium nitrate, treating the concentrated filtrate with lead nitrate, decomposing the resulting precipitate with hydrogen sulphide, and concentrating the solution filtered therefrom. Quinoleic acid is then deposited in small honey-yellow monoclinic crystals, having the axes $a : b : c = 0·5418 : 1 : 0·6075$ and $\beta = 64° 54'$. Observed faces, ∞P, $P\grave{\infty}$, $\infty P\grave{\infty}$, and a pyramidal face not determined. Cleavage, parallel to the clinopinacoïd.

Quinoleic acid is but slightly soluble in cold, rather more so in hot water, very slightly soluble in alcohol, insoluble in benzene, and is removed from its aqueous solution by ether. It is but very slightly attacked by potassium permanganate in alkaline solution, easily in acid solution. When heated to 100°, it gives off CO_2 and leaves nicotic acid, $C_6H_5NO_2$. Heated in capillary tubes, it begins to turn brown at 175°, and melts at 228—230°, but if rapidly heated it melts at about 180°, giving off gas and resolidifying, after which it melts at 228°. Heated with lime, it yields an oil smelling of pyridine.

A cold moderately dilute aqueous solution of this acid exhibits the following reactions. With—

$CaCl_2$: gelatinous pp., gradually becoming crystalline.
$BaCl_2$: gelatinous pp.
$ZnSO_4$: pp. of microscopic needles after a few hours.
$MnSO_4$: like the last, but smaller crystals.
$CO(NO_3)_2$: like the last; pp. rose-coloured.
$NiSO_4$ and $HgCl_2$: no pp.
$FeSO_4$: orange colour; yellow-brown crystalline pp. after some time.
Fe_2Cl_6: yellow-brown, amorphous.
$CuSO_4$: light-blue, apparently amorphous, nearly insoluble in water and acetic acid, even at boiling heat.
$Hg(NO_3)_2$: white pp.; microscopic needles.
$Pt(C_2H_3O_2)_2$; like the last.
$AgNO_3$: shining needles of acid salt (*infra*).

Quinoleic acid is a pyridine-dicarboxylic acid,

$$C_5H_3\overset{1}{N}(\overset{2}{COOH})(\overset{3}{COOH}).$$

It is therefore bibasic. The *acid potassium salt*, $C_7H_4NO_4K,2H_2O$, forms limpid triclinic crystals, which give off their water at 100°. The *normal barium salt*, $C_7H_3NO_4Ba$, obtained by adding a soluble barium salt to a cold solution of the acid neutralised with ammonia, crystallises sometimes with $1\frac{1}{2}$, sometimes with $2\frac{1}{2}$ mols. H_2O, part of which goes off at 100°, the last semi-molecule only at 260°. The *normal silver salt*, $C_7H_3NO_4Ag_2$, is obtained by adding silver nitrate to a cold neutralised solution of the acid, as a gelatinous precipitate which becomes granular or crystalline on standing. The *acid salt*,

$$C_7H_4NO_4Ag + H_2O,$$

is obtained by adding a hot aqueous solution of the acid to an acid solution of silver nitrate diluted with boiling water, and separates on cooling in concentric groups of shining needles. Sometimes, however, a *hyper-acid salt*, $C_7H_4NO_4Ag,C_7H_5NO_4$, is deposited under these conditions, in concentric groups of small needles.

Quinoleic acid, when heated at 120—140° and upwards, gives off water and carbonic anhydride, and is converted into nicotic acid, $C_6H_5NO_2 = C_7H_5NO_4 - CO_2$. The same result is obtained by heating quinoleic acid with acetic acid. The nicotic acid thus produced agrees in character with that which is obtained by other methods. Its calcium salt, $(C_6H_4NO_2)_2Ca$, forms monoclinic crystals; $a : b : c = 1{\cdot}5372 : 1 : 0{\cdot}6293$. $\beta = 62{\cdot}50$. Observed faces, ∞P, $P\breve{\infty}$. H. W.

Nitro- and Amido-bromoquinoline. By W. La Coste (*Ber.*, 15, 1918—1922).—Bromoquinoline (prepared from parabromaniline) is added gradually to a mixture of two parts sulphuric acid and one part fuming nitric acid, the whole being cooled if necessary. On pouring the product into water and neutralising with sodium carbonate, nitrobromoquinoline is precipitated, and can be purified by crystallisation from alcohol. It forms long yellowish-white needles, which melt at 133°. It dissolves readily in ether and in boiling alcohol, and is slightly soluble in boiling water, from which it crystallises in long thin colourless needles. With platinum chloride, nitrobromoquinoline gives a bright-yellow crystalline precipitate,

$$[C_9H_5NBr(NO_2),HCl]_2,PtCl_4.$$

Bromoquinoline, obtained by the bromination of quinoline, also yields a nitro-compound which melts at 133°. It crystallises from hot alcohol in short yellowish needles, grouped together in nodules. It gives a yellow granular precipitate with platinum chloride.

For the reduction of nitro- to amido-bromoquinoline, it is best to heat it in alcoholic solution with an acid (HCl) solution of stannous chloride. The double salt which crystallises out on cooling is dissolved in water, and treated with dilute soda-solution, when amidobromoquinoline separates in flocks, and may be crystallised from boiling water. It forms long almost colourless needles, containing 1 mol. H_2O, which it loses over sulphuric acid. It melts (anhydrous) at 164°. Amidobromoquinoline is a weak base, which forms salts with acids. The *nitrate*, $C_9H_5NBr(NH_2),HNO_3$, forms gold-coloured groups of needles; it explodes on heating. The *hydrochloride* crystallises in very soluble red prisms, which contain water of crystallisation; it forms a platinochloride. *Acetamidobromoquinoline*, $C_9H_5NBr.NH.COMe$, crystallises in colourless plates melting at 104—105°.

A. K. M.

Hydroxyquinoline. By O. FISCHER (*Ber.*, **15**, 1979—1981).— Quinoline yields two isomeric monosulphonic acids, of which the ortho-acid, as previously described (Abstr., 1882, 869), yields the hydroxyquinoline of melting point 75—76°. The meta-acid crystallises in long thin colourless needles, and is more readily soluble in water than the ortho-acid; it is best separated by the difference of solubility of the calcium salts, the meta-salt being the more soluble. The best yield of the meta-acid is obtained by conducting the reaction at 140—150°, the yield being then 10—15 per cent.

Metahydroxyquinoline forms colourless silky needles, melting at about 230°, it is readily soluble in alcohol and benzene, sparingly in water, ether, and light petroleum. With ferric chloride, it yields no coloration in the cold, but on heating a faint red tint appears. The platinochloride forms brownish-yellow prisms.

Metamethoxyquinoline, prepared in a similar manner to the ortho-compound (*loc. cit.*), is a limpid oil, boiling with partial decomposition at 275° under 720 mm. pressure. The platinochloride crystallises in long brownish-yellow prisms; the picrate crystallises in tufts of thin needles, both salts are sparingly soluble in water. The oxalate forms silky needles, readily soluble in water.

On distilling sodium quinolinorthosulphonate with potassium cyanide, the distillate was found to contain a mixture of ortho- and meta-cyanoquinolines, the latter being in excess, intra-molecular change having occurred. A. J. G.

Synthetic Researches in the Quinoline Series. By Z. H. SKRAUP (*Monatsh. Chem.*, **3**, 531—569).—HYDROXYQUINOLINES,

$$C_9H_7NO = C_6H_3N \vdots C_6H_3OH.$$

These bases (ortho, meta, and para, according to the relative positions of the N-atoms and the OH-group) are formed by heating a mixture of an amidophenol (or better its hydrochloride) and the corresponding nitrophenol, with sulphuric acid and glycerol, according to the equation $C_6H_4(NH_2).OH + C_3H_8O_3 = C_9H_6NOH + 3H_2O + H_2$. The amidophenols used for the purpose must be pure, as even small quantities of foreign substances greatly diminish the yield of hydroxyquinoline.

Ortho-hydroxyquinoline is but very slightly soluble in water, easily soluble in absolute alcohol, less soluble in aqueous alcohol. From water and from dilute alcohol, it separates in anhydrous brittle prisms, from absolute alcohol in more compact crystals. Ether dissolves it with difficulty, warm benzene in all proportions. The solutions in nearly absolute alcohol and in benzene are colourless; the former becomes deep yellow on addition of a small quantity of water, colourless again when mixed with a large quantity of alcohol. The solutions in acids and alkalis are yellow.

o-Hydroxyquinoline quickly becomes reddish on exposure to sunshine; it has a peculiar phenolic odour and burning taste; sublimes very easily both from its solutions and in the solid state, softens at 72°, melts at 73—74°, and usually solidifies at 53—55°. Under a pressure of 752 mm. it boils at 258·2° (corr.). The impure substance decomposes on distillation, the pure substance scarcely at all. The dilute alcoholic solution is coloured blackish-green by ferric chloride, the colour becoming darker on addition of sodium carbonate, which ultimately throws down a dingy brownish-green flocculent precipitate. The coloration is prevented by the presence of free hydrochloric acid but not by acetic acid. Ferrous sulphate forms a dark brown-red precipitate soluble in acetic acid with silver nitrate. The solution of this hydroxyquinoline in potash gives a yellow flocculent precipitate becoming crystalline on standing; with mercuric chloride an orange-yellow crystalline precipitate; with lead nitrate a light yellow flocculent precipitate, and with barium chloride a white pulverulent precipitate. The *acid sulphate*, C_9H_7NO,H_2SO_4, crystallises in light yellow prisms containing 2 mol. H_2O, 1 mol. of which is given off over sulphuric acid. The *hydrochloride*, $C_9H_7NO,HCl + H_2O$, forms yellow prisms easily soluble in water and in alcohol; the *platinochloride*, $(C_9H_7NO,HCl)_2PtCl_4 + 2H_2O$, forms long golden-yellow sparingly soluble needles; the *picrate*, $C_9H_7NO,C_6H_2(NO_2)_3.OH$, crystallises in yellow prisms very slightly soluble in cold alcohol, caking together at 170° and melting at 203—204°. A characteristic *copper-compound*, $(C_9H_6NO)_2Cu$, is precipitated as a siskin-yellow powder on adding cupric acetate to an alcoholic solution of the hydroxyquinoline.

The acetyl-compound, $C_{11}H_9NO = C_9H_6\overline{Ac}NO$, prepared by boiling the hydroxyquinoline with acetic anhydride and sodium acetate, is a nearly colourless oil which remains fluid at −20°, boils at about 280°, is gradually decomposed by exposure to the air, more quickly by bases, with separation of *o*-hydroxyquinoline; it dissolves readily in hydrochloric acid, and the solution mixed with platinic chloride forms the salt $(C_9H_6\overline{Ac}NO,HCl)_2PtCl_4 + 2H_2O$, which separates in tufts of small yellow needles.

Nitro-compounds.—Strong nitric acid converts *o*-hydroxyquinoline into a mixture of the mono- and dinitro-derivatives, $C_9H_6(NO_2)O$ and $C_9H_5(NO_2)_2O$, the latter greatly predominating. The mixture dissolves in hot dilute potash-ley, forming a deep yellow solution, which on cooling deposits a potassium derivative in slender yellow needles. The alcoholic solution is coloured deep garnet-red by ferric chloride.

Bromine-compound, $C_9H_5Br_2NO$.—This compound separates on dropping bromine (1 mol.) into an alcoholic solution of *o*-hydroxyquinoline, as a mass of needles, and may be obtained by recrystallisation from alcohol or benzene in white brittle prisms. It appears to be converted into a bromine addition-product by excess of bromine.

o-Methoxyquinoline or *o*-Quinanisoïl, $C_{10}H_9NO = C_9H_6NOMe$, is prepared, not from the hydroxyquinoline, but directly by treating a mixture of *o*-amidanisoïl and *o*-nitranisoïl with glycerol and sulphuric acid. It is a nearly colourless oil, which boils at 265—268°, turns brown on exposure to the air and forms a platinochloride—

$$C_{10}H_9NO,H_2PtCl_6 + 2H_2O,$$

which crystallises in short reddish-yellow prisms.

Hydro-*o*-hydroxyquinoline, $C_9H_{11}NO$, previously obtained by Bedall u. Fischer (*Ber.*, **11**, 1368), is prepared by the action of tin and hydrochloric acid on the hydroxyquinoline. The aqueous solution of its hydrochloride gives a blood-red colour with ferric chloride, and is distinguished from that of the para-derivative by not emitting the odour of quinone when boiled.

Para-hydroxyquinoline.—This base, prepared like the *o*-compound, is best purified by recrystallisation of its hydrochloride. The free base crystallises from alcohol in small brittle prisms, melts at 193°, boils above 360°, dissolves very sparingly in water and ether, still less in benzene and in chloroform, more freely in alcohol, easily in acids and alkalis. Ferric chloride colours the alcoholic solution faintly yellow; ferrous sulphate produces no coloration. The alkaline solution gives with silver nitrate a yellowish gelatinous precipitate; with mercuric chloride a light yellow, with lead nitrate a nearly white precipitate, with barium nitrate none; with cupric acetate, after neutralisation with ammonia, a green precipitate.

The *hydrochloride*, $C_9H_7NO,HCl + H_2O$, is colourless when pure, very soluble in water, sparingly in absolute alcohol, insoluble in ether, very slightly soluble in strong hydrochloric acid, and in a saturated solution of sodium chloride; it gives off its crystal-water easily at 100°. The *platinochloride*, $(C_9H_7NO,HCl)_2,PtCl_4 + 2H_2O$, is a reddish-yellow crystalline precipitate. A *copper-quinoline acetate*, $(C_2H_6NO_2)_2Cu,2C_2H_4O_2$, separates gradually from an alcoholic solution of *p*-hydroxyquinoline mixed with a dilute solution of cupric acetate, in groups of acute wedge-shaped crystals nearly black by reflected, amethyst-blue by transmitted light.

Nitro-*p*-hydroxyquinoline is obtained as a nitrate—

$$C_9H_6(NO_2)NO,HNO_3 + H_2O,$$

on adding *p*-hydroxyquinoline to 4—5 parts strong nitric acid, warming the liquid till the whole is dissolved, and diluting the red-brown solution with water. The salt then separates in orange-red acute prisms which become whitish at 100°. It dissolves easily on heating with a small quantity of water, less easily in a larger quantity, easily in alcohol. By dissolving it in sodium carbonate and acidulating with acetic acid, the free nitrohydroxyquinoline, $C_9H_6(NO_2)NO$, is obtained in small yellow needles, insoluble in water, sparingly in cold, easily in hot alcohol, easily also in acids and alkalis. It melts at 139—140°, and sublimes when cautiously heated. Its alcoholic solution is coloured reddish by ferric chloride, gives a yellow-brown precipitate with cupric acetate, and orange-yellow with silver nitrate. Its potassium salt forms yellowish-brown brittle needles; the barium salt, orange-yellow needles slightly soluble in cold water.

Bromo-*p*-hydroxyquinoline, C_9H_6BrNO, is obtained on slowly adding bromine to an alcoholic solution of *p*-hydroxyquinoline, as a hydrobromide, C_9H_6BrNO,HBr, which separates in reddish-yellow heavy granules. This salt dissolves sparingly in absolute, easily in hot aqueous alcohol, and with partial decomposition in a large quantity of hot water. Its dilute alcoholic solution, when treated with sodium carbonate, deposits the free bromhydroxyquinoline, C_9H_6BrNO, in nearly colourless needles, easily soluble in hot dilute alcohol, melting at 184—185°. With silver nitrate, on addition of ammonia, it gives a yellowish flocculent precipitate; with cupric acetate, after neutralisation, an olive-green precipitate.

The acetyl-compound, $C_9H_6\overline{Ac}NO$, prepared like the corresponding ortho-compound, is a light yellow scentless oil, boiling at 298°, easily soluble in alcohol and ether, soluble also in hot water. When cooled to −20°, it remained liquid for nearly half an hour, but began to crystallise soon after its removal from the freezing mixture. The white crystals thus obtained melted between 36° and 38° to a colourless liquid which solidified only in contact with the solid substance. The *platinochloride*, $(C_{11}H_9NO_2,HCl)_2,PtCl_4$, is a yellow crystalline precipitate. The benzoyl-compound, $C_9H_6\overline{Bz}NO$, prepared by boiling the hydroxyquinoline with benzoic chloride, crystallises from glacial acetic acid in white slender needles, nearly insoluble in water, alcohol, ether, and hydrochloric acid, slightly soluble in alkalis, and melting at 230—231°.

p-Quinanisoïl, $C_9H_6N.OMe$, prepared like the ortho-compound, is a non-solidifying-oil. This *hydrochloride* crystallises in long white prisms, deliquescing in water, moderately soluble in alcohol, sparingly in ether alcohol. The *platinochloride*, $(C_9H_6N.OMe,HCl)_2,PtCl_4 + H_2O$, crystallises in acute orange-red prisms, easily soluble in hot water.

Hydro-*p*-hydroxyquinoline, $C_9H_{11}NO$, has been obtained as a hydrochloride, though not quite pure, by the action of tin and hydrochloric acid on *p*-hydroxyquinoline. The hydrochloride is easily soluble in water and separates by evaporation over sulphuric acid, in feathery groups of large white prisms, afterwards in small white needles. The free base is coloured reddish-violet by ferric chloride, becoming brownish on boiling, and emitting a strong odour of quinone.

Meta-hydroxyquinoline.—This base is most readily purified by fractional precipitation of the acid oxalate. It crystallises from absolute alcohol in prisms, from dilute alcohol and from ether in needles, from chloroform, and by spontaneous evaporation of its aqueous solution, mostly in granular aggregates. It melts, with partial blackening, at 235—238°, sublimes undecomposed when quickly heated, and boils with rapid decomposition at a higher temperature than the para-compound. It is inodorous and nearly tasteless, slightly soluble in water, much less soluble in alcohol than *p*-hydroxyquinoline, more soluble in chloroform, moderately in other solvents. Its solutions in alkalis and acids have a deep yellow colour, so long as any of the undissolved substance is present, but they become colourless when the whole is dissolved. It dissolves readily in caustic potash and baryta, sparingly in ammonia. All the solutions, especially the dilute alcoholic, have a distinct green fluorescence. Ferric chloride added to the dilute alcoholic solution, produces a fine brown-red colour, becoming lighter on addition of sodium carbonate; ferrous sulphate produces no reaction. The meta-compound withstands the action of potassium dichromate more completely than its isomerides, which are thereby oxidised.

The *hydrochloride*, $C_9H_7NO,HCl + 1\frac{1}{2}H_2O$, crystallises in prisms, colourless when quite pure, but mostly light yellow, freely soluble in water, very sparingly in alcohol; the *platinochloride*—

$$(C_9H_7NO,HCl)_2,PtCl_4 + 2H_2O,$$

in orange-yellow needles; the picrate, in light yellow needles melting with decomposition at 244—245°. The *copper-compound*—

$$(C_9H_6NO)_2Cu,2C_2H_4O_2,$$

is obtained in violet crystals when an alcoholic solution of hydroxyquinoline mixed with an equivalent quantity of cupric acetate and a small quantity of acetic acid, is left to evaporate.

Nitro-*m*-hydroxyquinoline, $C_9H_6(NO_2)NO$, is obtained on adding *m*-hydroxyquinoline to fuming nitric acid, precipitating with water, and recrystallising the yellow granules thereby thrown down from hot water, in yellow shining laminæ which melt with evolution of gas at 255°, and unite with acids, forming salts which are decomposed by water.

Bromine-compound.—On adding bromine-water to the hydrochloride of *m*-hydroxyquinoline, a bromide of bromhydroxyquinoline is obtained, which when boiled with alcohol, is converted into a hydrobromide, C_9H_6BrNO,BrH.

A benzoyl-derivative is obtained in the same manner as the corresponding para-compound in the form of an oil which slowly solidifies, melting at 88—89°, and yields a platinochloride having the composition $(C_9H_6\overline{Bz}NO,HCl)_2,PtCl_4$.

Hydro-*m*-hydroxyquinoline.—The hydrochloride of this base is obtained in colourless well-defined prisms by heating a solution of *m*-hydroxyquinoline in hydrochloric acid with excess of metallic tin, precipitating the excess of tin with hydrogen sulphide, and evaporating. When heated with ferric chloride, it first turns light yellow, then brown-red, and gives off an odour slightly resembling that of quinone.

H. W.

Quinoline-derivatives. By A. Rhoussopoulos (*Ber.*, **15**, 2006—2009).—By the union of quinoline with ethyl monochloracetate, a compound, $C_{13}H_{14}NO_2Cl = C_9H_7N(CH_2.COOEt)Cl$, is obtained, crystallising in stellate groups of white needles. It is extraordinarily soluble in water, readily soluble in alcohol, insoluble in ether. The platinochloride, $C_{13}H_{14}NO_2Cl_2,PtCl_4$, crystallises in small thin needles. The compound, $C_{13}H_{14}NO_2Cl$, treated with freshly precipitated silver oxide, yields *quinoline-betaïne*, according to the equation—

$$C_9H_7N(C_2H_2O_2Et)Cl + AgOH + H_2O = AgCl + EtOH + C_9H_7NC_2H_2O_2,H_2O.$$

Quinoline-betaïne forms short thick crystals, readily soluble in water and alcohol. It begins to decompose at 168°, and fuses at 171°. Hydrochloric acid converts it into the hydrochloride, which unites with platinum chloride, yielding stellate groups of orange-coloured needles of the formula $(C_{11}H_9NO_2,HCl)_2,PtCl_4$.

A. J. G.

Bromoquinolinesulphonic Acids. By W. La Coste (*Ber.*, **15**, 1910—1918).—Bromoquinoline, prepared as previously described by the author (Abstr., 1882, 978), was gradually added to five times its weight of warmed fuming sulphuric acid, and the product when cold was mixed with a considerable quantity of water and well stirred; the heavy crystalline precipitate consisted of two isomeric bromoquinolinesulphonic acids, which can be easily separated by means of their potassium salts. The acid from the less soluble potassium salt is called by the author α-, and that from the more readily soluble salt β-bromoquinolinesulphonic acid.

The α-acid crystallises from boiling water in short thin anhydrous needles, sparingly soluble in cold water and in alcohol. The *potassium* salt, $C_9H_5NBr.SO_3K$, forms short prisms, which decrepitate on heating. The *barium* salt, $(C_9H_5NBr.SO_3)_2Ba$, is a sparingly soluble crystalline precipitate. The *magnesium* salt, $(C_9H_5NBr.SO_3)_2Mg + 10H_2O$, forms colourless plates, which lose their water at 120°. The *zinc* salt, $(C_9H_5NBr.SO_3)_2Zn + 4H_2O$, slender needles, which lose their water at 120° F. The *manganese* salt, $(C_9H_5NBr.SO_3)_2Mn + 4H_2O$, forms short greenish-yellow needles; and the *silver* salt, $C_9H_5NBr.SO_3Ag$, anhydrous needles.

β-Bromoquinolinesulphonic acid crystallises in short needles with 1 mol. H_2O, which it loses at 150—160°. It is sparingly soluble in cold water, although considerably more soluble than the α-acid. The *potassium* salt, $C_9H_5Br.SO_3K + 1\frac{1}{2}H_2O$, crystallises in plates of moderate size, which are easily soluble in water. The *barium* salt, $(C_9H_5NBr.SO_3)_2Ba$

$+ 2H_2O$, forms crystalline groups of needles; the *magnesium* salt, $(C_9H_5NBr.SO_3)_2Mg + 9H_2O$, small needles, and the *zinc* salt, $(C_9H_5NBr.SO_3)_2Zn + 9H_2O$, large transparent six-sided plates, easily soluble in hot water. The *manganese* salt, $(C_9H_5NBr.SO_3)_2Mn + 6H_2O$, crystallises in colourless plates, easily soluble in hot water, and the *silver* salt, $C_9H_5NBr.SO_3Ag$, forms colourless needles. The α- and β-acids both form crystallisable salts with aniline. A. K. M.

Caffeine. By TANRET (*J. Pharm. Chim.* [5], **5**, 591—595).—The salts of caffeine which it is generally supposed to form, are here shown for the most part not to exist. Owing to its weak basic properties and neutral reaction, it does not neutralise the smallest trace of acid, and even relatively concentrated solutions of it do not give a precipitate with potassium-mercuric iodide.

Caffeine does not form salts with the organic acids. Acetic, valeric, lactic, and citric acids merely dissolve it, and on cooling the solution, pure caffeine separates out. Caffeine crystallised from valeric acid retains the odour of the acid, which, however, may be removed by washing, so that the substance sold for caffeine valerate is only the base, whilst caffeine citrate is a mixture of caffeine and the acid. To dissolve one equivalent of caffeine, three equivalents of citric acid are required, which is the inverse of the proportion which would be required for the formation of the citrate.

With mineral acids, however, caffeine does form salts, the sulphate being crystallised with difficulty, whilst the hydrochloride and hydrobromide crystallise well. They are, however, decomposed by water into caffeine, which is precipitated, and the free acid; the hydrochloride decomposes even on exposure to the air. Such compounds, as well as its solutions in organic acids, are useless for hypodermic injections.

It appeared, however, that the compound which exists in coffee, chlorogenate of potassium and caffeine might be used for this purpose; but the difficulty of preparing it in large quantities, its instability, and sparing solubility in water, prohibit its use. It was found, however, that caffeine forms with benzoate, cinnamate, and salicylate of sodium, compounds similar to the natural compound, and very soluble in water. They are prepared by treating caffeine with its equivalent of the sodium salt, dissolved in a small quantity of water. One equivalent of sodium cinnamate dissolves one equivalent of caffeine, yielding a compound containing 58·9 per cent. caffeine. The double benzoate contains 48·5 per cent., and the salicylate 61 per cent. These compounds are not stable, however, being readily decomposed by chloroform. 100 parts of water dissolve 2 parts of the benzoate and cinnamate, and 3 parts of the salicylate.

Similar compounds have been obtained with sodium acetate, lactate, citrate, sulphate, and chloride.

By means of these compounds, caffeine may be used for hypodermic injections. L. T. O'S.

Hydrocinchonidine. By O. HESSE (*Annalen*, **114**, 1—17).—Hydrocinchonidine, $C_{19}H_{24}N_2O$, is contained in considerable quantities in the aqueous mother-liquor from the preparation of homocinchonidine sulphate. The alkaloïds are precipitated from this solution by ammonia and recrystallised from alcohol. The crystalline mass is dissolved in hydrochloric acid, and by fractional precipitation with sodium tartrate the homocinchonidine is separated from the hydrocinchonidine tartrate; the latter is contained in the last precipitate. The tartrate is converted into the neutral chloride: this is purified by recrystallisation from water, and then decomposed by ammonia, when it yields pure hydrocinchonidine. The pure alkaloïd melts at 230° (uncorr.), and does not decolorise potassium permanganate immediately. The sulphuric acid solution is not fluorescent. Hydrocinchonidine is deposited from an alcoholic solution in six-sided plates or prisms, which are insoluble in boiling chloroform, and but sparingly soluble in ether or in water. It is scarcely attacked by strong hydrochloric acid at 160°. The following salts were prepared:—$C_{19}H_{24}N_2O,HCl + 2H_2O$, short six-sided prisms, soluble in water and in alcohol. $(C_{19}H_{24}N_2O)_2,H_2PtCl_6, + 3H_2O$, yellow amorphous precipitate. $C_{19}H_{24}N_2O,H_2PtCl_6$, orange-coloured six-sided plates. The *thiocyanate* and the *neutral oxalate* form anhydrous needles. The *salicylate* does not crystallise. The *quinate* crystallises in anhydrous needles, soluble in water. The *tartrate*, $(C_{19}H_{24}N_2O)_2,C_4H_6O_6 + 2H_2O$, is sparingly soluble in cold water. The crystals of the *thiosulphate* containing 1 mol. H_2O dissolve in 117 parts of water at 10°. $C_{19}H_{24}N_2O,H_2SO_4 + 4H_2O$, is deposited in lustrous prisms, sparingly soluble in cold water. $(C_{19}H_{24}N_2O)_2,H_2SO_4 + 7H_2O$, dissolves freely in alcohol and hot water. At 10° one part of the sulphate requires 57 parts of water for solution. The *phenol sulphate*, $(C_{19}H_{24}N_2O)_2SO_3,C_6H_6O + 5H_2O$, forms white prisms, sparingly soluble in cold water. The *acetic derivative*, $C_{19}H_{23}\overline{Ac}N_2O$, is a hygroscopic amorphous powder, soluble in alcohol, ether, acetone, and chloroform.

Amorphous hydrocinchonidine is formed when the acid sulphate of this base is heated at 160° with hydrochloric acid, and is precipitated in the form of a resin on the addition of soda to the aqueous solution of the crude product. The pure base melts below 100°. It is easily soluble in ether, alcohol, chloroform, and acids. Hydrocinchonidine deviates the ray of polarised light to the left much more powerfully in an acid than in a neutral solution. W. C. W.

Xeronic and Pyrocinchonic Acids. By W. Roser (*Ber.*, **15**, 2012—2014).—In a previous communication (Abstr., 1882, 1114) the author has shown that pyrocinchonic acid is probably dimethylfumaric acid, and stated his belief that xeronic acid is the homologous diethylfumaric acid. In accordance with this view, he now finds that calcium xeronate yields propionic acid when oxidised.

By heating pyrocinchonic acid with hydriodic acid, an acid, $C_6H_{10}O_4$, is obtained, which from its reactions is probably identical with the unsymmetrical dimethylsuccinic acid of Pinner (*Ber.*, **15**, 582). As acetic acid is obtained by the oxidation of pyrocinchonic acid (2 mols.), pointing to a symmetrical constitution, intermolecular change must have occurred in one or other of these reactions.

A. J. G.

Strychnine. By A. GOLDSCHMIDT (*Ber.*, **15**, 1977).—A preliminary notice that the author has obtained indole by fusing strychnine with caustic potash. A. J. G.

Distillation of Strychnine with Zinc. By S. SCICHILONE and O. MAGNANIMI (*Gazzetta*, **12**, 444—448).—By heating strychnine with zinc-powder in small glass retorts to a temperature near the melting point of the glass, a distillate is obtained, separable by treatment with ether and fractional distillation, into two portions, boiling respectively at 165—180° and 230—300°. In a second distillation the first of these fractions yielded a light yellow fragrant oil boiling at 173°, and the second yielded two yellow liquids, one boiling at 240—250°, the other at about 292°, and crystallising in a mixture of snow and salt.

The liquid boiling at 173° gave by analysis numbers agreeing with the formula C_7H_9N, which was confirmed by its vapour-density, determined by Meyer's method (exp. 3·89; calc. 3·70); and from the odour of this base and the pyridic nature of strychnine, the authors infer that it is a lutidine, distinguishing it as γ-lutidine (α-lutidine boils at 145°, β-lutidine at 163—168°). This base is insoluble, or nearly so, in water, soluble in alcohol and ether, and smells somewhat like liquorice. The other two liquids, which were obtained in very small quantity only, are also nitrogenous compounds, and the second, which boils at about 292°, solidifies in a mixture of snow and salt, whereas the first remains liquid.

The behaviour of the three bases with the usual tests for alkaloïds, is shown in the following table:—

	γ-Lutidine (b. p. 173°).	Liquid, b. p. 240–250°.	Liquid, b. p. about 292°.
Sodium phosphomolybdate.	Dark-yellow precipitate soluble in NH_3 with faint blue colour.	White precipitate soluble in ammonia without coloration.	Light yellow precipitate soluble in ammonia, without coloration.
Potassio-mercuric iodide.	Yellow amorphous precipitate.	Dirty yellow precipitate.	Red-brown precipitate.
Iodised potassium iodide.	Crimson precipitate insoluble in dilute hydrochloric acid.		
Mercuric chloride.	White curdy precipitate soluble in NH_4Cl.	White precipitate soluble in NH_4Cl.	White precipitate soluble in NH_4Cl.
Auric chloride	Dirty white precipitate.	Brown precipitate.	Brown precipitate.
Fröhde's reagent ..	Faint red colour.		
Picric acid	—	Yellow amorphous precipitate.	Yellow amorphous precipitate.
Platinic chloride ..	—	Reddish precipitate.	Red-brown precipitate.

H. W.

Action of Dehydrating Agents on Lupinine. By G. Baumert (*Annalen*, **214**, 361—376).—*Anhydrolupinine*, $C_{21}H_{38}N_2O$, and *dianhydrolupinine*, $C_{21}H_{36}N_2$, are formed by the action of phosphoric anhydride or of fuming hydrochloric acid at 200° on lupinine, $C_{21}H_{40}N_2O_2$. Anhydrolupinine is an oily liquid insoluble in water. It turns brown on exposure to the air, and begins to decompose at 150°. The platinochloride, $C_{21}H_{38}N_2O,H_2PtCl_6$, forms quadratic plates, soluble in water and in alcohol. Dianhydrolupinine is an oily liquid (b. p. 220°), which rapidly absorbs oxygen from the air. It yields a platinochloride, $C_{21}H_{36}N_2,H_2PtCl_6$ crystallising in dark red needles.

Oxylupinine, $C_{21}H_{40}N_2O_5$, prepared by the action of phosphoric anhydride on lupinine hydrochloride at 175°, is an unstable oily liquid. The platinochloride $C_{21}H_{40}N_2O_5,H_2PtCl_6$, forms orange-coloured plates, insoluble in water and alcohol. This salt is decomposed by prolonged boiling with water. If the mixture of phosphoric anhydride and lupinine hydrochloride is heated at 185—190° for five hours, hydrochloric acid is evolved, and anhydrolupinine is produced.

W. C. W.

Colouring Matter (Ruberine) and Alkaloïd (Agarythrine) in Agaricus Ruber. By T. L. Phipson (*Chem. News*, **46**, 199).—Ruberine is insoluble in water and in alcohol; it is rose-red by reflected, bright blue by transmitted light, and gives two wide and dark absorption-bands in the green. As it is soluble in water, a heavy fall of rain washes it out from the head of the fungus. Frequently the upper surface of *A. ruber* is eaten through by slugs, which, however, do not penetrate deep. A yellowish-white alkaloïd (agarythrine) is extracted by ether from the fungus itself, after removal of the skin. It has a bitter taste at first, which changes to a burning sensation, resembling that produced by aconitine; the chloride is soluble in water, but the sulphate, although insoluble in water, is soluble in alcohol. Nitric acid solutions become red. Bleaching powder produces also a red coloration with agarythrine, but the colour is soon bleached. When the solution is shaken up with ether, it is oxidised by the air to a red colouring matter; this is probably the cause of the red colour of the surface of the fungus, the alkaloïd being oxidised by the air in presence of light.

E. W. P.

Bases formed by Putrefaction. By A. Gautier and A. Étard (*Bull. Soc. Chim.* [2], **37**, 305—307).—The authors have extracted from putrid animal matter two liquid alkaloïds, which have a strongly alkaline reaction, attack tissues in the same manner as potash, saturate strong acids, and appear to absorb carbonic anhydride from the atmosphere with formation of crystalline carbonates. One of these alkaloïds boils at about 210°, and is a colourless, syrupy, bitter, and very caustic liquid; its sp. gr. at 0° is 1·0296. Its hydrochloride forms slender needles, somewhat stable when pure, but rapidly reddened by excess of acid. It is very soluble, and has a very bitter taste. The platinochloride is also stable, and crystallises well. It is precipitated immediately from moderately concentrated solutions, dissolves on heating, but separates out again on cooling in slightly curved needles. The aurochloride is very unstable, and rapidly deposits metallic gold.

The various salts of this base rapidly reduce ferric chloride to the ferrous state.

The second alkaloïd boils at a higher temperature, but decomposes on boiling into ammonia and products which have a carbolic odour, and are only slightly soluble in ether.

These alkaloïds appear to be accompanied in the putrid matter by other more complex and more unstable basic compounds. When the crude ethereal solution of the alkaloïds is evaporated to dryness, and the residue treated with potash, a strong odour of carbylamine is given off. The carbylamines are doubtless produced by the action of the potash on the complex basic compounds. C. H. B.

Formation of Alkaloïds from Normal Human Fluids. By A. GAUTIER (*Bied. Centr.*, 1882, 710).—If saliva be evaporated and the residue dried for some hours, it will act as a poison on birds; this substance, like the ptomaines, turns potassium ferricyanide and ferrichloride blue. An easily oxidisable alkaloïd, which combines and forms crystalline compounds with gold and platinum chloride, has been prepared from urine. E. W. P.

Urorosein. By M. NENCKI and N. SIEBER (*J. pr. Chem.* [2], **26**, 333—336).—The urine of a diabetic patient was found to become bright pink on the addition of pure hydrochloric acid. The colouring matter is extremely unstable. It dissolves in amylic alcohol, and the solution shows a characteristic absorption-band between the lines D and E, the maximum of intensity corresponding to 557 millionth millimetres wave-length. O. H.

Behaviour of Unorganised Ferments at High Temperatures. By F. HUPPE (*Bied. Centr.*, 1882, 718).—Pepsin, when dry and heated to 100°, is not injured, but at 170° its power is diminished, although not entirely destroyed.

Malt diastase is not affected by a temperature of 100°. Pancreatin still dissolves albumin, even after being heated to 160°; the temperature at which all are killed is about 160—170°. E. W. P.

The Temperature most Favourable to the Action of Invertin. By A. MAYER, W. HAGEMANN, and W. HEUBACH (*Bied. Centr.*, 1882, 706).—In a previous communication, it has been shown that precipitation by alcohol destroys the fermenting power of invertin, and further experiments have not resulted in the discovery of any method for the separation of this ferment in the pure state. The temperature at which action is most intense is about 30°, but if an acid be present, then the temperature may be raised to boiling; with various preparations the temperature may be different, ranging from 31—± 48°.
E. W. P.

Influence of Invertin on the Fermentation of Cane-sugar. By E. BAUER (*Bied. Centr.*, 1882, 707).—It is generally stated that the fermentation of cane-sugar induced by invertin proceeds with equal rapidity, whether it is previously inverted before the ferment is introduced or not; such a supposition is incorrect, as unless the sugar be previously inverted, the fermentation will proceed but slowly, although the complete change does finally take place, and the time occupied is longer. E. W. P.

Physiological Chemistry.

Nutritive Value of Skim Milk. By J. König (*Bied. Centr.*, 1882, 693—696).—Comparing skim milk (N.R. 1 : 2) with whole milk (N.R 1 : 3·5), the author shows that skim milk is by far the cheapest and most nutritious food for adults; also it is shown that the price paid for the albuminoïds in skim milk is lower than that paid for them in any of the ordinary foods which appear in the markets, excepting stockfish; as for example 1000 nutritive units in skim milk cost 41·7 pfennings, whilst in pork they cost 71·4; in butter, 81·7; and in eggs, 201·2. Stohmann has calculated that 1 litre skim milk corresponds in nutritive value to 160 grams boneless meat, the latter costing 19·2 pfennings, whilst the former costs only 8·10. E. W. P.

Skim Milk as Food. By Ritthausen (*Bied. Centr.*, 1882, 641). —Skim milk is a valuable food for man and beast, as 2·8 litres of it contain as much nitrogenous matter as a pound of meat, and it is much cheaper. E. W. P.

Feeding Horses with Flesh Meal. By Findeisen (*Bied. Centr.*, 1882, 671).—Old horses fed with Huch's flesh meal increased in weight, and this food was found to be very satisfactory in cases of illness. E. W. P.

Researches on the Digestibility of Purified Lupine Seeds by the Horse, and Observations on the Working Power of the Horse when Fed with Lupines and Oats. By O. Kellner (*Bied. Centr.*, 1882, 588—592).—The digestive coefficients of lupine seeds when eaten by horses, in combination with hay, are as follows:—

Dry matter.	Org. matter.	Albuminoïds.	Fibre.	Fat.	Extractives.
70·63	72·29	94·16	50·82	27·32	50·79

Lupine seeds therefore approach in feeding power to peas, beans, and maize, being more easily, and oats less easily digested. To determine the comparative value of oats and lupines as food during labour, a horse was fed with 6 kilos. purified lupine seeds, corresponding to 2·77 dry untreated seeds, and 8·5 kilos. hay. After the performance of certain labour in a wheel, the amount of labour being so regulated that the live weight remained the same, the lupines were replaced by 4 kilos. oats daily, and again labour was performed under the same conditions. The labour performed during the "oat" period was in excess of that done during the "lupine" period by 380,300 kilogram-meters, the nutrient ratio in the oat period being 1 : 738; during the other, 1 : 304. From the calculations given it would appear that 1 kilo. oats produces the same working power in a horse as 1 kilo. of air-dried and purified lupines, but as the ratio in the lupines is so narrow, it is not advisable to replace more than 2·5 kilos. oats by lupines, otherwise a great decrease in fat is likely to take place.

E. W. P.

The Gastric Juice. By J. Chapoteaut (*Compt. rend.*, **94**, 1722). —On evaporating an aqueous solution of gastric juice, prepared from the stomach of a sheep, a pepsin is obtained capable of dissolving 3000 times its weight of fibrin. Alcohol precipitates from the solution a white neutral pulverulent substance, while the liquid acquires an acid reaction: the liquid freed from alcohol is without solvent power, but the white substance when acidified possesses a considerable power of dissolving fibrin, and indeed appears to retain the special properties of pepsin. It precipitates metallic salts and solutions of lime and baryta, and froths with a solution of albumin. The acid liquid is, however, certainly one of the active elements of pepsin, for the solvent powers of the white substance are much inferior to those of the original liquid. R. R.

Decomposition of Hydrogen Peroxide by certain Organised Bodies. By A. Béchamp (*Compt. rend.*, **94**, 1601—1604).—The paper discusses previously published observations by the author (*Compt. rend.*, **59**, 713) in relation to investigations by Dumas, Thénard, Bert, Regnard, and others. He will shortly show that the granulations which decompose oxygenated water can be isolated from blood without formation of fibrin, and that the more the serum of blood is deprived of microzymas and globules, the less energetic is its action in decomposing oxygenated water. R. R.

Microzymas the Cause of the Decomposition of Hydrogen Peroxide by Animal Tissues. By A. Béchamp (*Compt. rend.*, **94**, 1653—1656).—The paper discusses some observations of Thenard's on the decomposition of hydrogen peroxide by various animal tissues, and the results of the author's experiments are given in a tabular form. The removal of the microzymas of the blood itself from the several tissues presented some difficulties, but the author conceives that he has proved by these experiments that the microzymas of the different tissues are not only functionally different, but that they act on hydrogen peroxide with different degrees of energy. R. R.

Action of Hydrogen Peroxide on the Red Colouring Matter of the Blood, and on Hæmatosin. By A. Béchamp (*Compt. rend.*, **94**, 1720—1722).—The serum of ox blood freed from microzymas by passing it through a filter covered with barium sulphate is without action on hydrogen peroxide; but the red solution obtained from the blood globules, even after passing through a similar filter, disengages oxygen. Hæmoglobin is distinguished from fibrin and from tissues that act like it, in that it is capable, after coagulation by alcohol or by heat, of being dried at 120° without losing its power of decomposing hydrogen peroxide and becoming colourless. This phenomenon corresponds with a profound chemical reaction, and the oxygen disengaged is due to an action analogous to those observed by Thénard, in which the action of hydrogen peroxide on sugar and starch gave rise to both oxygen and carbonic anhydride at the same time. Blood contains two causes for this decomposition, the microzymas and hæmoglobin, and if hydrogen peroxide is ever formed in the blood it is immediately employed in effecting transformations similar to those described. R. R.

Rattlesnake Poison. By H. H. Croft (*Chem. News*, **46**, 165).—A favourite antidote for rattlesnake poison, in Mexico, is a strong solution of iodine in potassium iodide. The author has tested some of the poison itself with this solution, and finds that a light brown amorphous precipitate is formed, the insolubility of which explains the beneficial action of the antidote. When iodine cannot be readily obtained, a solution of potassium iodide, to which a few drops of ferric chloride has been added, can perhaps be used as an antidote to snake poison; it is a very convenient test for alkaloïds. D. A. L.

Physiological Action of β-Collidine. By Marcus and O. de Coninck (*Bull. Soc. Chim.* [2], **37**, 457).—β-collidine exerts a strong poisonous action, and in this respect has no analogy with the cinchonine from which it is derived. Subcutaneous injection of 0·05—0·15 gram produce general and progressive weakness, with paralysis of the psychomotor centres. Reflex motions are not affected, with the exception of that of the cornea, which is destroyed. The blood pressure diminishes, the cardiac muscle becomes weaker and weaker, the temperature decreases, and the heart stops from diastole.

Weak doses produce a temporary effect characterised by the same symptoms. The alkaloïd is eliminated by the organs of secretion, which it excites, and the organisms reassume their normal functions. The reflex action of the cornea, however, does not return.

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Alcohol on the Development of Yeast. By M. Hayduck (*Bied. Centr.*, 1882, 635—637).—From this continuation of former experiments (Abstr., 1882, 761) we learn that the presence of alcohol retards the development of yeast, and that fermentation proceeds more slowly in proportion as the amount of alcohol originally present is greater. E. W. P.

Nature and Formation of Dextran. By E. Bauer (*Bied. Centr.*, 1882, 630).—The microscopic appearance of the organisms which induce the formation of dextran is described, and it is stated that mucus fermentation can occur only in neutral or slightly alkaline solutions; it does not occur, therefore, in the fermentation of must, as much acid is present; but it does occur in the fermentation of molasses, owing to the presence of alkali in small quantity.

E. W. P.

Elimination of Oxygen from Plant Cells. By T. W. Engelmann (*Bied. Centr.*, 1882, 673).—By means of his bacteria method (Abstr., 1882, 335) and with a microspectroscope, the author finds that the action of the light between the B and C lines is the most intense, and not, as according to other authors, in the yellow.

E. W. P.

Elimination of Carbonic Anhydride by Plants in Absence of Oxygen. By W. P. Wilson (*Bied. Centr.*, 1882, 674).—Diminution of the amount of oxygen admitted to plants is accompanied by a reduction in the quantity of carbonic anhydride expired. For example, in air, *Lupinus luteus* expired 5·7 CO_2 in the first half-hour, whereas in hydrogen only 1·5 CO_2. Plants, whether in air or in hydrogen, are not influenced by the presence or absence of light. E. W. P.

Action of Various Gases, especially Nitrous Oxide, on Plant Cells. By W. Detmer (*Bied. Centr.*, 1882, 675—677).—Seeds of *Pisum sativum* and *Triticum vulgare* cannot germinate in pure nitrous oxide, but they do not lose the power of germinating afterwards in air, if they be not kept too long in the former gas; still to a certain extent harm is inflicted on the embryo, reducing its energy and the intensity of evolution, and this reduction in its activity is the greater the longer it has been in contact with the gas, and the higher the temperature. Seeds can germinate in a mixture of air and nitrous oxide, but the growth ceases as soon as the free oxygen is absorbed, and decomposition of nitrous oxide never occurs. Heliotropic motion does not take place, neither do etiolated plants become green in nitrous oxide. These observations were also made when the atmosphere consisted of pure hydrogen or carbonic anhydride. Chloroform vapour kills germinating plants, or at least stops their growth, breathing however, still continues. Dead cells do not breathe, so that respiration is dependent on the presence of living protoplasm; but it sometimes occurs that carbonic anhydride is eliminated from dead plants: this must be due to the action of lower but live organisms acting on the dead cellulose matter. E. W. P.

Influence of the Electric Light on the Development of Plants. By P. P. Déhérain (*Annales Agronomiques*, **7**, 551—575).—The author's experiments were made at the Palais d'Industrie during the Electric Exhibition of August, 1881. A greenhouse was constructed and divided into two compartments, one of which was glazed with blackened perfectly opaque glass, whilst the other was exposed to the ordinary diffused daylight of the Exhibition building. The darkened chamber was illuminated continuously, night and day, by a

2000-candle arc-light from a Gramme machine, driven by an Otto gas-engine. The transparent chamber was illuminated at night only by the electric light. Five series of comparative observations were made, viz.:—

1. Plants exposed night and day to the electric light alone.
2. Plants exposed during the day to the diffuse daylight of the Palais, and during the night to the electric light.
3. Plants living during the day in the open air, and receiving the electric illumination at night.
4. Plants passing the day in the diffuse daylight of the Palais, and the night in darkness.
5. Plants living normally in a garden.

The plants submitted to experiment were barley, flax, beans, and a number of garden and greenhouse plants.

Action of the Unprotected Light.—At the end of seven days the naked electric light was seen to have an injurious effect both on those plants which were constantly subjected to it, and in a less degree on those which were exposed to it during the night only. The leaves blackened, withered, and dropped off; the injury was confined to the epidermal layers, and was due to the direct impact of the luminous radiations (and not to the formation of nitrogen oxides); for where one leaf was partly shaded by another, a sharp line was photographically impressed.

Experiments on *Elodea canadensis*, submerged in flasks of water, showed that whilst the diffuse daylight of the building was unable to cause decomposition of carbonic anhydride and evolution of oxygen, the direct rays of the electric light were able to do so, about as much oxygen being obtained during an exposure of four or five days and nights to the electric light as could be obtained in an hour or so in bright sunlight. At the end of 15 days the arc lights were enclosed in globes of transparent glass, Siemens' just published experiments having shown that the injurious action of the direct radiations was thereby modified.

Action of the Protected Light.—A number of fresh and uninjured plants were placed in the greenhouse, and in addition sowings of barley, oats, peas, maize, beans, which had just appeared above the ground. All the seedlings exposed exclusively to the electric light perished sooner or later, and the leaves of some of them were blackened as with the naked light. The mature plants, on the other hand, continued to vegetate, but in no case, save a plant of barley, were flowers and seeds produced, the vegetation being purely foliaceous. The barley grains were normal, and germinated on being sown. The electric light employed was clearly insufficient by itself to determine the assimilation of any considerable quantity of material; direct experiments also proved that it is not more powerful in exciting transpiration of water, a leaf exposed to it giving off in an hour only about one-fiftieth of the quantity of water evaporated under similar circumstances in sunlight. As the evaporation of water by the leaves is one of the chief agencies in causing the migration of material necessary for the maturation of seed, the failure of the plants to produce flowers and seeds receives its explanation. It is known that yellow and red rays are most powerful in causing transpiration, whilst the electric light is particularly rich in blue and violet rays. The author considers the electric light employed as too feeble to allow of any conclusion as to the necessity of a nocturnal rest to plants. It was, however, evident that the electric illumination during the night was advantageous to those plants which passed the day in the rather feeble diffused daylight of the palace. In a third series of experiments, the intensity of the electric light was practically augmented by placing the plants nearer the lamp. The experiment was again fatal to young seedlings receiving the electric light exclusively, but many of the hardier and more mature plants survived, although the leaves of some were blackened by their too great proximity to the light; and again the nocturnal electric illumination was decidedly favourable to the plants which passed the day in the light of the palace. The author sums up his conclusions thus:—

1. The electric arc-light emits radiations which are injurious to vegetation.
2. Most of these radiations are arrested by colourless glass.
3. The electric light emits radiations powerful enough to maintain mature plants in vegetation for two months and a half.
4. The beneficial radiations are not sufficiently powerful to cause the growth of germinating seeds, or to allow of the maturation of fruit in older plants.

J. M. H. M.

Embryos of Ungerminated Rye. By K. NACHBAUR (*Monatsh. Chem.*, **3**, 673—676).—Analyses of the sample of Russian rye employed, and of the embryos carefully separated from it, gave the following results:—

	Rye.	Embryos.
Water	11·92	9·58
Proteïn substances	14·12	42·12
Fat	1·16	12·04
Ash	1·63	4·44
Gum, starch, dextrin, and woody fibres	71·17	—
Soluble matter	—	45·11
Sp. gr.	1·245	1·13

The especial object of the investigation was to ascertain if the diastatic ferment observed in the grain was contained in the embryo, which for this purpose was extracted by glycerol according to Gorup-Besanez's method, but with negative results.

A. J. G.

Analyses of Indian Wood. By W. R. CRIPER (*Chem. News*, **46**, 187).—After exposure to the sun, the woods chiefly used for fuel have the following composition:—

	Mango.	Sál.	Dháka.
Carbon	42·72	43·58	40·61
Hydrogen	5·70	5·45	5·11
O + N	36·23	38·09	35·36
Ash	2·88	1·24	6·25
Sand	2·97	0·44	1·00
Water	9·50	11·20	11·67
	100·00	100·00	100·00
Heat-units calc. from analysis, not including sand	3634	3458	3259

During the rainy season, the wood contains about 20 per cent. of water; the heat-units for Sál would be 3054; therefore for equal weights coal has 2·32 times the heating power of ordinary wood.

E. W. P.

Inorganic Constituents of some Epiphytic Ferns. By W. A. Dixon (*J. Roy. Soc. New South Wales,* **15**, 175—183).—The ferns examined were *Platicycerium grande*, *P. alcicorne*, and *Asplenium nidus*, from the Clarence River, and a specimen of the second from Newcastle, N.S.W. The following table exhibits the results obtained by analysis of the ash of these ferns, the live fronds and the humus mass, consisting mainly of dead fronds mixed with rootlets, being analysed in each case. Contrary to what might have been expected from their mode of growth, the amount of ash in the growing fronds is quite as high as in the leaves of most plants; and those of *Asplenium nidus* are rather rich in inorganic matter. Of *Platycerium alcicorne*, two specimens were examined, one growing on a rock, the other on a tree. The humus mass of the rock specimen contains a considerable quantity of sand, consisting almost wholly of white quartz. The withered fronds and humus of the tree-plant contain copper oxide, proceeding from the smoke of copper-works situated about three-quarters of a mile from the locality in which the fern grew. In the table, the sand and copper oxide have been deducted.

The high percentage of sand in the ashes of the humus masses, as well as the copper oxide in the specimens from Newcastle, show that the ferns must obtain much of their inorganic matter in the form of dust, as with the exception of *P. alcicorne*, which grew upon a rock, they could not obtain it directly. They are all plants requiring considerable quantities of alkalis, and when these are deficient, the growing parts take up as much as possible from the withered fronds and humus. The humus being partly composed of rootlets, must necessarily retain some of the inorganic constituents. Thus *P. alcicorne*, growing upon a rock, is very deficient in potash and soda, and, as will be seen from the table, has extracted almost the whole of these constituents from the humus and dead fronds, and has made up for its deficiency of alkalis by assimilating a large quantity of magnesia, lime, and alumina. The same species from Newcastle contains more than double the quantity of alkalis, which it has removed chiefly from

Quantities of Different Constituents in 10,000 *parts of the Dried Plants.*

	Platycerium grande.		*Platycerium alcicorne* from rock.		*Platycerium alcicorne* from tree.			*Asplenium nidus.*	
	Live fronds.	Humus mass.	Live fronds.	Humus mass.	Live fronds.	Withered fronds.	Humus mass.	Live fronds.	Humus mass.
Potash	292·04	22·72	92·50	—	191·87	3·54	14·34	349·01	29·06
Soda	97·66	7·29	80·73	—	102·76				
Potassium chloride	—	—	—	12·84	—	16·62	—	285·28	4·48
Sodium chloride	15·26	7·29	54·43		48·15	6·77	18·41	163·76	
Lime	189·55	85·93	61·92	51·72	23·84	34·58	76·19	229·22	133·87
Magnesia	48·10	7·29	65·71	11·38	22·60	8·58	15·83	82·99	24·62
Alumina	70·34	41·51	47·39	47·13	34·50	26·31	25·60		
Ferric oxide	21·29	5·86	5·68	42·13	3·22	5·69	8·84	10·74	21·35
Manganese oxide	3·87	—	7·85						
Phosphoric „	79·13	4·07	14·12	16·62	21·81	6·46	8·42	46·29	29·01
Sulphuric „	12·67	20·40	11·63	32·94	18·72	12·45	23·34	13·70	25·12

the withered fronds, but has still left considerable quantities in them and in the humus, whilst, although lime and magnesia are present in the humus in greater abundance than in the other plant, the living plant has not taken up so much. *P. grande* seems to have had an abundant supply of all its constituents, whilst *A. nidus* has been deficient only in sodium salts, which it has removed completely from the humus. H. W.

Percentage of Ash in the Sugar-cane. By W. Knop (*Dingl. polyt. J.*, **245**, 435).—The following is an analysis of a sample of sugar-cane from Pernambuco, the cane having been overgrown with fungi. It contained 80 per cent. of water. 100 parts of the dried substance gave—

SiO_2.	P_2O_5.	SO_3.	Cl.	K_2O.	Na_2O.	CaO.	MgO.	
0·81	0·07	0·08	0·29	0·86	traces	0·06	0·16	parts

also traces of ferric and manganic oxides.

It is a remarkable coincidence that the ash, although small in quantity, contains so large an amount of magnesia and chlorine. Whether this peculiarity in the composition of the ash favours the spreading of fungoid disease cannot be ascertained without making a number of ash determinations of sound canes. D. B.

Parasitic Diseases of Plants, and their Prevention. By L. Danger and others (*Bied. Centr.*, 1882, 615—619).—Cabbages and cauliflowers suffer from a sudden fall in the temperature; the damage is due to rending of the epidermis cells, whereby the flow of sap is impeded.

Sugar-beet is frequently destroyed by the larvæ of *Atomaria linearis* or of the centipede, which eat the rootlets, but so long as the inner bundle of rootlets remains unattacked, the beets will flourish. To provide other food for these larvæ, J. Kühn recommends that the weeds should be allowed to grow up to the fifth leaf, and that the beet seed should be pickled with a mixture of 5 parts of magnesium sulphate dissolved in 100 of water, to which may be added 1 part of phenol. Hess describes the slightly known larva of *Silpha reticulata*, which destroys the cotyledon leaves; this larva prefers, however, to feed on *Atriplex hortensis* and the Chenopodiaceæ, which should therefore be carefully weeded out.

Prillieux describes a fungoid growth belonging to the Discomycetes, which attacks beans, hemp, clover, carrots, and chicory. The unusable portion of these plants should be burnt, and not placed in compost heaps. G. Kreiss states that all plants of berberry, buckthorn, blackberry, and several belonging to Boraginaceæ should be removed from the neighbourhood of fields bearing grain, as these plants harbour the germs of Accidium, which produces rust in the grain. E. W. P.

Vine Diseases, and Remedies. By F. v. Thümen and others (*Bied. Centr.*, 1882, 688—690).—Thümen recommends a mixture containing one-twelfth road dust, one-twelfth ferrous sulphate, and five-sixths gypsum as a remedy against *Peronospora viticola*, the winter spores of which Prillieux has found on leaves to the number of 200 per square mm. of surface. Clissey burns all portions of the vines affected with *Sphaceloma ampelinum*. Thümen describes the appearance of a new disease, called in France "Aubernage," which is produced by *Sphaerella pampini*. J. Kübler describes the effects of disease produced in Switzerland by *Cicada* or *Typhlociba vitis*.

E. W. P.

Diseases of Sugar-beet. By J. Kühn and H. Joulie (*Bied. Centr.*, 1882, 607—612).—Various methods were tried for the destruction of nematodes, which destroy sugar-beet. The most satisfactory plan is to sow some fine-rooted variety of garden-cabbage, or the same mixed with cress. The nematodes feed on this, and the larvæ then remaining may be burnt when this supplementary crop is removed, which should be in about 30 days after brairding.

Experiments show that this method relieves a soil of beet-sickness. Joulie has noticed that sugar-beet does not thrive on reclaimed forest lands without the addition of manures containing potash, such as farmyard dung, &c.; the roots being feeble and wanting in sugar, and the leaves weakly. The ash of these weak roots on analysis shows that potash is decidedly in too small a quantity, and consequently the plant is enfeebled. E. W. P.

Composition of Fodders. By A. Petermann (*Bied. Centr.*, 1882, 642).—Tables of analyses of a dozen kinds of fodder.

Specific Gravity of Cereal Grains. By Drechsler (*Bied. Centr.*, 1882, 715).—The sp. gr. of cereal grains has no connection with their agricultural value, which is determined by their absolute weight, the heavier corns producing the highest yield. To estimate the actual weight, it is necessary to weigh at least 400 grains. It has been found, from an extended series of experiments, that 100 grains of winter rye, wheat, and oats weigh 4 grams, and 100 grains of barley 6 grams. E. W. P.

Composition of Malt from 1877 Barley. (*Bied. Centr.*, 1882. 632—634.)—Tables showing the composition of the original and malted barley from various districts, as also of the ash of the barley and malt. Malt contains more lime than barley. E. W. P.

Cotton Cake. By A. Renouard (*Annales Agronomiques*, **7**, 511—524).—Since 1872 the consumption of cotton cake in France has been extending, and it is now largely used for feeding cattle. In 1880 the amount of cotton cake imported was 446,467 kilos., and of cotton seed 21,588,363 kilos. In the same year the quantity of cotton cake exported (almost entirely to England) was 2,704,807 kilos. The chief supply, both of cake and seed, is derived from Egypt, Turkey, and Italy, very little coming into France from the United States. England, on the other hand, imports cotton cake chiefly from the United States, and cotton seed chiefly from Egypt. The cotton-seed oil, expressed at Marseilles and Rouen, is used by painters and varnish makers, and in soap making. The extraction of this oil on a commercial scale dates from 1860, before which time vast heaps accumulated and perished on the cotton plantations; at the present day the seed is often more profitable to the planter for its oil and oil-cake than for its cotton, of which it contains only about 25 per cent. by weight. In the United States, the cotton-seed harvest takes place in October and November, and the seed, after having been carefully gathered by women, is spread out to dry until hard to the teeth: the cotton wool is then separated from the remainder of the seed by suitable machines. The earlier seeds are of inferior quality to those gathered later in the season; they are more watery, the kernel is greener and softer, the cotton less easily removed, and they are apt to be crushed by the decorticators: the oil obtained from them contains more water, resin, and mucilage, clarifies with difficulty and easily becomes rancid. In order to extract the oil, the seeds are screened, crushed between fluted rollers, ground into a paste which is heated in an oven to coagulate the albumin; then submitted to a pressure (in England) of 8500 lbs. per square inch in a hydraulic press. The greater part of the oil is extracted at the first pressure, which lasts five minutes; the cakes are then crushed, with addition of 5 per cent. water, dried by steam-heat, and re-pressed; the pressing is sometimes repeated a third time, after which the cake does not retain more than 9—10 per cent. of oil. The cakes are finally trimmed and allowed to dry for about 20 days, when they become hard enough for transport. French cotton cakes are generally square, 35 × 35 × 0·5 centimetre, and weigh 2·4 kilos. There are three qualities:—

1. *Cottony*, so called because they contain *débris* of cotton. The Syrian cakes contain more cotton than the Catanian.

2. *Brown.* Levantine or Alexandrian cakes are made from Egyptian seed, and are free from cotton.

3. *Purified* cake, made at Marseilles, and consisting of the brown cake deprived of a portion of the husks by a summary method.

In England, the only qualities are rough or common cotton cake (answering to the *tourteaux bruts*), and decorticated cotton cake, which is unknown in France.

Cottony Cake has a deep-brown colour and granular fracture, showing fibres of cotton.

	Catanian.	Syrian.
Water	8·4	7·4
Oil	5·2	6·92
Organic matter	79·81	80·33
Ash	6·59	5·28
	100·00	100·00
Nitrogen	3·23	2·86
Phosphoric acid	2·02	1·12

Cottony cake is chiefly used in the south of France as manure. If given to stock, the cotton-fibres are apt to collect into balls which obstruct the intestines. Cottony cake is sometimes adulterated with earthy matter.

Brown Cake.—The fresh cake has a greenish colour which becomes brown with age. The fracture shows a large number of hard, black fragments of the testaceous covering of the seed. It is used solely for feeding stock, in admixture with pulped potatoes or mangel, and with hay or chaff after maceration for 12 hours. It is never given to pigs. In England and America, it has to a considerable extent taken the place of linseed cake. Cotton cake should never be boiled, for it then developes an essential oil which animals dislike.

	Composition.
Water	10·98
Oil	6·09
Organic matter	77·03
Ash	6·00
	100·00
Nitrogen	4·03
Phosphoric acid	2·07

Purified Cake is yellow, sprinkled with numerous dark spots. Cattle like it better than the preceding, and it is excellent for fattening, and, above all, for producing milk, being preferred even to rape cake for this purpose.

	Composition.
Water	11·26
Oil	4·80
Organic matter	78·76
Ash	5·28
	100·00
Nitrogen	4·43
Phosphoric acid	1·96

Decorticated Cotton Cake has a pale-yellow colour, and is made only in England and America. The seeds are crushed by decorticators and the husks then winnowed from the kernels, which are ground to meal and then made into cakes in the ordinary manner. The husks are used to make paper. The cakes are hot pressed only when the oil is to be used for industrial purposes; virgin oil for use at table is always obtained by pressing in the cold.

In the United States, a salad oil is obtained by cold pressing equal parts of sesame meal and cotton-seed meal. The semi-solid fat, which is a bye-product in this operation, is used for making artificial butter.

	Ordinary decorticated cotton cake.	Cold-pressed (Voelcker).	Hot-pressed (Voelcker).
Water	9·52	9·08	9·28
Oil	11·58	19·34	26·05
Organic matter	73·27	64·2	66·62
Ash	6·63	7·38	8·05
	100·00	100·00	100·00
Nitrogen	7·64	6·93	6·58

The varieties of cotton cake in the market vary so much in composition, that buyers should always require a specification and guarantee of quality. J. M. H. M.

Cultivation of Lupines. By J. König (*Bied. Centr.*, 1882, 642).—Continuous cropping with lupines cannot be carried on for more than 5—10 years. E. W. P.

Potato Culture. By A. Leydhecker and others (*Bied. Centr.*, 1882, 598—605).—Leydhecker finds that the best yield of potatoes is obtained by removal of the side eyes rather than of the end eyes, whether the sets be planted shallow or deep; also that deep setting lowers the yield of tubers and haulms. E. Wollny having planted potatoes, of which the sets were half-potatoes cut either along the long diameter or short diameter, found that the pointed half produced the highest, the other half the lowest yield; that the tubers from the pointed sets were larger than those produced from medium-sized whole sets; and that large whole sets gave a larger yield than halved potatoes. The rest of this article consists of tables merely showing the yields and percentage of starch of varieties of potatoes grown by several experimenters. E. W. P.

Sugar-beet Culture. By W. Rimpau and others (*Bied. Centr.*, 1882, 594—598).—Rimpau notices that the earlier the beet is sown, the greater will be the number of young shoots, and that their growth is aided by the cold frosty nights of March; also that a greater number of shoots will be thrown up if the seed be planted deep. From France it is reported that it is best to plant deep, as the percentage of sugar is then higher, and that the shallow-sown roots generally grow up forked. Desprez reports that the beets with compact flesh and wrinkled skin contain a higher percentage of sugar than other kinds. E. W. P.

Cultivation of the Sugar-beet. By A. Ladureau (*Annales Agronomiques*, **7**, 575—587).—In this paper are detailed the results of experiments carried out in 1880. The manuring experiments are the only ones of chemical interest.

The soil of the experimental plots has received no manure for many years, and is remarkable as being quite destitute of phosphoric acid. Sample taken to a depth of 40 cm. contained per cent.:—P_2O_5, none; N as NH_3, 0·012; organic N, 0·065; nitric N, 0·022 (total N, 0·099); K_2O, 0·035; CaO, 0·370; MgO, 0·151; Al_2O_3 and Fe_2O_3, 3·259; Na_2O, 0·084; Cl, 0·091; SO_3, traces.

Nitrogenous Manures.—These were employed in equivalent quantities, at the rate of 200 kilos. nitrogen per hectare, the size of each experimental plot being one "are." The leather used in experiment No. 9 had been torrefied by superheated steam. The "azotine" used in No. 9 is prepared by the action of steam on torrefied wool-waste (*Annales Agronomiques*, **7**, 28), and contains organic nitrogen in a soluble form; it can be bought at 2 francs per kilo. of contained N. The trimethylamine of No. 10 is produced by the destructive distillation of certain beet-distillery residues, and is sold as a brown, badly smelling liquid, containing about 10 per cent. nitrogen, at a price equivalent to 1·50 francs per kilo. of N; the principal results are embodied in the annexed table.

Manure.	N per cent. of Manure.	Kilos. Manure per hectare.	Kilos. Beet per hectare.	Kilos. Sugar per hectare.
1. Unmanured	—	—	32,400	3292
2. Ammonium sulphate	20·8	960	47,400	4569
3. Sodium nitrate	15·8	1265	54,800	5310
4. Potassium nitrate	13·33	1500	51,200	4392
5. Arachida cake	7·27	2750	52,400	5622
6. Wool refuse	4·54	4440	49,600	4925
7. Torrefied wool	3·30	6660	50,100	4954
8. Torrefied leather	6·07	3330	48,100	5334
9. Azotine	9·20	2170	60,100	5775
10. Trimethylamine	9·56	2090	43,600	4407

The seed was sown on April 7th, and the roots lifted November 13th.

These experiments show clearly the superiority of nitrate of soda to sulphate of ammonia, and even to nitrate of potash (for this soil), and the value of the organic nitrogen in such manures as arachida cake, wool refuse, and azotine.

Phosphatic Manures.—The quantity of each was so adjusted as to represent 100 kilos. phosphoric anhydride per hectare. To the superphosphate in No. 5 was added the same quantity of ammonium sulphate as was used in No. 2 of the preceding experiments.

Manure.	P_2O_5 per cent. of Manure.	Kilos. Manure per hectare.	Kilos. Beet per hectare.	Kilos. Sugar per hectare.
1. Unmanured	—	—	32,400	3292
2. Ardennes phosphates	34·8	280	33,800	3596
3. Burgundy phosphate	29·5	340	33,400	3610
4. Superphosphate	13·5	750	44,700	4559
5. Superphosphate and ammonium sulphate.	13·5	750 960	55,400	5246

J. M. H. M.

Nitrification in Soils. By R. WARINGTON (*Bied. Centr.*, 1882, 660—663; from *Jour. Soc. Arts*, 1882, 532—544).—The following table represents the average quantity of nitrogen as nitrates in the drainage-water which flowed from depths of 20 and 60 inches of unmanured and uncultivated soil at Rothamsted during the years 1877—1882 :—

Rainfall in inches.		Drainage in inches from		Nitrogen as nitrates			
				in 1,000,000.		Kilos. per acre.	
		20 ins.	60 ins.	20 ins.	60 ins.	20 ins.	60 ins.
January	1·57	1·26	1·34	9·8	11·1	1·25	1·51
February	2·85	2·74	2·39	8·6	9·8	2·39	2·38
March	1·36	0·53	0·61	6·0	9·2	0·32	0·57
April........	2·51	1·03	1·33	9·5	9·1	1·00	1·13
May.........	2·68	0·63	0·68	11·6	11·5	0·74	0·86
June	2·62	0·56	0·62	9·3	10·5	0·54	0·66
July.........	3·04	0·75	0·68	16·4	14·2	1·25	0·98
August	4·20	1·86	1·64	15·9	14·0	3·01	2·34
September ...	2·83	1·23	1·14	17·2	13·3	2·15	1·54
October	2·95	1·68	1·50	15·5	13·0	2·66	1·99
November ...	3·38	2·55	2·40	11·8	11·8	3·05	2·89
December....	2·51	2·01	2·01	8·9	0·9	1·82	2·24
Total....	32·50	16·83	16·34	11·8	11·05	20·17	19·09

The greatest amount is eliminated during the summer and autumn period, the summer being the season when nitrification proceeds most rapidly. The analyses of drainage of fallows, at a depth of 27 inches, show a loss of nitrate nitrogen amounting to about 26 kilos. per acre; but although the nitrates are formed in the upper portion of the soil, rain has carried them down, and they appear in larger quantities in the second 9 inches of soil below the surface. The conclusions drawn from these and other analyses are, that so long as the winter is not wet, no great loss of nitrates occurs, but that nearly all are removed if the winter be otherwise, consequently the crops will suffer. To avoid this loss, it is recommended that some rapid growing crop, as mustard, be sown during the summer; this will retain the nitrates, and convert them into an insoluble form which can then be utilised by the crop sown during the winter months. E. W. P.

Nitrification in the Soil. By MARIÉ-DAVY (*Bied. Centr.*, 1882, 663).—Water containing 20·6 mgrm. N as ammonia, and 0·8 as nitrates, was brought in contact with a mixture of sand and flint; 31 litres of this water appeared after its passage through the soil (in 31 days) as 25·2 litres clear water, which contained only 1·7 mgrm. N as ammonia, but 21·5 mgrm. per litre N as nitrates. In another experiment ryegrass was allowed to grow in the soil, and was watered with the same water, which, after its passage through, contained only 0·8 mgrm. N as ammonia, and 20·5 mgrm. N as nitrates per litre; nearly all the phosphoric acid present in the water was absorbed. E. W. P.

Comparative Manuring Experiments. By A. SALFELD (*Bied. Centr.*, 1882, 585—587).—At three different stations on sandy soils, the effects of various combinations of lime, kainite and bone-meal with Chili saltpetre, &c., were tried on oats, grass, and rye. Kainite and lime alone were nowhere found to be a financial success, but mixtures of kainite and bone-meal with a little saltpetre, and of kainite with Mejillones phosphate gave satisfactory returns. E. W. P.

Influence of the State of Division of Manures on their Action. By P. WAGNER (*Bied. Centr.*, 1882, 665).—With the exception of sodium nitrate, all manures should be in a fine state of division, whereby they can be more readily absorbed by the soil. Even superphosphates, when finely ground, produce better crops than the same in a coarse state of division, as experiments on peas show (Comp. Abstr., 1882, 90, 550). E. W. P.

Manuring Potatoes with Potassium Nitrate. By EDLER (*Bied. Centr.*, 1882, 577—580).—In previous communications from the agricultural station at Göttingen, it was shown that the use of potassium nitrate raised the yield above that produced by sodium nitrate, that both manures produce larger tubers, and that with potash manures the disease was less than with the sodium compound. Moreover it was shown that the percentage of starch was lowered by sodium nitrate, but not by the potassium salts. The experiments have been continued during the two succeeding seasons (1880 and 1881), but owing to the bad season of 1880 the results obtained were inconclusive; the season of 1881, however, was more favourable, and the results obtained corroborate those obtained in 1879. Potash saltpetre distinctly increased the total yield, as also the yield of large tubers, and it did not lower the percentage of starch in the large tubers, whereas sodium nitrate did; the percentage of starch in the medium and small-sized tubers grown on the unmanured plots, was, however, higher than that contained in the corresponding sized tubers, but which had been manured. The application of potassium nitrate was also a financial success. E. W. P.

Composition of Pig Dung. By G. LECOUTEUX (*Bied. Centr.*, 1882, 640).—According to Gassend, pig dung consists of water 80·57 per cent., N 0·711, P_2O_5 0·187, K_2O 1·859. The pigs were fed with barley and potatoes, and the production of the manure cost 7·11 M per 1000 kilos. The value of the manure, calculated from the market prices of its components, was 24·66 M per 1000 kilos. (7·11 kilos. N = 14·22 M, 1·87 P_2O_5 = 1·52 M, 18·59 K_2O = 8·92 M), consequently there was a gain of 17·5 M per 1000 kilos. E. W. P.

Analysis of Mud from the Mouth of the Eider. (*Bied. Centr.*, 1882, 639.)

Hydrochloric acid extract of the air-dried mud.

CaO.	CaO combined with CO_2.	K_2O.	P_2O_5.	SO_3.
4·89	4·42	0·15	0·15	0·18
4·09	3·63	0·07	0·08	0·06

	H_2O.	N.	Cl.	Loss on ignition.
I......	2·91	0·26	0·56	8·88
II......	0·79	0·10	0·09	3·25

I. Within harbour of Töning. II. Outside harbour.

E. W. P.

Mineral Phosphates on Arable Soil. By L. GUILLAUME (*Annales Agronomiques*, 7, 587—591).—Experiments were undertaken by the author to test Déhérain's statement that soils containing less than 0·04 per cent. of phosphoric anhydride are benefited by the addition of mineral phosphate. Déhérain considers that most arable soils which have been cultivated for a long time with the aid of farmyard manure, are by that means sufficiently supplied with assimilable phosphoric acid, and that addition of mineral phosphate is useless. The soil on which the author's experiments were conducted is a loam of jurassic origin, and has been for a long time under cultivation and in receipt of a large dressing of farmyard manure. It contains 0·05 per cent. phosphoric anhydride, 3·61 per cent. calcium carbonate, and a considerable amount of ferric oxide. The experimental plots were fifteen in number, each of 1 acre, and a mineral phosphate from Auxois was used, containing 24 per cent. P_2O_5.

The results, per hectare, are annexed:—

	Unmanured.	15,000 kilos. farmyard manure.	15,000 kilos. farmyard manure and 1,000 kilos. phosphate.
1. Wheat (Bordeaux)—			
Straw	4,900 kilos.	5,600	5,700
Grain	708 „	1,596	1,760
2. Oats (Yellow Flanders)—			
Straw	4,900 „	5,900	5,950
Grain	2,544 „	3,256	3,397
3. Maize.................. (cut green August 22nd)	15,200 „	17,360	17,800
4. Potatoes	160 hectolitres	265	240
5. Beet	26,400 kilos.	27,600	27,900

Thus, in no case was the increase sufficient to cover the cost of the mineral phosphate applied. The author intends to repeat the experiments with superphosphates. J. M. H. M.

Analytical Chemistry.

A New Condensation Hygrometer. By A. CROVA (*Compt. rend.*, 94, 1514—1516).—The hygrometers now in use are subject to several causes of errors more or less considerable. To obviate these, the author has contrived an instrument consisting of a tube of highly polished nickel, closed at each end by discs of glass, one clear, the other ground.

Through this tube the air is slowly drawn, and the moment of deposition of moisture can be very sharply observed by viewing the interior of the tube through a lens. The cooling is effected by passing a current of air through bisulphide of carbon contained in a vessel surrounding the tube. R. R.

Direct Estimation of Chlorine in Presence of Bromine and Iodine. By G. VORTMANN (*Monatsh. Chem.*, **3**, 510—530).—Two years ago the author published a short notice on the detection of chlorine in presence of bromine and iodine, depending on the reactions of chlorides, bromides, and iodides with the peroxides of lead and manganese, in presence of acetic acid of various degrees of dilution (Abstr., 1880, 509); and more recently he has given a sketch of the application of these reactions to quantitative analysis (*ibid.*, 1882, p. 1230). In the present paper, the reactions concerned in these processes are more fully discussed, and the methods of estimation are described in detail, and illustrated by numerous examples.

Estimation of Chlorine in Presence of Bromine.—When the quantity of bromine present is but small, it is sufficient to heat the mixture of chloride and bromide with lead dioxide and acetic acid of 2—3 per cent. two or three times on the water-bath. With larger quantities of bromine, complete separation is somewhat difficult; the method of effecting it will be further considered in connection with the separation of chlorine from bromine and iodine together.

Estimation of Chlorine in Presence of Iodine.—This is effected in the same manner as in the last case, lead dioxide being used when the quantity of iodide present is but small, manganese dioxide being preferable when it is large. In this case also, the evaporation with dilute acetic acid must be repeated several times. The expulsion of the iodine may be accelerated by first boiling the liquid for a few minutes in a small flask; this, however, can be done only when lead dioxide is employed, as the use of manganese dioxide quickly gives rise to violent percussive ebullition. In the latter case, the liquid must be heated in a beaker on the water-bath, while a stream of air is passed through it. The estimations come out sharp, even when large quantities of iodine are present. In using lead dioxide when small quantities of chlorine are to be estimated in presence of much iodine, the results are apt to come out too high.

Estimation of Bromine in Presence of Iodine.—This estimation is very easily performed by evaporating down the mixture of bromide and iodide with manganese dioxide and dilute acetic acid several times on the water-bath, the evaporation being accelerated, if desired, by passing a stream of air through the liquid.

Estimation of Chlorine in Presence of Bromine and Iodine together.—This may be effected either by boiling with lead dioxide and dilute acetic acid, whereby the iodides and bromides are decomposed simultaneously; or by first expelling the iodine by evaporating down with manganese dioxide and acetic acid, and then the bromine by repeating this operation after addition of lead dioxide. In operating by the first method, the mutual action of iodine and bromine gives rise to the formation of iodic acid, to prevent which, as far as possible, it is advisable to add the lead oxide to the boiling solution by small portions at a time. The liquid having been boiled for about half an hour, and the water as it evaporates renewed from time to time, the dissolved lead is precipitated by hydrogen sulphide, without previous filtration; and the liquid, after being once more treated with hydrogen sulphide, is warmed for some time on the water-bath and filtered. The filtrate is then evaporated to complete dryness on the water-bath, the residue drenched with dilute acetic acid, and the liquid evaporated down after addition of a small quantity of lead dioxide. The evaporation to dryness is then once more repeated, the residue finally dissolved in water, and the chlorine precipitated from the filtrate by nitrate of silver. In working by the second of the methods above mentioned, the mixture of the halogen-compounds is several times evaporated down on the water-bath with lead dioxide and acetic acid, and the chlorine in the residue is estimated in the usual way. This method is preferable to the former, in so far as it affects the expulsion of all the iodine and bromine without formation of oxy-acids, and may also afford the means of estimating these two halogens at the same time. Moreover, it gives more exact results than the first method; but on the other hand it has the disadvantage that in decomposing the iodides by manganese dioxide, manganese passes into solution and is precipitated in the subsequent treatment with lead dioxide, in the form of manganese dioxide, or rather of a compound of this oxide with dioxide of lead, $MnO_2,4PbO_2$: this precipitate is difficult to wash, and it is only after prolonged treatment with boiling water that filtrates are obtained which no longer become opalescent on addition of silver nitrate.

The numerous analyses given in the paper show that the method therein described is applicable in all cases to the separation of chlorine from bromine and from iodine. Moreover it gives satisfactory results in the estimation of relatively large quantities of chlorine in presence of small quantities of bromine. When on the other hand much bromine is present, the results, even with careful working, come out too high by several units per cent.

Finally the author observes that it is not necessary to bring the chlorine into combination with an alkali-metal by decomposing the lead chloride obtained in the process with potassium sulphate, inasmuch as the entire process is performed with hot dilute solutions, and the solubility of the lead chloride is very considerably increased by the presence of the dilute acetic acid and solution of lead acetate, so that an incomplete solution of the lead salt is not to be apprehended. The manganese dioxide and lead dioxide added in excess are very easy to wash, and the filtrates after a short time give not the slightest turbidity with silver nitrate.

The bromine or iodine given off in these processes of separating chlorides from bromides and iodides may be collected and estimated. With regard to the estimation of iodine in presence of chlorine or bromine, the author has already obtained satisfactory results. For bromine, the numbers hitherto obtained are less satisfactory; but he hopes soon to arrive at more exact results, which may form the subject of a further communication. H. W.

Estimation of Carbonic Anhydride in the Air at Cape Horn. By A. MÜNTZ and E. AUBIN (*Compt. rend.*, **94**, 1651).—The scientific mission to Cape Horn has been provided with an apparatus for estimating the carbonic anhydride in the air. There are two sheet-iron aspirators, representing 300 litres of air; and drawn-out tubes containing potassium hydroxide are fixed in metallic cases, to guard them from accident, and are so arranged that they need not be removed from the cases when the air is being drawn through them.

R. R.

Estimation of Phosphoric Acid. By O. V. D. PFORDTEN (*Ber.*, **15**, 1929—1930).—This method depends upon the conversion of phosphoric acid into ammonium phosphomolybdate, and subsequent estimation of the molybdenum (see p. 122). A. K. M.

Estimation of Sulphur in Iron and Steel. By G. E. CRAIG (*Chem. News*, **46**, 199).—The method now recommended is more rapid and quite as accurate as that in which potassium chlorate and hydrochloric acid are employed; 100 grains of the metal are placed in a 10 oz. flask, with $\frac{1}{2}$ oz. water, $1\frac{1}{2}$ oz. hydrochloric acid is added by means of a stoppered funnel; the gas evolved is passed by means of tubes, &c., through an empty flask or test-tube (to condense vapours) into a nitrogen bulb containing $\frac{1}{8}$ oz. hydrogen peroxide, and $\frac{1}{2}$ oz. ammonia; when the action becomes sluggish heat is to be applied. After blowing air through, the contents of the nitrogen bulbs and the preceding condensing flask are washed out into a beaker, and barium chloride is added after acidifying the solution with hydrochloric acid and boiling. A blank experiment should be made with each new sample of hydrogen peroxide. The presence of copper has no influence on the results. E. W. P.

Estimation of Oxygen and Carbon in Iron. By A. LEDEBUR (*Dingl. polyt. J.*, **245**, 293).—The author found oxygen in many kinds of malleable iron, wrought iron containing ferrosoferric oxide as a mixture principally, whilst ingot iron contains ferrous oxide, either in the dissolved state or as an alloy. The oxygen, especially in the latter case, has a marked influence on the properties of the iron: hence its determination in ingot iron is almost as important as that of the sulphur and phosphorus. For analysis, clean dry iron filings free from fatty constituents should be employed. For the removal of the last traces of moisture and organic matter, the filings are heated in a current of pure dry nitrogen gas, obtained by heating a mixture of 1 pt. sodium nitrite, 1 pt. ammonium nitrate, 1 pt. potassium dichromate, and 10 pts. water, passing the gas through a solution of ferrous sulphate, and over red hot copper turnings, and finally drying it by means of phosphoric anhydride. The hydrogen gas is made from zinc and sulphuric acid. It is passed through soda-lye and an alkaline solution of lead, then through a heated tube filled with platinised asbestos, and eventually dried over concentrated sulphuric acid and phosphoric anhydride; 15 grams of iron borings are placed in a porcelain boat, and pushed into a glass tube of which one end is connected by means of a **T**-piece with the nitrogen and hydrogen tubes, whilst the other end is drawn out and communicates with the absorption-tube containing phosphoric anhydride. In commencing the analysis, the tube with the copper turnings is heated, and a slow stream of nitrogen passed through the apparatus. After two hours the tube with the iron borings is heated, nitrogen gas being passed over continuously, in order to expel all volatile constituents. The absorption-tube is then attached to the apparatus, the current of nitrogen stopped, and hydrogen passed through. After 30—45 minutes' heating, the apparatus is cooled slowly, hydrogen still being passed over. The absorption-tube is then removed, and after expelling the hydrogen in the tube by means of air dried over phosphoric anhydride, it is weighed. The porcelain boat and contents are also weighed, and the weight of the oxygen of the water absorbed should agree with the loss in the weight of the porcelain boat. Analyses of a variety of samples of iron are given, the high percentage of oxygen in wrought iron being explained by the admixture of slag. The determination of oxygen is therefore said to afford a means of determining approximately the quantity of slag present. For determining the carbon, the author recommends M'Greath and Ullgren's method. D. B.

Electrolytic Estimation of Zinc. By A. MILLOT (*Bull. Soc. Chim.* [2], **37**, 339—341).—2·5 grams of the mineral are dissolved in 50 c.c. of hydrochloric acid, and a small quantity of potassium chlorate is added to the boiling solution in order to precipitate the iron. If the mineral contains much silica, it is previously evaporated to dryness with hydrochloric acid. The liquid is cooled, diluted, and mixed with 100 c.c. of ammonia and 50 c.c. of a saturated solution of ammonium carbonate in order to precipitate the lead and calcium. The liquid is diluted to 500 c.c., filtered, and 100 c.c., corresponding to 0·5 gram of the mineral and containing from 0·2 to 0·3 gram of zinc, are mixed with 1 gram of pure potassium cyanide and placed in a beaker in which is suspended a cylinder of platinum gauze which acts as the positive pole, and a platinum cone like that in Riche's apparatus which acts as a negative pole. Two Bunsen cells or a Clamond thermo-electric pile of 150 elements may be used to effect precipitation, which is complete in about ten hours. The firmly adhering deposit is washed with water, then with alcohol, and dried. If the mineral contains copper the latter is deposited with the zinc. The deposit on the cone must in this case be dissolved in nitric acid and the copper precipitated from the acid solution. If cadmium is present, it must be removed by treatment with hydrogen sulphide. The potassium cyanide should be used in the proportion given above; if more is added, the metal is deposited very slowly, whilst if less is added the deposit of zinc is not adherent. Any action on the electrodes may be prevented by mixing the solution with ammonium acetate or nitrate. The latter, however, retards the precipitation of the zinc. C. H. B.

Reduction of Molybdenum Compounds. By O. v. D. PFORDTEN (*Ber.*, **15**, 1925—1929).—The author has examined Pisani's method for estimating molybdenum. He finds that the end-product of the reduction of molybdic acid with zinc and hydrochloric acid is not

Mo_2O_3, but $Mo_5O_7(= 2Mo_2O_3 + MoO)$. This, however, becomes oxidised, by exposure to air, to Mo_2O_3. A method for the volumetric estimation of molybdic acid is founded on this reduction, and subsequent oxidation with standard potassium permanganate.

A. K. M.

Otto's Method for the Estimation of Fusel Oil in Brandy. By C. Krauch (*Bied. Centr.*, 1882, 718).—Krauch does not find Otto's method of any use. The oxidation-products, which according to Otto contain valeric acid, the author finds to be acetic acid.

E. W. P.

Estimation of Glycerol in Fatty Matters. By J. David (*Compt. rend.*, **94**, 1477—1479).—100 grams of the fat are melted; 65 grams of barium hydrate, $BaO,9H_2O$, are added with brisk stirring; when most of the water has been expelled, the heating is discontinued; 80 c.c. of alcohol of 95° are poured on the mass, and the whole is well stirred; 1 litre of water is then added, and the whole boiled for an hour. The barium soap remains insoluble, whilst the glycerol is dissolved by the water, which is freed from the excess of barium, reduced in volume by boiling, and finally evaporated in a vacuum at a low temperature; or, preferably, the quantity of glycerol is inferred from the density of the solution. The barium soap after being boiled with water is decomposed by hydrochloric acid and the fatty acid separated and weighed. Its melting point will indicate approximately the proportions of stearic and oleic acids it contains.

R. R.

Estimation of Dextrose, Maltose, and Dextrin in Starch-sugar. By H. W. Wiley (*Chem. News*, **46**, 175—177).—The method employed was as follows:—(1) 10 grams undried sugar dissolved in 1000 c.c. water; (2) 10 grams dissolved in 100 c.c. and polarised in 200 mm. tube; (3) 10 c.c. of the solution (2) is treated with excess of mercurous cyanide (120 grams $HgCy_2$ and 120 grams NaHO per litre) boiled, and excess of strong hydrochloric acid added and made up to 50 c.c.; this solution is polarised in 500 mm. tube and the angular rotation multiplied by 2. Solution (1) reduced by Fehling gives the total percentage of reducing matter, viz., dextrose with reducing value of 100, maltose 62. The first polarisation gives the apparent specific rotation due to all optically active bodies present, viz., dextrose = 52, maltose = 139; dextrin = 193. The second reduction (3) leaves only dextrin unaffected, and the amount of this is determined by the second polarisation. If solid starch-sugar is employed, it must be boiled for some time to destroy birotation; after reduction by cyanide, it is unnecessary to use charcoal, as the addition of the acid destroys the red colour generally present.

Calculation of the results: from (1) we obtain the reducing per cent. of dextrose d, + that of maltose m, which latter, compared with the former, is only 0·62.

(1.) $R = d + 0{\cdot}62\,m.$
(2.) $P = 52\,d + 139\,m + 193\,d'.$
(3.) $P' = 193\,d'.$ (Second polarisation).

To find d and m.

(4.) $P - P' = 52\,d + 139\,m$.

Multiply (1) by 52 and substract from (4).

(5.) $P - P' - 52\,R = 106{\cdot}76\,m$.

(6.) Whence $m = \dfrac{P - P' - 52\,R}{106{\cdot}76}$.

(7.) $d = R - 0{\cdot}62\,m$.

(8.) $d' = \dfrac{P'}{193}$.

This process agrees well with that proposed by Allen. Several analyses are given. E. W. P.

Diffusion of Sugar in Beet. By G. Mareck (*Dingl. polyt. J.*, **245**, 345—350).—In determining the differences in the sp. gr. of whole roots and of roots cut into sections, the author found that the weight of the former was generally below that of the separate parts of the root, the differences being greater the smaller the sp. gr. of the whole root. The valuation of beet according to the density of the juice is said to give more accurate results than the determination of the sp. gr. of the roots. A table is given showing the results of experiments on the distribution of sugar in the beet. D. B.

Estimation of Rice-starch. By F. Salomon (*J. pr. Chem.* [2], **26**, 324—333).—The results of a series of experiments are given which show that while potato-starch, when heated with hydrochloric acid, yields the full theoretical amount of glucose (111·11 per cent.), rice-starch cannot be made to yield more than about 107 per cent. The sp. gr. of the inverted solution is, however, identical with that obtained from potato-starch, proving that about 4 per cent. of substances are formed which have no reducing action on Fehling's solution. O. H.

Volumetrical Estimation of Phenol. By T. Chandelon (*Bull. Soc. Chim.* [2], **38**, 69—77).—The introduction of phenol as an antiseptic has necessitated a rapid and easy method for its estimation. Koppershoor has proposed to act on phenol with a standard solution of bromine in potassium bromide so as to convert the phenol into tribromophenol. The excess of bromine used may be determined by sodium thiosulphate; or a mixture of potassium bromide and bromate acidified by hydrochloric acid may be substituted for bromine-water. Giacosa used a solution of bromine-water which has been standardised by a phenol solution of known strength, but as the precipitate of tribromophenol invariably retains a certain quantity of bromine, the results are far from being exact.

The author proposes potassium hypobromite which, like bromine, converts the phenol into tribromophenol. The method of operation is as follows:—The hypobromite solution is prepared by dissolving 14—15 grams pure potassium hydroxide in 1 litre of water and adding gradually to it 10 grams bromine. The solution is then diluted until it is of such a strength that 50 c.c. corresponds to 10 c.c. of a normal solution of phenol of 10·5 per cent. or 0·05 gram of pure phenol. In order to ascertain the strength of any phenol solution, 50 c.c. of the hypobromite is placed in a flask and the phenol solution is added until a drop of the solution gives no blue coloration with potassium iodide and starch solution. The method is sufficiently exact for clinical purposes, the error being about 1·2 per cent. If it is required to estimate phenol in urine, the latter is distilled with dilute sulphuric acid: in the case of lint or cotton, the vapours of water, slightly acidulated with hydrochloric acid, are passed over them and subsequently condensed, and the phenol in the distillate estimated after neutralisation with potassium hydroxide. V. H. V.

Ammoniacal Alkaline Silver Solution as a Test for Formaldehyde. By B. TOLLENS (*Ber.*, **15**, 1828—1830). — Salkowski having noticed the formation of fulminating silver in a solution of silver which had been treated with caustic soda and ammonia, the author states that this has not occurred with his solution when prepared in the way described. If, however, it is allowed to evaporate in a shallow dish, small quantities of a detonating compound are formed, but not when it is kept in a stoppered bottle. The best way is to keep the component parts separate, and mix them when required. With regard to the quantitative determination of aldehydes by the above solution, for each molecule of formaldehyde 2 atoms of silver in general are thrown down; but irregularities have occurred which have not yet been avoided. The best proportions for the solution as yet have been found to be equal weights of a solution of 1 part silver nitrate in 10 parts water, and 1 part caustic soda in 10 parts of water mixed together, and the ammonia added drop by drop until complete solution of the silver oxide is effected. J. K. C.

Examination of Fat. By H. Y. DE SCHEPPER and A. GEIBEL (*Dingl. polyt. J.*, **245**, 295—302).—In order to ascertain the value of a fat, it is necessary to determine the non-fatty constituents, *i.e.*, the amount of water, sand, fibrous matter, &c., the total quantity of fatty acids and glycerol, and the amount of "candle material," *i.e.*, the solid fatty acids present in the latter. The water is determined by placing 50—60 grams of the substance in a tared beaker and drying it at 110° for one hour, stirring the mixture occasionally with a tared glass rod. The temperature is then increased to 125°, and after two hours' heating the beaker with contents is weighed, the loss in weight giving the amount of water. The sand and other substances are determined by filtering 50—60 grams of the fat through a tared filter at 60—70°, washing with hot benzene, drying and weighing. If, owing to the presence of glycerol, the dried product is deliquescent, it is washed with alcohol before weighing. The process for determining the fatty acids and glycerol is based on the following conclusions. From the equation indicating the decomposition of fats in general:

$$C_3H_5(O_2C_nH_{2n+1})_3 + 3H_2O = C_3H_5(OH)_3 + 3C_nH_{2n+1}O_2H,$$

it follows that (calling a the molecular weight of the fatty acid) an equivalent of fat, expressed by $(3a + 92 - 3 \times 18)g$, gives $3a$ grams fatty acids and 92 grams glycerol (g). If a represents the mean molecular weight of the different fatty acids contained in fat, we obtain the following formulæ for the quantity of fatty acids and glycerol calculated as per cent. on the fat:—

$$f = \frac{300a}{3a + 38} \text{ and } g = \frac{9200}{3a + 38}.$$

To ascertain the factor a in a fat, 50 grams of the latter are saponified with 40 c.c. potash-ley of sp. gr. 1·4 and 40 c.c. alcohol; boiled in a litre of water for about an hour, decomposed with sulphuric acid, and the fatty acids, after washing and drying, titrated with standard potash-ley, 10 c.c. neutralising exactly 1 gram margaric acid, or 100 c.c. = 1000 : 270 = 37·037 c.c. standard acid. By calling α the tenths of c.c. necessary to neutralise 1 gram of fatty acid, we obtain the following ratio between a and α:—$a = \frac{270 \times 100}{\alpha}$. To determine the amount of neutral fat N, 1 gram of dried and filtered fat is titrated with the above solution. By taking n to indicate the tenths of c.c., and assuming that the various triglycerides are all decomposed in the same manner, the amount of free fatty acids is equal to the following:—

$$F = \frac{100n}{\alpha}, \text{ also } N = 100 - \frac{100n}{\alpha} \text{ per cent. of the fat.}$$

By making use of these formulæ we obtain the following general equations:—

$$f = \frac{100\,[1 - (n:\alpha)]}{100}\;\frac{300a}{3a + 38} + 100\,\frac{n}{\alpha} \text{ and}$$

$$g = \frac{100\,[1 - (n:a)]}{300}\;\frac{9200}{3a + 38}.$$

It was found that the molecular weight of fatty acids from tallows ranged between 280 and 274—hard tallows being nearest to the higher number. For palm oils, the molecular weight is 270: without, therefore, causing too serious an error, this number may be taken to represent the molecular weight of tallows and palm oils, or mixtures of both, which simplifies the above method. The percentage of neutral fat in this case is $N = 100 - n$, whilst the above formulæ may be modified as follows:—

$$f = 95{\cdot}52\,\frac{100 - n}{100} + n \text{ per cent., and } g = 10{\cdot}85\,\frac{100 - n}{100} \text{ per cent.}$$

By taking into consideration the fact that all fats contain from 1 to 1·5 per cent. albumin or cellulose, and that the percentage of fatty acids in tripalmitines is less than 95·5, and the glycerol more than 10·85, the above formulæ require a further alteration, viz.:—

$$f - 94{\cdot}5\,\frac{100 - n}{100} + n, \text{ and } g = 10{\cdot}5\,\frac{100 - n}{100},$$

or, $f = 94{\cdot}5$ and $g = 10{\cdot}5$ if $n = 0$, ond $f = 100$, and $g = 0$ if $n = 100$, *i.e.*, an increase in the percentage of neutral fat N from 0 to 100 raises the percentage of fatty acids 5·5, whilst the glycerol is reduced by 10·5 per cent.; so that the following formulæ are obtained which may be used for determining the percentages of fatty acids and glycerol:—

$$f = 100 - 0{\cdot}055\ \mathrm{N}, \text{ and } g = 0{\cdot}105\ \mathrm{N}.$$

The value of the fatty acids is ascertained by determining the crystallising points. It is, however, necessary to test the acids for neutral fat by dissolving 1 gram in hot alcohol and adding strong ammonia to the solution. In the presence of mere traces of neutral fat, the solution is rendered turbid on the addition of ammonia. D. B.

Occurrence of Organic Bases in Commercial Amyl Alcohol. By L. HAITINGER (*Monatsh. Chem.*, **3**, 688—692).—With reference to the use of amyl alcohol in testing for alkaloïds, the author calls attention to the fact that pyridine and other bases are frequently present, even in the commercially "pure" alcohols. A. J. G.

Technical Chemistry.

Influence of Coal-dust in Colliery Explosions. By W. GALLOWAY (*Proc. Roy. Soc.*, **33**, 437—445, and 490—495).—A continuation of the author's experiments. The apparatus finally adopted to investigate the influence of coal-dust consists of (1) an explosion chamber 6 feet by 2 feet, lined with strips of wood, with three openings for admitting the fire-damp, letting out the air displaced, and for igniting the mixture respectively. It is provided with a small centrifugal fan for mixing the air and the fire-damp. (2.) A gallery 126 × 2 × 2 feet, consisting of seven pieces, each 18 feet long, placed end to end and hooped by iron bands, one side of which, of dimensions 18 feet by 2 feet 3 inches, can be opened like a door. Before an experiment, these doors are opened and coal-dust strewed on the floor to a thickness of one-eighth to a quarter of an inch, and some laid on shelves in the several sections. The method of procedure is as follows:—The explosion chamber is drawn back, and several sheets of paper inserted between it and the gallery to act as a diaphragm; the chamber and gallery are then bolted together, the fire-damp introduced from a measuring cylinder, and mixed with the air by the aid of the fan, and the mixture exploded. When no coal-dust was introduced, or the floor or shelves damped, the fire-damp explosion travels along the gallery for about 12 feet; if the coal-dust was dry, and all the sections closed so as to make the gallery continuous, the flame extended to 50 or 60 feet (experiments showed that the greater or less moisture in the atmosphere exerted an appreciable effect on the coal-dust), and finally if the doors and the fourth and fifth sections were opened, the flame reached to 60 or 70 feet. In all cases, a thick cloud of coal-dust and air was driven by the explosion-wave through the gallery, and on emerging into the open air assumed large proportions, and exhibited all the phenomena of incipient explosive combustion. Crusts of coked coal-dust were found on the shelves the farthest removed from the explosion chamber, which corroborated the hypothesis proposed in connection with explosions at collieries, that these crusts are deposited during a retrograde movement of the air, travelling back towards the origin of the explosion. From observations made by the author at the Peny-graig Colliery after an explosion, similar crusts of coked coal-dust were found deposited in a direction opposite to that of the explosion.

The results of the experiments given in the papers confirm the view put forward by the author as to the manner in which the flame of an explosion is originated and propagated, but they further show that the presence of fire-damp is unnecessary, provided that the scale of the experiments be large, and the coal-dust be sufficiently fine and dry. V. H. V.

Water of Rangoon. By R. Romanis (*Chem. News*, **46**, 187).—In the water stored in reservoirs at Rangoon, the vegetation increases largely during the hot season, but the quantity of free ammonia is highest during March. Albuminoïd ammonia sometimes reaches as high as 0·82 in July, the minimum quantity during two years being 0·24. E. W. P.

Action of Water on Lead. By A. H. Allen (*Chem. News*, **46**, 145—146).—In a recent trial (J. J. Milnes against the Huddersfield Corporation), the question arose as to the influence which the presence of sulphuric acid had on the intensity of the action of water on lead; and from the scientific evidence given it was inferred that a trace of free sulphuric acid was rather beneficial than otherwise, as it would tend to protect the pipes from the action of the water by depositing insoluble lead sulphate. The author has proved this suggestion fallacious, for he has found by experiment that water containing free sulphuric acid dissolves more lead than water which is either altogether free from acid or which has been neutralised. The experiments were made by adding definite quantities of decinormal sulphuric acid to 250 c.c. of water, and then immersing in the liquid equal sized pieces of sheet lead, scraped clean immediately before use. The results vary. Some water after standing in lead pipes all night contained 0·61 grain of lead per gallon. Water taken from the main, having marked acid reaction to Poirier's orange, left in contact with clean lead, dissolved 0·42 to 0·56 grain per gallon, but when previously rendered faintly alkaline with lime-water, only 0·14 of lead was dissolved. The author is of opinion that the free acid in drinking-water is more likely to be hydrochloric than sulphuric acid. D. A. L.

Antiseptic Action of Salicylic Acid. By E. Robinet and H. Pellet (*Bied. Centr.*, 1882, 637).—Salicylic acid added to must in quantities of 0·3 gram per litre preserves it perfectly from fermentation, and when yeast has been added to the must, 0·5 gram per litre is sufficient to destroy its action. E. W. P.

Certain Properties of Hydrogen Cyanide. By C. Brame (*Compt. rend.*, **94**, 1656).—Aqueous solution of hydrocyanic acid copiously precipitates albumin from its aqueous solutions. Bodies of animals poisoned by hydrocyanic acid have been preserved for a year. When the bodies of animals injected with hydrocyanic acid have been preserved in closed receptacles for several months, they lose all odour of the acid, and acquire that of ammonium formate, which salt may be found in the serous liquids. In embalming by means of hydrocyanic acid, it is necessary to introduce into the body, after the acid, a small quantity of zinc chloride. R. R.

Boiler Explosions. (*Dingl. polyt. J.*, **245**, 517.)—It is mentioned that a silent boiling of liquids is due to the formation of gases. If instead of feeding a boiler with fresh water, boiled or condensed water be used, which contains less absorbed air, explosive boiling may occur after heating the boiler for some time, and as in this case a large amount of steam is formed in a short time, the plates of the boiler are endangered, owing to the sudden increase in the pressure of steam. D. B.

Recovery of Sulphur by Mond's Process. By Schaeppi (*Dingl. polyt. J.*, **245**, 341—345, and 387—392).—The following is a summary of the author's results and conclusions:—The longer the time the liquors and oxidised residue are allowed to remain in contact, the more sulphide is dissolved. It is best to oxidise in as concentrated a solution as possible, and to lixiviate for two or three hours. The weaker the liquor, the more sulphides does it contain; the stronger it is the larger is the quantity of thiosulphates: hence the longer the liquor is oxidised the greater is the importance of working with weaker solutions. In the commencement, a solution was used of 16° T.; subsequently this was reduced to 12°, so that it was possible to oxidise with twice the quantity of air without over-oxidising the liquor, whereby a considerable increase in the yield of sulphur was obtained. A further modification was the use of hot water, which not only dissolves a larger proportion of sulphides in a shorter time, but prevents the cooling of the residue. Formerly this residue required four to six hours' heating to render it effective, whilst at the present time it can be used at once for a further oxidation. By mixing the liquor and acid in closed vessels before bringing them into the decomposer, the loss of sulphuretted hydrogen due to defective decomposition is reduced, whilst, owing to the possibility of working with smaller vessels, the operation is considerably facilitated. It is necessary, however, to heat the liquor to 80—90°, otherwise the sulphur is deposited in a form difficult to filter. D. B.

The Currents of the Gases in Sulphuric Acid Chambers. By K. Abraham (*Dingl. polyt. J.*, **245**, 416—421).—The success of the manufacture of sulphuric acid depends largely on the uniformity of the admixture of the reacting gases, not only at the point of entrance but throughout the chamber. Schwarzenberg's theory is that these currents move in horizontal strata from the roof to the floor of the chamber. His views are based on observations of the temperature and sp. gr. of the gaseous mixture at successive points. The author from his own investigations concludes that Schwarzenberg's theory is untenable. He states that the gases on entering come into contact with a gaseous mixture which differs only slightly from them in sp. gr., and therefore undergo a uniform distribution over the first portion of the chamber considered in vertical section, the production of sulphuric acid showing a corresponding uniformity. The cooling action of the sides and roof of the chamber effects a decrease in the temperature: hence the gases travel upwards from the centre and downwards along the side walls of the chamber. The author formulates these phenomena in the following manner:—The gases move in vertical strata perpendicular to the exit, each gaseous molecule describing a spiral line whose axis is parallel to the length of the chamber. The practical conclusions arrived at are these:—The inlet of the gases should be at the middle height of the chamber, and to determine the point of origin of the screw motion as closely to the fore side of the chamber as possible and prevent the ingress of the gases in too rapid a manner, the tube is enlarged with a conical opening. The outlet tube is arranged in a similar manner. The steam should not be introduced in jets along the chamber, but should be admitted through several openings in the roof, each tube to supply two perpendicular jets, the orifices of the tubes being sufficiently large to prevent the entrance of the steam in powerful jets. D. B.

Utilisation of the Nitrogen-compounds from the Manufacture of Sulphuric Acid. By G. Wachtel (*Dingl. polyt. J.*, **245**, 517).—Although the loss of potassium nitrate in the manufacture of sulphuric acid has been greatly diminished, about 50 per cent. of the total nitrogen in the potassium nitrate still escapes with the exit gases from the Gay-Lussac tower. For recovering these nitrogen compounds, the exit gases are drawn by means of a Körting's injector through cast iron or clay retorts filled with iron filings heated to redness. The oxygen compounds of the nitrogen are thereby converted into ammonia, which may be absorbed by means of sulphuric or hydrochloric acid. This process is specially adapted for sulphuric acid works not using the Gay-Lussac tower. D. B.

Preparation from Bauxite of Aluminium Sulphate free from Iron. By C. Fahlberg (*Bull. Soc. Chim.* [2], **38**, 154—156).—Attempts to prepare aluminium sulphate free from iron from bauxite have hitherto been unsuccessful, for the methods proposed have been found to be too costly or too complex. The author, in conjunction with Semper, has practically solved the problem by the use of lead peroxide, which is prepared by first triturating a mixture of 2 parts lead monoxide and 1 part sodium chloride, until the mass assumes the white tint of lead oxychloride; the product is then boiled with bleaching powder until lead peroxide is formed, which is washed and preserved in the damp state. This paste is added to a neutral or slightly alkaline solution of bauxite in sulphuric acid; for every part of iron contained in the solution 20 parts of the dioxide are required. It is necessary to work with concentrated solutions and to avoid a rise of temperature; the iron must also be as a ferric salt. In order to recover the peroxide employed, the solid matter is separated by a filter-press, suspended in water, and then dilute sulphuric or nitric acid added, which leaves the peroxide undissolved, so that it can be employed a number of times without losing any of its properties.

V. H. V.

Japanese Soils: a Natural Cement. By O. KORSCHELT (*Chem. News*, **46**, 187).—The soil below Tokio yields to hot hydrochloric acid as much as 80 per cent., and this contains about 30 per cent. SiO_2 and 30 per cent. $Al_2O_3 + Fe_2O_3$, and 1·5 to 3·0 per cent. K_2O was found in the lower layers; it contains little or no quartz, but 50 to 60 per cent. of zeolites. The tufa soils have a low sp. gr., varying from 2·097—2·291. Full analyses of many samples taken from different depths are given. When mixed with lime paste, they form a satisfactory cement, the temperature rising 7° during the mixing; the proportions used are 1 vol. lime to 6 vols. earth. The analyses show a decrease of nitrogen from the surface downwards: in the top layer it amounts to 0·521 per cent.

E. W. P.

On Cement and its Application. (*Dingl. polyt. J.*, **245**, 381—387, 456—464, and 499—506).—Delbrück mentions that in tendering for large cement contracts it no longer suffices to give the price only, but that the strength of extension forms an important item. The value of cement is determined, therefore, according to the price and the guaranteed weight which 1 part cement mixed with 3 parts sand bears after 28 days' setting. In comparing cements differing in the rate of setting (slow, medium, and rapid), it is necessary to consider the time. According to G. Dyckerhoff, the packing of cement in bags is 10 per cent. cheaper than in casks. It is also mentioned that when rollers are used in the grinding of cement, the motive power consumed is less than in the case of the ordinary cement mills. This is confirmed by Heyn, Delbrück, Nagel, and Kaemp, who add, that not only is a more finely divided product obtained, but the wear and tear of the machinery is considerably reduced. For sifting the ground cement, Nagel and Kaemp recommend the use of shaking sieves, made of perforated sheets of steel, the holes being 1 mm. in diameter. These are said to be stronger than wire sieves, but, like the latter, do not produce a cement fine enough to pass through a sieve with 5000 meshes per sq. cm., without leaving a residue of about 30 per cent. on the sieve. The air sieve constructed by Michaelis is said to overcome this difficulty. The cement is put into a centrifugal machine and whirled, the fine dust produced being collected in a chamber in communication with the machine. The process, however, is not practicable, owing to the excessive consumption of motive power and the enormous wear and tear of the machine. According to Heintzel, cement made up with $33\frac{1}{3}$ per cent. water hardens in $9\frac{1}{4}$ hours; with 30 per cent. in $7\frac{1}{2}$ hours; with $26\frac{1}{2}$ per cent. in 4 hours; with $23\frac{1}{3}$ per cent. in 37 minutes; and with 20 per cent. in 4 minutes. In comparing the time which cement requires for setting, it is usual to mix it with water to the consistency of a thick paste. It is difficult, however, to fix the quantity of water necessary to effect this result, as some kinds of cement absorb more water than others. It is best, therefore, to use an excess of water in all cases. Herzog has found that in preparing a large block of cement, the temperature increases considerably, especially after the mass has been beaten down. In buying cement, it is often stipulated that during the hardening the temperature should not rise more than 3° to 5°, although the quantity of cement to be used to determine this point is not mentioned, so that by using larger quantities greater differences are obtained, the result being the rejection of good samples of cement. In order to economise heat, Tomei, in burning cement, uses a battery of shaft furnaces connected with one another, and worked continuously. Dyckerhoff has made a series of useful experiments as to the profitable application of Portland cement to the preparation of mortar and concrete. He shows that concrete, when beaten down in the air, requires twice as much flint as sand, and that it is not economical to throw concrete direct into water. For concreting under water, not more than equal parts of sand and flint should be used, otherwise the firmness of the concrete will not be the same as that of the mortar used in its preparation. The firmness of mortar and concrete, when beaten down or brought into water depends on the quantity of sand used and the quality of the cement. Mortars were examined as to their impermeability to water and resistance to atmospheric influences. The following mixtures were found to give good results:—1 part cement with 1 part fine sand, or 2 parts ordinary sand and 0·5 part lime, or 3 parts sand and 1 part lime, or 6 parts sand and 2 parts lime. D. B.

Iron Industry. (*Dingl. polyt. J.*, **245**, 392—394.)—In 1877 the Prussian Chamber of Commerce made a series of tests with a view of comparing Rhenish-Westphalian foundry pig with English and Scotch brands. It was shown that the prevailing prejudices against German cast iron were no longer tenable, so that since that time the imports of foreign foundry pig into Germany have decreased by about 12 per cent., whilst the home production has been doubled.

Analysis of flue-dust from a Whitwell apparatus:—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	ZnO.	MnO.
17·05	9·53	25·95	2·31	0·91	1·30	0·37

S.	SiO_2.	Al_2O_3.	CO_2, H_2O, CN, and residue.
1·71	24·05	10·09	6·73

The silica is partly free, partly combined; the sulphur is present as potassium and calcium sulphides, also as alkaline thiosulphate. The potash and soda are in combination with silicic acid, thiosulphuric acid, thiocyanates, cyanides, and ferrocyanides.

The following table gives the chemical analysis of the various irons examined in the comparison mentioned above:—

Name of pig iron.		Silicon.	Phosphorus.	Sulphur.	Graphite.	Carbon combined.	Copper.	Manganese.	Iron.
Coltness No. 1		3·50	0·984	0·022	3·30	0·20	0·099	1·58	90·24
Langloan No. 1		2·93	0·752	0·041	3·40	0·46	0·071	1·62	90·51
Clarence No. 3		2·52	1·490	0·055	3·39	0·13	0·038	0·68	91·40
Clarence No. 3		3·08	1·800	0·025	3·33	0·12	0·045	0·82	89·82
Rhen.-Westphalian.	No. 1. Foundry A	2·45	0·977	0·011	3·28	0·26	0·060	0·18	92·40
	No. 3. Foundry A	1·87	0·935	0·008	2·93	0·50	0·055	0·16	93·45
	No. 1. Foundry B	2·45	0·988	0·035	3·40	0·19	0·039	1·48	91·10
	No. 3. Foundry B	1·75	0·812	0·034	3·12	0·15	0·039	1·92	91·80
	No. 1. Foundry C	2·11	0·850	0·021	3·16	0·49	0·040	0·97	92·00
	No. 3. Foundry C	1·61	0·790	0·044	2·97	0·61	0·055	0·86	92·78
	No. 1. Foundry D	1·30	0·930	0·005	3·22	0·23	0·055	0·72	93·32
	No. 1. Foundry D	2·01	0·850	0·018	3·33	0·42	traces	0·99	91·50
	No. 3. Foundry D	3·50	0·966	0·010	3·27	0·15	0·039	0·79	91·10
No. 3 from Lorraine		2·70	1·830	0·040	3·08	0·11	0·060	0·63	91·20
No. 2 from Luxemburg		1·86	2·210	0·058	2·88	0·55	0·820	0·099	91·50

The following is an analysis of the slags from samples Nos. 1 to 3 compared with slag obtained from fibrous puddled iron:—

	No. 1.		No. 2.		No. 3.	Puddled iron.
SiO_2	27·50	28·30	31·37	33·30	31·20	32·20
Al_2O_3	9·75	11·61	13·09	13·09	10·81	8·17
CaO	58·90	54·94	52·04	52·04	53·17	48·92
MgO	1·37	0·98	1·16	1·16	1·08	4·79

The ratio of the oxygen of the silicic acid to that of the bases in slag No. 1, is as 2 : 3; in No. 2, 3 : 4; in No. 3, 4 : 5, and in puddled iron, 8 : 9.
D. B.

Utilisation for Agricultural Purposes of the Basic Slag obtained in the Dephosphorising Process. (*Dingl. polyt. J.*, **245**, 513.)—At a large steel works in Westphalia some investigations were made as to the possibility of using the slag from the dephosphorising process for agricultural purposes, in the place of phosphate. The cinder gave on analysis:—

SiO_2.	CO_2.	S.	P_2O_5.	Fe.	Mn.	CaO.	Al_2O_3 and sand, alkalis, magnesia, &c.
6·20	1·72	0·56	19·33	9·74	9·50	47·60	2·68

It was found that 10·94 per cent. phosphoric acid, corresponding to 56·6 per cent. of the total phosphoric acid, was soluble in ammonium citrate, and therefore present in a form which will allow it to be assimilated readily by plants (compare Abstr., 1882, p. 1229).

D. B.

Desilvering of Lead. By HAMPE (*Dingl. polyt. J.*, **245**, 515).—The author mentions that while the refining of copper by means of electricity is being worked with success on a large scale, Keith's process of desilverising lead by electrolysis has not made much progress. This is mainly due to the fact that the refined lead does not answer the requirements of commercially pure lead, and that lead precipitated electrolytically from acid solutions does not give a compact substance, but forms lamellar masses, diffused over the whole of the solution. To obtain crystals of lead sufficiently large to fall to the bottom of the solution, it is necessary to increase the distance between the electrodes; however by doing this the resistance, and with it the consumption of electricity required to surmount it, are proportionately increased.

D. B.

Reactions of the Mexican Amalgamation Process. By A. K. HUNTINGTON (*Chem. News*, **46**, 177).—Mercury worked up with silver sulphide and sodium chloride extracted seven-eighths of the silver chloride, which was three times as much as that extracted when sodium chloride was absent: ferric oxide causes loss when sodium chloride is present, as calomel and ferric chloride are formed; very little iron causes much loss. When cupric sulphate is present in the mixture, loss of mercury is greater, and the yield of silver less. The action of cuprous and cupric chlorides on silver sulphides occurs in two stages:—

$$Ag_2S + CuCl_2 = 2AgCl + CuS$$
$$CuS + CuCl_2 = Cu_2Cl_2 + S,$$

which results in the formation of silver chloride and free sulphur. The amount of free sulphur and cuprous chloride formed depends on the strength and quantity of a solvent for cuprous chloride present, such as sodium chloride or $CuCl_2$, the temperature and the pressure. The action of the air in facilitating the action is due to the conversion of cuprous chloride into insoluble oxychloride:

$$3Cu_2Cl_2 + 3H_2O + 3O = 3CuO,CuCl_2,3H_2O + 2CuCl_2.$$

Cuprous chloride and free sulphur are formed when cupric chloride and silver sulphide are heated in a closed vessel to a high temperature, and if heated long enough, the sulphur is oxidised to sulphuric acid; if, however, all air be excluded, no sulphur is formed, but cupric sulphate and cuprous chloride instead. Cuprous chloride and silver sulphide yield silver chloride and cuprous sulphide. This is contrary to the statements of Malaguti and Durocher, who obtained metallic silver, but it was because they employed ammonium as a solvent, and not sodium chloride.

E. W. P.

Extraction of the Precious Metals from all Kinds of Ores by Electrolysis. By BLAS and MIEST (*Chem. News*, **46**, 121—122).—The authors have discovered that if, in electrolysis, compressed sulphur-ores are used as anode in a bath of an electrolyte containing the same metal as the metal of the ore, on the passage of the current the ore is decomposed, the sulphur, &c., being precipitated at the anode, whilst the metal collects at the cathode. Thus with pure galena in a lead nitrate bath, the separation is complete and easy. If the ore contains silica as well, then the silica is deposited along with the sulphur, and remains uncombined; antimony and arsenic, if present, behave in a similar manner, being precipitated as insoluble oxides; they are very easily separated by subsequent electrolysis. When large quantities of arsenic are present, a part of it combines with the sulphur, and forms realgar or orpiment. When ores containing several metals are operated on, the precious metals, being most easily precipitated, are thrown down first in the metallic state at the cathode under the action of a moderate current. The final separation of these metals requires very little battery power, for the mass of metal when dissolved under the action of the current regenerates sufficient heat for the ulterior separation of each metal separately. The products at the anode are extracted and purified by treatment with carbon bisulphide, and afterwards by separate electrolysis. The decanted carbon bisulphide solution of sulphur is distilled, the latter being left pure. If the ore is a polysulphide, and is mixed with much iron, sulphur and iron oxide are obtained in the first operation. These are best separated by electrolysing in a dilute sulphuric acid-bath; pure sulphur is obtained at the anode and basic iron sulphate at the cathode. By this process, 1½ horse-power is required to produce 1 kilo. of copper from a sulphurous ore in one hour. As an example of the working with a complex ore, they describe the treatment of an argentiferous lead ore containing iron, copper, and zinc. The current being sufficiently strong, the iron and zinc will dissolve as readily as the other metals, but will not be precipitated so easily, therefore the solution will gradually become saturated with iron and zinc; the current is then regulated so that only the lead, silver, gold, and copper are precipitated on the cathode, while the zinc remains dissolved as nitrate. As the bath becomes saturated, the iron yields to the zinc, and is precipitated to the bottom as ferric oxide, and as soon as the solution is nearly saturated with zinc nitrate, it is syphoned off; the metals are then removed from the cathode, the sulphur and silica from the anode, and the iron oxide from the bottom, of course all separately. The sulphur, &c., and the metals are treated as above described. The zinc nitrate solution is treated with a small quantity of zinc oxide, which throws down the iron; the lead, copper, and silver retained (if any) are precipitated by passing a current through the solution, using a zinc anode.

The pure zinc nitrate may be treated by a stronger electric current if metallic zinc is required, or chemically if zinc oxide is wanted.

D. A. L.

Freezing of Wine. By J. MORITZ (*Bied. Centr.*, 1882, 716).—Wine shows a tendency to remain liquid below its true solidifying point; the percentage of alcohol present determines the freezing point; the higher the percentage the lower will be that point, ranging from 3·3—5·9° for an alcoholic strength of 7·8—12·5 of alcohol by volume.

E. W. P.

Preservation of Beer. By A. H. BAUER (*Bied. Centr.*, 1882, 719). Unless salicylic acid is present in large quantities, it will not preserve beer, but Pasteurising and a small addition of acid preserves beer for 3—6 months. Borax is useless as a preservative. E. W. P.

Beer-grains. (*Bied. Centr.*, 1882, 717.)—To estimate the amount of wort removed in the grains, 50 grams of the grains are shaken up with 200 c.c. water for 10 minutes, the sp. gr. of the liquid after filtering is then taken, and the percentage of extract deduced. To estimate the starch left in the grains, a sample is weighed and dried and powdered, and then submitted to the action of diastase at 60°; an extract is then made, and the difference between the sp. gr. of the first and second extract corresponds to the starch in the grains. E. W. P.

Loss of Sugar by long Steaming of the "Mash." By V. GRIESSMAYER (*Bied. Cenlr.*, 1882, 717).—This loss has been attributed to the formation of furfural, but the author believes it to be due to the phosphoric acid in the nucleïn, which converts the starch into lævulinic acid. Maltose is converted by acids under pressure into dextrose, and then furfural and formic acid may be produced. In sugar-beet, however, the action of the acid is to produce dextrose and lævulose, and from the latter lævulinic acid is formed. E. W. P.

Does Potato-sugar contain any Deleterious Matter? By v. MERING (*Bied. Centr.*, 1882, 699).—It has been stated by Schmitz and Nessler that in the unfermentable portion of potato-sugar there is some substance which produces ill effects on animals. By experiments the author proves that this unfermentable substance is not deleterious, but that it is a compound allied to the carbohydrates, and is of some nutritive value. E. W. P.

Purification of Sugar-beet Juice. By SCHOTT and others (*Bied. Centr.*, 1882, 697).—According to Schott's patent, the amount of potassium present in the juice must first be estimated, and then if there is not a sufficiency of lime present, gypsum is to be added, so as to have 0·593 part CaO for every 1 part K_2O, then a dilute solution of ferrous sulphate is poured in, and the whole heated nearly to boiling, finally allowing it to settle, filtering through "charred peat," and evaporating.

Siegert in his patent states that after boiling the juice with lime a fresh supply of lime is to be added, and after passing it through a filter-press, the lime is to be removed by carbonic anhydride. By this process, treatment with charcoal may be avoided. Licht has patented a "barium chloride" method, whereby the organic acids are precipitated as salts of barium. A similar patent is that of Kottmann, in which strontium chloride is employed. E. W. P.

General and Physical Chemistry.

Observations on the Solar Spectrum. By LANGLEY (*Compt. rend.*, 95, 482—487).—The observations were made on Mount Whitney, which is almost as high as Mont Blanc, and overlooks the dryest and most deserted district of South California. Observations of the total solar radiation were made with the spectro-bolometer, and also with Pouillet's heliometer, and Violle's actinometer. The calculations are not yet completed, but the author obtains a value of about 3 cal.; in other words, if the terrestrial atmosphere were removed, the sun's rays would raise the temperature of 1 gram of water through 3° C. for every square centimeter of earth's surface exposed under normal conditions. This number is higher than that obtained by Pouillet (1·7 cal.), or by Soret, or Crova and Violle (2·2—2·5 cal.). The author has already shown that Pouillet's formula is only applicable to homogeneous rays, and gives results too low.

On Mount Whitney, and also at the Alleghany Observatory, the author has examined both with a prism and with a diffraction grating the distribution of energy in the spectrum from λ 3,500 to λ 28,000. The length of the ultra-red portion of the spectrum is much greater than was supposed. If the terrestrial atmosphere were entirely removed, this portion of the spectrum would doubtless extend much further, whilst the ultra-violet portion would not be affected to anything like the same extent, there being but little terrestrial absorption in this region. The actual results obtained with the prism and with the grating are given in the form of two curves. One-fourth of the total energy is situated in the visible and ultra-violet portion of the spectrum, the remaining three-fourths being in the ultra-red region. In the latter region, there are several broad absorption-bands or cold spaces, probably made up of a number of lines which are not separated by the bolometer. In the visible spectrum, the maximum energy is in the orange.

Contrary to the usual opinion, the author finds that in a dry climate the general terrestrial absorption diminishes up to the extreme infrared. In both the terrestrial and solar atmospheres absorption increases as the wave-lengths diminish. Combining, by means of Maxwell's discs, the colours which would be visible at the surface of the photosphere if all intervening absorbing layers were removed, it is found that the true colour of the photosphere is similar to that of the spectrum near F, *i.e.*, blue. C. H. B.

Absorption Spectrum of the Earth's Atmosphere. By EGOROFF (*Compt. rend.*, 95, 447—449).—The electric light at Mont Valérien, 10 kilos. distant, was observed at the Paris Observatory by means of a spectroscope with two Thollon's prisms attached to the

Foucault telescope. The brilliant spectrum thus obtained was crossed by a large number of absorption lines. Four could easily be distinguished between D and D_2, and on either side of D, but especially on the less refrangible side, they are very numerous and distinct. The group *a* is almost complete, and the region of C contains a large number of lines. B is partially resolved into eleven pairs separated by equal distances, and A can be easily distinguished by using a cobalt glass. All the groups are characteristic and easily distinguished.

With a Drummond light, at a distance of 1600 meters, B, *a*, and A could be clearly distinguished, between B and *a* there were two faint nebulous lines, and traces of absorption lines could be seen between D and C. With a Drummond light, at a distance of 240 meters, the only lines visible were: A very distinct, and *a* very feeble, but apparently intensified by a heavy shower of rain. When the light was 80 meters from the end of the telescope, A could still be seen, although with difficulty; all the other lines had disappeared. C. H. B.

Reflection of Actinic Rays: Influence of the Reflecting Surface. By DE CHARDONNET (*Compt. rend.*, **95**, 449—451).—The author has photographed the spectrum of sunlight reflected from the surfaces of a large number of substances, including white and black enamel, uranium glass, crude hæmatite, polished hæmatite, diamond, compressed carbon both rough and polished, vermilion, gold, lead, nickel, Arcet's alloy, copper, polished steel and rough steel, Prussian blue, green leaves, speculum metal, mercury, and mercury covered with a plate of quartz. His results show that there is no selective absorption, precisely the same spectrum being obtained in all cases. Silver at first appears to be an exception, because it becomes transparent to the second half of the ultra-violet; but with sufficiently long exposure this part of the spectrum also becomes distinctly visible. In this case it is better to push the exposure to the first degree of inversion pointed out by Janssen. A positive impression is thus obtained in the neighbourhood of H, and a negative in the neighbourhood of P.

Similar results were obtained with a number of liquids, including water, solution of magenta, quinine acetosulphate, ammonio-copper sulphate, potassium dichromate, milk, and ink. The author confirms the statement of Cornu that platinum mirrors, speculum metal, and mercury covered with quartz, do not absorb any of the more refrangible rays radiated from the sun.

With regard to the visible rays, the author arrives at the following conclusions. Every surface reflects in varying proportion all the rays of the spectrum; pure colours can consequently never be obtained by reflection. The reflecting power of a liquid is independent of the substances which it holds in solution or in suspension. This law apparently holds good for solid media, for a mirror of black enamel gave the same spectrum as a mirror of white enamel. It is not necessary to conclude that the incident rays do not penetrate into the reflecting surface to a depth comparable with the wave-lengths. These lengths would be too small to produce appreciable absorption. A layer of quinine acetosulphate showing Newton's rings (yellow of the first and blue of the second order) has no absorptive effect on the solar spectrum. The same substance gives the same reflection whether rough or polished: the polished surface increases the total quantity of reflected rays, but the relative intensity of different regions of the spectrum, *i.e.*, the *actinic colour* of the substance, depends on the nature of the substance employed. C. H. B.

Widening of the Lines in the Hydrogen Spectrum. By D. v. MONCKHOVEN (*Compt. rend.*, **95**, 378—381).—The author employed a vacuum tube in the shape of a capital H, the horizontal part being a capillary tube 0·5 mm. in diameter, whilst the vertical limbs were wider and were provided at each end with an electrode, of which there were consequently two pairs. Under varying degrees of pressure, and with induction coils of different power, he found that the widening of the hydrogen lines begins at different pressures, but always at the point where the silent discharge passes into a spark discharge. Under constant pressure, variations in temperature obtained by using different coils, produced no effect on the width of the hydrogen lines. When the current from a powerful coil is passed through a hydrogen tube under low pressure for one minute, the temperature rises considerably but the lines remain narrow. If, however, the coil is connected with a Leyden jar, the gas is scarcely warmed, but the lines C and F are broad. If the current from an induction coil connected with a Leyden jar is passed through the tube previously described, the tube being filled with hydrogen at a pressure of 1—2 mm., the hydrogen lines are broad. If now a current from a powerful coil is passed through the tube, by means of the other pair of electrodes, the lines do not thicken, but a bright fine line is seen down the centre of each broad line; in other words two spectra are superposed. Since the use of vacuum tubes and disruptive discharges gave no satisfactory proof as to whether the widening of the hydrogen lines is due to pressure or to temperature, the author passed an electric arc, obtained from a continuous current, through pure hydrogen contained in a tube connected with a Sprengel pump. At atmospheric pressure the hydrogen lines, C and F, are seen on the continuous spectrum of the incandescent carbon particles, F is considerably widened, C less so. The lines are uniformly brilliant, and have an appearance identical with that of the hydrogen lines in the sun and some stars; whereas in the vacuum tubes the widened lines decrease in brilliancy from the centre to the edges. At 0·25 m., the width of the lines C and F decrease, and at 0·09 m. they are almost narrow, Hγ is invisible, but the arc and the lines increase considerably in brilliancy. At 0·02 m., C and F are quite narrow and very brilliant, and Hγ becomes visible. At 0·008 m., Hγ becomes still more brilliant. By varying the distance between the electrodes, or by altering the power of the current, the temperature was made to vary considerably, but the breadth of the lines always remained the same. The author therefore concludes that *the widening of the lines in the spectrum of hydrogen is due solely to pressure and is absolutely independent of temperature.* C. H. B.

Spectrum of Water. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **33**, 274—276).—This paper is illustrative of a photograph of the spectrum of an oxyhydrogen flame; in no cases were lines of a wave-length less than λ 2200 observed. V. H. V.

Influence of Temperature on the Spectra of Non-metals. By D. v. MONCKHOVEN (*Compt. rend.*, **95**, 520—522).—Plücker has shown that most of the non-metals give two perfectly distinct spectra, one of which he regards as being due to a high, the other to a low temperature. If the H-shaped tube with four electrodes, previously described (preceding page), is filled with oxygen or some other non-metal, and the gas is subjected to the simultaneous action of two currents, one from an induction-coil alone, the other from a coil connected with a Leyden jar, the high temperature spectrum and the low temperature spectrum are seen superposed. According to Plücker's hypothesis, the gas must therefore be at two different temperatures at the same instant, a supposition which is inadmissible. The superposition of the two spectra is not due to the fact that the contact breakers of the two coils do not vibrate in unison, thus producing alternations of the two spectra which appear to be superposed, owing to the persistence of the images, for in some tubes, especially if the tube be filled with oxygen, the light is radiated for several tenths of a second after the current is interrupted. The author attributes the changes in the spectra of the non-metals to a particular state of vibration of their molecules, depending directly on the nature of the electricity employed. A hydrogen vacuum tube subjected to the action of ordinary sparks presents an appearance very different from that produced by induction sparks. The stratification in a vacuum tube changes entirely according as it is produced by ordinary sparks, by induction sparks, or by a battery of high tension. Further, each variation in the appearance of an incandescent gas (*i.e.*, change of stratification, alteration of the colour of the light emitted, &c.) always corresponds with a partial, often an entire, change in the character of the spectrum, the effect being certainly independent of the temperature. C. H. B.

Note by Abstractor.—The author's supposition that the change in the spectra of the non-metals is due to a particular form of molecular vibration, depending on the nature of the electricity employed, is supported by Schuster's observation of the peculiar spectrum of oxygen in the neighbourhood of the negative pole. C. H. B.

Circular Polarisation of Quartz. By J. L. SORET and E. SARASIN (*Compt. rend.*, **95**, 635—638).—In continuing their researches, the authors have adopted the following improved method of determining the original plane of polarisation. Between the polariser and the analyser is placed a first quartz plate, say lævogyrate, of thickness E, a black band is brought into coincidence with a line in the spectrum, and the position of the analyser noted. The first quartz being left in position, a second quartz is added of inverse rotation, and of a thickness equal to 2E. The general appearance of the spectrum is not modified in the least, but there is a rotation to the right equal to 2Eϕ degrees, where ϕ denotes the angle of rotation for a thickness of 1 mm. A black band is brought into coincidence with the same spectral line, and from the angle through which it is necessary to turn the analyser, plus a certain multiple of 180°, the value of ϕ is deduced. The results obtained by this method agree with those previously published. A table is given of the values of the angle of rotation for different rays at 20°, deduced from observations on two pieces of quartz, one 30 mm., the other 60 mm. thick. The observed values agree closely with those calculated by Boltzmann's formula reduced to its two first terms,

$$\phi = \frac{7 \cdot 1082930}{10^6 \lambda^2} + \frac{0 \cdot 1477086}{10^{12} \lambda^4},$$

λ being the length in millimeters of the wave in air, and this formula may be used to calculate the angle of rotation of a ray of any wave-length between A and O. For rays more refrangible than O, the formula no longer holds good, even though three or four terms of the series are taken. By substituting l, the wave-length in quartz, for λ, the wave-length in air, a formula is obtained, which when reduced to two terms, approximately represents the observed rotation throughout the entire spectrum. The agreement between the observed and calculated values is not, however, complete, and the differences are greater than errors of observation would be. No better results are obtained by using three terms. By addition of a third term, Hl^2, the divergence usually becomes greater.

The influence of temperature on the rotation is not constant for all rays, as is generally supposed, but increases with the refrangibility. For line 24 of cadmium, the formula for correction between 0° and 20° is $\phi = \phi_0 (1 + 0 \cdot 000179t)$. This coefficient is greater than the number 0·000149 obtained by several observers as the mean coefficient between 0° and 100° for sodium light, and is, of course, still greater than the coefficient for the same light between 0° and 20°.

C. H. B.

The Metallic Galvanic Circuit of Ayrton and Perry. By B. J. Goossens (*Ann. Phys. Chem.* [2], **16**, 551—554).—According to Perry and Ayrton (*Proc. Roy. Soc.*, **27**, 219) a galvanic circuit is obtained by dipping strips of platinum and magnesium into mercury, but they were unable to obtain a similar effect with other metals. The author shows that the current obtained as above by Ayrton and Perry is a true thermo-current, caused by the evolution of heat in the formation of the magnesium amalgam (compare Obach, *Pogg. Ann.*, *Suppl.*, **7**, 300).

T. C.

Electricity of Flame. By J. Elster and H. Gertel (*Ann. Phys. Chem.* [2], **16**, 193—222).—The longitudinal polarisation of flame is only apparent, and is caused by the unequal immersion of the wires serving as electrodes. In its cross section, however, the flame appears to be strongly polarised, the electrode in the zone of air immediately surrounding the flame being always positive towards the one in the flame. The electromotive power is independent of the size of the flame. The change in the polarity of the flame may be produced by a suitable shifting of the electrodes. The electromotive force of the flame is dependent on the nature of the metals used as electrodes, and on the nature of the burning gas. It is especially great with electrodes of aluminium or zinc, and very weak if the electrode situated in the surrounding zone of air is covered with a salt, such as potassium chloride. An undoubted electrical action is obtained by the use of water electrodes and exclusion of metals, the electrode in the air being positive towards that in the flame. Flames may be combined like galvanic elements, and a number of them may be united so as to form a flame battery. The following theory is advanced in explanation of the above facts. Free electricity is not produced within the flame during combustion; but the gases from the flame, and the zone of air surrounding the flame, have the property in contact with metals or liquids, of exciting the latter like an electrolyte; and in addition to this there is a thermoelectric excitement determined by the glowing condition of the electrodes. This being so, the amount and nature of the electric excitement is independent of the size of the flame, but dependent on the nature and superficial condition of the electrodes, on the nature of the burning gases, and on the glowing condition of the electrodes. These conclusions have been confirmed by numerous experiments.

The authors conclude therefore that Hankel's (*Pogg. Ann.*, **81**, 212) theory as to the electricity of flames is incorrect. T. C.

Electrolysis of Hydrochloric Acid. By D. TOMMASI (*Compt. rend.*, **95**, 689—691).—With platinum electrodes and concentrated acid, the positive electrode is attacked by the chlorine, and consequently behaves as a soluble electrode; with dilute acid, on the other hand, chlorine compounds are liberated at the positive pole, but the platinum is not attacked.

Concentrated Acid.—The decomposition of 2 mols. of hydrochloric acid in solution absorbs 78·6 cals., but since the positive electrode is attacked, the heat of formation of platinum chloride must be subtracted from this number. The electromotive force necessary to effect decomposition is consequently much less than 78·6 cals. A single Daniell element is indeed sufficient to produce very slow decomposition, but a Daniell element (49 cals.) and a zinc-cadmium element (16·6 cals.) decompose the acid rapidly, with liberation of hydrogen at the negative pole, but no liberation of gas at the positive pole. After 20 hours, the evolution of gas continues at the negative pole only. With two Daniell elements (98 cals.) decomposition is very rapid. At first there is no evolution of gas at the positive electrode, but after about an hour bubbles of gas begin to form. After 20 hours, decomposition continues with evolution of hydrogen at the negative and oxides of chlorine at the positive pole. Similar results are obtained with acid of different degrees of concentration, but the limit is reached with acid of 10 per cent., when the amount of platinum dissolved is very small.

Dilute Acid.—On closing the circuit, gas is evolved at the negative pole, whilst the liquid round the positive pole becomes coloured faintly yellow, and bleaches litmus-paper. Even after continuous passage of the current for 100 hours, no trace of platinum is dissolved.

Similar results were obtained with acid of different strengths down to 1 per cent. The chlorine appears at the positive pole in the form of oxides of chlorine, with probably hypochlorous acid, and perhaps traces of free chlorine. Whether the oxides of chlorine are produced by the decomposition of the hydrate $HCl,6H_2O$, or by the action of the oxygen of the water on the hydrochloric acid, cannot be ascertained.

C. H. B.

Distribution of Heat in the Ultra-red Region of the Solar Spectrum. By P. Desains (*Compt. rend.*, 95, 433—436).—The author has continued his measurements of the distribution of heat in that portion of the solar spectrum less refrangible than the red (Abstr., 1879, 864), using respectively flint glass and crown glass prisms with a refracting angle of 60°. In the following table *d* and *d'* indicate in minutes the angular distance of the cold band from the line D, *i* and *i'* the relative intensities of the bands. It must not be assumed, however, that the intensity of the band at 15' from D with a crown glass prism is equal to that of the band at 42' from D with a flint glass prism.

Crown Glass (*July* 11*th*, 12*th*, 13*th*, 1881).

d.	15·0	18·0	24	31·0	34·5	44·5	50·5
i.	20·0	19·0	22	26·6	23·5	17·0	19·0
d.	60·5	80·5	92	117·4	127·4	147·0	
i.	15·0	5·5	10	—	2·5	—	

Flint Glass (*July* 17*th*, 19*th*, 1881).

d'.	42	45·0	55	58·0	68·0	73	77·2	82	88	92·5	96
i'.	20	18·0	16	23·0	26·5	24	25·0	24	16	20·0	16
d'.	100	103·0	108	122·0	130·0	142	157·0	170	175	185·0	
i'.	25	21·5	26	16·5	20·0	6	15·5	7	2	—	

With prisms of flint and crown glass, the spectrum extends to a much greater distance beyond the extreme red than with a prism of rock salt. With rock salt, the limit is only 80' from the extreme red, whilst with flint glass it extends as far as 1° 40'. C. H. B.

Law of Thermal Constants of Substitution. By D. Tommasi (*Compt. rend.*, 95, 453—456).—It has been stated that the author's law (Abstr., 1882, 1257) does not hold good in the case of soluble salts formed by weak acids. He therefore cites a number of examples to show that wherever the calculated number differs from that actually obtained, the difference is due to the dissociation which takes place on solution, the coefficient of dissociation of the particular substance not being the same as that of the corresponding potassium salt. The close agreement between the calculated and actual numbers in the case of sodium, ammonium, lithium, strontium, and calcium sulphides shows that the coefficient of dissociation of these compounds is the same as that of potassium sulphide. The difference between the numbers found and calculated is considerable in the case of ammonium carbonate and ammonium phenate, where also the dissociation is considerably greater than that of the potassium compounds. For the same reason there is a considerable difference between the two numbers in the case of mercuric cyanide. C. H. B.

Law of Cooling. By C. Rivière (*Compt. rend.*, **95**, 452—453).—The radiating body was a platinum wire heated by means of an electric current. The temperature was calculated from variations in its conductivity, and the quantity of heat lost was calculated by Joule's law. Under the low pressures at which the experiments were made, the cooling effect due to the gas present becomes of considerable importance. The quantity of heat carried off by the air under a pressure of 0·12 mm. of mercury is given approximately in the following table:—

	Heat radiated in a vacuum.
A 200	10 times.
A 400	3 ,,
A 600	1 ,,
A 800	$\frac{2}{3}$,,
A 1000	$\frac{1}{4}$,,

With a platinum thread 0·1 mm. diameter placed horizontally in a glass cylinder 0·17 mm. in diameter, and surrounded by air under a pressure of less than 0·0001 mm. of mercury, the cylinder being cooled by a current of cold water, the following numbers were obtained:—

Temperature of the cylinder 17·3°.

Excess.	Heat lost.	$ma^{\theta}(a^{t}-1)$.	$nT^{2}(T-\Theta)$.
50°	38·5	38·4	35·4
100	94·8	94·7	93·0
150	175·6	177·4	177·6
200	284·0	298·7	293·6
250	448·0	476·7	445·7
300	708·0	738·0	638·0
400	1610·0	1684·0	1164·0
500	3300·0	3721·0	1907·0
600	6035·0	8107·0	2904·0
700	10160·0	17552·0	4193·0
800	15980·0	37891·0	5808·0
900	24110·0	81688·0	7788·0
1000	34800·0	176006·0	10168·0

The values in the third and fourth columns are calculated from the formulæ of Dulong and Petit, and of Rosetti respectively, the constants being obtained from an experiment in which the excess of the temperature of the wire was 136·3° above that of the surrounding space. These results afford further proof of the fact that the numbers given by Dulong and Petit's formula increase far too rapidly.

C. H. B.

Comparison of Mercurial Thermometers with the Hydrogen Thermometer. By J. M. Crafts (*Compt. rend.*, **95**, 836—839).—

The table of corrections for mercurial thermometers, which is to be found in ordinary text-books, was compiled 30 years ago by Regnault, but that experimenter himself pointed out that owing to the great variation in the composition of glass, errors might arise from the application of his tables to all mercurial thermometers. Regnault's instruments have been destroyed, and the manufactory in which they were made has ceased to exist; moreover the composition of the glass now used in France differs very considerably from that of the glass used by Regnault. The author has therefore undertaken a revision of the table. The boiling of water at different pressures gives the means of determining accurately temperatures between 80° and 150°. Between 140° and 350° the author uses naphthalene and benzophenone at varying pressures. He has described elsewhere the methods used for determining with the aid of a hydrogen thermometer the exact pressures corresponding to any given boiling points of these liquids. By tabulating these results, he obtains the pressure under which it is necessary to boil either liquid to maintain for any required time a constant temperature. By these means, he has compared 15 thermometers with hydrogen thermometers. Two sets of seven of these thermometers were of flint glass, by two different French makers, and the other of soda glass, by a German maker. A table* showing the amount of error of the mercurial thermometers for temperatures from 110—330° accompanies the paper. The same table gives the comparison of these errors with those given by Regnault. The results have been confirmed by experiments with twelve other thermometers of peculiar construction. E. H. R.

Limit of the Liquid State. By J. B. HANNAY (*Proc. Roy. Soc.*, **33**, 294—321).—A continuation of the author's researches (Abstr., 1882, 268). After some remarks on the uncertainty of our knowledge of the exact condition of a fluid immediately above and below its critical point, the author proceeds to divide fluids into three classes—(1) *liquids*, which exhibit surface tension, as capillarity or a permanent limiting surface; (2) *gases*, which cannot be reduced to liquids by pressure alone; and (3) *vapours*, which can be so reduced. A further distinction of gases and vapours lies in the fact that the curve representing pressure and volume of a gas is a continuous straight line, whereas a part of the curve representing pressure and volume of a vapour is asymptotic. The author proposes to show that the gaseous state is entirely dependent on the mean velocity, and not on the free path of the molecule. Numerous experiments were made to ascertain the critical temperature and pressure of alcohol under its own vapour, and under that of certain gases, as hydrogen and nitrogen, which do not attack and are not dissolved by the alcohol. A modified form of Andrews's apparatus was used. The manometers were filled with hydrogen, as the only gas which follows Boyle's law at high pressures, and the alcohol was carefully purified by an elaborate method.

The mean of over 100 experiments gave a critical point for alcohol

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* The author has informed the editor that there is a misprint in the table in the original; the letters B and C should be transposed.—C. E. G.

under its own vapour of 235·47° under a pressure of 67·07 atmospheres. In order to study the critical temperature of alcohol under greater pressures, hydrogen was introduced over the alcohol, in order to allow of the limiting surface of the liquid to be seen; but it was found that the critical temperature was practically unaltered, even under a pressure of 178·8 atmospheres. Similar results were obtained when nitrogen was substituted for hydrogen. The method of measuring the capillary height of a liquid under various temperatures and pressures was also tried, and it was shown that the capillary height of a liquid is lowered by a gas under pressure impinging on its surface; this phenomenon would follow naturally from a constant disturbance of the surface of the liquid, owing to the high velocity of the hydrogen molecules striking it. Capillarity is not then a true measure of the cohesion of a fluid, for were the pressure sufficiently high, the surface of the liquid might be made to disappear while its interior was in a truly liquid condition.

Similar experiments were made with carbon bisulphide and tetrachloride and with methyl alcohol, the same general results being obtained. The critical point of carbon bisulphide under its own vapour was found to be 277·68° at 78·14 atmospheres; under hydrogen, 274·93° at 171·54 atmospheres; under nitrogen, 273·12° at 141·45 atmospheres; this last result is probably affected by the solubility of the nitrogen in the carbon bisulphide. The capillary action of this liquid is also weakened by a gas impinging upon its surface.

Determinations of the critical point of methyl alcohol under its own vapour gave the following results:—232·76° at a pressure of 72·85 atmospheres; under hydrogen 230·14° at 128·60 atmospheres; and under nitrogen, 277·92° at 191·40 atmospheres, or 225·82° at 262 atmospheres. With carbon tetrachloride, the results were 282·51° at 57·57 atmospheres under the pressure of its own vapour, and 277·56° at 142·82 atmospheres under nitrogen. It was found impossible to use hydrogen, for it attacked the tetrachloride, with formation of chloroform, and other compounds. In conclusion, the author views the four states of matter thus:—1st, the gaseous, which exists from the highest temperature down to an isothermal passing through the critical point, and depending on temperature or molecular velocity; 2nd, the vaporous, bounded on the upper side by the gaseous, and on the lower by absolute zero, and dependent upon the length of the mean free path of the molecule; 3rd, the liquid, bounded on the upper side by the gaseous, and on the lower by the solid state; 4th, the solid. The gaseous state is thus the only one which is not affected by pressure alone, or in which the molecular velocity is so high that the collisions cause a rebound of sufficient energy to prevent grouping. Another distinction between the gaseous and vaporous states lies in the fact that the former is capable of acting as a solvent of solids (Abstr., 1882, 271).

V. H. V.

Expansion of Isomorphous Salts. By W. Spring (*Ber.*, **15**, 1940—1945).—Between 0° and 100° the expansions of ammonium and rubidium sulphates are sensibly equal, potassium chromate only expands at a slightly greater rate, but in the case of potassium sulphate the expansion is about 10 per cent. greater. The discrepancy is explained by the fact that a given volume of potassium sulphate contains a larger number of molecules than the other salts, for on dividing the sp. gr. by the molecular weight of each salt there is obtained: K_2SO_4 : ·015316; Am_2SO_4 : ·013664; Rb_2SO_4: ·013657; K_2CrO_4 : ·01412. Taking the ratio of the molecules of K_2SO_4 to Am_2SO_4, there is obtained $0·015316 \div 0·013664 = 1·21$, whilst the ratio of the expansions of the same two salts is about the same figure, $0·012645 \div 0·011191 = 1·29$. From these results, it is probable that the expansions of the alums are not absolutely the same, although the differences fall within the limits of error (cf. Spring, Abstr., 1882, 1020; Petterson, Abstr., 1882, 1259). A. J. G.

Modification of the Usual Statement of the Law of Isomorphism. By D. Klein (*Compt. rend.*, **95**, 781—784).—Mitscherlich stated the law of isomorphism as follows:—1. Two bodies are called isomorphous when, having the same crystalline form, they can crystallise together in the same crystal. 2. Isomorphous bodies have an analogous chemical composition. The author gives in the order of their discovery certain exceptions to the second part of this law. He goes on to state that in previous communications he has described a tungstoboric acid, $9WO_3,B_2O_3,2H_2O + 22Aq$, *isomorphous* with Marignac's octohedral silicotungstic acid, $12WO_3,SiO_2,4H_2O + 29Aq$; also a monosodium tungstoborate, $9WO_3,B_2O_3,Na_2O + 23Aq$, *isomorphous* with the acids just mentioned; and further a diammonium tungstoborate, $9WO_3,B_2O_3,2NH_4O + 19Aq$, *isomorphous* with an ammonium metatungstate described by Marignac, and a dibarium tungstoborate, $9WO_3,B_2O_3,2BaO + 18Aq$, *isomorphous* with the corresponding metatungstate. The author states that the tungstoboric acid employed by him contained only a trace of silica, and that his analyses have in this respect been confirmed by Marignac. In consequence of these facts, a modification of Mitscherlich's law has become necessary, and the author therefore gives the following, already proposed by Marignac, as a substitute for the second part of the law in question:—*Isomorphous bodies have either a similar chemical composition, or possess only a slightly different percentage composition, and all contain either a common group of elements or groups of elements of identical chemical functions, which form by far the greater part of their weight.*

E. H. R.

Observations on Crystallisation. By G. Brügelmann (*Ber.*, **15**, 1833—1839).—After giving a short account of the development of the theories of isomorphism, dimorphism, &c., with special reference to their bearing on chemical composition, the author proceeds to show at some length that crystallisation of two substances in the same form or the same crystal does not always depend on any relation in their chemical composition, a fact which has already been pointed out in several instances, notably by G. Rose, in the case of sodium nitrate and calcspar. The examples brought forward by the author are copper sulphate and potassium dichromate, copper sulphate and cobalt chloride, borax and potassium chlorate; in most cases the cold saturated solutions were mixed in varying proportions, but in some crystals of the one substance were introduced into saturated solutions of the other. In all cases coloured solutions were used, and perfect co-crystallisation was observed, the colours being different in various parts of the same crystal. Compounds therefore of the most dissimilar atomic constitution can crystallise together, their power of so doing being a function of the physical conditions in which they are found, and not of their chemical composition. The occurrence therefore of a body in a definite crystalline form is no criterion of its individuality, and the conception of isomorphism possesses only a nominal significance, as it cannot be used as a separate means of classification, but only in confirmation of facts otherwise obtained. J. K. C.

Experiments in Crystallisation Exemplifying Berthollet's Law of Affinity. By G. Brügelmann (*Ber.*, **15**, 1840—1841).—The following experiments are of interest as touching Berthollet's law, that a liquid in which two salts have been dissolved contains the acids and bases of each reciprocally combined. Equal volumes of cold saturated solutions of cobalt chloride and nickel sulphate were mixed and allowed to evaporate spontaneously; the crystals obtained consisted of both metals in the form of sulphates, and the chlorides of the two metals were left in solution. Similar results were obtained with copper sulphate and cobalt chloride, as well as with copper sulphate and potassium dichromate; in the former case, the first crop of crystals contained both metals as sulphates, together with small quantities of chlorides; in the latter, crystals of the mixed sulphates of copper and potassium were first deposited, then various mixtures of the chromates and sulphates, and finally a mixture of chromates of the two metals. In every case the crystallisation seems to have proceeded in a liquid containing four different salts. J. K. C.

Nature of the Vibratory Movements which accompany the Propagation of Flame in Mixtures of Combustible Gases. By Mallard and Le Chatelier (*Compt. rend.*, **95**, 599—560; see also Abstr., 1881, 971).—The authors employed a tube 3 meters long and 0·03 meter in diameter. The combustible gas was a mixture of nitric oxide and vapour of carbon bisulphide. An image of the tube was thrown on to a cylinder covered with sensitive paper and rotating with a known velocity. The photographs show that the flame travels at first with a uniform velocity, but afterwards performs a series of very rapid oscillations, the regularity, duration, and amplitude of which vary at different parts of the tube. Uniform motion continues with a velocity of 1·10 meter per second to a distance of 0·75 meter from the mouth of the tube. Beyond this point the flame, and consequently the mass of gas, is thrown into vibration, the vibrations being both simple and compound. The points at which the vibration is simple are generally spaces of one or two-fifteenths the length of the tube. The duration of successive vibrations varies between 0·025 and 0·0034 of a second. The durations are in the simple ratios of 1, 2, 3, 4, 5, 6, but no relations could be traced between these times and the position of the flame in the tube. As a matter of fact, the vibrating mass of gas is composed of two distinct columns, one of burnt gas, the other of cold gas, the lengths and densities of which vary at every instant. The amplitude appears to be greatest for vibrations of long period, and is particularly great in the last third of the tube, at the point where one of the vibrating segments is situated when the tube gives the first harmonic from its fundamental note. The amplitude at this point is as high as 1·10 meter. Since the oscillations of the flame are simply those of layers of burning gas, these experiments gave the first precise idea of the amplitude of the vibrations of a mass of gas emitting a sound. These vibratory movements necessarily correspond with high pressures. From calculations based on the variation in volume, measured by the oscillation of the flame, it is found that the mean pressure is at least five atmospheres, and for mixtures in which the initial velocity is greater than 1 meter, the pressures will be considerably higher. The mean velocity of propagation appears to increase with the amplitude and rapidity of the vibrations. In one experiment, the limits were 1·10 meter and 5·40 meters, in another, 0·97 meter and 8·60 meters. In another experiment, the explosive wave was formed at a distance of two-thirds the length of the tube from the mouth, *i.e.*, at the point where the amplitude of vibration was greatest, and the last third of the tube was completely shattered. The brilliancy of the flame varies at successive phases of the same vibration, being greater when the flame moves forward than when it moves backward; these differences increase with the amplitude of vibration, and are undoubtedly connected with variations in pressure.

With a tube 0·01 meter in diameter, the flame is extinguished at a distance of about 1·5 meter from the mouth. The vibratory movement is produced at a distance of 0·18 meter from the mouth of the tube, instead of at 0·75 meter, and the amplitude of vibration increases more rapidly. The mean velocity of propagation is at first very small, but attains a rate of 4·50 meters per second at a distance of 0·5 meter, and becomes almost nothing just before the extinction of the flame. The narrowing of the tube favours the development of the vibratory motion with all its consequences. C. H. B.

Inorganic Chemistry.

Action of the Galvanic Current on Chlorides and Chlorates. By A. Lidoff and W. Tichomiroff (*Jour. Russ. Chem. Soc.*, 1882, 341—349).—In a former paper (Abstr., 1882, 925) the authors have found that by the action of the electric (galvanic) current on a solution of chlorides, hypochlorites are first formed, which, by an elevation of temperature, are converted into chlorates. But later on they found that even at the ordinary temperature, as soon as the solution becomes more concentrated, hypochlorites are converted into a mixture of chlorates and chlorides by the sole action of the current. They propose to apply this process to the manufacture of chlorates, more especially of the sodium salt, which is difficult to prepare in the ordinary way. On acting with a current of a powerful Gramme machine for 25 hours, on a solution of 400 grams of potassium chloride in 900 grams of water, 210 grams of crystals, containing 70 per cent. of chlorate, were obtained. The crystals contain, together with potassium chlorate, a considerable quantity of the chloride, and 5—12 per cent. of carbon from the electrodes. As soon as about 30 per cent. of the original salt is transformed into the chlorate, the positive electrode is most strongly corroded, and no further separation of the crystals from the liquid takes place.

If, instead of a high tension-current (2 electrodes) a divided current (8 electrodes) is employed, far less chloride is converted into chlorate in the same space of time. The corrosive action of the liquid on the positive electrode is due to its oxidation by the oxygen of the potassium chlorate, which is reduced to chloride (about 30 per cent. in 10 hours). For this reason, potassium chloride cannot be completely converted into chlorate, but a limit is reached after some time, when the energy of formation of potassium chlorate from the chloride becomes equal to the energy of its decomposition. Electrodes of another material than carbon cannot be used for the conversion of chlorides into chlorates, for all metals, even platinum, are corroded by the chlorine which is set free at the same time. If, however, a solution of potassium *chlorate* be electrolysed by means of platinum electrodes, no chlorine, but *ozone*, is evolved on the positive pole. At the same time crystals of potassium *perchlorate* separate from the liquid, and only traces of potassium chloride are formed at the same time. In this respect the action of electricity on potassium chlorate is analogous to the action of heat on the same salt; in both cases oxygen is evolved, and potassium chlorate and chloride are formed, although the proportion in the quantities of these two salts is widely different. The corrosion of carbon in the above case is due to the action of ozone, and the products of this action in presence of water are mellitic and hydromellitic acids. B. B.

Oxidation of Carbonic Oxide by Palladium Hydride and Oxygen. By M. TRAUBE (*Ber.*, **15**, 2325—2326).—The changes which occur when carbonic oxide is converted into the anhydride by the action of palladium hydride and oxygen are as follows:—In the first place palladium hydride and moist oxygen form hydrogen peroxide, and this compound in presence of metallic palladium oxidises carbonic oxide to carbonic anhydride. W. C. W.

Compressibility of Nitrogen. By E. H. AMAGAT (*Compt. rend.*, **95**, 638—641).—A summary of the experiments made by Cailletet and by the author with a view to determine the compressibility of nitrogen. Curves are given representing the results obtained by both observers. The author considers Cailletet's method inferior in accuracy to his own. The curve representing Cailletet's results is very irregular, whilst that representing the author's results is perfectly regular. C. H. B.

Black Phosphorus. By P. THENARD (*Compt. rend.*, **95**, 409—410). —A quantity of phosphorus was being cast in the usual way, and a dozen sticks had been obtained of the usual colour, when the thirteenth suddenly blackened at the moment of congelation. Subsequently a second stick, about 20 cm. long, blackened for about 4 cm. of its length, the remainder being unchanged. A portion of the black phosphorus was brought in contact with ordinary phosphorus, in a state of superfusion at 10° under ice. In the first experiment, the white phosphorus became black on solidifying, but the same effect was not again obtained once in more than twenty experiments under precisely similar conditions. The specimen of black phosphorus became white when fused, and remained white if cooled suddenly, but if super-cooled it again became black when brought in contact with either black or white phosphorus. Black phosphorus dissolves almost entirely in carbon bisulphide, leaving a slight yellow residue apparently consisting of amorphous phosphorus. C. H. B.

Neutral Phosphates of the Alkalis. By E. FILHOL and SENDERENS (*Bied. Centr.*, 1882, 641).—Careful neutralisation of phosphoric acid with sodium hydroxide results in the formation of a mixture which reacts on red or blue litmus; crystals obtained from the solution contain 1 mol. of the mono- and 1 mol. of the di-sodium phosphate. Neutral potassium or ammonium phosphates have not been obtained, whilst potassium sodium and sodium ammonium phosphates crystallise readily. E. W. P.

Calcium Chloride. By A. WEBER (*Ber.*, **15**, 2316—2317).—Calcium chloride dried at 180—200° is practically anhydrous. It contains from 0·12 to 0·24 per cent. of water and 0·047 per cent. CaO. W. C. W.

Properties of Pure Aluminium. By J. W. MALLET (*Chem. News*, **46**, 178).—Sp. gr. at 4° = 2·583; atomic vol., 10·45; sp. heat = 0·2253 between 0—100°; atomic heat, 6·09°; less fusible than the commercial metal, and less easily acted on by alkalis and acids. It is nearly pure tin-white, with no bluish tinge, and has a lustre like that of tin. It is more malleable and less easily hardened by hammering than ordinary aluminium. E. W. P.

Decomposition of Phosphate by Potassium Sulphate at High Temperatures. By H. GRANDEAU (*Compt. rend.*, **95**, 921—922).—Debray (*Bull. Soc. Chim.*, **3**, 251) has shown that on heating to a high temperature aluminium phosphate with excess of an alkaline sulphate, an alkaline phosphate and crystallised aluminium are obtained. This reaction has been used by Derôme (*Compt. rend.*, **89**, 925, and this Journal, **38**, 286) for the separation of phosphoric acid from iron and aluminium. To determine the conditions of the reaction, a mixture of aluminium phosphate and potassium sulphate was heated for several hours in a platinum crucible. At a high temperature, not only is alumina formed, but also a crystalline double phosphate of aluminium and potassium. At a still higher temperature, the quantity of alumina increases, but even on very vigorous heating it is impossible to completely decompose the double phosphate. Similar results were obtained by substituting phosphates of glucinum, cerium, and didymium for aluminium phosphate. But when phosphates of calcium, magnesium, &c., were used, the double phosphate alone was formed under the conditions of the experiment; whilst with nickel and cobalt phosphates results similar to those with aluminium phosphates were obtained. With chromium and uranium phosphates, the final products are potassium chromate and uranate. The investigation is being continued. L. T. O'S.

Determination of the Equivalent of Thorium. By L. F. Nilson (*Compt. rend.*, **95**, 729—730).—As a mean of ten determinations, the author finds 58·10 to be the equivalent of thorium, that of oxygen being 8, and of sulphur 16. He makes the atomic weight, therefore, to be 232·36. These results were obtained by calcining two different specimens of the sulphate, *a* and *b*. Specimen *b* was obtained from the mother-liquors of *a*. The first six determinations were made on specimen *a*, which contained nine molecules of water. In these six experiments the author used the hydrated salt, because the dehydrated substance was found to be extremely hygroscopic. In the other four experiments this was impossible, because specimen *b* (the crystals of which differed from those of specimen *a*) contained only eight molecules of water, and absorbed water during the process of weighing. In the latter four experiments, therefore, the anhydrous sulphate was used. The two specimens gave practically identical results.

		Sulphate a.			
	Water.	SO_3.	ThO_2.	Equiv.	At. Wt.
Mean of six experiments	27·573	27·336	45·091	58·11	232·43
		Sulphate b.			
Mean of four experiments	—	37·703	62·297	58·09	232·30

The author concludes by drawing attention to the wide discrepancies in the values of the atomic weight as determined by other chemists.

E. H. R.

Metallic Thorium. By L. F. Nilson (*Compt. rend.*, **95**, 727—729).—The author obtains metallic thorium by heating with sodium in an iron crucible a mixture of the anhydrous double chloride of thorium and potassium with sodium chloride. After treatment of the residue with water, metallic thorium remains as a heavy greyish brilliant powder. Examined under the microscope, the powder is seen to consist of minute crystals, more or less brilliant and united in groups. The metal is brittle and almost infusible. The powder assumes a metallic lustre under pressure, is unalterable in air up to 120°, takes fire in air or oxygen below a red heat, and burns with dazzling brilliancy, leaving a perfectly white oxide. It takes fire when heated with chlorine, iodine, bromine, and sulphur. It is not attacked either by hot or by cold water. Dilute sulphuric acid causes a feeble evolution of hydrogen in the cold, becoming more rapid on the application of heat, but the metal is attacked slowly; hot concentrated sulphuric acid also acts but slowly, disengaging sulphurous anhydride. Nitric acid, whether hot or cold, strong or dilute, exerts no sensible action. Dilute hydrochloric acid dissolves the metal slowly even when heated, but concentrated acid attacks it very easily. Aqua regia acts like hydrochloric acid. Alkalis have no action. The metal obtained by the author behaves, therefore, exactly like that obtained by Berzelius. The mean sp. gr. is nearly 11; this is much higher than that found by Chydenius (7·657 to 7·795): hence the specimen obtained by the latter chemist must have contained much impurity, probably derived from the glass tube in which it was prepared. The densities of two different specimens of the oxide were 10·2207 and 10·2198 respectively. These numbers are again much higher than those obtained by Berzelius, Damour, and Chydenius (9·402, 9·366, 9·288). Admitting that the metal is quadrivalent, the atomic volume is 21·1. This number coincides with the atomic volume of zirconium (21·7), cerium (21·1), lanthanum (22·6), and didymium (21·5); and this fact serves to confirm the author's opinion that the rare earth-metals form a series of quadrivalent elements. E. H. R.

Magnesia Alba. By K. KRAUT (*Arch. Pharm.* [3], **20**, 180—187).—In this criticism of Beckurts' paper on the composition of *magnesia alba* (this vol., p. 13), the author shows that analytical errors have crept in, as no direct estimation of the water lost by heating was made, &c.; the formula proposed by Beckurts therefore is incorrect, and the original formula $5MgO4CO_2,H_2O$, as proposed by Kraut, is the right one; also by boiling for some time, the composition may be altered to $4MgO,3CO_2,6H_2O$, but never to $7MgO,5CO_2$.

E. W. P.

Separation of Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, **95**, 410—413; 503—506. See also Abstr., 1882, 897, 1323).—*From Indium.*—Precipitation of the gallium by potassium ferrocyanide, in presence of hydrochloric acid, is to be recommended only when it is required to separate a little indium, together with other metals, such as aluminium and chromium. The following is the only trustworthy method:—The moderately concentrated solution is boiled for some minutes with a slight excess of potassium hydroxide; the precipitated indium hydroxide retains small quantities of gallium, which may be removed by a repetition of the process. The alkaline solutions contain only very slight traces of indium; to remove these, hydrochloric acid is added in slight excess, and the gallium and indium are precipitated together by boiling with an excess of ammonia, or better, by means of cupric hydroxide. The gallium and indium chlorides are then converted into sulphates; the slightly acid solution mixed with a quantity of ammonium sulphate rather more than sufficient to convert the gallium into alum is evaporated to small bulk, and, after cooling, mixed with four or five times its volume of alcohol of 70 per cent. Gallium alum is thus thrown down as a crystalline powder, which is washed once or twice with alcohol, dissolved in warm water containing a minute quantity of sulphuric acid, and reprecipitated. By several repetitions of this process, the gallium is obtained in the form of alum, free from indium. The alcoholic washings, which contain small quantities of gallium and indium, are evaporated to small bulk, the metals precipitated by boiling with ammonia or by means of cupric hydroxide, the precipitate dissolved in hydrochloric acid, and the solution boiled with a slight excess of potassium hydroxide; a small quantity of indium hydroxide is thus obtained free from gallium. The gallium remaining in solution may be separated as alum. Usually the indium dissolved by the potash is removed by four crystallisations of the ammonium-gallium alum; but if the gallium hydroxide contains more than 4 per cent. of indium hydroxide, seven or eight crystallisations are necessary.

From Cadmium.—In presence of much free hydrochloric acid, cadmium is not completely precipitated by hydrogen sulphide, whilst if the solution is but feebly acid, the cadmium sulphide contains gallium. The somewhat acid solution is treated with hydrogen sulphide, the precipitate redissolved in hydrochloric acid, the solution diluted, and again treated with hydrogen sulphide. By two or three repetitions of the process, the greater part of the cadmium is obtained as sulphide free from gallium. The filtrates which contain the gallium, mixed with a little cadmium, are evaporated to expel excess of acid, diluted with water, and saturated with hydrogen sulphide. The cadmium sulphide thus thrown down is reprecipitated two or three times.

Excess of boiling potassium hydroxide precipitates cadmium oxide, and dissolves gallium hydroxide; the cadmium oxide is redissolved and again precipitated, in order to separate the last traces of gallium. If the amount of cadmium is large, this process must be repeated four or five times. The alkaline solution which contains gallium and a small quantity of cadmium is slightly acidified with hydrochloric acid, and the gallium precipitated by means of cupric hydroxide, the filtrate is mixed with ammonium acetate, and treated with hydrogen sulphide, which throws down copper and cadmium: this precipitate is dissolved in aqua regia, evaporated with hydrochloric acid, and hydrogen sulphide is passed into the strongly acid solution; copper sulphide is thus precipitated, whilst cadmium remains in solution.

The following methods are more rapid:—(1.) The solution, which must contain a sufficient quantity of ammonium chloride, is boiled with excess of ammonia: cadmium then remains in solution, and gallium hydroxide is precipitated; this precipitate is redissolved and again precipitated, in order to remove the last traces of cadmium. (2.) Gallium is precipitated by means of potassium ferrocyanide in a solution which contains at least one-third of its volume of strong hydrochloric acid; the cadmium ferrocyanide remains in solution. (3.) Cupric hydroxide precipitates gallium on gently warming; the precipitate retains small quantities of cadmium, which may be removed by a repetition of the process. (4.) When it is necessary to remove iron as well as cadmium, the warm solution is reduced by metallic copper and then mixed with a slight excess of cuprous oxide: the precipitated gallium hydroxide contains traces of cadmium, which may be removed by reprecipitation.

The reactions with cupric hydroxide, and with metallic copper and cuprous oxide, are the most satisfactory.

From Uranium.—(1.) The boiling slightly acid solution of the chloride is treated with cupric hydroxide; the precipitate is then dissolved in hydrochloric acid, diluted, and again precipitated with cupric hydroxide, the treatment being repeated four or five times. (2.) If it is required to separate iron at the same time, the solution is reduced with metallic copper, and then boiled with excess of cuprous oxide; the precipitate is redissolved and the treatment repeated about four times. Neither of these methods is affected by the presence of considerable quantities of alkaline salts. (3.) The slightly acid solution of the chloride is mixed with an excess of acid ammonium acetate, zinc chloride free from gallium added, and the liquid is treated with hydrogen sulphide: the zinc sulphide formed carries down the gallium, whilst the uranium remains in solution. The precipitate is difficult to wash and must be redissolved in hydrochloric acid, and again precipitated in presence of an acetate. The zinc and gallium are separated by the method previously described. (4.) The uranium is precipitated in the form of alkaline uranate by adding a slight excess of potassium hydroxide, the precipitate dissolved in hydrochloric acid, and again precipitated. To remove traces of uranium from the filtrate, the latter is slightly acidified with hydrochloric acid, and boiled with cupric hydroxide. When the potassium hydroxide contains carbonate, the quantity of uranium in the filtrate is increased.

From Lead.—(1.) The slightly acid solution of the chloride is boiled with cupric hydroxide, the last trace of lead being removed by a second precipitation. The reagents must be free from sulphuric acid. This method is very accurate, and may be used to separate gallium sulphate from the minute quantities of lead which remain in solution after precipitation of lead as sulphate. (2.) The solution of chloride or sulphate is boiled with metallic copper and then with cuprous oxide, traces of lead being removed by a second precipitation. If a solution of the chlorides is used, the presence of sulphuric acid in the reagents must be avoided. (3.) The moderately acid solution is treated with hydrogen sulphide, the filtrate evaporated almost to dryness to expel free acid, diluted with water, and again treated with hydrogen sulphide. If sulphuric acid is present, it should be partially neutralised with ammonia. To extract the gallium retained by the lead sulphide, the latter is treated with strong hydrochloric acid, alcohol is added, the liquid is filtered, and the filtrate, after evaporation to expel water and alcohol, is diluted, and saturated with hydrogen sulphide. (4.) The gallium is then precipitated as ferrocyanide by means of potassium ferrocyanide in a solution containing one-third or one-fourth its volume of strong hydrochloric acid. A second precipitation is sometimes necessary in order to remove the last traces of lead. (5.) The solution is mixed with sulphuric acid, and two volumes of alcohol of 90° added; the precipitated lead sulphate, after being washed with alcohol acidified with sulphuric acid, is suspended in dilute hydrochloric acid and treated with hydrogen sulphide; and the filtrate, after being boiled to expel excess of the gas, is treated with cupric hydroxide to precipitate the last traces of gallium. The gallium in the alcoholic solutions is precipitated by cupric hydroxide, after boiling off the alcohol. (6.) The solution is mixed with twice its volume of 90 per cent. alcohol; a slight excess of hydrochloric acid is added, and the precipitated lead chloride is washed with acidulated alcohol, whereby it is obtained free from gallium. The filtrate is evaporated to small bulk, the nitric acid removed, and the liquid treated either with hydrogen sulphide, with cupric hydroxide, or with metallic copper and cuprous oxide. C. H. B.

Separation of Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, 95, 703—706).—*Separation from Tin.*—Sulphide of tin precipitated from a hydrochloric acid solution containing tin and gallium, retains none of the latter metal. On adding hydrochloric acid in excess to a solution of the sulphides of tin and gallium in an alkaline sulphide, sulphide of tin free from gallium is thrown down. Salts of manganese added to a solution of the mixed sulphides in an alkaline sulphide give a precipitate of manganese sulphide, which contains gallium: this makes it possible to extract the latter metal from large quantities of sulphide of tin. The author draws attention to one or two points, of which notice must be taken in analysing mixtures containing gallium. A solution containing even a considerable amount of gallium is not precipitated by potassium ferrocyanide if a large amount of stannic chloride is present; so that tin must be separated before attempting to estimate gallium by ferrocyanide. Tin and gallium, when alloyed, cannot be completely separated by nitric acid, because the metastannic acid formed retains sensible quantities of gallium, even after prolonged washing with nitric acid. It is difficult to obtain a complete separation of gallium and tin by precipitating the latter metal with zinc, because in a solution strongly acid the tin is not entirely thrown down, and in a nearly neutral solution a certain quantity of gallium becomes insoluble. Finally, tin dioxide, precipitated by boiling with sulphuric acid, retains much gallium.

Separation from Antimony.—Gallium may be separated from antimony by sulphuretted hydrogen, or by addition of an acid to a solution of the sulphide in an alkaline solution, just as described in the case of tin, except that in the case of the solution in the alkaline sulphide, it is advisable to repeat the process. Potassium ferrocyanide precipitates gallium from a solution containing antimony, but the precipitate contains traces of the latter metal, which must be removed by dissolving it in potash and reprecipitating by addition of a large excess of hydrochloric acid and a few drops of ferrocyanide. Salts of manganese can be used to separate traces of gallium from antimony, just as in the case of tin. Precipitation of the antimony by zinc does not answer well. E. H. R.

Compounds of Tin Disulphide and Diselenide. By A. DITTE (*Compt. rend.*, 95, 641—644).—*Potassium thiostannate,*

$$SnS_2,K_2S,3H_2O,$$

forms transparent colourless or very slightly yellow prisms, very soluble in water, but decomposed by a large quantity of that liquid, with precipitation of hydrated stannic sulphide. It is obtained by dissolving stannous sulphide in a solution of potassium polysulphide, or more easily by boiling a concentrated solution of potassium monosulphide with the theoretical amount of sulphur and a slight excess of tin, and evaporating the clear yellow solution by boiling or in a vacuum. *Potassium seleniothiostannate*, $SnSe_2,K_2S,3H_2O$, is obtained by substituting selenium for sulphur in the preceding operation. It forms yellow octohedrons, very soluble in water, with formation of a rose or red solution, according to the degree of concentration. Both the solution and the crystals alter when exposed to air, black crystalline selenium being liberated. *Potassium seleniostannate*,

$$SnSe_2,K_2Se,3H_2O,$$

is obtained by saturating a solution of potassium selenide with tin diselenide and evaporating in a vacuum. It forms crystals which alter rapidly when exposed to air. *Sodium thiostannate* and *sodium seleniostannate* are obtained in the same way as the corresponding potassium compounds, and have similar properties. *Ammonium thiostannate*, $3SnS_2,(NH_4)_2S,6H_2O$, is obtained by heating sheet tin with a solution of ammonium polysulphides, and evaporating the clear yellow liquid in a vacuum over potassium hydroxide and sulphuric acid. It forms yellow plates, which are decomposed by water with separation of hydrated stannic sulphide. The crystals alter quickly even in a vacuum, losing water and acquiring a superficial violet tint. When gently heated, they lose water, ammonium sulphydrate, and sulphur, a residue of tin sulphide being left. *Ammonium seleniothiostannate*, $3SnSe_2,(NH_4)_2S,3H_2O$, is obtained by treating an excess of hydrated tin diselenide with a concentrated solution of ammonium sulphydrate in the cold, filtering, and evaporating the red filtrate in a vacuum over potassium hydroxide and sulphuric acid. It forms yellowish-red plates, less stable than the preceding compound. The crystals are decomposed by water, with separation of red flakes of tin diselenide.

Tellurium dissolves in boiling concentrated solutions of the alkaline sulphides, but yields no compounds with tin analogous to those already described. Tellurium is deposited in crystals when the solution cools.

Barium thiostannate, $SnS_2,BaS,8H_2O$, obtained by dissolving tin in a boiling solution of barium polysulphides and evaporating the solution in a vacuum, forms transparent citron-yellow crystals, soluble in cold water without decomposition. From this solution dilute acids immediately precipitate yellow stannic sulphide. *Strontium thiostannate*, $SnS_2,SrS,12H_2O$, produced in a similar manner, forms bulky, transparent, colourless prisms, soluble in cold water without decomposition. *Calcium thiostannate*, $SnS_2,2CaS,14H_2O$, also obtained in a similar manner, forms transparent citron-yellow crystals, soluble in cold water without decomposition. C. H. B.

Preparation of Lead Dioxide. By A. FEHRMANN (*Ber.*, **15**, 1882). —A concentrated solution (60—70° C.) of lead chloride is treated with solution of chloride of lime until a filtered sample does not show further separation of the dioxide; the latter is then filtered off and washed out of contact with air. Lead dioxide so prepared is quite pure and nearly black, and keeps best in the moist state. When prepared from sugar of lead it is not so cheap, and liable to undergo decomposition from the impurities of the lead acetate. J. K. C.

Barium Compounds of Bismuth Peroxide. By I. MESCHTCHERSKY (*Journ. Russ. Chem. Soc.*, 1882, 280—281).—On fusing a mixture of bismuth trioxide, baryta, and potassium chlorate, a black mass is obtained, which, when washed with water, begins to decompose, with evolution of oxygen. The black or reddish-brown residue remaining after the extraction of soluble salts by water consists of compounds of bismuth peroxide with barium, and decomposes hydrochloric acid with evolution of chlorine. Analogous compounds with calcium or magnesium could not be obtained. If the above compound has been well washed with water, it does not lose oxygen under pure water, but decomposition takes place suddenly in contact with barium peroxide or solution of potassium chlorate. Fusion with potassium nitrate gives rise to compounds containing more oxygen, *e.g.*, one of the following composition: $14BaO, 5Bi_2O_5, BiO_2, 3H_2O$. B. B.

A Hydrate of Molybdic Acid. By F. PARMENTIER (*Compt. rend.*, **95**, 839—841).—The author has examined the yellowish crystalline substance which always separates after a time from solutions of alkaline molybdates in nitric acid. He finds that it contains no nitrogen, but is a hydrate of molybdic acid, having the composition $MoO_3,2H_2O$. This substance is not formed in hydrochloric acid solutions of alkaline molybdates. It is very sparingly soluble in water, a litre dissolving only 0·5 gram at 15°. The crystals are efflorescent, and lose half their water in a vacuum over sulphuric acid. Heated to 200°, they lose all their water, and leave a white residue which sublimes completely on further heating. E. H. R.

Mineralogical Chemistry.

Mechanical Separation of Minerals. By L. PEBAL (*Monatsh. Chem.*, **3**, 723—725).—In this paper, which is partly a reply to Doelter's remarks on the same subject (Abstr., 1882, 656, 1173), the author recommends the following modification of his method of moving the electromagnet about in water holding the finely pulverised mineral in suspension. To avoid the formation of lumps, arising from the enclosure of air-bubbles, the fine powder of the mineral is made slowly to absorb water—or alcohol if water will not wet it—from one side only, after which it is treated as follows:—A number of moderate-sized beaker-glasses are filled with distilled water; the moistened rock-powder is introduced into the first; into this powder is thrust the end of the iron rod surrounded with a coil of wire; and the circuit is closed, while the water is briskly agitated. The electromagnet is then dipped into the second glass; the circuit is broken; and this treatment is repeated till the magnet in the first glass no longer attracts any particles. After all the magnetic particles have thus been transferred to the second glass, the process is repeated in exactly the same manner with the second and third glass, then with the third and fourth, and so on till the magnetised bar no longer leaves any residue in the last glass but one. The contents of the last glass are then collected on one filter, and those of all the others on a second filter. With a moderate amount of care in carrying out this process, it is easy to avoid loss of substance. One point, however, must not be overlooked, namely, the behaviour of solid diamagnetic bodies in diamagnetic liquids, whereby, if the diamagnetism of the liquid is stronger than that of the solid body, repulsion becomes converted into attraction. H. W.

Application of a Solution of Potassium and Mercury Iodides to Mineralogical and Petrographical Researches. By V. GOLDSCHMIDT (*Jahrb. f. Min.*, 1881, **1**, Beil. Bd., 179—238).—It is to be regretted that the subject of the separation of the constituents of a rock has been neglected of late, in consequence of the success which has attended microscopic investigation, as there are cases in which the latter method cannot be relied on. The separation may be effected chemically or mechanically; in the latter case advantage is taken of the difference in the sp. gr. of the substances. In 1877 Church ("On a Test of Sp. Gr.," *Min. Mag.*, 1877) proposed to separate the constituents of a rock according to their sp. gr. by the help of an aqueous solution of the iodides of potassium and mercury. The paper gives at some length an account of J. Thoulet's researches on the same subject (*Bull. Soc. Min.*, 1879, No. 1).

On investigating the subject further, the author decided to employ a solution in which the weight of potassium iodide present is to the mercury iodide as 1 is to 1·239; and this solution has a sp. gr. of 3·196, so that fluorspar floats in it; while the solutions of Thoulet and Church gave as the maximum sp. gr. 2·77 and 3·01 respectively. The maximum density is, however, not constant. It depends on the moisture of the atmosphere and on the temperature. In summer the maximum was 3·196, whilst in winter it was only 3·17.

The difficulties which attend this simple method of separation of the rock constituents according to the sp. gr. are due to the variation in the sp. gr. of the predominating mineral; the close combination of the constituents; the smallness of the grains; the great similarity, or, in some cases, identity of sp. gr. of different minerals occurring together, such as quartz and oligoclase; the tendency of the lighter grains when they are in great excess to bring the heavier with them to the top; and the liability of the solution to change by evaporation or by taking up water.

In considering this method, the question arises: Is the value of the sp. gr. constant enough for the mineral to be determined by it, and if a separation is effected between narrow limits of weight, can it with certainty be asserted that the mineral sought for has been separated? Theoretically it is so. In order to answer the question practically, the author submitted the felspar-group to the strictest investigation, and came to the conclusion that, with fresh material and perfect separation, the determination of the sp. gr. gives an exact conclusion as to the nature of the felspar.

The apparatus used for the separation of the rock-constituents proposed by Thoulet is described, but the author prefers to effect the separation in small beakers of about 40—50 c.c. capacity, the principal advantage of which is that the parts swimming above can be better manipulated with the glass rod, and, consequently, the heavier grains which are enclosed more easily separated. A number of minerals whose sp. gr. has been exactly determined, are used as indicators in the solution. The powdered rock and the indicators are introduced into about 30 c.c. of the concentrated solution and stirred, then allowed to subside, and the lighter parts removed. The success of the separation depends on the skill of the experimenter, on the choice of the indicators, but, above all, on the nature of the substance to be separated.

It is evident, then, that Thoulet's opinion that the constituents of a rock can be qualitatively and quantitatively separated, holds good only very rarely, and it would be necessary also in most cases to make use of auxiliary methods, such as treating the powder with various reagents or with the magnet. B. H. B.

Native Palladium-Gold from Taguaril, Brazil. By W. H. Seamon (*Chem. News*, **46**, 216).—Sp. gr. = 15·73. Analysis:—

Au.	Pd.	Ag.	Fe.
91·36	8·21	trace	trace

E. W. P.

Alloys of Gold, Silver, &c., found in Grains along with the Native Platinum of Columbia. By W. H. Seamon (*Chem. News*, **46**, 215).—Occurring with native platinum, alloys were found having the following composition:—$(Ag + Cu')Au_3$, $(Cu' + Ag)_4Au_6$, $(Ag + Hg')_2Au_8$, Ag_4Au_{10}. Analyses are given, together with the donsities; but the results are not of much value, owing to the smallness of the quantity of material at hand. E. W. P.

On a Bed of Coal discovered in Algiers, and on the Layers of White Sand accompanying the same. By G. Pinard (*Compt. rend.*, **95**, 708—709).—The author states that the results of experiments made with the coal of Bou-Saada in Algiers show that, both in respect of the amount of gas yielded and the illuminating power of the latter, it is quite equal to the best English and French coals. The yield of coke varies from 60 to 66 per cent. of the coal used.

The coal is always accompanied by beds of white sand arising from the disintegration of bands of sandy loam. This sand can be used for the manufacture of superior glass. E. H. R.

Dopplerite from Aussee. By W. Demel (*Monatsh. Chem.*, **3**, 763—769).—A perfectly homogeneous specimen of this mineral freed from adhering peat and dried at 100—120°, gave by analysis 56·42 and 56·51 per cent. carbon and 5·34—5·20 hydrogen, leading to the formula $C_{12}H_{14}O_6$, which requires 56·69 C, 5·52 H, and 37·79 O. It yielded also 5·1 per cent. ash having the following composition:—

CaO	72·67	SO_3	4·36
MgO	2·03	Cl	1·09
K_2O,Na_2O	0·99	Insoluble	6·80
Al_2O_3,Fe_2O_3	12·02		
			99·96

The high percentage of lime seems to show that this base may be present as carbonate, but the percentage of CO_2 directly determined was only 0·16; and this, together with the smallness of the amounts of SO_3 and Cl, shows clearly that the greater part of the lime must be combined with the organic matter, a conclusion which is confirmed by the behaviour of the mineral with caustic potash. On suspending the dopplerite in water and treating it with strong potash-lye, the mass becomes thick, pasty, and very hot, and the alkali appears to be saturated, as it no longer absorbs carbonic acid from the air. On boiling the liquid the dopplerite dissolves, yielding a dark brown-red solution, and from this, after filtration, acids throw down a brown flocculent precipitate which, after thorough washing and drying, becomes shining and brittle, and very much like the original dopplerite. This substance dried at 110° gave 0·73 per cent. ash, and its combustion yielded 56·86—56·99 per cent. C and 4·90—4·97 H, leading to the formula $C_{12}H_{12}O_6$, which contains 2 at. hydrogen less than that of the original dopplerite.

The alkaline solution of dopplerite gives with calcium salts a brown precipitate containing calcium, which when dried forms a blackish-brown mass like dry dopplerite; it contains about 2·71 per cent. $CaCO_3$, and, deducting this, the composition of the salt is found to agree very nearly with the formula $C_{26}H_{22}CaO_{12}$, thereby affording further evidence that the substance isolated from dopplerite in the manner above described has the composition $C_{12}H_{12}O_6$.

Dopplerite fused with potassium hydroxide is converted into protocatechuic acid (m. p. 199—201°), together with resinous and dark-coloured products containing more than 70 per cent. carbon.

Ulmin (prepared from cane-sugar) also gave, on fusion with potash, protocatechuic acid, together with black amorphous masses very rich in carbon.

From the similarity of the compounds above described to humus-substances in general, and from the mode of occurrence of dopplerite in peat-beds, this mineral may be regarded as the calcium salt of one or several acids belonging to the series of humus-substances.

H. W.

New Sulphide received as Tetrahedrite from Great Eastern Mine, Colorado. By W. T. PAGE (*Chem. News*, **46**, 215).—Steel-grey metallic lustre; structure crystalline but indefinite, brittle. Hardness = 4: sp. gr. = 4·89. Composition:—

S.	Sb.	Cu.	Zn.	Fe.	Pb.	Silicious residue.	
26·88	34·47	23·20	7·14	1·38	1·19	5·86	= 100·12

This corresponds to—

$$\{\tfrac{2}{3}Cu'_2S + \tfrac{7}{3}(Cu'',Zn,Fe,Pb)S\}Sb_2S_3.$$

This mineral might be considered as a distinct species of stylotypite, but it is better to class it as a variety of bournonite.

E. W. P.

Martite of the Cerro de Mercado, or Iron Mountain of Durango, Mexico, and certain Iron Ores of Sinaloa. By B. SILLIMAN (*Am. J. Sci.* [3], **23**, 375—379).—This remarkable hill exposes masses of the ore all over its surface; they appear to be derived from one or more immense beds of specular iron standing nearly vertical; the fragments form a talus on the slopes of the mountain and conceal the underlying porphyry. There is nothing to show that it is a pseudomorph of pyrites. An average sample contained—

Fe_3O_4.	Fe_2O_3.	Mn_2O_3.	TeO_2.	CaO.	MgO.	SO_3.	P_2O_5.	SiO_2.	H_2O, &c.	Al_2O_3.
2·07	77·57	0·11	0·71	5·05	0·36	0·21	3·04	7·76	1·98	—

In the ores from Sinaloa there still remains in the martite about one-third of the original magnetite.

H. B.

New Locality for Hayesine. By N. H. DARTON (*Am. J. Sci.* [3], **23**, 458—459).—This very rare mineral occurs with datholite and calcite in the trap rock of Bergen Hill. Slender acicular crystals grouped on the calcite crystals; they are probably a decomposition-product of datholite; the rock is soft, and permeable to water.

	CaO.	B_2O_3.	H_2O.	
Found	18·39	46·10	35·46	= 99·95.

H. B.

Occurrence and Composition of some American Varieties of Monazite. By S. L. PENFIELD (*Am. J. Sci.* [2], **24**, 250—255).—(1.) The specimen was apparently homogeneous. Sp. gr. = 5·20—5·25; locality, Pelton's Quarry, Portland, Conn. (2.) Picked grains from the monazite sand from gold washing in the Brindletown district, Burke Co., N. Carolina; sp. gr. = 5·10. (3.) A specimen, also apparently pure, from Yale College.

	P_2O_5.	Ce_2O_3.	$(La,Di)_2O_3$.	ThO_2.	SiO_2.	Ignition.	
(1.)	28·18	33·54	28·33	8·25	1·67	0·37	= 100·34
(2.)	29·28	31·38	30·88	6·49	1·40	0·20	= 99·63
(3.)	26·12	29·89	26·66	14·23	2·85	0·67	= 100·42

These numbers are in most cases the mean of two or three determinations.

The ratios $(Ce,La,Di)_2O_3 : P_2O_5$ are 1 : 1·06, 1 : 1·08, and 1 : 1·07; those of ThO_2 to SiO_2 1 : 0·90, 1 : 0·92, and 1 : 0·88 respectively. The varying amounts of ThO_2 and SiO_2, and their chemical difference from the cerite metals, made it probable that the thorium silicate exists as an impurity; this was proved by microscopic examination, the mechanically mixed thorite being distinguished by its darker colour and easy decomposition by acids.

The thoria was separated by sodium thiosulphate; the remaining oxides were heated with dilute sulphuric and oxalic acid, and the evolved carbonic anhydride collected in potash bulbs. The joint atomic weight of the oxides obtained from the Portland specimen was 140·1, which number was also used to calculate the results of the other analyses. H. B.

Colourless Mimetite from the Richmond Mine, Nevada. By F. A. Massie (*Chem. News*, **46**, 215).—Slender acicular hexagonal prisms, colourless, transparent, and with adamantine lustre. Hardness = 3; sp. gr. 6·92, easily fusible. Composition:—

As_2O_5.	P_2O_5.	PbO.	$PbCl_2$.
23·41	trace	68·21	8·69 = 100·31

agreeing with the known formula $PbCl_2,3Pb_3As_2O_8$. E. W. P.

Notes on some N. Carolina Minerals. By W. E. Hidden (*Am. J. Sci.* [3], **24**, 372—377).—In Alexander Co., emerald and beryl crystals, on which the rare forms $3P\frac{3}{2}$ and $4P\frac{4}{3}$ are largely developed, are occasionally found.

The supposed *æschynite* from Ray's Mine, Yancey Co., is columbite.

Uraninite from Mitchell Co. has sp. gr. = 8·97—9·22, and hence is not entirely free from alteration.

Euxenite from Wiseman's mica mine has been reanalysed by J. W. Mallett; titanic acid is absent; it is therefore probably altered samarskite, with which it is intimately associated.

Fergusonite from Burke Co. has also been analysed by Mallett.

Nb_2O_5.	Ta_2O_5.	SnO_2,WO_3.	Y_2O_3, &c.	C_2O_3.	Di_2O_5,La_2O_3.
43·78	4·08	0·76	37·21	0·66	3·49

U_2O_3.	FeO.	CaO.	H_2O.
5·81	1·81	0·65	1·62 = 99·87.

Allanite has recently been found at two new localities, viz., Alexander Co. with the above-mentioned emerald crystals, and Wiseman's mica mine, Mitchell Co.; in both cases the crystals are well developed.

SiO_2.	Al_2O_3.	Y_2O_3.	Ce_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.
39·03	14·33	8·20	1·53	7·10	5 22	4·29	17·47	2·78 = 99·95

H. B.

Composition of Two Specimens of Jade. By C. L. Allen (*Chem. News*, **46**, 216).—The first specimen came from the Karakash Valley, on the borders of Turkestan; it is of a pale green colour, translucent; hardness = 6·5; sp. gr. = 2·98, and contains—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.
57·35	1·03	1·22	22·73	13·40	0·25	0·23	2·69 = 98·9

The other specimen came from Hokotika, New Zealand, and is subtranslucent, with hardness = 6; sp. gr. 3·026. Composition:—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	
56·34	1·60	4·86	20·23	13·51	0·27	0·31	3·57	= 100·69

These specimens therefore represent the nephrite variety of amphibole, and the first analysis corresponds to $(\frac{7}{10}Mg + \frac{3}{10}Ca)SiO_3$, whilst the second corresponds to $(\frac{2}{3}Mg + \frac{1}{3}Ca)SiO_3$. E. W. P.

Analysis of a Mineral allied to Orthite. By W. H. Seamon (*Chem. News*, **46**, 215).—Crystals flat, well defined, imbedded in soft kaolin, pitch-black, submetallic lustre; brownish-grey streak; imperfect conchoïdal fracture; hardness = 6; sp. gr. 3·15. Composition:—

SiO_2.	Al_2O_3.	Y_2O_3.	Ce_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.	
39·03	14·33	8·20	1·53	7·10	5·22	4·29	17·47	2·78	= 99·95

Distribution of elements $(\frac{6}{12}M' + \frac{9}{12}M'' + \frac{8}{12}M''')SiO_4$.

E. W. P.

Communications from the U. S. Geological Survey, Rocky Mountains Division. 1. Minerals, mainly Zeolites, occurring in the Basalt of Table Mountain, near Golden, Colorado. By W. Cross and W. T. Hillebrand (*Am. J. Sci.* [3], **23**, 452—458, and **24**, 129—138).—Leucite does not occur. The formation of the mountain is due to two protecting sheets of lava, an upper and a lower one, of 115 feet in thickness. In the cavities of the upper portion of the lower sheet (felspar basalt) are many beautifully crystallised zeolites, associated with calcite and arragonite. The zeolites are often found together; the following have been determined, viz., analcite, apophyllite, chabasite, mesolite, natrolite, stilbite, and thomsonite. *Chabasite* is apparently the oldest zeolite, as it generally lines the cavities, and the other zeolites are formed upon it. *Thomsonite*—Crystals, thin rectangular blades, grouped together in various ways; where calcite crystals are not covered by chabasite, thomsonite never fails to coat them. Toward the close of the zeolitic formation, a second generation of thomsonite, and sometimes also of chabasite, was deposited.

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	
I.	40·68	30·12	11·92	4·44	12·86	= 100·02
II.	42·66	29·52	10·90	4·92	12·28	= 100·01
III.	41·60	—	—	—	—	
IV.	40·88	—	—	—	—	

I is of the older growth, and II of the newer. No. I was most carefully freed from any chabasite. No. II contained a comparatively few crystals of mesolite, and their *complete* removal was impossible. III is of the *ends* of the thin blades, and the microscope showed the presence of irregular rounded isotropic particles imbedded in the outer parts of the crystals. No. IV was from some very fine crystals, containing but a very few of these rounded particles. The silica is higher than that allowed by the generally accepted formula; the oxygen ratios being—

	RO	:	Al_2O_3	:	SiO_2	:	H_2O.
I.	1	:	3·09	:	4·76	:	2·51
II.	1	:	3·10	:	5·17	:	2·48
Accepted formula....	1	:	3·00	:	4·00	:	2·50

Analcite follows thomsonite in time of deposition. Form 2O2 and also $\frac{3}{2}$O, which is very characteristic for this locality. The double refraction was very regular. A second generation of small and clear crystals upon apophyllite was observed. Analcite is often found alone in the cavities; natrolite is almost invariably deposited on analcite. *Apophyllite*, form ∞P . P. Crystals large and rough, or small and smooth; the terminal edges of the pyramid are slightly furrowed. Sections parallel to 0P exhibit between crossed Nicols a square dark centre, whose sides are parallel to the traces of the prism faces, and from whose corners dark lines proceed to the margin; the appearance must be caused by internal tensions. The composition is quite normal.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Fl.	O for Fl.
51·89	1·54	0·13	24·51	3·81	0·59	16·52	1·70	−0·72 = 99·97

Much of the apophyllite is altered to a white pearly substance containing much silica, alumina, and water. *Calcite* has been deposited in three stages—firstly, wine-yellow crystals, preceding chabasite and deposited directly on the basalt; secondly, colourless or only slightly yellow; and lastly, aragonite as a snow-white incrustation, mostly on chabasite, sometimes on apophyllite and thomsonite.

Mesolite is the last mineral deposited; it occurs in groups of exceedingly delicate needles, too small to recognise any crystalline form.

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.
46·14	26·88	8·77	6·19	12·17 = 100·15.
46·02	26·87	—	—	12·17
46·33	—	—	—	12·13

This corresponds very nearly with 1 mol. of natrolite substance plus 2 mols. scolecite substance, *i.e.*, Naumann's formula.

A second series of zeolites differing in time and manner and also in composition, are found as semi-stratified deposits in the bottoms of many cavities, forming a kind of floor. The sandstone-like substance is crystalline, granular, and yellow, or white in colour, and in one large cavity this consisted entirely of laumontite, as was shown by optical and chemical examination—(*a*), white crystals; (*b*), yellow crystals:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.
(*a*.) ..	51·74	21·65	0·95	11·95	0·19	0·35	13·30 = 100·13.
(*b*.) ..	52·84	21·62	—	11·41	0·48	0·42	13·32 = 100·09.

The low amount of water is due to only some of the grains being clear, others being turbid; laumontite easily loses some of its water.

In other cases a mixture of laumontite and stilbite grains was present, often accompanied by reddish spherules of thomsonite, as shown by analysis; this mineral is also similarly deposited alone on the lower lava sheet. In many cases, fissures filled with these three minerals have been found leading into cavities also containing them; they were certainly deposited previously to the other zeolites, whose crystals are *attached* to the walls of the cavities, or to this older deposit. H. B.

Garnet and Cordierite in the Trachytes of Hungary. By J. Szabó (*Jahrb. f. Min.*, 1881, 1, Beil. Bd., 302—326).—Red garnet has often been found in the trachytes of Hungary, and the researches of Szabó prove that the garnet represents a type of trachyte which is characterised by its associated minerals, as well as by its relative age and the manner of its origin. He also found that the Hungarian trachytes very frequently contain cordierite. The garnet is almost always red. The grains are usually so large that they can be distinguished with the naked eye. The predominating form of the crystals is an ikostetrahedron, with subordinate rhombic dodecahedron. It fuses easily before the blowpipe, thus indicating the almandine variety. The minerals accompanying it are felspar, amphibole, biotite, magnetite, and cordierite. The latter has previously been found in the trachytes of Spain and Tuscany, but was first discovered in the Hungarian trachytes by Vogelsang, having formerly been mistaken either for quartz or for felspar. The cordierite has a violet-blue colour, and resembles amethyst-coloured quartz. It gave on analysis—

SiO_2.	Fe_2O_3 and Al_2O_3.	MgO.	CaO.	Total.
56·85	28·76	11·84	1·06	98·51 per cent.

The remainder is probably soda. It is dichroic, and scratches quartz. It is associated with an orthoclase rich in soda, also with biotite, amphibole, and almandine.

The author employs a new method of distinguishing cordierite for petrographic purposes. The dichroism alone is not sufficient, as it is not distinctly marked in light-coloured varieties, and although the mineral is harder than quartz, the difference in this respect is too small to afford any serviceable distinction: for these reasons chemical tests are to be preferred. Before the blowpipe it shows the presence of soda by faintly colouring the flame. The amount of soda is so slight, that it would in a chemical analysis be regarded merely as a trace; but it is here of the greatest importance, since it serves, together with the fact of its being slightly fusible, to distinguish the mineral from quartz.

Garnet is not found in the trachytes of Servia, of Auvergne, or of the Rhine district. It has, however, been found in the trachytes of the Rocky Mountains (*United States Geol. Exploration of the 40th Parallel.* C. King, 1877, p. 561).

The trachyte family may be classed according to the felspar present, as follows:—(*a*) orthoclase trachyte; (*b*) oligoclase trachyte; (*c*) labradorite trachyte; (*d*) anorthite trachyte. Most of the Hungarian trachytes are biotite trachytes, in which the predominating felspar is labradorite, but andesine (oligoclase) also occurs subordinately: hence it can be seen that the garnet indicates the presence of a lime-soda felspar, and therefore, if garnet is found in a Hungarian trachyte the latter may be considered a biotite-labradorite trachyte, or, in other words, a garnet trachyte.

Cordierite occurs under quite different conditions; it is not bound to any particular felspar; it may be found or be wanting, in any of the types of trachyte mentioned above. The presence of cordierite is of importance, as it indicates with certainty that the trachyte has undergone metamorphism. B. H. B.

The Lugano Eruptive District. By Toyokitsi Harada (*Jahrb. f. Min.*, 1882, **2**, Beil. Bd., 1—48).—The paper gives a topographical and geological review, and a petrographical description of the Lugano eruptive rocks.

1. *The Black Porphyry.*—This is an intermediate rock, with an exclusively felspathic ground-mass. The minerals which compose it, according to the relative age in which they separated out, are the following:—Zircon, titanite, apatite, magnetite, biotite, hornblende, plagioclase, orthoclase, quartz, and lastly, the various products of decomposition, especially kaolin, mica, chlorite, and epidote. The plagioclase is proved to be oligoclase, with a sp. gr. of 2·65. An exact determination of the sp. gr. of the black porphyry itself cannot be expected, on account of its state of decomposition. The comparatively undecomposed rock had a sp. gr. of 2·672—2·675. The chemical analysis of the rock gave the following result:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	H_2O.	
59·44	17·26	7·35	3·47	3·60	3·28	3·23	0·62	2·22	= 100·87

The black porphyry may be regarded as a quartz porphyrite, the structure of which varies between that of quartz diorite and quartz felsophyrite.

2. *The Red Porphyry.*—This is widely different from the black porphyry; it is very acid, and has a magma rich in recent quartz. The four essential constituents are biotite, plagioclase, orthoclase, and quartz, and besides these zircon, apatite, and magnetite occur. The latter are always found enclosed in the other minerals, especially in the biotite. Kaolin, potash mica, epidote, ferric hydrate, calcite, quartz, chalcedony, pyrites, and chlorite appear as secondary constituents. The order in which the minerals separated out from the magma is the following:—1. Zircon and apatite. 2. Magnetite. 3. Biotite. 4. Oligoclase. 5. Orthoclase. 6. Quartz.

The chemical analyses of the red porphyry gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	72·32	13·37	0·57	2·34	—	1·88	3·57
II.	73·71	12·20	2·42	1·55	trace	0·40	3·63

	K_2O.	Na_2O.	H_2O.	
I.	2·30	2·76	0·68	= 99·79
II.	2·28	1·83	1·69	= 99·71

The sp. gr. is 2·59.

Tourmaline is to be regarded as a secondary constituent both of the red and black porphyries.

3. *The Tufas.*—These originate from the comminution of the red porphyry, as is shown by the fact that fragments of the latter are found in its deepest beds, and that the red porphyry and the tufa beds exhibit perfect conformability. B. H. B.

Sericite Rocks occurring in Ore Deposits. By A. v. GRODDECK (*Jahrb. f. Min.*, 1882, Beil. Bd., [ii], 72—138).—The "white rock" of Holzappel, on the Lahn, Wellmich and Werlau, on the Rhine, the slate bed of Mitterberg, in the Salzburg Alps, and the white slate of Agordo, in the Venetian Alps, which up to the present time have been described as talc slates, are sericite rocks.

The analyses of the sericite gave the following result:—

SiO_2.	Al_2O_3.	FeO.	MgO_2.	CaO.	K_2O.	N_2O.	H_2O.	Phosphoric acid.	
45·58	36·76	1·13	0·85	0·03	9·29	1·36	5·16	trace	= 100·16

Sp. gr. 2·87—2·88. The analysis thus corresponds pretty exactly with the formula of potash mica, $H_2(KNa)Al_3(SiO_4)_3$, which confirms Laspeyre's theory that sericite is not a distinct mineral, but a cryptocrystalline potash mica.

A part of the "white rock" contains pseudomorphs after felspar, augite, magnetite, and titanic iron ore, and is hence an altered eruptive rock, probably a diabase. In the white rock of Wellmich large crystals of apatite are enclosed, which are without doubt of secondary origin.

The sericite rocks of Mitterberg and Agordo are very probably metamorphic rocks from normal clay slates, or Greywacké slates.

An exact knowledge of these rocks seems suitable for opening up new points of view for several most important questions regarding ore deposits, as it is highly probable that the sericite rocks described always occur with ore-deposits where there is conformability between the deposit and the strata of the surrounding rocks. The ore-deposits of Holzappel, Wellmich, Werlau, and Mitterberg are doubtless veins resembling interstratified beds. It had long been doubtful whether the Salzburg and Tyrol copper ore deposits of Mitterberg, &c., were true beds or lodes resembling beds, but the general opinion now is that all the occurrences belong to the group of lodes resembling beds. These seem to be always accompanied by sericite rocks. The Agordo deposit resembles in a remarkable degree that of Mitterberg; it is therefore very probable that it is also a bed-like lode. The white slates of Agordo correspond, according to v. Cotta, with the rock at Fahlun, in Sweden, so it is very possible that the latter also belongs to the sericite rocks. Although sericite rocks occur with such typical bed-like lodes as those of Holzappel and Mitterberg, they are entirely absent in the case of typical stratified pyrites deposits, as the beds of Goslar, Schmöllnitz, and Meggen.

It has long been a moot question whether ore deposits, which are conformably interstratified in sedimentary rocks, must be considered as beds, or lodes resembling beds. To settle this question, the character of the surrounding rock has never yet been taken into account, but the author is of the opinion that if the sericite rocks are truly the original surrounding rock altered by the formation of a mineral vein, they can only occur in the presence of mineral veins, and their absence must confirm the opinion as to the bedded nature of the deposit.

B. H. B.

Basalt Rocks containing Hornblende. By H. SOMMERLAD (*Jahrb. f. Min.*, 1882, Beil. Bd. [ii], 139—185).—The hornblende basalts, characterised macroscopically by their richness in porphyritic amphibole crystals, contain microscopically as essential constituents, plagioclase, augite, hornblende, magnetite, and olivine. In the Rhön rocks, nepheline occurs, although never in distinct crystals, and is of no special importance for the composition of the rock, as the chemical analysis also proves. A glassy basis is rarely met with.

The hornblende basalts form a subdivision of the felspar basalts. When nepheline is present in greater quantity, they pass into basanites; in the absence of plagioclase, and with predominence of a glass basis they approach the limburgites. The most interesting constituent, the hornblende, frequently shows remarkable peculiarities of structure. Rounded crystals are specially characteristic of it. It was without doubt an original ingredient of the rock, which has separated very early out of the magma. The hornblende basalts of the Rhön-mountains, where they seem to be most widely distributed, never form high peaks. They are of older origin than the basalts, which are free from hornblende, as can at least be proved in the case of the Rhön and the Vogelsberg.

The chemical composition indicates that the hornblende basalts are tolerably basic, owing to their richness in magnetite, hornblende, and augite. The percentage of silica scarcely rises above 44; that of soda varies between 2·57 and 3·25; thus it may be seen that it is not greater than in other felspar basalts, and this proves that the nepheline does not play a special part in the hornblende basalts. The percentage of potash varies between 1·36 and 1·54. Only a few varieties from the Rhön gelatinise weakly with hydrochloric acid, with separation of little cubes of sodium chloride.

The rocks from Beuelberg, near Kircheip, and from Naurod, near Wiesbaden, contain hornblende and augite, but no felspar can be found microscopically in them as an essential constituent, and they contain large amounts of olivine; they belong to the group of the tertiary picrite porphyries. B. H. B.

Examination of certain Meteorites. By W. FLIGHT (*Proc. Roy. Soc.*, **33**, 343—347).—I. The Bruce meteorite, found at Cranbourne, near Melbourne, is shown by the author to consist entirely of metallic minerals; the iron contains no combined carbon, from 7—9 per cent. nickel, some cobalt, silicon, and copper. On the surface were metallic plates of a flexible mineral of composition Fe_5Ni_2, which the author proposes to name *Edmondsite*. Among other minerals present were rhabdite, Fe_4Ni_3P, a brittle coarse powder, probably identical with a schreibersite of formula $(Fe_2Ni)_7P$, brass-coloured oblique crystals of composition $Fe_9Ni_2B_2$, and square, black metallic prisms of composition Fe_7Ni_2P, together with triolite and graphite; the occluded gases amounted to 3·59 times the volume of the iron, and consisted of—

CO_2.	CO.	H.	CH_4.	N.
0·12	31·88	45·79	4·55	17·66

II. The Rowton siderite fell on April 24th, 1876, at Rowton, near Wellington, Salop. It is covered with a thin black crust of the magnetic oxide; some fragments of the block were found on analysis to contain—

Fe.	Ni.	Co.	Cu.
91·145	8·582	0·371	trace

thus closely resembling the iron of Nevagolla, in India. The occluded gas was 6·38 times the volume of the iron, and consisted of—

CO_2.	H.	CO.	N.
5·155	77·778	7·345	9·722

III. The Middlesborough siderite fell at Middlesborough on March 14th, 1881; it is in the form of a low pyramid, slightly scolloped, the summit and side being deeply grooved and polished. It contained 9·379 per cent. of nickel iron, containing iron, 76·99; nickel, 21·32; cobalt, 1·69 per cent; the remaining constituents consist of a soluble silicate identical with olivine, and an insoluble silicate, bronzite.

V. H. V.

Deposits of Manganese on the Surfaces of Rocks. By BOUSSINGAULT (*Compt. rend.*, **95**, 368—373).—The author has found manganese in the magnesia prepared from sea-water by Schloesing's process. Dieulafait has detected manganese in considerable quantity in the ashes of marine plants, and the "Challenger" expedition dredged up, from the bottom of the deep sea, nodules containing a large proportion of manganese dioxide. There can, therefore, be no doubt that manganese is present in sea-water. The manganese found in such large quantity on the sea bottom by the "Challenger" is apparently of volcanic origin, for it was always found where pumice stone was present. The nodules have an oolitic appearance, and frequently consist of concentric layers of manganese dioxide surrounding a nucleus of red clay, but they show no trace of organic structure. Buchanan regards the nodules as due to the intervention of animal substances, which reduce the sulphates in the sea-water to sulphides. Gümbel supposes that the manganese is derived from submarine springs which rise in volcanic districts, and contain manganese carbonate in solution. The manganese carbonate is deposited, and is oxidised by the oxygen dissolved in the water. This explanation is very similar to that which the author has advanced to account for the deposits of manganese dioxide on the surface of rocks on the banks of the Orinoco and in other localities (Abstr., 1882, 1270).

C. H. B.

The Orchard Alum Spring. By J. C. Thresh (*Pharm. J. Trans.* [3], **13**, 361).—This spring, which issues from an old coal mine near the summit of Axe Edge, in the Peak country, has long been valued as a vermifuge, but it is not adapted as a tonic, owing to the amount of aluminium sulphate present. The water has a decided red tint, which varies according to the wetness of the season; it is acid in reaction, but contains no free acid. When heated to 66° it becomes opaque, basic ferric sulphate separating, but the deposit redissolves as evaporation proceeds; the water is colourless if the deposit is allowed to settle. The sp. gr. = 1·00351, and the composition per gallon is as follows:—

Fe_23SO_4	174·426	grains.
Fe_2O_3	6·275	,,
Al_23SO_4	72·908	,,
$MgSO_4$	21·055	,,
$CaSO_4$	14·381	,,
$FeSO_4$	1·596	,,
Na_2SO_4	0·537	,,
K_2SO_4	0·822	,,
$AlPO_4$	0·456	,,
KCl	0·282	,,
NH_4Cl	0·125	,,
KNO_3	0·170	,,
SiO_2	5·776	,,
	298·809	,,

The source of the spring is above the millstone grit, which is overlaid by aluminous shale. The author proceeds to show theoretically the formation of ferric sulphate from the ferric sulphide in the shale.

E. W. P.

Analysis of Waters accompanying Petroleum and of those Ejected by Mud Volcanoes. By A. Potilitzin (*Jour. Russ. Chem. Soc.*, 1882, 300—310).—The author has analysed waters of the above kind from the Caucasian and Caspian petroleum district. The waters have an alkaline reaction, and contain large quantities of sodium chloride, besides sodium bromide and iodide, the latter in such quantities as have never been found before in any mineral water, viz., 0·098—0·118 gram NaI in 1000 grams. The author found also considerable quantities of a free organic acid belonging to the fatty series, most probably capric acid. He regards the above petroleum wells as a new source of iodine.

B. B.

Organic Chemistry.

Action of Hydrocarbons of the Acetylene Series on Mercuric Salts. By M. G. KUTCHEROFF (*Jour. Russ. Chem. Soc.*, 1882, 326—327).—On shaking aqueous solutions of mercuric salts with allylene, white, dense, and sometimes crystalline precipitates of the general formula $m\mathrm{HgX_2}, n\mathrm{HgO}, p(\mathrm{C_3H_4HgO})$ separate out. The coefficients m, n, and p are different for different salts, *e.g.*, for $\mathrm{HgCl_2}: m = 3, n = 1, p = 2$; for $\mathrm{Hg(C_2H_3O_2)_2}: m = n = 1, p = 2$; for $\mathrm{HgSO_4}: m = 1, n = 2, p = 3$. The formation of the precipitates from the acetate, sulphate, and chloride takes place as easily as the reaction between allylene and an ammoniacal solution of cuprous or silver salts, both reactions being equally delicate. A solution of mercuric bromide gives a slight precipitate, but mercuric iodide in water or in potassium iodide gives no precipitate. The precipitates are insoluble in water, easily soluble in acids, acetone being set free at the same time. They do not explode when heated. The author regards these compounds as combinations of basic salts of mercury with acetone, the two hydrogen-atoms of which are replaced by one atom of mercury. A solution of mercuric iodide in potassium iodide and hydroxide, however, absorbs allylene with formation of a crystalline precipitate; this is soluble in acids with separation of *allylene*.

The author explains the hydration of hydrocarbons of the acetylene series by means of mercuric salts, already announced by him in a former paper, by the formation of the above intermediate compounds.

B. B.

Transformation of Propyl Bromide into Isopropyl Bromide under the Influence of Heat. By L. ARONSTEIN (*Rec. Trav. Chim.*, 1, 134—142).—The author has already shown (Abstr., 1882, 567) that normal propyl bromide, $\mathrm{CH_2Me.CH_2Br}$ or $\mathrm{Pr^{\alpha}Br}$, heated in sealed tubes at 280°, is converted into isopropyl bromide, $\mathrm{CHMe_2Br}$ or $\mathrm{Pr^{\beta}Br}$.

Supposing then, in accordance with the received theory of dissociation, that the number of molecules dissociated remains constant at a given temperature, the recomposition of dissociated molecules and the dissociation of pre-existing molecules going on simultaneously at the same rate, the author was led to expect that normal propyl bromide, if exposed for a sufficient time to the temperature of dissociation, might be completely converted into isopropyl bromide. Experiment, however, does not confirm this expectation, but shows, on the other hand, that after propyl bromide has been exposed to the temperature of dissociation for 20 hours, further heating does not increase the quantity of isopropyl bromide formed, the transformation not being complete even if the heating be continued for 100 hours.

This result, which appears at first sight to be at variance with the fundamental principles of the theory of dissociation, may, according to the author, be reconciled with that theory in two ways, viz.:—(1.) By supposing that the propylene and hydrobromic acid resulting from the decomposition of the propyl bromide recombine partly as $Pr^{\alpha}Br$ and partly as $Pr^{\beta}Br$. If this be the case, $Pr^{\beta}Br$ heated in sealed tubes should be partly converted into $Pr^{\alpha}Br$. Such, however, is not the case: for the author finds that $Pr^{\beta}Br$ may be heated in sealed tubes at 280° for a week with scarcely any alteration, nearly the whole afterwards distilling over at 59—62° (b. p. of $Pr^{\beta}Br$), and only a few drops of dark-coloured high-boiling liquid remaining in the retort, probably consisting of hydrobromides of polymeric propylenes.

(2.) Another cause capable of preventing the complete transformation of $Pr^{\alpha}Br$ into $Pr^{\beta}Br$ may, in the author's opinion, be found in the pressure to which the liquid in the sealed tubes is subjected. It is known indeed that dissociation is retarded by increased pressure, and the author finds, by determination of the vapour-densities of the products obtained by the action of heat on the two propyl bromides, that at any given temperature, $Pr^{\beta}Br$ decomposes more quickly than $Pr^{\alpha}Br$: consequently, as the proportion of $Pr^{\beta}Br$ in the mixture becomes greater, so also will there be an increase in the number of molecules resolved in a given time into C_3H_6 and HBr, the pressure exerted on the yet undecomposed molecules, increasing in proportion thereto; and this increase of pressure will retard the decomposition of the normal propyl bromide, and consequently prevent its complete conversion into the isopropyl compound.

Similar results have been obtained by Eltekoff (*Ber.*, **8**, 1144; *C. J.*, 1876, 541), with regard to the conversion of isobutyl bromide into tertiary butyl bromide.

Attempts to convert other propyl compounds into isopropyl compounds by heating in sealed tubes were unsuccessful. Propyl chloride, propyl alcohol, and propyl acetate, heated for several days above 300°, showed no sign of alteration; and the same was the case with the dibromide of ethylene (? propylene). H. W.

α-Monochlorallylic Alcohol and its Derivatives. By L. HENRY (*Compt. rend.*, **95**, 849—851).—On boiling the compound $CH_2 : CCl.CH_2Cl$ (b. p. 95°) with a dilute solution of potassium carbonate for some hours in a wide flask with reflux condenser, the chloride gradually disappears; and on distilling the product the alcohol, $CH_2 : CCl.CH_2.OH$, comes over in the first portions of the distillate, and may be completely separated from the water by means of potassium carbonate. It forms a perfectly limpid colourless liquid, having a faint smell. Its sp. gr. at 19° is 1·164, and it boils unaltered at 136° under a pressure of 763 mm. It dissolves easily in water, but less easily than allylic alcohol. The ethereal acetate, $CH_2 : CCl.CH_2\overline{Ac}$, produced by the action of acetic chloride, boils at 145°. The bromide, $CH_2 : CCl.CH_2Br$, formed by the action of phosphorus tribromide, boils at 121°. The corresponding thiocyanate obtained by the action of the chloride on potassium thiocyanate, boils at 180—181° without decomposition. When freshly distilled, it is colourless, and recalls exactly the odour of oil of mustard, but after a time it becomes brown. By the action of ammonia upon it, monochlorothiosinnamine is obtained, melting at 90—91°. A mixture of concentrated nitric and sulphuric acids, well cooled, converts the alcohol into the compound $CH_2 : CHCl.CH_2.NO_3$.

α-Monochlorallylic alcohol dissolves easily in sulphuric acid with development of heat, and hydrochloric acid is evolved. Distilled with a large quantity of water, the liquid yields a product having all the properties of pyruvic alcohol, $CH_3.CO.CH_2.OH$.

The author draws attention to the great difference in physiological properties between the compound above described and β-monochlorallylic alcohol, described by Van Romburgh (*Bull. Soc. Chim.*, **36**, 557), the latter being intensely caustic. E. H. R.

Ethylene Oxide. By BERTHELOT (*Bull. Soc. Chim.*, **39**, 488—491).—The basic properties of ethylene oxide, as evidenced by its ready combination with hydrochloric acid, have been pointed out by Wurtz; this reaction the author has made the subject of a thermochemical study.

The equation $C_2H_4O + HCl = C_2H_5ClO$ develops heat $= + 36{\cdot}0$ cal., a number comparable in value to $C_2H_4 + HCl = C_2H_5Cl = + 38$ cal., although in the first case a compound analogous to the hydrate and alcoholates of hydrochloric acid is at first formed, whilst no such intermediate product is possible with ethylene. But the values for the combination of ethylene oxide and ammonia with hydrochloric acid are approximately equal: for $NH_3 + HCl = NH_4Cl = + 42{\cdot}5$, if the heat of solidification of ethylene chlorhydrin be taken into account; and further, $C_2H_4O_2$ (very dilute) + HCl (very dilute) = C_2H_5ClO (dissolved) $= + 12{\cdot}4$, a value equal to the heat of combustion of ammonia or potash with hydrochloric acid under the same conditions.

Attention is also drawn to the fact that ethylene oxide combines with hydrochloric acid in the presence of a large quantity of water with evolution of a considerable amount of heat; this phenomenon explains the reaction between ethylene oxide and the metallic chlorides observed by Wurtz; for in the presence of water a certain quantity of hydrochloric acid is formed, and an equilibrium is established dependent upon the heat of formation of the metallic chloride and oxychloride, and the degree of dissociation of the hydrate and the oxychloride in presence of water.

Ethylene oxide, doubtless, combines with the other haloïd acids, but this is not the case with the organic acids, for dilute acetic acid is not appreciably neutralised by the oxide even after the lapse of many hours. V. H. V.

Strobometric Determination of the Rate of Inversion of Cane-sugar, and Transition of the Birotation of Milk-sugar into its Normal Rotation. By F. URECH (*Ber.*, **15**, 2130—2133).—In continuation of his former work on this subject (Abstr., 1881, 242), the author finds that although the ultimate result of the inversion is unaffected by the concentration of the solution, strength of acid used, or temperature, the *rate* of inversion varies very greatly under variations of these conditions. The volume of the solution remaining constant, increase in the percentage of acid present decreases the time required for the inversion. The percentage of acid to water being constant, increase of volume decreases the time, but percentage of acid to sugar being constant, increase of volume (*i.e.*, dilution with water) increases the time. Increase of temperature shortens the time of reaction. In the case of sugar of milk, the rate of transition of the birotation to the normal seems independent of the proportion of water to sugar. An addition of a small quantity of hydrochloric acid quickens the action at first, but does not shorten the total time of reaction. When 3 grams of sugar of milk were dissolved in 50 c.c. of hydrochloric acid of sp. gr. 1·155, the rotation was at once reduced from 10° 6′ to 6°, but after two hours had returned to 10°. (See also Schmöger, *Ber.*, **13**, 1927.) L. T. T.

Anhydrous Grape-sugar from Aqueous Solution. By O. HESSE (*Ber.*, **15**, 2349—2350).—A question of priority.

Transformation of Amides into Amines. By BAUBIGNY (*Compt. rend.*, **95**, 646—648).—When a primary or secondary amine is heated with an ethereal salt, an amide is formed and the alcohol of the ethereal salt is set free. Ethylamine and methyl acetate, for example, yield ethylacetamide and methyl alcohol. Under certain conditions, these amides combine with water, reproducing the original salt. The author finds that when the amides are heated at a temperature higher than that necessary for their formation, they combine with alcohol, forming the original salt, in which, however, the amine is replaced by a substituted amine derived from the alcohol employed. Acetamide, heated with ethyl alcohol, yields ethylamine acetate; and ethylacetamide, under the same conditions, yields diethylamine acetate. The reaction has been observed with methyl, ethyl, and amyl alcohols, with alcohols of the benzene series, and with acetic, valeric, and benzoic acids. The amide and the compound amine can be formed in successive stages of the same operation by heating first at a low, then at a high temperature. When ammonium benzoate is heated with ethyl alcohol, or when ammonia in alcoholic solution is heated with ethyl benzoate, benzamide is first formed, with elimination of water, and then after some hours' heating at a higher temperature, ethylamine benzoate is formed by the action of the amide on the alcohol. With a mixture of aniline, glacial acetic acid, and methyl alcohol, phenylacetamide and water are first formed, then methylaniline and acetic acid, the salt formed by their union being very unstable. This change can be repeated so as to produce successively, for example, ethylamine benzoate, diethylamine benzoate, and triethylamine benzoate. The final product contains either the tertiary amine alone or a mixture of different amines, according to the proportion of alcohol employed. Ammoniums are not formed, and in this respect the reaction differs from the action of the amines on alcoholic chlorides, &c. It is worthy of note, that no aniline is formed by the action of acetamide on phenol, even after heating at 300° for eight hours. It is possible that the cyanides derived from the amides by loss of water will combine with alcohol in a similar manner. A large series of new compounds would thus be formed. C. H. B.

Action of Anhydrous Aluminium Chloride on Acetone. By E. Louise (*Compt. rend.*, **95**, 602—603).—If acetone is gently heated and aluminium chloride added in successive portions, the mixture, after about 20 hours, is converted into a blackish solid and liquid. This product, when distilled in steam, yields a yellow liquid, amounting to about 35—40 per cent. of the acetone used. It consists of condensation-products from acetone, mixed with unstable chlorine-derivatives of the same products. When treated with potash and distilled, it yields a more volatile portion, consisting mainly of mobile colourless mesityl oxide $C_6H_{10}O$, (b. p. 128—130°, vapour-density found, 3·51, calculated, 3·39), and a less volatile portion, which contains crystallisable phorone, $C_9H_{14}O$ (m. p. 28°, b. p. 195—196°, vapour-density found, 4·51, calculated, 4·77), mixed with higher condensation-products which will not crystallise.

The double chloride of aluminium and sodium acts on acetone in a similar manner. C. H. B.

Action of Nitric Acid on Fatty Acids containing the Isopropyl-group. By J. Bredt (*Ber.*, **15**, 2318—2325).—When isovaleric acid is acted on by nitric acid, a mixture of methylmalic acid [identical with the *methoxysuccinic acid* described by Demarçay (*Compt. rend.*, **82**, 1337) and Morris (this Journal, 1860, 6)], and β-nitrovaleric acid is produced. The two acids are easily separated by recrystallisation, the nitro-acid being much less soluble than methylmalic acid. β-nitroisovaleric acid crystallises in glistening plates belonging to the monoclinic system, $a : b : c = 1·8346 : 1 : 1·7442$ $\beta = 87° 28'$. On reduction with tin and hydrochloric acid, β-amidoisovaleric acid is obtained. It is identical with the acid described by Heintz (*Annalen*, **198**, 42). Nitroisovaleric acid is decomposed by strong nitric acid, yielding dinitroisopropane (m. p. 50°, b. p. 187°), which has been described by Meyer and Locher (*ibid.*, **180**, 147). This hydrocarbon is also obtained as a bye-product of the action of nitric acid on isovaleric acid from valerian root. Under similar treatment, isovaleric acid from fermentation amyl alcohol yields methylmalic acid, nitroisovaleric acid, and dinitroisopropane. W. C. W.

Solidification of Different Mixtures of Naphthalene and Stearic Acid. By H. Courtonne (*Compt. rend.*, **95**, 922—924).—The results of Heintz and of Gottlieb on the melting points of mixtures of fatty acids are borne out by mixtures of bodies widely differing in their chemical properties, such as stearic acid and naphthalene.

Commercial stearic acid was used; the results are, therefore, only relative: but if it be admitted that a definite compound is formed (m. p. 47°) by melting 100 parts stearic acid with 40 parts naphthalene*, by a simple calculation the solidifying points of the three first mixtures given in the following table may be found. These numbers are given in the fourth column:—

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* These numbers were taken as approaching most nearly the relation between the molecular weights of the two bodies.

		Point of solidification.	
Stearic acid.	Naphthalene.	Found.	Calculated.
100·0	0·00	56·00	—
"	7·50	53·50	53·80
"	15·00	51·50	51·90
"	22·50	50·00	50·20
"	40·00	47·00	—
"	45·00	47·50	48·00
"	50·00	47·60	—
"	"	"	—
"	79·00	55·60	—
"	90·00	58·50	—
"	135·00	66·00	—
"	270·00	73·00	—
"	"	"	—
0·0	100·00	79·00	—

The solidifying point of the last four mixtures is not constant.

What reaction takes place between these two bodies? Whether a compound analogous to that of stearic acid with glucose or those of naphthalene with di- and tri-nitrophenol is formed, will form the subject of further research. L. T. O'S.

Conversion of Acetonechloroform into Hydroxyisobutyric Acid. By C. WILLGERODT (*Ber.*, **15**, 2305—2308).—Acetonechloroform, $OH.CMe_2.CCl_3$, is decomposed by water at 180°, forming hydrochloric and hydroxyisobutyric acids, $CMe_2(OH).COOH$.

W. C. W.

Bye-products in the Preparation of Acetonechloroform. By C. WILLGERODT (*Ber.*, **15**, 2308—2313).—On acidifying the residue obtained in the preparation of acetonechloroform, an oily liquid is liberated (b. p. 192—212°), which contains *acetonaloxyisobutyric* acid, $COOH.CMe_2.O.CMe_2.O.CMe_2.COOH$. This acid probably owes its formation to the action of potash on a mixture of acetonechloroform and diacetonechloroform, potassium acetonate and acetoneoxyisobutyrate being formed in the first instance. Two molecules of the latter salt lose a molecule of water, and form potassium acetonaloxyisobutyrate. W. C. W.

Halogen Substitution-compounds of Ethyl Acetoacetate. By M. CONRAD (*Ber.*, **15**, 2133—2134).—In reference to the denial by Duisberg (Abstr., 1882, 1192) of the existence of ethyl dibromacetate dibromide described by the author (*Annalen*, **186**, 232), he is inclined to look upon this body as identical with the tetrabromacetoacetic ether, $C_6H_6Br_4O_3$, obtained by Duisberg, instead of $C_6H_8Br_2O_3.Br_2$, as originally proposed by himself. L. T. T.

The Addition of Bromine to Ethyl Acetoacetate. By E. LIPPMANN (*Ber.*, **15**, 2142—2144).—The author upholds the correctness of his ethyl acetoacetate dibromide, $C_6H_{10}O_3Br_2$ (*Wien. Akad.*

Ber., 1868, **58** [2], 310), the existence of which is denied by Duisberg (Abstr., 1882, 1192). This dibromide is very unstable, and he believes Duisberg's preparation, which was kept 14 days before analysis, to be a decomposition-product formed according to the equation $C_6H_{10}O_3Br_2 = C_6H_9BrO_3 + HBr$. L. T. T.

Decomposition of Tertiary Amyl Acetate by Heat. By N. MENSCHUTKIN (*Compt. rend.*, **95**, 648—651).—The author has previously found (Abstr., 1881, 36) that the etherification of acetic acid and tertiary amyl alcohol takes place very slowly and only to a very limited extent. He has therefore investigated the dissociation of tertiary amyl acetate at 155° by the method described in a former paper. During the first 20 hours, the rate of decomposition is very slow; it then rapidly increases and attains a maximum after 48 hours; then again decreases until, after 92 hours, the decomposition almost ceases. The decomposition, $C_5H_{11}.C_2H_3O_2 = C_5H_{10} + C_2H_4O_2$, is limited by the inverse change, $C_5H_{10} + C_2H_4O_2 = C_5H_{11}.C_2H_3O_2$; but the effect of this inverse change is very slight, for the limit of decomposition at +53° is as high as 97·42 per cent. The limit of etherification of acetic acid and tertiary amyl alcohol at the same temperature was previously found (*loc. cit.*) to be 2·53 per cent. The rate of decomposition is materially affected by the temperature. At 100° there is no decomposition; at 125° it is only perceptible after some days' continuous heating, and even at 140° it is extremely slow. The higher the temperature, the more quickly does decomposition commence, and the greater is its rapidity in all phases; but under the most favourable conditions decomposition is not perceptible until after two hours' heating; and whatever the temperature, the rate of decomposition is at first very slow, then increases and attains a maximum, then decreases until the limit of decomposition is reached. The author was unable to ascertain definitely whether the limit depends on the temperature; at 145° it was found to be 96·59 per cent., at 155° 97·42 per cent. C. H. B.

Action of Ammonium Cyanate on Glyoxal. By N. LJUBAVIN (*Jour. Russ. Chem. Soc.*, 1882, 281—291).—The author describes experiments by which he proves that the compound obtained in the above reaction, and formerly regarded by him as diamidosuccinic acid, is in reality glycocine; but up to the present time he has not been able to ascertain the course of the reaction. B. B.

Series of Salts containing Chromium and Urea. By W. T. SELL (*Proc. Roy. Soc.*, **33**, 267—274).—When urea is moistened with chromium oxychloride, there is considerable development of heat, and on treating the product with water a green crystalline powder is obtained; this compound is insoluble in alcohol and ether and dissolves in hot water with decomposition, another salt separating out in olive-green needles; this latter body is a dichromate of a base containing urea and chromium, and has the composition

$$\{(CON_2H_4)_{12}Cr_2\}(Cr_2O_7)_3,3H_2O:$$

it is sparingly soluble in cold, more freely in hot water; its aqueous solution gives crystalline precipitates with platinum chloride and potassium ferrocyanide. The *platinochloride*,

$$\{(CON_2H_4)_{12}Cr_2\}(PtCl_6)_3,2H_2O,$$

crystallises in green silky needles, sparingly soluble in cold water; the chloride, $(CON_2H_4)_{12}Cr_2Cl_6,6H_2O$, obtained by decomposing the dichromate with lead chloride and water, crystallises in slender silky needles, sparingly soluble in cold, readily soluble in hot water. Its aqueous solution is precipitated by potassium dichromate and ferrocyanide and by platinum chloride. The *sulphate*,

$$(CON_2H_4)_{12}Cr_2(SO_4)_3,10H_2O,$$

obtained from the chloride by the action of silver sulphate, crystallises in dark-green prisms; the *nitrate*, $(CON_2H_4)_{12}Cr_2(NO_3)_6$, also presents a similar form. The formation of a hydroxide was suspected, but it was not obtained in a state sufficiently pure for analysis.

V. H. V.

Synthesis of Uric Acid. By J. HORBACZEWSKI (*Monatsh. Chem.*, **3**, 796).—Pure glycocine (from hippuric acid) was finely pulverised and mixed with ten times its weight of pure urea prepared from ammonium cyanate, and the mixture was heated in a small flask placed in a metal bath at 200—230° till, the liquid, at first colourless and transparent, became brownish-yellow and turbid. The melt when cold was dissolved in potash, and the solution, after supersaturation with sal-ammoniac, was precipitated with a mixture of ammoniacal silver solution and magnesia-mixture. The resulting precipitate was well washed with ammoniacal water and decomposed with potassium sulphide, the liquid filtered from silver sulphide, and the filtrate, after acidulation with hydrochloric acid, was concentrated on the water-bath, whereby uric acid was separated. The crude product thus obtained was redissolved in potash-lye, and the above-described process twice repeated, whereby ultimately a yellowish crystalline powder was obtained exhibiting the composition, physical properties, and all the reactions of uric acid.

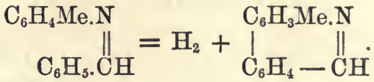
H. W.

Crystallographic Examination of α-β-Dinitroparaxylene and of the Dinitroparaxylene which melts at 93°. By F. BARNER (*Ber.*, **15**, 2302—2305).—The crystals melting at 99·5°, which Jannasch and Stünkel (Abstr., 1880, 808) obtained on crystallising a mixture of α- and β-dinitroparaxylenes from glacial acetic acid, or preferably from benzene, belong to the rhombic system and exhibit sphenoidal hemihedry. The ratio of the axes $a : b : c$ is $0·69649 : \bar{1} : \bar{1}·06850$. Dinitroparaxylene (m. p. 93°) is deposited from a solution in benzene in lustrous prisms belonging to the monoclinic system, $a : b : c = 0·869502 : 1 : 0·63818$; $\beta = 81° 14' 52''$.

W. C. W.

Benzyleneorthotolylamine and Methylphenanthridine. By A. ÉTARD (*Compt. rend.*, **95**, 730—732).—When orthotoluidine and benzaldehyde are mixed in molecular proportions, heat is evolved, water is separated, and a substance is produced which boils at 314°

(uncorr.). Analysis and determination of vapour-density lead to the formula $C_6H_4Me.N\colon CHPh$. Water, especially at 100°, decomposes this substance into orthotoluidine and benzaldehyde. Concentrated hydrochloric and nitric acids give rise to the products of the action of these acids on orthotoluidine and benzaldehyde respectively. When benzyleneorthotolylamine is allowed to fall drop by drop into an iron tube at a bright red heat, two simultaneous decompositions result. One of these is represented by the equation $C_6H_4Me.N\colon CH.C_6H_5 = C_6H_5Me + C_6H_5.CN$; the other consists in the removal of 2 atoms of hydrogen from the original substance and the formation of a new body which the author terms *methylphenanthridine.*



$$\begin{array}{r} C_6H_4Me.N \\ \| \\ C_6H_5.CH \end{array} = H_2 + \begin{array}{l} C_6H_3Me.N \\ |\qquad\quad\ \| \\ C_6H_4 - CH \end{array}.$$

The new substance bears the same relation to methylphenanthrene that pyridine does to benzene. To isolate the new base, the mixed product is steam-distilled, by which means the toluene and benzonitrile are removed, and the residue is distilled. The substance is easily purified, by crystallisation from ether, when it melts at 170° and boils above 360°. It is insoluble in water, slightly soluble in alcohol, very soluble in ether. Aqueous hydrochloric acid does not dissolve it, but in alcoholic solution a hydrochloride is obtained which gives a crystalline double salt with platinic chloride. The author has obtained similar results with ortho- and para-toluidine and other aldehydes.

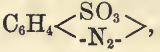
E. H. R.

Azoxylene. By N. SAMONOFF (*Jour. Russ. Chem. Soc.*, 1882, 327—328).—On adding a mixture of potassium hydroxide and ferrocyanide to xylidine sulphate (b. p. 198—210°), an orange precipitate separates out at first, and later on resinous compounds are formed: the precipitate is separated from the liquid, dissolved in alcohol, and treated with chlorine in order to destroy the resinous bodies. Dark-red crystals separate from the solution, which after purification by repeated crystallisation melt at 128°. This compound is identical with the azoxylene which Werigo obtained in 1864 by reducing the unsymmetrical nitroparaxylene with sodium-amalgam. The author proposes to examine the azoxylenes.

B. B.

Klinger's Method of Preparing Azoxybenzene. Note by N. MOLTCHANOFFSKY (*Jour. Russ. Chem. Soc.*, 1882, 350).—On repeating Klinger's method for obtaining azoxybenzene, the author could not get more than 32 per cent. of the theoretical yield, though Klinger would seem to have got a yield of 100 per cent. (48 grams from 60 grams of nitrobenzene); moreover the preparation obtained by the above method was far from being pure. The author recommends therefore the use of his own method (Abstr., 1882, 965), the yield of which is over 87 per cent. of the theoretical.

B. B.

Diazo-compounds. By P. GRIESS (*Ber.*, **15**, 2183—2201).—This is the first of two papers in which the author intends summarising the results of several years' work on this subject. In the present notice he details the results of the action of paradiazobenzenesulphonic acid (parabenzene-diazine sulphite),  $C_6H_4<\begin{smallmatrix}SO_3\\ -N_2-\end{smallmatrix}>$, on various primary amido-compounds.

When molecular proportions of paradiazobenzenesulphonic acid and aniline hydrochloride are heated together in aqueous solution for about 24 hours, the product is found to consist of diazobenzene hydrochloride, sulphanilic acid, and a new compound, which the author names *amidoazobenzenesulphonic acid.* The reactions probably take place according to the two equations—

$$\text{(i.)}\ C_6H_4SO_3N_2 + C_6H_5.NH_3Cl = C_6H_4(SO_3H).N_2.C_6H_4.NH_2 + HCl,$$
$$\text{(ii.)}\ C_6H_4SO_3N_2 + NH_3PhCl = Ph.N_2Cl + C_6H_4(SO_3H).NH_2.$$

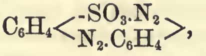
When free aniline was used instead of the hydrochloride, the diazobenzene hydrochloride formed in the above reaction was replaced by diazoamidobenzene.

Azoamidobenzenesulphonic acid,

$$C_6H_4(SO_3H).N_2.C_6H_4.NH_2\ [SO_3H : N_2 : NH_2 = 4 : 1 : 4],$$

is precipitated from a solution of its ammonium salt in glittering yellowish-white microscopic needles, which are almost insoluble in water, alcohol, ether, and chloroform. When heated, it carbonises and gives off SO_2. Reduced with tin and hydrochloric acid, it splits up into sulphanilic acid and paraphenylenediamine. The *barium salt,* $(C_{12}H_{10}N_3.SO_3)_2Ba + 6H_2O$, crystallises in reddish-yellow needles, sparingly soluble in water.

Diazoazobenzenesulphonic acid (azobenzenediazine sulphite),



$$C_6H_4<\begin{smallmatrix}-SO_3.N_2\\ N_2.C_6H_4\end{smallmatrix}>,$$

is obtained when azoamidobenzenesulphonic acid suspended in water is treated for some time with nitrous acid. It forms pale yellow microscopic needles, almost insoluble in the usual neutral solvents. It is dissolved by potash, and reprecipitated unchanged by mineral acids. It has scarcely any taste, and decomposes with explosive violence at high temperatures. If boiled for some time with water, it is converted into *phenolazobenzeneparasulphonic acid,*

$$C_6H_4(SO_3H).N_2.NC_6H_4(OH)\ [N : SO_3H = 1 : 4],$$

already described by the author (Abstr., 1879, 315). Heated with dilute alcohol, an azobenzenesulphonic acid, $C_6H_4(SO_3H).N_2.C_6H_5$, is produced identical with that previously obtained by the author (*Annalen,* **154**, 208) by the action of fuming sulphuric acid on azobenzene.

Azoamidobenzenedisulphonic acid, $C_6H_4(SO_3H).N_2.C_6H_3(SO_3H).NH_2$, is produced on heating azoamidobenzenesulphonic acid with four times its weight of fuming sulphuric acid at 100° until water no longer causes a precipitate. This acid crystallises in glistening violet-coloured needles, easily soluble in boiling, sparingly so in cold water, but easily soluble in alcohol, from which it is reprecipitated by ether; on exposure to the air, it effloresces to a brown powder. It dyes silk and wool a fine yellow. Reduced with tin and hydrochloric acid, it splits up into sulphanilic acid and an acid crystallising in white needles, which the author believes to be diamidobenzenesulphonic acid. *Barium azoamidobenzenedisulphonate*, $C_{12}H_7N_2(NH_2)(SO_3)_2Ba + 7\frac{1}{2}H_2O$, is easily soluble in boiling water, and on cooling, crystallises out in reddish-yellow needles.

Diazoazobenzenedisulphonic acid is obtained from the foregoing acid by the action of nitrous acid, and is precipitated from its alcoholic solution by ether in dirty yellow needles, which carbonise easily when heated. An *azobenzenedisulphonic acid*, $SO_3H.C_6H_4.N_2.C_6H_4.SO_3H$, is formed on heating it with alcohol.

The author finds that the above-mentioned azoamido-mono- and di-sulphonic acids are identical with those prepared according to Grässler's patent by heating azoamidobenzene with 3 to 5 times its bulk of fuming sulphuric acid. The author also states that the process for preparing azoamidobenzenemonosulphonic acid patented by Grässler was described by himself as early as 1876, and that, moreover, this process is valueless from a technical point of view.

Action of Paradiazobenzenesulphonic Acid on the Isomeric Toluidines.—The general reactions (taking the chlorides as examples) are—

$$\text{(i.)}\ C_6H_4SO_3N_2 + C_7H_7.NH_3Cl = C_6H_4(SO_3H).N_2.C_7H_6.NH_2 + HCl,$$
$$\text{(ii.)}\ C_6H_4SO_3N_2 + C_7H_7.NH_3Cl = C_7H_7.N_2.Cl + C_6H_4(SO_3H).NH_2.$$

With orthotoluidine, the reaction takes place principally according to (ii), orthodiazotoluene chloride and sulphanilic acid being the chief products. With metatoluidine, reaction (i) plays the principal part, azo-*o*-amidotoluene-*p*-benzenesulphonic acid forming the greater part of the product. With paratoluidine, reaction (ii) alone takes place, no trace of azo-*p*-amidotoluene-*p*-benzenesulphonic acid having been found. The author notes here the incorrectness of the generally received idea that in hydrated and amidated benzenes the *para*-compounds are incapable of reacting with diazo-compounds to form azo-compounds, because the hydrogen-atom in the para-position to the OH or NH_2 group is always the one acted on: parahydroxybenzoic acid and paradiazobenzenesulphonic acid, for instance, combine to form azo-*p*-sulphobenzene-*p*-hydroxybenzoic acid,

$$C_6H_4(SO_3H).N_2.C_6H_3(OH).COOH,$$

in which $[SO_3H : N = 4 : 1]$ and $[OH : COOH = 1 : 4]$. This acid crystallises in pale yellow needles, easily soluble in boiling, sparingly in cold water, and very much resembling the corresponding azo-acid obtained from salicylic acid.

Paradiazobenzenesulphonic acid combines very readily with *α- and β-naphthylamine* to form *azoamidonaphthalenebenzenesulphonic acid*, no secondary reactions taking place, as in the case of the toluidines and aniline.

Azo-α-amidonaphthaleneparabenzenesulphonic acid (*Ber.*, **12**, 224) forms a potassium salt crystallising with $3H_2O$, and a barium salt also with $3H_2O$.

Azo-β-amidonaphthaleneparabenzenesulphonic acid,

$C_6H_4(SO_3H).N_2.C_{10}H_6.NH_2$ [$SO_3H : N = 4 : 1$] and [$N : NH_2 = 1 : 2$],

prepared by acting on β-naphthylamine hydrochloride with paradiazobenzenesulphonic acid, is obtained in yellowish-red needles or groups of needles, slightly soluble in boiling water. It is very soluble in alcohol, thus differing from its isomeride. It carbonises easily, giving off naphthylamine. The potassium salt crystallises in yellowish-red flakes with $7\frac{1}{2}H_2O$.

Both these acids split up under the action of tin and hydrochloric acid into the corresponding diamidonaphthalenes and sulphanilic acid.

Diamidonaphthalene from the α-acid crystallises in white needles or small prisms, which quickly turn green, especially if moist. It is easily soluble in alcohol, ether, and chloroform, sparingly in boiling water; its aqueous solution decomposes quickly. It has an extremely burning taste, producing on the tongue soreness lasting for days. It melts at 120° to a brown oil having an odour similar to that of quinone. Ferric chloride produces α-naphthaquinone in a hydrochloric acid solution of this body. The hydrochloride crystallises in white glistening flakes, easily soluble in hot water, almost insoluble in hydrochloric acid. This diamidonaphthalene is almost certainly identical with that obtained by Perkin (this Journal, **18**, 181) from azo-α-amidonaphthalene, and that which Liebermann and Dittler prepared (*Annalen*, **183**, 239) from α-amidonitronaphthalene.

Diamidonaphthalene from the β-acid is equally soluble with its isomeride in alcohol, ether, and chloroform, more sparingly so in hot water, from which it separates in white rhombic plates (m. p. 95°) having a silvery lustre, soon turning to grey. Ferric chloride produces change of colour in its solution, but no quinone or other crystalline body could be detected. The chloride is easily soluble in water, and is reprecipitated by hydrochloric acid. The author assigns to the first mentioned diamidonaphthalene (from the α-acid, as also Perkin's, and Liebermann and Dittler's), the formula $C_{10}H_6(NH_2)_2$ [$NH_2:NH_2=1:4$], and that from the β-acid [$NH_2 : NH_2 = 1 : 2$], and to Aiguar's (*Ber.*, **7**, 307) α-diamidonaphthalene (m. p. 189°), [$NH_2 : NH_2 = 1 : 4'$], and to the same investigators β-diamide (m. p. 66°) [$NH_2 : NH_2 = 1 : 1'$].

With the isomeric *amidonaphthalenesulphonic acids*, paradiazobenzenesulphonic acid forms compounds analogous to those with the isomeric naphthylamines.

Azo-α-amidosulphonaphthalene-p-*benzenesulphonic acid*,

$$NH_2.\alpha C_{10}H_5(SO_3H).N_2.C_6H_4(SO_3H),$$

(the only one of these compounds which the author has investigated in detail), is easily soluble in alcohol and water, insoluble in ether, and colours silk and wool yellow. With barium it forms an acid salt, $(C_{16}H_{12}N_3S_2O_6)_2Ba + 8H_2O$, very sparingly soluble in boiling water, and a neutral salt, $(C_{16}H_{11}N_3S_2O_6)Ba + 7\frac{1}{2}H_2O$, easily soluble in boiling water. Treated with tin and hydrochloric acid, *diamidonaphthalenesulphonic* and *sulphanilic acids* are produced.

When paradiazobenzenesulphonic acid acts on either of the isomeric diamidobenzenes, nitrogen is evolved, and a brown gummy mass results. If *orthodiamidobenzene chloride* be used instead of the free base, small quantities of *sulphanilic acid* and *azimidobenzene*,  $C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NH$, are produced identical with that which Ladenburg obtained by acting on orthodiamidobenzene with nitric acid.

δ-Diamidobenzoic acid, [$COOH : NH_2 : NH_2 = 1 : 3 : 5$], combines directly with the diazo-acid to form *azo-*p*-sulphobenzene-δ-diamidobenzoic acid*, $C_6H_4(SO_3H).N_2.C_6H_2(NH_2)_2.COOH$. This acid is sparingly soluble in water, alcohol, and ether, and decomposes very easily, even on boiling with water. Treated with tin and hydrochloric acid, it gives sulphanilic acid and a new triamidobenzoic acid,

$$C_6H_2(NH_2)_3COOH\ [COOH : NH_2 : NH_2 : NH_2 = 1 : 2 : 3 : 5].$$

This acid crystallises from hot water in colourless compact crystals, very sparingly soluble in alcohol, insoluble in ether, and having a bitter taste. On attempting to distil it, it almost entirely carbonises, but a small quantity of a base distils over, which may be triamidobenzene. Sulphuric acid gives a salt, $C_7H_9N_3O_2,H_2SO_4$. Taking into account the origin of this acid, and that the only other known triamidobenzoic acid (Salkowsky, *Annalen*, **163**, 12) has the formula [$COOH : NH_2 : NH_2 : NH_2 = 1 : 3 : 4 : 5$], the formula given above must be the correct one. From this it would appear that the azo-acid must have the formula—

$$C_6H_5(SO_3H).N \vdots N.C_6H_2(NH_2)_2COOH\ [COOH : N : NH_2 : NH_2 = 1 : 2 : 3 : 5].$$

L. T. T.

Azylines. By E. LIPPMANN and F. FLEISNER (*Ber.*, **15**, 2136—2142).—The authors give the name of azylines to a series of bodies obtained by the action of nitric oxide on tertiary bases of the aromatic series, and containing the tetrad-group $\equiv N—N \equiv$. They intend also to try whether similar bodies can be obtained from secondary amines, and from amines belonging to the fatty series.

These bodies are obtained by passing nitric oxide into a solution of a tertiary amine in alcohol or benzene, whereupon carbonic acid is freely given off, and red crystals are deposited. They are insoluble in water, soluble in hydrochloric acid with reddish-purple, in acetic acid with emerald-green coloration. They crystallise from alcohol and benzene in well-formed red crystals. Their fusing point descends as the molecular weight ascends (except the propyl compound, which melts lower than the butyl and amyl bodies). With the chlorides of platinum, gold, zinc, cobalt, &c., they form double salts. By the action of stannous chloride, or of phosphorus and hydriodic acid, unstable hydrogenised bodies are produced, which, however, yield crystallisable platinochlorides. Mineral acids decompose the azylines, splitting off ammonia. Picric acid gives sparingly soluble crystalline salts. Bromine and iodine readily yield substitution-products. The haloïd ethers combine with them at 100°. Nitrous acid produces nitroso-compounds, giving Liebermann's colour reaction with phenol and sulphuric acid. The following equation expresses the reaction in the case of dimethylaniline, $2C_8H_{11}N + N_2O_2 = 2H_2O + C_{16}H_{18}N_4$. The authors believe the general constitutional formula to be $R_2N.C_6H_3 \vdots N.N \vdots C_6H_3.NR_2$.

Dimethylanilineazyline, $C_{16}H_{18}N_4$, first obtained by Frankland (*Annalen*, **99**, 342) fuses at 266°. By careful oxidation with potassium permanganate in the cold, it yields carbonic and oxalic acids. This, according to Wallach and Claissen's researches (*Ber.*, **8**, 1237), tends to show the correctness of the above formula. The picrate, $C_{16}H_{18}N_4,C_6H_2(NO_2)_3OH + EtOH$, forms green needles, which contain alcohol of crystallisation. It decomposes at 100°.

Diethylanilineazyline, $C_{20}H_{26}N_4$, forms red needles melting at 170°, deliquescent in chloroform, and sparingly soluble in cold alcohol. The picrate, $C_{20}H_{26}N_4,[2C_6H_2(NO_3)_2.OH]$, crystallises in yellow needles, sparingly soluble in alcohol and ether.

Dipropylanilineazyline, $C_{24}H_{34}N_4$, fuses at 90°. The crystals belong to the rhombic system ($a : b : c = 1 : 0{\cdot}629 : 0913$), their principal faces being ∞P, $\infty \breve{P} \infty$, $\bar{P} \infty$.

Dipropylaniline boils at 240—242°, and forms a yellow crystalline platinochloride, which is decomposed by water.

Dibutylanilineazyline, $C_{28}H_{42}N_4$, crystallises in needles, and fuses at 158°.

Diamylanilineazyline, $C_{32}H_{50}N_4$, fuses at 115°. L. T. T.

Phenylenethiocarbamides. By E. LELLMANN (*Ber.*, **15**, 2146—2147).—Orthodiamidobenzene thiocyanate, formed by evaporating an aqueous solution of orthodiamidobenzene hydrochloride with ammonium thiocyanate, is further heated in an air-bath at 120—130°, and the dry residue extracted with water; *orthophenylenethiocarbamide*, $C_7H_6N_2S$, remains undissolved. This body is easily soluble in alcohol, sparingly so in water, and crystallises in violet plates. It melts at about 280°, but becomes brown at 260°. Metadiamidobenzene gives a similar body which, with the corresponding para-compound, is now under investigation. The author proposes the constitutional formula

$C_6H_4<{NH \atop NH}>CS$ for these bodies. L. T. T.

Formation of Phenylxanthogenamide. By E. BAMBERGER (*Ber.*, **15**, 2164—2166).—In a previous paper (Abstr., 1882, 394) the author described some crystalline bodies obtained by heating phenylthiocarbimide with various acid amides in alcoholic solution. He now finds that in all cases the body formed is *phenylxanthogenamide*, and that the character of the acid amide has no influence on the reaction. L. T. T.

Aromatic Isophosphines. By A. MICHAELIS and L. GLEICHMANN (*Ber.*, **15**, 1961—1964).—In the course of the investigation of the mixed aromatic phosphines, the authors endeavoured to obtain the corresponding phosphonium iodides without the use of the zinc alkyls, by heating together alkyl iodides, phosphenyl chloride, and metallic zinc, and obtained good results. On substituting benzyl chloride for the alkyl iodides, however, a new class of bodies, the *isophosphines*, were obtained.

Isobenzylphenylphosphine is prepared by gently warming a mixture of 2 parts benzyl chloride and 1 part phosphenyl chloride, with granulated zinc in a vessel provided with a reflux condenser; a violent reaction takes place, and is completed without further heating. The excess of benzyl chloride is then decanted, the residual zinc compound decomposed by soda, and the isophosphine purified by solution in alcohol, precipitation by water, and crystallisation from glacial acetic acid, from which it separates in long, fine, interlaced needles (m. p. 70—71°), of the formula $C_{13}H_{13}P$ or $C_{25}H_{24}P_2$. Its properties render it improbable that it is an ordinary secondary phosphine. It does not unite with the alkyl iodides, nor is it changed by heating with them and zinc oxide in sealed tubes. It unites with acetic anhydride, forming an unstable compound, completely resolved into its components by long exposure to air or by heating at 60—70°. It dissolves in benzyl chloride, but is not further affected by it even on heating at 200° for 15 hours. Strong oxidising agents convert it into benzoic and phosphoric acids; on heating it with soda-lime, phosphoric acid, benzene, and toluene, are formed; nascent hydrogen does not act on it. In an atmosphere of chlorine, isobenzylphenylphosphine liquefies to a viscous yellow mass, from which, after treatment with soda to remove the chlorine taken up, an oxide, $C_{13}H_{13}PO$ or $C_{25}H_{22}P_2O_2$ (m. p. 154—155°) is obtained, crystallising from acetic acid or alcohol in long, colourless, matted needles. It is insoluble in alkalis, and is similarly indifferent to reagents. Isobenzylphenylphosphine would appear to be closely related to the dibenzylphosphine, $C_{14}H_{15}P$, obtained by Hofmann (*Ber.*, **5**, 100) by heating together benzyl chloride, phosphonium iodide, and zinc oxide.

Isotolylbenzylphosphine is prepared in a manner similar to isobenzylphenylphosphine, and closely resembles it in properties; it crystallises in light, colourless, felted needles (m. p. 187°) of the formula $C_{14}H_{15}P$ or $C_{27}H_{28}P_2$. A. J. G.

Phenylarsine Sulphides. By C. SCHULTE (*Ber.*, **15**, 1955—1960).—*Phenylarsine monosulphide*, AsPhS, is obtained by the action of sulphuretted hydrogen on phenylarsine oxide or chloride; it crystallises in fine white needles, is sparingly soluble in benzene, alcohol, and ether, readily soluble in hot benzene and in carbon bisulphide. Nitric acid oxidises it to phenylarsenic acid. It is but slightly soluble in ammonia, but dissolves in hot soda, and is reprecipitated by hydrochloric acid. It is sparingly soluble in ammonium monosulphide or sulphydrate, but dissolves readily in the yellow sulphide; addition of an acid to the solution precipitates phenylarsine sesquisulphide. The monosulphide melts at 152° to a yellow liquid, and on dry distillation in a stream of carbonic anhydride, yields arsenic sulphide and triphenylarsine. By the action of mercury-ethyl, it is converted into phenyldiethylarsine and mercury sulphide.

Phenylarsine sesquisulphide, $AsPh_2S_3$, is best prepared by the action of hydrogen sulphide on an ammoniacal solution of phenylarsenic acid, and subsequent precipitation with hydrochloric acid. When crystallised from benzene, it forms pale yellow transparent prisms, readily soluble in benzene and carbon bisulphide, moderately in boiling glacial acetic acid, sparingly soluble in hot alcohol and ether. It melts at

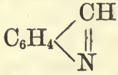
130° to a clear liquid, and decomposes at higher temperatures. Nitric acid converts it into phenylarsenic acid. It is nearly insoluble in ammonia, sparingly soluble in soda, but dissolves readily in yellow ammonium sulphide.

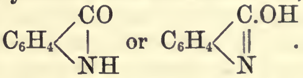
Disodium phenylsulpharsenate, $AsPhS(SNa)_2,6H_2O$, is obtained by dissolving phenylarsine mono- or sesqui-sulphide in sodium sulphide containing excess of sulphur; on evaporation and addition of absolute alcohol to the thick liquid, it separates in slender needles. It is readily soluble in water, sparingly in alcohol. A. J. G.

Arsenobenzene, Arsenonaphthalene, and Phenylcacodyl. By A. MICHAELIS and C. SCHULTE (*Ber.*, **15**, 1952—1955).—In addition to the method previously given (Abstr., 1881, 722), arsenobenzene can be prepared by the reduction of monophenylarsenic acid. It reacts readily with sulphur, yielding the phenylarsine sulphides (preceding Abstract). If fused with excess of sulphur, it gives arsenic sulphide and phenyl sulphide. When heated with mercury ethyl in sealed tubes at 150°, it gives mercury and diethylphenylarsine. Attempts to reduce arsenobenzene to phenylarsine, $AsPhH_2$, have so far failed, as when heated with alcoholic ammonium sulphide it yields benzene, arsenic sulphide, and metallic arsenic, whilst hydriodic acid has no action in the cold, and on heating, gives benzene, arsenic iodide, and metallic arsenic.

Arsenonaphthalene, $(C_{10}H_7)_2As_2$, is obtained by the reduction of naphthylarsineoxide as a powder composed of slender yellow needles (m. p. 221°); it is sparingly soluble in alcohol, benzene, carbon bisulphide and chloroform, insoluble in water and in ether. It unites with chlorine, forming naphthylarsine chloride; with sulphur, forming naphthylarsine sulphide; and is oxidised by nitric acid to naphthylarsenic acid. On dry distillation, it decomposes, with formation of naphthalene and arsenic, and separation of much carbonaceous matter.

Phenylcacodyl, As_2Ph_4, as obtained by the reduction of diphenylarsine oxide with phosphorous acid, forms a white crystalline mass melting at 135°, and soluble in alcohol, less readily in ether. It quickly oxidises in the air, forming diphenylarsenic anhydride. With chlorine it forms diphenylarsine trichloride, $AsPh_2Cl_3$. It yields arsenic and triphenylarsine on dry distillation. A. J. G.

Reduction of Orthonitrobenzaldehyde. By P. FRIEDLÄNDER and R. HENRIQUES (*Ber.*, **15**, 2105—2110).—Rudolph (*Ber.*, **13**, 310) obtained a base,  $C_6H_4\left\langle\begin{matrix}CH\\ \|\\ N\end{matrix}\right.$, by the reduction of orthonitrobenzaldehyde (obtained by the nitration of benzaldehyde, and containing the meta-compound). The authors have repeated and extended these experiments, employing *pure* orthonitrobenzaldehyde, obtained from ethyl nitrocinnamate (Abstr., 1882, 840). They are unable to confirm Rudolph's results, having obtained a body C_7H_5NO.

If soda solution in excess be added to the product of the action of tin and acetic acid on orthonitrobenzaldehyde, and the whole distilled with steam, scarcely anything passes over, but anthranilic acid is found in the residue. If, however, the acid mixture is neutralised with sodium carbonate and distilled with steam, an oil is obtained of the formula C_7H_5NO, which the authors propose to call *anthranil.* Anthranil is a colourless mobile liquid, slightly soluble in hot water, easily so in the usual solvents. It does not solidify at − 18° C., has an odour resembling that of benzaldehyde, and of the vegetable bases, and is easily volatile with steam. Exposed to air and light, it becomes brown and resinous. It begins to boil at 210—215°, but decomposes at the same time. Anthranil has feeble basic properties, dissolving easily in concentrated mineral acids, but is reprecipitated on adding water. Its salts and double salts are very unstable, the only compound obtained being $C_7H_5NO,HgCl_2$; this compound fuses at 174°, and is readily decomposable. Dilute soda dissolves anthranil slowly in the cold, quickly on heating; ammonia requires a temperature of 120°, and water has scarcely any action at 130°. In these reactions *anthranilic acid* is produced: $C_7H_5NO + H_2O = NH_2.C_6H_4.COOH$. Boiled with acetic anhydride and mixed with H_2O, it gives *acetylanthranilic acid*, $C_7H_6NO_2\overline{Ac}$. These reactions render it probable that anthranil is an internal anhydride of anthranilic acid, having one of the two following formulæ:  $C_6H_4\left\langle\begin{matrix}CO\\ |\\ NH\end{matrix}\right.$ or $C_6H_4\left\langle\begin{matrix}C.OH\\ \|\\ N\end{matrix}\right.$. No halogen-, methyl-. or nitroso-substitution-compounds could be obtained. Further reducing action gave an amorphous compound, probably a condensed amidobenzaldehyde; also, small quantities of amidobenzyl alcohol.

With zinc and hydrochloric acid in alcoholic solution, an amorphous substance was obtained, which dissolved in hydrochloric acid, but was partly reprecipitated by water, entirely by sodium acetate. It bears great resemblance to the amorphous meta- and para-amidobenzaldehyde, and is probably a corresponding condensed orthamidobenzaldehyde. This body is undergoing further investigation. L. T. T.

Metahydroxybenzaldehyde and some of its Derivatives. By F. Tiemann and R. Ludwig (*Ber.*, **15**, 2043—2059).—Metahydroxybenzaldehyde has been obtained by Sandemann (*Ber.*, **14**, 969) by partial reduction of metahydroxybenzoic acid with sodium-amalgam. It is best obtained, however, from metamidobenzaldehyde by the diazo-reaction. For this purpose metanitrobenzaldehyde, prepared by the method of Friedländer and Henriques (*Ber.*, **14**, 2802), is mixed with exactly the necessary quantity of zinc chloride and hydrochloric acid, and after the reaction is finished a solution of potassium nitrite is added, the mixture being kept cold. A double salt, having the composition $(COH.C_6H_4.N_2.Cl)_2,SnCl_4$, then separates, and this on being decomposed with water easily gives metahydroxybenzaldehyde. The latter crystallises in white needles, melting at 104°. It yields metahydroxybenzoic acid on fusion with potash. The potassium compound suspended in ether and heated with acetic anhydride, yields the acetyl-derivative, an oil boiling at 263°. Metahydroxybenzaldehyde, when boiled for some hours with excess of acetic anhydride, yields a compound, $CH(O\overline{Ac})_2.C_6H_4.O\overline{Ac}$, melting at 76°.

Methylmetahydroxybenzaldehyde is a liquid boiling at 230°.

Acetometacoumaric acid is prepared by heating a mixture of metahydroxybenzaldehyde, anhydrous sodium acetate, and acetic anhydride. It crystallises from water in white needles melting at 151°. On heating it with solution of potash, it yields *metacoumaric acid*, which crystallises from hot water in white prisms melting at 191°. This acid can also be obtained by the diazo-reaction from metamidocinnamic acid. On treatment with sodium-amalgam, it is reduced to *hydrometacoumaric acid*, which crystallises in long needles, melting at 111°.

Methylmetacoumaric acid melts at 115°, and *methylhydrometacoumaric acid* at 51°.

Nitration of Metahydroxybenzaldehyde. — When this aldehyde is warmed with 10 parts of nitric acid (sp. gr. 1·1), and the product poured into water, a yellow crystalline mass separates out, which is partly soluble in benzene and chloroform. After being recrystallised from water, the portion insoluble in benzene melts at 166°, and is termed by the author β-nitrometahydroxybenzaldehyde. The portion soluble in benzene is separated by a mixture of benzene and light petroleum into two bodies, the less soluble melting at 138°, termed the γ-compound, and the other, melting at 128°, the α-compound. These are all mononitro-derivatives, and easily yield methyl ethers.

Nitration of Methylmetahydroxybenzaldehyde.—On nitrating this compound under different conditions, a mixture of two isomeric dinitro-compounds is always obtained. These may be separated by boiling water, in which the β-compound (m. p. 155°) is almost insoluble, the α-compound (m. p. 110°) being easily soluble.

Constitution of the Nitro-derivatives.—Four mononitro-derivatives of metahydroxybenzaldehyde are theoretically possible, in which the NO_2-group occupies respectively the two ortho-, the para-, and the meta-position with reference to the hydroxyl. According to the known laws of substitution in phenol-like bodies, the authors think it probable that the three nitro-derivatives prepared by them are those in which the NO_2-group occupies the three former positions. In this case the methyl ethers should, by reduction and the diazo-reaction, yield respectively β-metamethoxysalicylaldehyde (*Ber.*, **14**, 2022), vanillin, and α-metamethoxysalicylaldehyde. Now, the so-called γ-compound yields by this treatment a body smelling like vanillin, and the authors therefore ascribe to it the constitution $C_6H_3(COH)(OMe)(NO_2)$ [1 : 3 : 4]. The β-compound yields, however, a body which does not agree in its properties with either of the metamethoxysalicylaldehydes, and therefore the authors think that it probably has the constitution $C_6H_3(COH)(OMe)(NO_2)$ [1 : 3 : 5]. The α-compound does not yield any well-defined product. E. H. R.

New Derivatives of Salicylaldehyde. By H. VOSWINCKEL (*Ber.*, **15**, 2021—2027).—Tiemann and Reimer have shown (*Ber.*, **9**, 1268; **10**, 1562) that, by the chloroform reaction, salicylic acid yields both para- and ortho-aldehydosalicylic acids, but parahydroxybenzoic acid only one product, namely, orthoaldehydosalicylic acid. Applying the same reaction to salicylic and parahydroxybenzaldehydes, the author has obtained analogous results. In the former case two bodies are formed, the one easily, the other sparingly, soluble in light petroleum. The former, *α-hydroxyisophthalaldehyde*,

$$C_6H_5(OH)(COH)_2\ [OH : COH : COH = 1 : 2 : 6],$$

crystallises from water in tufts of needles melting at 88°, the latter, *β-hydroxyisophthalaldehyde*, $C_6H_5(OH)(COH)_2$ [OH : COH : COH = 1 : 2 : 4], in long needles melting at 108°. When parahydroxybenzaldehyde is used, only one body is formed, namely, the α-compound.

The constitution of these dialdehydes is determined by fusing them with potash, whereby they are converted into *hydroxyisophthalic acid*. Attempts to form bodies containing a third COH-group proved fruitless.

Methylsalicylaldehyde.—The author finds that the reaction between the sodium compound of salicylaldehyde and methyl iodide is completed by digestion on the water-bath. By removing every trace of salicylaldehyde, the methyl-derivative is obtained in prisms melting at 35°.

Salicylaldehyde cyanhydrin, $C_6H_4(OMe)[CH(OH).CN]$ [1 : 2]. This compound is easily obtained by the action of potassic cyanide and hydrochloric acid on salicylaldehyde dissolved in ether. It separates from benzene in colourless transparent crystals melting at 71°. Attempts to obtain the corresponding amide were unsuccessful, and *orthomethoxymandelic acid* was obtained only as a syrup in an impure condition. By the action of the equivalent quantity of a 10 per cent. solution of ammonia in closed vessels at 60—70°, the compound $(OMe.C_6H_4.CH.CN)_2N_2H$, is produced. It melts when freshly prepared at 123°, but soon alters on exposure to air.

Nitrile of orthomethoxyphenylphenamidoacetic acid,

$$C_6H_4(OMe)[CH(NHPh).CN\ [1 : 2].$$

This body is easily obtained by the action of aniline on the cyanhydrin of methylsalicylaldehyde. It forms colourless six-sided tables melting at 61°.

Nitromethylsalicylaldehyde, $C_6H_3(NO_2)(OMe).COH$.—The author has prepared this compound by dissolving the aldehyde in fuming nitric acid, and precipitating by water. It forms fine white needles melting at 88°. The author is engaged in investigating its constitution.

E. H. R.

Isovanillin. By R. Wegscheider (*Monatsh. Chem.*, **3**, 789—795). This compound is formed, together with others, by the action of dilute hydrochloric acid on opianic acid. When these two substances are heated together in a sealed tube at 160—170°, a mixture of dark and nearly colourless crystals is obtained, together with a reddish-yellow liquid; and on filtering, boiling the crystals with water, and filtering again, a black mass remains undissolved, and the light red filtrate, boiled with animal charcoal and evaporated, yields crystals of isovanillin. On further evaporation, a small quantity of unaltered opianic acid separates out, and the last fraction gives with ferric chloride a green colour, probably due to the formation of a trace of protocatechuic aldehyde.

Isovanillin recrystallised from water forms anhydrous prisms having a vitreous lustre, softening at 115°, melting at 116—117°. These crystals are monoclinic, having the axial ratio $a : b : c = 0·6370 : 1 : 0·9228$; $\beta = 96·9$. Observed faces $\infty P\grave{\infty}$, $0P$, $2P\grave{\infty}$, ∞P, $+ P$. Habit, tabular by predominance of the clinopinacoid. Face of cleavage $P\grave{\infty}$.

Isovanillin is not much more soluble in caustic soda than in water, but dissolves easily in ammonia and still more in potash-lye, forming yellow solutions. From concentrated alkaline solutions, it is precipitated by acids. Strong sulphuric acid colours it yellow, then yellowish-red, and slowly dissolves it, both at ordinary temperatures and at 100°; on raising the temperature to the boiling point of the acid, a blood-red colour is produced. The aqueous solution is neutral, and gives no reaction with ferric chloride or lead acetate. It reduces ammoniacal silver nitrate very slightly in the cold, more abundantly at boiling heat.

Isovanillin is inodorous in the cold, but when heated, and especially when its aqueous solution is boiled, it emits a pleasant odour like that of vanilla, or fennel, or anise-oil. When heated on platinum-foil, it gives off a stronger odour like that of vanilla, and still more like that of burning opianic acid.

It decomposes slightly when sublimed, and volatilises to a small extent when its aqueous solution is distilled. Like vanillin, it forms soluble compounds with alkaline bisulphites, and may be separated from solution in ether by agitation with strong solution of sodium hydrogen sulphite.

If the action of hydrochloric acid on opianic acid be carried beyond the point at which isovanillin is formed, the product subsequently obtained is protocatechuic aldehyde, a result which, when viewed in connection with the fact that isovanillin must differ in constitution from vanillin, shows that the former must be represented by the formula $C_6H_3(COH)(OH)(OMe)$ [1 : 3 : 4].

In the formation of isovanillin from opianic acid, as well as in that of methylnoropianic acid from opianic acid, and of methylnorhemipinic acid from hemipinic acid, it appears that whenever a single methyl-group is detached from hemipinic or opianic acid, the methoxyl-group attacked is always that which stands in the ortho-position relatively to the carboxyl. H. W.

Preparation of the Three Isomeric Nitracetophenones. By H. Gevekoht (*Ber.*, **15**, 2084—2086).—By acting on ethylic sodacetoacetate with the three isomeric nitrobenzoic chlorides (*Ber.*, **12**, 351), the three corresponding ethylic nitrobenzacetoacetates are produced, and these on saponification yield the three nitracetophenones. The meta- and para-nitracetophenones thus produced agree exactly with those obtained in other ways. The ortho-compound is now for the first time obtained pure. It is a pale yellow oil, which can be distilled in a vacuum, and does not solidify at −20°. It is easily reduced by tin and hydrochloric acid to the corresponding amido-compound, which is a pale yellow oil possessing basic properties, and capable of being distilled unchanged in a vacuum. E. H. R.

Action of Cyanogen Chloride on Amido-Acids. By J. TRAUBE (*Ber.*, **15**, 2110—2122).—The author hoped in this way to obtain cyanamido-acids, none of which have hitherto been known in the free state.

Cyanogen chloride acts but very slightly on an aqueous solution of alanine, producing small quantities of lacturamic acid. When a stream of cyanogen chloride is passed through fusing sarcosine, water is evolved, and methylhydantoïn is produced, as also an anhydride, formed by the abstraction of one molecule of water from two molecules of sarcosine. *Sarcosine-anhydride*, $C_6H_{12}N_2O_3$, crystallises in hexagonal colourless plates, melting at 143—146°: it is easily soluble in water, alcohol, and ether: it has a bitter taste, and is reconverted into sarcosine by dilute hydrochloric acid. This anhydride differs from sarcosine in giving no crystalline compound with zinc chloride, and by its double platinochloride, $(C_6H_{12}N_2O_3)_2,H_2PtCl_6$, containing no water of crystallisation.

Cyanogen chloride acts very readily on an alcoholic solution of metamidobenzoic acid, and if the product of the reaction is at once poured into a large quantity of water, metacyanamidobenzoic acid is produced—a secondary reaction sets in very quickly if the alcoholic solution is allowed to stand before dilution.

Metacyanamidobenzoic acid, $CN.NH.C_6H_4.COOH$, crystallises in flat white rounded needles, containing $\frac{1}{2}$ mol. H_2O: it is almost insoluble in cold, moderately soluble in boiling water: very soluble in boiling alcohol, ether, and chloroform, sparingly so in benzene. Cyanamidobenzoic acid begins to decompose at 140°, but does not fuse below 200°, when gas is evolved. Its taste is decidedly acid, and it decomposes carbonates. When heated at 140° with solution of barium hydroxide, it is decomposed into amidobenzoic acid, ammonia, and carbonic anhydride. Boiling it with water causes no decomposition, and even strong soda solution is slow in its action. Acids decompose it much more readily. Most of its salts are easily soluble, but the lead salt forms a white flocculent precipitate, soluble in excess of lead acetate and in boiling water. Ferric chloride produces a pale yellow amorphous precipitate; silver nitrate a white gelatinous one insoluble in cold water, soluble in ammonia: it is a mixture of the salt, $CN.NH.C_6H_4.COOAg$, with small and varying quantities of

$$NAg(CN).C_6H_4.COOAg.$$

A brown amorphous copper salt was also obtained. This production of a brown copper salt appears to be a common property of the cyanamides, and serves to distinguish cyanamidobenzoic acid from all other known derivatives of metamidobenzoic acid.

Heated alone, metacyanamidobenzoic acid decomposes slowly at 140°, quickly at 210—220°, evolving cyanic acid freely, and leaving a white amorphous product insoluble in water, alcohol, ether, and hydrochloric acid, but easily soluble in concentrated sulphuric acid, from which it is reprecipitated on dilution with water. Analyses show the composition of this body to be a mixture of bodies of the general formula $mC_8H_6N_2O_2 - nCNOH$. This decomposition appears to be analogous to that observed by Bässler (*J. pr. Chem.*, **16**, 125) in the case of ethyl cyanocarbamate. A similar mixed product is obtained by the action of cyanogen chloride on fusing metamidobenzoic acid, but here $CO(NH.C_6H_4.COOH)_2$ is also amongst the products of the reaction. With dilute hydrochloric acid, a similar reaction takes place, as in the case of cyanocarbamic acid compounds, *metauramidobenzoic acid* being formed.

Hydrogen sulphide is absorbed very slowly by metacyanamidobenzoic acid, but with ammonium sulphide a rapid and quantitative reaction takes place, *thiouramidobenzoic acid*, identical with that obtained by Arzruni (this Journal, **24**, 570), being produced.

Thiouramidobenzoic acid crystallises in groups of needles melting at 187°, and at the same time evolving ammonia and hydrogen sulphide, and leaving products free from sulphur.

Several of the salts of metacyanamidobenzoic acid decompose slowly in contact with boiling water. A concentrated solution of barium cyanamidobenzoate heated for several days on the water-bath, gives off ammonia and leaves the barium salt of an acid corresponding tolerably closely with the formula $C_{24}H_{17}N_5O_7$. It is easily soluble in ether, alcohol, and water, and gives insoluble zinc, lead, copper, and mercury salts.

No addition-product of ammonia could be obtained from cyanamidobenzoic acid. By digesting it with aniline, *phenylbenzocreatine*,

$$NHPh.CNH.NH.C_6H_4.COOH,$$

is produced. *Phenylbenzocreatine* is nearly insoluble in ether and alcohol, easily soluble in boiling water, from which it crystallises in compact groups. It fuses with decomposition at 165°; it forms compounds both with acids and with alkalis, and gives a yellowish-red platinochloride.

When cyanamidobenzoic acid is heated with acetamide, it gives a body, $C_{30}H_{29}N_5O_6$, only soluble in fuming nitric and concentrated sulphuric acids. The reaction is not analogous to that of acetamide and phenylcyanamide, studied by Berger (Abstr., 1881, 810).

Paracyanamidophenylacetic acid is produced by the action of cyanogen chloride on an alcoholic solution of paramidophenylacetic acid. It crystallises in colourless glittering plates, very easily soluble in water, ether, and alcohol, and fusing with decomposition at 134°. It is a strong acid, and gives a brown copper salt which, like that of metacyanamidobenzoic acid, quickly blackens in contact with water. The brown salt differs from that of the meta-acid in being very soluble in alcohol.

Paracyanamidophenylacetic acid is very unstable, decomposing even when recrystallised. Evaporated with a very small quantity of hydrochloric acid, it is converted into *para-uramidophenylacetic acid.*

Para-uramidophenylacetic acid crystallises in compact groups containing $1\frac{1}{2}$ mol. H_2O, which are given up at 110°. It is easily soluble in alcohol and ether, tolerably so in water. It fuses with decomposition at 174°. With the alkalis and alkaline earths it forms soluble salts; with copper, lead, zinc, and mercury insoluble. Ferric chloride gives a characteristic yellowish-red precipitate.

Cyanogen chloride has no action on tyrosine or hippuric acid in alcoholic solution. L. T. T.

Contributions to the Knowledge of Meta-uramidobenzoic Acid and Carbamido-dibenzoic Acid. By J. Traube (*Ber.*, **15**, 2122—2129).—This investigation was undertaken in order to clear up the divergent statements of Griess (*Ber.*, **2**, 147) and Menschutkin (*Annalen*, **153**, 85) on this subject. The author substantially confirms Menschutkin's remarks on uramidobenzoic acid, and believes Griess's preparation not to have been perfectly pure. Crystallised *uramidobezoic acid*, $NH_2.CO.NH.C_6H_4.COOH$, contains 1 mol. H_2O; the anhydrous acid is soluble in 139 parts of 96 per cent. alcohol; and in 786 parts of ether.

Uramidobenzoic acid decomposes at 200°, producing a body to which Menschutkin gave the formula  $C_6H_4<\begin{matrix}CO.NH\\NH.CO\end{matrix}>$, and Griess,

$$CO(NH.C_6H_4.COOH)_2.$$

The author finds that Griess's formula is the correct one. This decomposition would be represented by the equation—

$$2(NH_2.CO.NH.C_6H_4.COOH) = CO(NH.C_6H_4.COOH)_2 + CO(NH_2)_2.$$

He has also obtained this body according to the two equations—

$$\text{(i.) } NH_2.CO.NH.C_6H_4.COOH + NH_2.C_6H_4.COOH = CO(NH.C_6H_4.COOH)_2 + NH_3, \text{ and}$$

$$\text{(ii.) } 2(NH_2.C_6H_4COOH) + CO(NH_2)_2 = CO(NH.C_6H_4.COOH)_2 + 2NH_3.$$

The latter equation explains at once the bad yield of uramidobenzoic acid by Griess's method of fusing together equal molecules of urea and amidobenzoic acid. The author therefore recommends Menschutkin's method of preparing this acid by the action of potassium cyanate on aqueous amidobenzoic acid hydrochloride. The yield is nearly quantitative, and the acid nearly pure. L. T. T.

Diamidocumic Acid. By E. Lippmann (*Ber.*, **15**, 2144—2146).—By the reduction of *dinitrocumic acid* (*Monatsh.*, **1**, 822), the author obtained *diamidocumic acid*, $C_6H_2Pr^\beta(NH_2)_2.COOH$, crystallising from ether in yellowish plates melting at 192°. Crystallised from water it contains 1 mol. H_2O, which is given off at 100°. The silver salt, $C_{10}H_{13}N_2O_2Ag + H_2O$, is slightly soluble in water, and decomposes readily. *Diamidocumic acid hydrochloride*, $C_{10}H_{14}N_2O_2,HCl + H_2O$, crystallises in pale brown prisms, soluble in water, but reprecipitated on the addition of hydrochloric acid. No hydroxy-acid could be obtained by the action of nitric oxide. L. T. T.

Constitution of the Halogen Cinnamic Acids. By J. Plöchl (*Ber.*, **15**, 1945—1946).—The position of the bromine-atom in the side-chain of the two bromocinnamic acids has never been determined with certainty. Glaser (*Annalen*, **143**, 330) termed the acid melting at 131° the α-acid, and that melting at 120° the β-acid, but did not determine their constitution. With the chlorocinnamic acids (Jutz, Abstr., 1882, 1073) the acid of highest melting point (142°) was also termed the α-acid.

The author has endeavoured to settle the question by synthesising an acid of the formula Ph.CH : CCl.COOH, and has effected this by heating a mixture of sodium monochloracetate, acetic anhydride, and benzaldehyde, when an acid melting at 142° and agreeing in all its other properties with Jutz's α-chlorocinnamic acid, was obtained. (β-Chlorocinnamic acid, unlike β-bromocinnamic acid, does not change into the α-acid even by repeated distillation, so that molecular interchange was not likely to have occurred at the low temperature [100—110°] of the reaction.) The supposition of Barisch (Abstr., 1880, 43) that the acid of β-position had the highest melting point is thus shown to be erroneous. A. J. G.

Hydrocinnamic and Cinnamic Acids. By S. Gabriel (*Ber.*, 15, 2291—2301).—Metanitroparamidohydrocinnamic acid (m. p. 145°) is converted into *diamidohydrocinnamic* acid by reduction with tin and hydrochloric acid. The hydrochloride of the new acid, although freely soluble in water, is sparingly soluble in strong hydrochloric acid. Diamidohydrocinnamic acid is deposited from a hot aqueous solution in transparent crystals containing 1 mol. H_2O, which is expelled at 100°. The anhydrous acid (m. p. 143°) is freely soluble in glacial acetic acid and in hot alcohol.

Bromacetoparamidohydrocinnamic acid is deposited in colourless needles (m. p. 160°), when bromine-water is added to a warm solution of paracetamidohydrocinnamic acid. The crystals are soluble in ether, warm alcohol, benzene, and acetic acid. The acetic group is expelled from this compound by strong boiling hydrochloric acid, the hydrochloride of bromamidohydrocinnamic acid being formed. The free acid, obtained by the cautious addition of ammonia to the hydrochloride, melts at 104·5°. On adding sodium nitrite to an alcoholic solution of the hydrochloride, *diazoamidobromhydrocinnamic acid*, $(C_6H_3Br.C_2H_4.COOH)_2N_3H$, is deposited in brown-coloured needle-shaped crystals. It is decomposed by hydrochloric acid, yielding *metabromhydrocinnamic acid*, $C_6H_4Br.C_2H_4.COOH$. This acid is deposited from an acetic acid solution in glistening prisms (m. p. 75°), soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, and hot water.

The nitrocinnamic acids can be converted into bromocinnamic acids, by acting on the nitro-acid with freshly precipitated ferrous oxide, which reduces it to the amido-acid. From the amido-acid, the diazo-compound is prepared, and this is converted into the bromocinnamic acid by the action of hydrobromic acid.

Orthobromocinnamic acid crystallises in needles or scales (m. p. 212°), soluble in hot alcohol, acetic acid, and ether. When treated with hydriodic acid and phosphorus, it yields orthobromhydrocinnamic acid melting at 98°. This acid is soluble in ether, alcohol, benzene, acetic acid, and chloroform. *Metabromocinnamic acid* forms pale-yellow needles, melting at 178°, and soluble in ether, alcohol, acetic acid, and also in hot benzene, chloroform, or carbon bisulphide. *Parabromocinnamic acid* also crystallises in needles of a pale-yellow colour, which melt about 252°. An aqueous solution of paradiazocinnamic acid decomposes at 100°, apparently yielding paracoumaric acid.

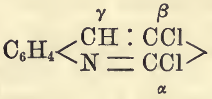
W. C. W.

Derivatives of Cinnamic Acid. By E. ERLENMEYER (*Ber.*, **15**, 2159—2160).—From the results of the further study of this subject, the author draws the following conclusions:—(1.) *Phenyldichloropropionic acid* prepared by the action of hydrochloric acid on Glaser's phenylchlorolactic acid, is identical with that formed by the addition of chlorine to cinnamic acid. (2.) The *phenylchlorobromopropionic acid*, obtained by the action of hydrobromic acid on Glaser's phenylchlorolactic acid, is isomeric but not identical with that obtained by acting on phenylbromolactic acid with hydrochloric acid. When boiled with water, the former gives chlorostyrol, the latter bromostyrol. (3.) The *phenylbromolactic acid*, prepared by the addition of hypobromous acid to cinnamic acid, is identical with that produced by boiling phenyldibromopropionic acid with water. (4.) The *halogen-cinnamic* (*phenyl-halogen-acrylic*) *acids* of higher fusing point contain the halogen in the α-position, those of lower fusing point in the β-position.

L. T. T.

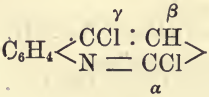
Orthamidophenylpropiolic Acid and its Derivatives. By A. BAEYER and F. BLOEM (*Ber.*, **15**, 2147—2155).—*Orthamidophenylpropiolic acid*, $NH_2.C_6H_4.C⋮C.COOH$, has been obtained by the authors by reducing orthonitrophenylpropiolic acid with ammonia and ferrous sulphate. It crystallises in pale-yellow microscopic needles, almost insoluble in water, chloroform, and light petroleum; sparingly soluble in ether, rather more so in cold alcohol. Boiling alcohol dissolves it freely, but it does not separate out on cooling, or on the addition of water. Heated to 125—130°, it decomposes with stormy evolution of carbonic anhydride, leaving a resinous residue, from which traces of orthamidophenylacetylene are extracted by acids. If boiled with water, it is decomposed, orthamidoacetophenone passing over with the steam. When boiled with potash, the acid gives a characteristic red colour on the addition of hydrochloric acid; excess of hydrochloric acid destroys this colour, but it is reproduced on adding alkali. The potassium, sodium, and ammonium salts are very soluble, the barium salt less so. The yellowish-white insoluble silver salt decomposes when exposed to the light and air, and explodes on heating. The ethyl salt crystallises in yellow needles, melting at 55°.

Boiled with dilute hydrochloric acid, amidophenylpropiolic acid gives *γ-chlorocarbostyril*, C_9H_6NOCl, crystallising in colourless needles, melting at 246°, and subliming at a higher temperature. In a similar way, *γ-bromocarbostyril*, colourless needles melting at 266°, and *γ-iodocarbostyril*, melting at 276°, can be obtained; both sublime unchanged. It being probable from the investigations of Friedländer and Ostermaier (*Ber.*, **15**, 332) that carbostyril is α-hydroxyquinoline, the authors acted on the chloro-derivative with phosphoric chloride, and succeeded in obtaining a dichloroquinoline, $C_9H_5NCl_2$, insoluble in water, easily soluble in alcohol, ether, benzene, and chloroform, and melting at 67°. This is different from that obtained by Baeyer (*Ber.*, **12**, 1320), m. p. 104°. This has probably the formula

I. 

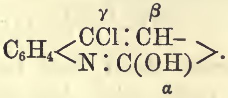
$$C_6H_4<\begin{matrix}\overset{\gamma}{CH}:\overset{\beta}{CCl}\\ N=\underset{\alpha}{CCl}\end{matrix}>$$

The new body would therefore be represented by the formula

II. 

$$C_6H_4<\begin{matrix}\overset{\gamma}{CCl}:\overset{\beta}{CH}\\ N=\underset{\alpha}{CCl}\end{matrix}>$$

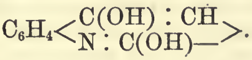
and would be an α-β-dichloroquinoline. The γ-chlorocarbostyril described above would then necessarily have the formula



$$C_6H_4<\begin{matrix}\overset{\gamma}{CCl}:\overset{\beta}{CH}-\\ N:\underset{\alpha}{C(OH)}\end{matrix}>.$$

Thus, on the addition of hydrochloric acid to amidophenylpropiolic acid, the chlorine goes to the carbon-atom nearest the benzene-nucleus.

Heated at 145° with concentrated sulphuric acid and the resulting product mixed with water, amidophenylpropiolic acid yields *hydroxycarbostyril*, $C_9H_7NO_2$, crystallising in colourless needles, which sublime above 320° without previous fusion. It differs from the isomeric amidopropiolic acid in subliming without fusing, and in its silver salt not exploding when heated. Treated with phosphoric chloride, it yields the same dichloroquinoline as chlorcarbostyril. The OH-group has, therefore, like the chlorine-atom, become attached to the carbon-atom next the benzene-nucleus, and the formula must be



$$C_6H_4<\begin{matrix}C(OH):CH\\ N:C(OH)-\end{matrix}>.$$

When it is heated with sulphuric acid at 200—220°, *hydroxycarbostyrilsulphonic acid*, $C_9H_7NO_5S$, is produced, easily soluble in boiling water, sparingly so in cold. Its barium and silver salts are soluble.

Of the three related acids, *orthamidohydrocinnamic acid*, *orthamidocinnamic acid*, and *orthamidophenylpropiolic acid*, the first forms an internal anhydride spontaneously, the second only with difficulty, and the third, so far as at present known, not at all. When the side nuclei close to a ring, this is always accompanied by the addition of HCl, HBr, HI, or H(OH), to the unsaturated pair of carbon-atoms.

When distilled with water, orthamidophenylpropiolic acid gives *amidoacetophenone* accompanied by traces of amidophenylacetylene. In this reaction, however, by far the greater part of the acid resinifies. A better way of preparing this body is from amidophenylacetylene, by Friedel and Balsohn's process (*Ber.*, **14**, 364).

Orthamidoacetophenone, $NH_2.C_6H_4.COMe$, is a thick light-yellow oil of basic properties. It distils almost without decomposition between 242° and 252°, and is very stable. The sulphate and hydrochloride are soluble in alcohol and water, and crystallise from the latter in prisms.

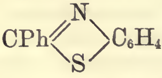
It forms a platinochloride. *Acetylorthoamidoacetophenone* is produced by the action of acetic anhydride on amidoacetophenone. It forms colourless needles melting at 76°. L. T. T.

Derivatives of Homoferulic Acid. By F. Tiemann and R. Kraaz (*Ber.*, **15**, 2070—2072).—The authors describe the following compounds, which are prepared by the usual methods, and present no peculiarities:—

	M. p.
Hydrohomoferulic acid, $C_6H_3(CH_2.CMeH.COOH)(OMe).OH$	114—115°
Methylic methylhomoferulate, $C_6H_3(CH : CMe.COOMe)(OMe)_2$	65—66
Methylhomoferulic acid, $C_6H_3(CH : CMe.COOH)(OMe)_2$	140—141
Methoxyhydrohomoferulic acid, $C_6H_3(CH_2.CMeH.COOH)(OMe)_2$	58—59

E. H. R.

Phenylphenamidoacetic Acid and its Amide and Nitrile. By F. Tiemann and K. Piest (*Ber.*, **15**, 2028—2034).—By heating together in a closed vessel for two hours at 100° a mixture of equal molecular weights of benzaldehyde-cyanhydrin and aniline dissolved in alcohol, and adding water to the product, a crystalline precipitate is obtained, which has the composition NHPh.CHPh.CN, and is formed according to the following equation:—$CHPh(OH).CN + NH_2Ph = NHPh.CHPh.CN + H_2O$. It crystallises from dilute alcohol in slender white needles, melting at 85°. This substance has already been prepared by Cech by the action of hydrogen cyanide on the compound NPh : CHPh. The authors find that the latter body melts at 48—49°, and not at 42° as stated by Cech, and they have prepared the above-mentioned nitrile by Cech's method. Heated by itself, it gives off hydrogen cyanide, and forms a polymeride of NPh : CHPh. When heated with concentrated or dilute hydrochloric acid, it splits up into aniline and benzaldehyde, whilst with caustic potash it yields aniline and mandelic acid; when dissolved in concentrated sulphuric acid, however, and allowed to stand two days and then gently heated, it yields the amide $NHPh.CHPh.CONH_2$, which is a crystalline substance, easily soluble in alcohol, ether, and concentrated acids. On further heating with dilute hydrochloric acid, it yields the acid NHPh.CHPh.COOH, melting at 173—175°. This substance combines with both acids and bases, and if heated quickly, yields aniline, resinous products, and a small quantity of benzylphenylamine. When the compound NHPh.CHPh.CN is treated with bromine in alcoholic solution, a dibromo-derivative is obtained, having the formula $C_6H_3Br_2.NH.CHPh.CN$ (m. p. 92°), which, on being warmed with concentrated sulphuric acid, splits up into benzaldehyde and dibromaniline, $C_6H_3(NH_2)Br.Br$ [1 : 2 : 4]. By heating the body NHPh.CHPh.CN with sulphur, the authors obtain a compound


$\mathrm{CPh}\overset{\mathrm{N}}{\underset{\mathrm{S}}{\lessgtr}}\mathrm{C_6H_4}$, to which they give the name benzenylorthamidophenylmercaptan. E. H. R.

α-Phenamidoisobutyric Acid and its Amide and Nitrile. By F. Tiemann (*Ber.*, **15**, 2039—2043).—The author has applied the reaction described in the foregoing abstracts to acetonecyanhydrin, and has obtained the following compounds which are analogous in every respect to those previously described:—

	M. p.
$NHPh.CMe_2.CN$	93—94°
$NHPh.CMe_2CONH_2$	137
$NHPh.CMe_2.COOH$	184—185

E. H. R.

Nitriles of α-Phenamido-, α-Paratoluamido-, and α-Orthotoluamidopropionic Acids and the corresponding Amides and Nitriles. By F. Tiemann and R. Stephan (*Ber.*, **15**, 2034—2039).—By methods precisely analogous to those described in the previous abstract, but using acetaldehyde-cyanhydrin and para- and orthotoluidine, as well as aniline, the authors have obtained the following compounds:—

		M. p.
Acetaldehyde-cyanhydrin, and aniline.	$(NHPh).CHMe.CN$	92°
	$(NHPh).CHMe.CONH_2$	140–141°
	$(NHPh).CHMe.COOH$	162°
Acetaldehyde-cyanhydrin, and paratoluidine.	$(NHC_7H_7).CHMe.CN$	81—82°
	$(NHC_7H_7).CHMe.CONH_2$	145°
	$(NHC_7H_7).CHMe.COOH$	152°
Acetaldehyde-cyanhydrin, and othotoluidine.	$(NHC_7H_7).CHMe.CN$	72—73°
	$(NHC_7H_7).CHMe.CONH_2$	125°
	$(NHC_7H_7).CHMe.COOH$	—

E. H. R.

Constitution of Æsculetin. By F. Tiemann and W. Will (*Ber.*, **15**, 2072—2084).—Coumarin, umbelliferone, and æsculetin are represented respectively by the following formulæ:—$C_9H_6O_2$, $C_9H_6O_3$, $C_9H_6O_4$. Since umbelliferone has been shown by Tiemann and Reimer (*Ber.*, **12**, 993) to be a hydroxycoumarin, it is obvious that æsculetin may be represented as a dihydroxycoumarin. When the hydrogen of the hydroxyl in umbelliferone is replaced by methyl, the ether thus produced shows all the properties of coumarin; the authors have therefore endeavoured to show that by replacing 2 atoms of hydrogen in æsculetin by methyl, a body is produced behaving exactly as coumarin. By the usual process the authors obtain a mixture of mono- and di-methylæsculetin, easily separable by ammonia, in which the latter is insoluble. *Monomethylæsculetin* melts at 184°. *Dimethylæsculetin* crystallises in shining white needles melting at 144°. Dimethylæsculetin, methylumbelliferone, and coumarin behave in an exactly similar manner towards reagents, solutions of potassium hydroxide for example. Further, all three exhibit fluorescence. These resemblances point to a similarity in constitution.

The authors have endeavoured to obtain further evidence on this point. Perkin has shown that by the action of methyl iodide on sodium coumarin in presence of methyl alcohol isomeric ethers may be obtained according to the conditions of experiment; and he has also obtained these two isomeric ethers and the corresponding acids by other methods (this Journal, **39**, 409). The authors have repeated Perkin's work, and fully confirm it, and they have further shown that by oxidation of both α- and β-orthocoumaric acids (Perkin, *loc. cit.*) one and the same methyl-salicylic acid is formed. They have applied these reactions to methylumbelliferone and æsculetin.

Methylic dimethoxyumbellate, $C_6H_3(CH \colon CH.COOMe)(OMe)(OMe)$ [1 : 2 : 4], produced by the usual process from methylumbelliferone, forms shining white needles melting at 87°. No isomeric ether could be obtained, although the temperature used did not exceed 100° (that used by Perkin); but the authors think it not impossible that an ether analogous to that of α-methylorthocoumaric acid may be produced, but, being much less stable than the latter, is transformed at once into its isomeride.

Dimethoxyumbellic acid, $C_6H_3(CH \colon CH.COOH)(OMe)_2$ [1 : 2 : 4], is prepared by saponification of the ether and melts at 184°. On oxidation it yields the acid $C_6H_3(COOH)(OMe)_2$ [1 : 2 : 4].

Methyl trimethoxyæsculeate, $C_6H_2(CH \colon CH.COOMe)(OMe)_3$, prepared from dimethylæsculetin in the same manner as the corresponding compound from methylumbelliferone, forms very pale-yellow glistening prisms melting at 109°. On saponification, it yields the corresponding acid, which melts at 168°. From want of material the oxidation-products of the latter could not be determined.

These researches show that methylumbelliferone and dimethylæsculetin give exactly analogous results, when their sodium-compounds are treated with methyl iodide in methyl alcohol solution, and hence there can be little doubt that æsculetin is a dihydroxycoumarin. The authors hope to determine from which trihydroxybenzene æsculetin is derived.
E. H. R.

Constitution of Eugenol. By F. TIEMANN and R. KRAAZ (*Ber.*, **15**, 2059—2070).—Some time since Tiemann and Nagai (*Ber.*, **10**, 201) showed that by oxidation of acetoeugenol under certain conditions, acet-α-homovanillic acid, $C_6H_3(CH_2.COOH)(OMeO\overline{Ac})$ [1 : 3 : 4], is obtained; and Erlenmeyer concluded (*Ber.*, **10**, 630) from these experiments that the C_3H_5-group in eugenol has the constitution $—CH_2.CH \colon CH_2$. The authors have endeavoured to determine this point.

Propiohomoferulic Acid.—By the action of sodium propionate and propionic anhydride on vanillin an acid is obtained melting at 128—129°, to which the authors ascribe the formula

$$C_6H_3(CH \colon CMe.COOH)(OMe)(OC_3H_5O)\ [1 : 3 : 4].$$

They discuss the changes which take place in Perkin's reaction, and come to the conclusion that in the formation of the homologues of cinnamic acid condensation takes place between benzaldehyde and the anhydrides of the higher fatty acids, which are either already present or are formed by the action of acetic anhydride on the sodium salts of those acids, and the following equations represent what takes place:—
$C_6H_5.COH + CH_2R.COO.CO.CH_2R = C_6H_5.CH \colon CR.CO.O.CO.CH_2R$ and $C_6H_5.CH \colon CR.CO.O.CO.CH_2R + H_2O = C_6H_5.CH \colon CR.COOH$

+ $CH_2R.COOH$. Since the homologues of cinnamic acid formed in this way, and also the hydro-acids derived from them by addition of 2 atoms of hydrogen, behave exactly as cinnamic and hydrocinnamic acids (*e.g.*, in the formation of the so-called inner anhydrides from their orthamido- and orthhydroxyl-derivatives), they must be represented as produced by substitution in the *side-chain* of cinnamic acid.

Homoferulic acid, $C_6H_3(CH \vdots CMe.COOH)(OMe)(OH)$ [1 : 3 : 4], is formed by saponification of the last-described compound. It crystallises in tables melting at 167—168°. By distilling it with lime a body is obtained which is isomeric with eugenol, and termed *isoeugenol*. It boils at 258—262°, the boiling point of eugenol being 247—249°. The two substances are further distinguished by their benzoyl-derivatives, which differ widely in melting point. From the formation of isoeugenol it follows that its formula is

$$C_6H_3(CH \vdots CHMe)(OMe)(OH) \ [1 : 3 : 4],$$

and therefore the formula $C_6H_3(CH_2.CH \vdots CH_2)(OMe)(OH)$ must be assigned to eugenol. The authors are endeavouring to synthesise it by the action of allyl chloride, &c., on guaiacol in presence of aluminium chloride. E. H. R.

Isatin. By A. BAEYER and S. ŒCONOMIDES (*Ber.*, **15**, 2093—2103).—The authors have prepared ethers of isatin and bromisatin, and studied their properties.

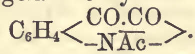
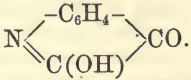
Ethers of Isatin.—By acting on isatin-silver with methyl iodide, using certain precautions (for an account of which reference must be made to the original paper), methylisatin can be obtained in large rhombic prisms of a blood-red colour. This body dissolves slowly in dilute potash, and acids precipitate unaltered isatin from the solution. It undergoes change spontaneously with the greatest readiness, and is converted into a yellow body of much higher melting point, 219° (methylisatin melts at 100—101°). If care be not used in the preparation of the methyl ether, the yellow body, which the authors term *methylisatoïd*, is obtained instead: the latter gives numbers on analysis agreeing with a formula intermediate between that of isatin and methylisatin, $C_8H_5NO_2 + C_9H_7NO_2 = C_{17}H_{12}N_2O_4$. It dissolves in boiling soda solution, and acids precipitate isatin therefrom.

Ethers of Bromisatin.—The ethers of bromisatin show less tendency to form isatoïd compounds. *Methylbromisatin* forms blood-red needles melting at 147°. It changes spontaneously into *methylbromisatoïd*, m. p. 230—231°.

Ethylbromisatin is similar to the methyl-compound, and melts at 107—109°. An alcoholic solution of the former, treated with a small quantity of potash, becomes reddish-violet, and on addition of more potash yellow, with formation of potassium bromisatate. Hence potassium bromisatin is first formed and then converted into the bromisatate. *Ethylbromisatoïd* is best obtained by allowing a solution of the ether in acetic anhydride to stand for some days. It behaves with boiling potash like the ether. *Acetylbromisatin* melts at 170—172°, and on treatment with dilute potash, forms a yellow solution, from which acids precipitate acetylbromisatic acid, melting at 178—

180°. *Isobutylbromisatoïd* melts at 210°. To account for the formation of these isatoïd compounds, the authors suppose that moisture causes a partial saponification, and condensation then takes place.

Ethers of Dibromisatin.—These differ from the ethers of isatin and bromisatin in not forming isatoïd compounds. The authors prepare dibromisatin by heating on the water-bath a saturated solution of bromisatin in glacial acetic acid, with twice the quantity of bromine necessary to produce dibromisatin. Since the melting point of dibromisatin (250°) is 5° lower than that of bromisatin, the second bromine-atom probably takes the ortho-position with reference to the nitrogen, the first bromine-atom having taken the para-position. *Ethyldibromisatin* melts at 87—89°. Treated in the cold with a 5 per cent. solution of potassium hydroxide, it forms a blue-violet powder, which is the potassium-derivative, but this soon becomes changed, without going into solution, into *potassium dibromisatate.* From the latter acids separate *dibromisatic acid*, which changes in a few days into dibromisatin. *Ethyl dibromisatate* crystallises in yellow tables, melting at 105°.

The authors discuss the formula of isatin considered in the light of these new facts. Acetylisatin, on treatment with potash, yields potassium acetylisatate. Ethylisatin, under the same conditions, yields first potassium isatin and then potassium isatate. It follows that the acetyl does not take up the same position as the ethyl, and that the latter must be attached to oxygen, whilst the former is directly attached to nitrogen. Only one constitution can be assigned to acetylisatin, viz.:  $C_6H_4\langle{}^{CO.CO}_{-NAc-}\rangle$. The most probable formula for isatin is  $N\langle{}^{-C_6H_4-}_{C(OH)}\rangle CO$. This method of representing it explains easily its formation and also the fact that isatin chloride is red and enters extremely readily into reaction.

The relation between ethylisatin or its bromine substitution-products and isatin chloride is further shown by the fact that the former, like the latter, yields indigo or substituted indigos. That isatin does not behave in a similar manner, shows that the formation of indigo depends on an alteration of the hydroxyl-group.

It follows from the above that the true acetylisatin, that namely in which the hydroxylic hydrogen is replaced by isatin, has not yet been prepared.

Finally, the authors call attention to the great similarity between the formation of isatin, as represented by the new formula, and that of carbostyril, which Friedländer and Weinberg (this vol., p. 204) have shown to be *hydroxyquinoline*, and not an imido-compound as hitherto supposed. The authors propose the name *lactam* for bodies formed like acetylisatin, and *lactim* for those formed like isatin.

E. H. R.

Metanitrodiphenylmethane. By P. Becker (*Ber.*, **15**, 2090—2093).—The author has obtained this body as a brownish liquid by agitating a mixture of metanitrobenzyl alcohol (prepared according to

R. Meyer's method, *Ber.*, **14**, 2394) and benzene, with a large excess of concentrated sulphuric acid, keeping the mixture well cooled. *Metadinitrodibenzylbenzene* is produced at the same time, and is a white crystalline substance melting at 165°. By nitration, metanitrodiphenylmethane yields a dinitro-compound melting at 94°, and isomeric with those described by Staedel. *Metamidodiphenylmethane*, obtained by reduction of the corresponding nitro-body with tin and hydrochloric acid, is a crystalline base melting at 46°. On oxidation with chromic mixture, metanitrodiphenylmethane yields *metanitrobenzophenone*, a bright yellow crystalline body melting at 92°. E. H. R.

Amarine. By A. CLAUS (*Ber.*, **15**, 2326—2336).—It has been previously pointed out by the author (*Ber.*, **13**, 1418) that a mixture of hydrodimethylamarine, methyl chloride, and hydromethylbenzylamarine is produced by the action of benzyl chloride on a boiling alcoholic solution of dimethylamarine, $2C_{21}H_{16}Me_2N_2 + C_7H_7Cl + 2H_2O = C_{21}H_{18}Me(C_7H_7)N_2O + C_{21}H_{18}Me_2N_2O.MeCl$.

Hydromethylbenzylamarine, $(C_{21}H_{18}Me)C_7H_7N_2O$, is deposited from an alcoholic solution in colourless crystals (m. p. 208°), which dissolve freely in chloroform, but are insoluble in water. The *hydrochloride* forms colourless transparent crystals which melt, with loss of water, at 102°. The dried salt, $C_{29}H_{28}N_2O,HCl$, melts at 205°. The *platinochloride*, $(C_{29}H_{28}N_2O)_2,H_2PtCl_6 + 2H_2O$, is deposited from a warm alcoholic solution in orange-coloured needles. The anhydrous salt melts at 168°.

Hydrodimethylamarine methyl chloride is a crystalline salt (m. p. 168°), freely soluble in water, alcohol, and chloroform, but insoluble in ether. The aqueous solution is not acted on by ammonia, but on treatment with potash or silver oxide, it yields *hydrotrimethylamarine*,

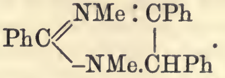
$$C_{21}H_{17}Me_3N_2O.$$

This base crystallises in transparent prisms (m. p. 158°), soluble in ether, alcohol, and chloroform. The *hydrochloride* (m. p. 204°) is insoluble in chloroform and sparingly soluble in water. On adding ammonia to the aqueous solution, the free base is precipitated. The *platinochloride*, $(C_{21}H_{17}Me_3N_2O)_2,H_2PtCl_6 + 2H_2O$, obtained as a yellow precipitate, soluble in alcohol, melts at 195°. The platinochloride of hydrodimethylamarine methyl chloride only contains 1 mol. H_2O. It is a bright yellow powder, melting at 244°, and soluble in alcohol, and in water containing a small quantity of acid.

Dibenzylamarine does not combine with alcoholic chlorides, bromides, or iodides. When ethyl iodide acts on dibenzylamarine, a mixture of hydriodide of dibenzylamarine and its di-iodide is produced. The *hydriodide*, $C_{21}H_{16}(C_7H_7)_2N_2,HI$, forms colourless plates, insoluble in water. The *di-iodide*, $C_{21}H_{16}(C_7H_7)_2N_2,HI,I_2$, is deposited from an alcoholic solution in golden needles.

Dibenzylamarine is not oxidised by chromic acid, but on treatment with dilute nitric acid (sp. gr. 1·13) it yields benzoic and paranitrobenzoic acids, and also two intermediate products, viz., a body crystallising in yellow needles melting at 142°, and a substance deposited from alcohol in pale yellow prisms melting at 95°.

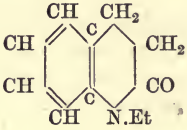
Dimethylamarine may be represented by the formula



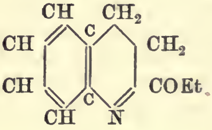
W. C. W.

Constitution of Carbostyril and Hydrocarbostyril. By P. FRIEDLÄNDER and A. WEINBERG (*Ber.*, **15**, 2103).—By the action of a concentrated solution of zinc chloride on ethyl orthamidocinnamate, an ethylcarbostyril is obtained identical with that produced directly from carbostyril or chloroquinoline. It follows, therefore, that ethylcarbostyril contains an ethoxyl-group; and carbostyril must be regarded as a *hydroxyquinoline.*

In a similar manner the authors obtain an ether of hydrocarbostyril which is easily saponified by dilute acids (*Ber.*, **15**, 1421). But when hydrocarbostyril is heated with potassium hydroxide and ethyl iodide in the usual way, an ethylhydrocarbostyril is obtained, which remains unaltered even when heated with concentrated sulphuric acid at 150°. The same body is obtained by heating ethylorthamidocinnamic acid with sodium-amalgam, ethylorthamidohydrocinnamic acid being thereby produced, which, on acidifying its alkaline solution, becomes converted into ethylhydrocarbostyril. The stable form of ethylhydrocarbostyril is therefore represented by Figure I, while Figure II indicates the constitution of its isomeride—



I.



II.

E. H. R.

New Compounds from Coal-tar: α- β- γ-Pyrocresoles. By H. SCHWARZ (*Monatsh. Chem.*, **3**, 726—744).—These compounds were prepared from a buttery distillate occurring amongst the last products of the rectification of carbolic acid in a tar-distillery at Angern near Vienna. The buttery mass, on rectification, began to boil at 180°, the boiling point often remaining stationary for a while at 207°, and then slowly rising to 225°. A small quantity passed over between 225° and 265°; more at 265—320°, the distillate then beginning to solidify. Between 320° and 330°, a copious light yellow distillate was obtained, which quickly solidified; at 330—350° the distillate was dark yellow, and above 350°, brown-yellow and softer. Finally, charcoal remained in the retort. On dissolving the crude distillate in glacial acetic acid at the boiling heat, and then heating it with zinc-dust, it becomes much lighter in colour, and if then distilled, yields a colourless product, which only gradually becomes coloured.

On heating the oily non-solidifying portion of the product with potash-ley, filtering from neutral oil, saturating the filtrate with hydrochloric acid, and distilling it with steam, collecting the oil which sinks to the bottom of the distillate, drying it with calcium chloride and rectifying, there passes over an acid oil, the chief part of which has the composition (77·34 per cent. carbon and 7·45 hydrogen) and boiling point (193—195°) of meta-cresol.

Preparation of Pure Pyrocresole (α, β, and γ).—The solid products of the distillation just described, as well as the press-cakes obtained on the large scale, and the buttery mass expressed therefrom, were found—after being subjected to a series of purifying processes by solution, especially at boiling heat, in benzene, light petroleum, carbon sulphide, chloroform, ether, and alcohol—to crystallise on cooling in silvery laminæ, which, after one more crystallisation, appeared to be pure enough for analysis. Nevertheless these apparently pure products exhibited very considerable differences of melting point and solidifying point, the latter—which admitted of more exact determination than the former—varying from 85° to 195°; and by washing with cold alcohol, boiling first with dilute and then with continually stronger alcohol, extraction with light petroleum and with ether in a percolator, &c., a number of isomeric bodies were obtained exhibiting different degrees of solubility. No separation could be effected by difference of boiling point.

The bodies of lowest melting point were also the most soluble, but the differences of solubility were not great enough to effect the definite separation of more than the products of highest and lowest melting point. The former were most readily separated by repeated crystallisation from boiling benzene, whereby, from the original press-cake solidifying at 127°, products were obtained solidifying at 147°, 157°, 169°, 181°, and finally at 195°, this last product crystallising in large laminæ having a silvery and satiny lustre, and dissolving without colour in benzene. The substance crystallised from this solution exhibited the same solidifying point, as did also that which was obtained from the mother-liquor by distilling off the benzene. It is, moreover, eminently sublimable, so much so indeed that it can scarcely be melted in an open vessel, the greater part subliming before it fuses. When quickly heated in a test-tube, it fills the tube with white coherent flocks, so that its boiling point cannot be determined. Dissolved in glacial acetic acid and oxidised by chromic acid, it yields a product crystallising in splendid needles. The other derivatives of this substance (to be described further on) are distinguished by great tendency to crystallise, relatively high melting point, and sparing solubility.

At the other end of the series is a substance which crystallises constantly at 104—105°. It may be separated by concentrating the mother-liquors, and is likewise obtained from the greasy mass which runs out on hot-pressing in the manufacturing process. It may be freed from colouring matter by treating it in the melted state with hot glacial acetic acid and zinc-dust. This substance is much more soluble than that which solidifies at 195°; it is not sublimable; its derivatives are less crystallisable; and its oxidation-product melts under hot water.

A third substance has also been separated, less well-defined than the two above mentioned. From a press-cake solidifying at 127—128°, the author, by repeated treatment with alcohol, ether, and benzene, obtained the bodies solidifying at 195° and 104°, but did not succeed in resolving the mass completely into these two compounds; and he supposes that it contained also a third substance solidifying at 124°, crystallising in smaller laminæ, and intermediate in solubility between the two former.

All these three substances were found by analysis to have the same elementary constitution, viz.:—

C.	H.	O.
84·87 to 85·24	6·61 to 6·84	7·97 to 8·48

agreeing most nearly with the formula $C_{14}H_{13}O$, which requires 85·28 C, 6·64 H, and 8·08 O. An uneven number of hydrogen-atoms being however inadmissible, the author assigns to these isomeric bodies the double formula $C_{28}H_{26}O_2$ (which is confirmed by some of the substitution-derivatives), and designates them as pyrocresoles, supposing them to be produced from cresol by elimination of water and hydrogen as shown by the equation, $4C_7H_8O = C_{28}H_{26}O_2 + 2H_2O + H_2$. They are distinguished as α, melting at 195, β at 124°, γ at 104°. They may perhaps be regarded as ditolyl-ditolylene dioxides, $C_7H_7.C_7H_6.O.O.C_7H_6.C_7H_7$.

PYROCRESOLE OXIDES, $C_{28}H_{22}O_4$, are obtained by treating the three pyrocresoles either with nitric acid of sp. gr. 1·40, or with a mixture of potassium dichromate and sulphuric acid, or with chromic anhydride in glacial acetic acid, the action being represented by the equation $C_{28}H_{26}O_2 + O_4 = 2H_2O + C_{28}H_{22}O_4$. The α-compound, which is especially fine, may be precipitated from its solution in glacial acetic acid by water, in groups of needles, and when washed, dried, and recrystallised from boiling alcohol, forms beautiful somewhat yellowish needles, becoming somewhat darker on exposure to light. It solidifies at 168°, *i.e.*, 27° lower than α-pyrocresole, and is more soluble than the latter in alcohol, &c. It distils unaltered, but shows little tendency to sublime.

The β- and γ-oxides solidify at much lower temperatures than the α-compound; they are also more soluble, and show less tendency to crystallise.

Oxynitro-products, $C_{28}H_{15}(NO_2)_7O_4$, are produced, with evolution of nitrous fumes, by treating the three oxides with a mixture of 1 vol. NO_3H and 2 vols. SO_4H_2, and separate as light yellow, more or less crystalline bodies, the separation being completed by addition of water. The washed and dried products melt when heated in test-tubes, and detonate at higher temperatures, leaving a large quantity of pulverulent charcoal. The α-nitro-compound crystallises from hot nitrobenzene or from glacial acetic acid in light yellow laminæ; from strong nitric acid on cooling and dilution, in nearly white laminæ and needles. The γ-modification is much more soluble in boiling acetic acid, and separates on cooling in yellow grains and nodules. The β-compound crystallises from a mixture of nitric and acetic acids in yellow laminæ. The analyses of these bodies show that they have not yet been obtained quite pure.

Amido-compounds appear to be formed by the action of tin and hydrochloric acid on the nitro-products, but they have not yet been isolated.

Bromine-compounds.—When a solution of α-, β-, or γ-pyrocresole in glacial acetic acid is treated with excess of bromine, likewise dissolved in glacial acetic acid, a reddish-yellow crystalline precipitate is formed, which after draining, washing with glacial acetic acid, and drying on earthenware plates over quicklime or potassium hydroxide, remains nearly unaltered. Part of the bromine contained in it is, however, very loosely combined, and may be removed by drying at 100°, or by washing with alcohol, or best by boiling with water, a white substance then remaining, which may be crystallised from boiling alcohol or glacial acetic acid.

Of the bromine-compounds thus formed, the α-product is the least soluble. On adding 6Br to 1 mol. α-pyrocresole, beautiful laminæ are thrown down, which contain only traces of free bromine, and may be rendered nearly colourless by treatment with a small quantity of alcohol. The γ-product obtained in like manner is best purified by recrystallisation from boiling alcohol. When on the other hand a larger quantity of bromine is added to γ-pyrocresole, torrents of hydrogen bromide are evolved, yellowish granular crusts separate out, and water throws down a yellowish compound, which melts even at the heat of boiling water. The analysis of the reddish-yellow α-compound thus obtained gave as a mean result, 32·62 per cent. C, 2·30 H, 60·32 Br, and 4·76 O, agreeing approximately with either of the three formulæ, $C_{28}H_{24}Br_8O_4$, $C_{28}H_{24}Br_8O_3$, and $C_{28}H_{24}Br_8O_2$, the first agreeing best with the quantity of bromine found by experiment, the third better with the carbon. The equation $C_{28}H_{26}O_2 + 10Br = 2BrH + C_{28}H_{24}Br_8O_2$, is in accordance with the experiment in which 1 mol. pyrocresole was acted upon with 10 at. Br, of which only a small quantity remained free.

By distilling the reddish-yellow α-compound with water, 61—62 per cent. of white residue was obtained, together with 24·10 to 12·55 per cent. hydrogen bromide, and 18·66 to 24·71 per cent. free bromine. The white residue exhibited a constant composition agreeing with the formula of tribromopyrocresole, $C_{28}H_{23}Br_3O_2$, its quantity agreeing closely with the calculated amount, viz., 61 per cent. The reddish-yellow body is its perbromide, and is converted into tribromopyrocresole by loss of HBr + Br. A similar perbromide is obtained from γ-pyrocresole, but has not yet been examined. β-pyrocresole does not appear to yield a bromine-compound.

To obtain pure *tribromopyrocresole*, it is sufficient to treat the solution of 1 mol. α- or γ-pyrocresole in glacial acetic acid with only 6 at. bromine, according to the equation $C_{28}H_{26}O_2 + 6Br = 3BrH + C_{28}H_{23}Br_3O_2$; the solution on cooling deposits the tribromo-compound in thin rhombic laminæ, which may be washed with water and recrystallised from alcohol.

γ-Pyrocresole treated at the boiling heat with a slight excess of bromine, yielded also another compound in yellow crusts, a further quantity of which was separated on dilution with water. This compound, not yet fully examined, melts under boiling water, whereas α-tribromopyrocresole solidifies at 200°, and the γ-compound at 183°.

On attempting to brominate pyrocresole oxide by treating its solution in glacial acetic acid with bromine, fine reddish-yellow needles were obtained, which turned white when exposed to light over solid potash, and when boiled with water quickly turned white, with formation of hydrobromic acid and evolution of bromine. The residual substance dissolved readily in warm alcohol, and crystallised therefrom in slender white needles, having the composition of pyrocresole dioxide, $C_{28}H_{22}O_6$.

Sulphonic Compounds.—α- and γ-Pyrocresole unite somewhat energetically with sulphuric acid, forming a red-brown syrup, which, however, on dilution with water, deposits nothing but the unaltered pyrocresole. The same solution saturated with carbonate and hydroxide of barium, then filtered and evaporated, yielded only in the case of α-pyrocresole, a salt which crystallised from the hot liquid in needles, giving by analysis 25·05 and 24·95 per cent. Ba, and 11·57 S, the formula of barium pyrocresole-tetrasulphonate requiring 27·84 Ba and 13·08 S. The salt was perhaps mixed with di- or tri-sulphonate. A sodium salt was likewise prepared containing 16·11 per cent. S, 10·33 Na, and 4·84 H_2O, the formula $C_{28}H_{22}Na_4S_4O_{14} + 2H_2O$, requiring 14·92 S, 10·72 Na, and 4·19 H_2O.

The solution obtained by treating α-pyrocresole oxide with sulphuric acid, deposited on dilution with water nothing but the unaltered oxide, and the filtered liquid treated with barium carbonate took up scarcely any traces of baryta. No sulphonic acid had therefore been formed.

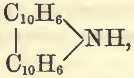
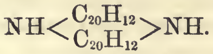
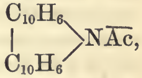
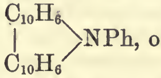
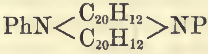
H. W.

α- and ι-Dichloronaphthalenes. By O. Widman (*Ber.*, **15**, 2160—2163).—In the hope of explaining the anomaly that the α- and *β-dichloronaphthalenes* both give the same dichloronaphthalene tetrachloride, which, when oxidised with nitric acid, gives the same dichlorophthalic acid as that obtained from β-dichlornaphthalene (*Bull. Soc. Chim.*, **28**, 505), the author has submitted *α-dichloronaphthalene* (obtained by acting on the pure tetrachloride with potash) to careful purification. The author has succeeded in separating from this α-compound a small quantity of ι-dichloronaphthalene fusing at 120°, and identical with that obtained by Leeds and Everhardt (*Amer. Chem. Soc.*, 1880, **2**, 205), by acting on naphthalene tetrachloride with moist silver oxide at 200°. No trace of β-dichloronaphthalene could be obtained. *α-Dichloronaphthalene* fuses at 38° (formerly the fusing point was given as 35—36°), and gives, by V. Meyer's method, the vapour-density 7·02 (theory 6·69), showing that it could contain no double-compound. Nevertheless, on treating this perfectly pure α-dichloronaphthalene with chlorine, β-dichloronaphthalene tetrachloride is produced. This point, therefore, is still obscure.

The author declines to allow as valid the arguments put forward by Claus in favour of his proposed new formula for naphthalene.

L. T. T.

β-Dinaphthol. By H. Walder (*Ber.*, **15**, 2166—2178).—The author has investigated many new derivatives of *β-dinaphthol.* The β-dinaphthol used was prepared by oxidising β-naphthol in ethereal solution with anhydrous ferric chloride. On distillation, β-dinaphthol decomposes, β-naphthol and some β-dinaphthol distilling over, and a carbonaceous residue being left in the retort.

β-Dinaphthol picrate, $C_{20}H_{14}O_2,2[C_6H_2(NO_2)_3.OH]$, melts at 174°, and is soluble in alcohol and benzene. α-Dinaphthyl is produced when β-dinaphthol is heated with zinc-dust. α-Dinaphthyl, heated with picric acid dissolved in benzene, yields a crystalline body melting at 145°; it crystallises from benzene in reddish-brown needles. By heating β-dinaphthol with zinc chloride at 270°, the author obtained a β-dinaphthalene oxide, which appears to be isomeric and not identical with that obtained by Dianin from β-naphthol and phosphoric anhydride. The oxide is soluble in the usual solvents, melts at 157°, and gives a picric acid compound, $C_{20}H_{12}O,2[C_6H_2(NO_2)_3.OH]$, melting at 135°. On heating β-dinaphthol with zinc ammonium chloride at 320—330° for 60 hours, a substance was obtained melting at 159°, and having the formula $C_{20}H_{13}N$. The author looks upon this body as *dinaphthylenamide*,  $\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}\!\!>NH$, or  $NH<\begin{matrix}C_{20}H_{12}\\ C_{20}H_{12}\end{matrix}>NH$. It is soluble in the usual solvents and yields rhombic crystals. It dissolves in concentrated sulphuric acid with blood-red coloration. With picric acid it gives a compound, $C_{20}H_{13}N,C_6H_2(NO_2)_3.OH$, melting at 217°. Heated with excess of acetic anhydride, it forms an acetyl-compound,  $\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}\!\!>N\overline{Ac}$, crystallising in greyish-white needles melting at 144°. Substituting zinc aniline chloride for zinc ammonium chloride, a *dinaphthylenephenylamine*,  $\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}\!\!>NPh$, or  $PhN<\begin{matrix}C_{20}H_{12}\\ C_{20}H_{12}\end{matrix}>NPh$, is obtained, soluble in benzene, ether, acetone, alcohol, and acetic acid, but not in dilute mineral acids. Sulphuric acid dissolves it with violet coloration. It crystallises in white needles melting at 144°. This amine also yields a picric acid compound, $C_{26}H_{17}N,2[C_6H_2(NO_2)_3.OH]$, melting at 169°. Acetic chloride attacks dinaphthylenamine, but not the tertiary dinaphthylenephenylamine. L. T. T.

Action of Amines on Quinone. Part VI. By T. ZINCKE and F. BRAUNS (*Ber.*, **15**, 1969—1972).—A continuation of the authors' researches on this subject (Abstr., 1880, 48; 1881, 595, 915; 1882, 735, 967). The ethers of β-naphthoquinonetoluide can be prepared from the silver salt by heating an alcoholic solution of the sodium salt with alcoholic bromides or iodides.

The *methyl* ether, $C_{17}H_{12}NO_2Me$, crystallises from alcohol in fine red crystals melting at 150°. The *ethyl* ether, $C_{17}H_{12}NO_2Et$, forms large red crystals melting at 135—137°. The *isopropyl* ether,

$$C_{17}H_{12}NO_2\beta Pr,$$

melts at 137—139°. These ethers, when boiled with acetic acid, yield ditoluide; they are saponified by hot concentrated sulphuric acid with formation of β-naphthoquinonetoluide. By the long continued action of hydrochloric acid, hydroxynaphthaquinones are formed.

Nitric acid dissolves the ethers; and on adding water precipitates are formed; in the case of the ethyl ether, a yellow crystallisable substance (m. p. 177—179°) being obtained.

Nitrous acid acts on β-naphthoquinonetoluide, and in presence of acetic acid and alcohol, gives a substance of the formula $C_{34}H_{22}N_4O_6$, crystallising from glacial acetic acid in small red needles, and appearing to be a nitroso-compound. It unites with alcohol, forming a white crystalline compound, which is decomposed by heat, the alcohol being driven off. On reduction, best by means of potassium bisulphite, a deep blue compound, $C_{34}H_{26}N_4O_4$, is formed; this forms red salts with acids, which are only stable in alcoholic solution; with alkalis it yields fine green salts, insoluble in alcohol; with acetic anhydride it yields a *tetracetyl*-derivative, $C_{34}H_{22}N_4(O\overline{Ac})_4$, forming yellow crystals, melting at 190—191°. On oxidation, the blue compound is converted into a yellowish-red substance, $C_{34}H_{22}N_4O_4$ (m. p. 260—265°), crystallising from acetic acid in needles; reducing agents reconvert it into the blue compound. By the action of soda on the nitroso-compound

$$C_{34}H_{22}N_4O_6,$$

a yellow crystalline body (m. p. 224°) is obtained; it is not attacked by the strongest oxidising agents; potassium bisulphite gives an unstable white reduction-product which readily reoxidises. Chromic acid converts the nitroso-compound into a body crystallising from alcohol in small yellow needles melting at 212—214°. A. J. G.

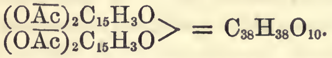
Lapachic Acid. By E. PATERNÒ (*Gazzetta*, **12**, 337—392).—This acid is extracted from the ground lapacho wood by boiling it with a dilute solution of sodium carbonate: the solution acquires a blood-red colour, and when cold is filtered and neutralised with hydrochloric acid; an abundant yellow precipitate of lapachic acid is then formed, amounting to about 8 per cent. of the original weight of the wood. In order to purify the crude product, it is crystallised successively from ether and from benzene, in which the resinous matters are insoluble; it then forms small well-defined monoclinic prisms of a fine canary-yellow colour, and very soluble in boiling alcohol, from which it separates in thin plates. It melts at 138°, and at a higher temperature decomposes, leaving an abundant carbonaceous residue. Lapachic acid, $C_{15}H_{14}O_3$, is easily soluble in solutions of the alkaline hydroxides and carbonates, giving bright red solutions. *Sodium lapachate*,

$$C_{15}H_{13}NaO_3 + 5H_2O,$$

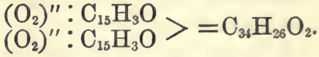
separates from concentrated solutions as a radiated crystalline mass of deep red colour, which after a time loses its crystalline structure and becomes almost black. It melts in its water of crystallisation at about 50°. *Potassium lapachate*, $C_{15}H_{13}KO_3$, closely resembles the sodium-compound in appearance. *Ammonium lapachate*, $C_{15}H_{13}O_3.NH_4$, crystallises in large brick-red needles, which lose ammonia quickly on exposure to the air, leaving a residue of pure lapachic acid. *Silver lapachate*, $C_{15}H_{13}AgO_3$, *calcium lapachate*, $(C_{15}H_{13}O_3)_2Ca + H_2O$, and *strontium lapachate*, $(C_{15}H_{13}O_3)_2Sr + 1\frac{1}{2}H_2O$, are obtained from the ammonium salt, by precipitation, as red amorphous powders. The *barium* salt, $(C_{15}H_{13}O_3)_2Ba + 7H_2O$, very sparingly soluble in cold, but more so in hot water, crystallises in long slender blood-red needles. The *lead* compound forms an orange-red precipitate. The aniline and toluidine salts were also prepared; they are orange-yellow crystalline compounds melting at 121—122° and 129·5—130° respectively.

Action of Bromine on Lapachic Acid.—On mixing bromine (35 grams), diluted with acetic acid with a solution of lapachic acid (50 grams), in the same solvent, a yellowish-brown solution is obtained, which yields an abundant orange-yellow precipitate when poured into a large quantity of water. The *monobromolapachic acid*, $C_{15}H_{13}BrO_3$, thus obtained is easily purified by washing it with ether and crystallising from boiling alcohol; it separates in large lustrous plates of an orange-red colour, melting at 139—140°. It has none of the characters of an acid, being quite insoluble in cold potash solution, and although alcoholic potash dissolves it, it is precipitated unchanged on diluting with water and adding hydrochloric acid. It dissolves in nitric or sulphuric acid at the ordinary temperature, and is precipitated unaltered on adding water to the solution. When boiled with nitric acid, however, it is gradually decomposed, bromine is given off, and the solution leaves phthalic acid on evaporation.

Acetyl-derivatives.—Lapachic acid is not altered by boiling with acetic chloride or anhydride under the ordinary atmospheric pressure, but on heating it with the anhydride at 150° for three hours, a *monacetic*-derivative, $C_{15}H_{13}O_3\overline{Ac}$, is formed; this may, however, be prepared more conveniently by heating a mixture of lapachic acid (2 parts), sodium acetate (2 parts), and acetic anhydride (5 parts), the liquid rapidly assumes a wine-red colour which passes into yellowish-brown, and finally becomes green; as soon, however, as the mixture begins to assume a green tinge, the reaction is stopped by adding water; this throws down a yellowish-brown oil which soon solidifies to a crystalline mass, the yield being almost the theoretical. It is easily purified by recrystallisation from alcohol, when it forms lustrous sulphur-coloured prisms, insoluble in water, but very soluble in ether; it melts at 82—83°. When heated with acetic anhydride in closed tubes, it yields a green resinous compound. It is not acted on by water at 120°, but is easily decomposed by alcoholic ammonia in the cold with formation of ammonium acetate and lapachate. With bromine, it yields monobromolapachic acid, and with nitric acid an *acetomononitrolapachic acid*, $C_{15}H_{12}(NO_2)O_3.\overline{Ac}$; this crystallises in orange-red plates which melt at about 166—168°, but undergo decomposition at the same time. If the mixture of acetic anhydride, sodium acetate, and lapachic acid above mentioned, instead of being heated until it commences to turn green, is boiled for about 15 minutes, it no longer contains a trace of monacetolapachic acid, but another compound which is precipitated as a brownish-green oil on adding water to the product; this becomes crystalline after some time, and is then powdered, washed with ether to remove a greenish resin, and finally purified by recrystallisation from alcohol or from dilute acetic acid. It forms dirty-white needles or minute prisms melting at 131—132°, and very sparingly soluble in ether or cold alcohol. Although the analytical results correspond very closely with the formula of biacetolapachic acid, yet, as it has not been found possible to reconvert it into lapachic acid, it is highly improbable that it is the biaceto-derivative. It is not altered by heating it with water at 150°, neither does it dissolve in solutions of the alkaline carbonates or of their hydroxides; it is decomposed, however, by alcoholic potash, which dissolves it with brownish-yellow colour, and on diluting the solution with water, and adding an acid, a new compound is obtained as a brownish-yellow precipitate. This is very soluble in alcohol, ether, and benzene, but may be crystallised from dilute alcohol, when it forms small, silky, flat needles of orange colour, melting at 140—141°. The author thinks it probable that these two compounds have the formulæ I and II respectively:—

I. 

$$\left.\begin{matrix}(O\overline{Ac})_2C_{15}H_3O\\(O\overline{Ac})_2C_{15}H_3O\end{matrix}\right> = C_{38}H_{38}O_{10}.$$

II. 

$$\left.\begin{matrix}(O_2)'' : C_{15}H_3O\\(O_2)'' : C_{15}H_3O\end{matrix}\right> = C_{34}H_{26}O_2.$$

The action of nitric acid on the acetic-derivative seems to give rise to two nitro-substitution-compounds, one of which crystallises in red needles melting at 147—148°, whilst the other, less soluble in ether, forms yellow needles melting at a somewhat higher temperature.

When lapachic acid is oxidised by potassium permanganate, it yields oxalic acid in small quantity; with ordinary nitric acid of sp. gr. 1·38 it yields phthalic acid in abundance, exceeding 75 per cent. of the lapachic acid taken.

On distillation with zinc-dust, lapachic acid yields naphthalene and a hydrocarbon boiling at about 250°, and melting at a lower temperature than naphthalene, probably a homologue of the latter; of the gaseous products, the portion absorbed by bromine gave two bromides, one isobutylene bromide, $CMe_2Br.CH_2Br$, the other derived apparently from a hydrocarbon containing C_6.

Action of Reducing Agents.—As the general conduct of lapachic acid and the fact that it yields naphthalene on distillation with zinc-dust, indicate that it is a hydroxyquinone derived from some homologue of naphthalene, it was of importance to examine the effect of reducing agents. The acid when dissolved with excess of an alkaline hydroxide and treated with zinc-dust, is acted on immediately, the intense red colour of the solution becoming pale yellow; the hydrolapachic acid formed, however, is oxidised so readily that it was found to be impossible to obtain it in a state sufficiently pure for analysis. It is soluble in boiling water, and crystallises in colourless needles melting at about 100°.

An energetic reaction takes place on heating lapachic acid with red phosphorus and concentrated hydriodic acid, and when it is complete the mixture separates into two layers, the lower of which is an oily hydrocarbon boiling at 304—306°. It combines with trinitrophenol, forming a compound which crystallises from boiling alcohol in large orange-red needles melting at 140—141°. From analyses of the picric acid compound, the hydrocarbon would seem to be an *amylnaphthalene*, $C_{10}H_7.C_5H_{11}$.

Action of Concentrated Acids.—Lapachic acid (1 part) dissolved in concentrated sulphuric acid (4 parts) in the cold gives a solution of the colour of bromine, and this, when poured into a large quantity of water, deposits an orange-yellow flocculent substance, which may be purified by crystallisation from alcohol. This new compound is *lapacone*, $C_{15}H_{14}O_3$, isomeric or polymeric with lapachic acid. It forms magnificent flattened needles melting at 155—156°, of orange-red colour and silky lustre. It is insoluble in water, easily soluble in benzene and alcohol, but less so in cold alcohol or ether. It dissolves also in concentrated sulphuric, nitric, and hydrochloric acids, and is precipitated unaltered on addition of water; it also dissolves in potash when heated. In like manner when lapachic acid is dissolved in well cooled concentrated nitric acid of sp. gr. 1·49, it is converted into lapacone, but a small quantity of another substance, more soluble in ether and cold alcohol, is formed at the same time; this crystallises from alcohol in canary-yellow needles melting at 116—117°. It does not contain nitrogen, and on analysis gave numbers nearly the same as those obtained with lapachic acid.

Lapacone is energetically acted on by acetic anhydride and sodium acetate; on heating the mixture, it becomes green and brilliant plates make their appearance in the liquid; the addition of water now throws down a dark green precipitate, which is washed with ether to remove a green resin, leaving the new compound in magnificent plates of metallic lustre with blue iridescence, bronze-red by reflected and golden-yellow by transmitted light; when pressed under a glass rod on paper they give an indigo-blue spot with coppery lustre like indigo. There is the greatest difficulty in purifying this substance, as it is almost insoluble in the usual solvents; it may, however, be recrystallised from a large quantity of boiling acetic anhydride. It is also slightly soluble in carbon bisulphide, yielding a beautiful blue solution, but on evaporation it is deposited in the amorphous state. It is not altered by boiling potash solution. Sulphuric acid dissolves it, but it is not reprecipitated on adding water; nitric acid dissolves it with red colour, but the product has not been examined. This substance is also formed by the action of acetic anhydride and sodium acetate on monobromolapachic acid.

These results incline the author to believe that it is an anhydride of lapacone, admitting—what is highly probable—that lapacone is a polymeride, $C_{30}H_{28}O_6$, of lapachic acid, analogous to the compound obtained by Stenhouse and Groves from β-naphthaquinone. In this case it would have the formula $C_{30}H_{26}O_5$.

The author then proceeds to discuss the identity of lapachic acid with taiguic acid and groenhartin, pointing out that these three substances are obtained from varieties of the same species, although not from the same plant; the properties of lapachic acid and also its melting point agree closely with those given by Arnoudon for taiguic acid; there is, however, a great difference in the amount of carbon, lapachic acid containing 74·5 per cent., whilst Arnoudon gives 70·9 for taiguic acid; it should be noted, however, that he does not consider the formula as absolutely settled. As regards groenhartin, the analyses given by Stein agree very closely with those of lapachic acid; Stein, however, says that he obtained an unstable bromo-derivative containing 37 per cent. bromine, whilst monobromolapachic acid contains but 25, and no definite dibromo-derivative could be obtained. The author suspects that the product analysed by Stein was not pure, but contained a resinous substance richer in bromine, the formation of which he himself has observed. It seems highly probable that these three substances are identical, and it is very desirable that Arnoudon and Stein should study taiguic acid and groenhartin so as to definitely settle this point. In an appendix, the author states that he has examined the acid obtained from a fragment of the very same piece of wood employed by Arnoudon, and finds it to be identical with lapachic acid.

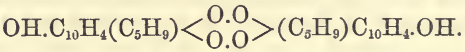
Constitution of Lapachic Acid.—The results of the analyses of lapachic acid and its substitution-products, and especially of the silver salt, closely agree with the formula $C_{15}H_{14}O_3$, whilst its chemical character and the action of reducing agents prove distinctly that it is a hydroxyquinone derived from naphthalene of the formula

$$C_5H_9.C_{10}H_4(O_2)''.OH.$$

The results obtained by the distillation of lapachic acid with zinc-dust, and the nature of the bromide obtained from the gaseous hydrocarbon evolved, indicate that the side chain C_5H_9 has the constitution

$$—CH\colon CH.CHMe_2.$$

The author assigns valid reasons for believing that in monobromolapachic acid the bromine takes the place of the hydrogen in the OH-group, and that its formula is $C_{15}H_{13}(O_2)''.OBr$, and that the acetate is $C_{15}H_{13}(O_2)''.O\overline{Ac}$. Finally, he discusses the formula of lapacone, and considers it highly probable that it is



$$OH.C_{10}H_4(C_5H_9)<\begin{matrix}O.O\\O.O\end{matrix}>(C_5H_9)C_{10}H_4.OH.$$

C. E. G.

A New Monochlorocamphor. By P. CAZENEUVE (*Compt. rend.*, **94**, 1530—1532).—When dry chlorine is passed into a mixture of camphor (760 grams) and absolute alcohol (230 grams), there is development of heat and the camphor dissolves. On cooling the product to about 15°, it becomes a pasty mass of crystals, which, after being collected, washed with water, and crystallised from alcohol, forms long colourless needles of *monochlorocamphor*, $C_{10}H_{15}ClO$. It has an odour resembling that of camphor, is sparingly soluble in water, but easily in ether and benzene. It softens at 75°, melts at 83—84°, and distils almost without decomposition at 244—247°. It is also easily volatile in the vapour of water. Its specific rotatory power $[\alpha]_j = + 90°$, is greater than that of camphor, or of the dichloro-derivative. It is not decomposed by an alcoholic solution of silver nitrate or by alcoholic potash, differing greatly in this respect from Wheeler's monochlorocamphor (*Bull. Soc. Chim.*, **10**, 289), which melts at 95°, and is readily decomposed when heated. C. E. G.

Contributions to the History of the Isomerism of the Dibromocamphors. By T. SWARTS (*Ber.*, **15**, 2135—2136).—By heating *α-dibromocamphor* for six hours at 120° in a sealed tube, in which hydrobromic acid was being evolved from a mixture of phosphorus bromide and syrupy phosphoric acid, the author has converted it into *β-dibromocamphor.* Hydrochloric acid does not produce the change.

α-Dibromocamphor forms a liquid compound with chloral hydrate; β-dibromocamphor has no action. The bromine-atoms in the α-body appear very immobile; one at least of those in the β-body is easily replaced, producing, with silver acetate, silver bromide and a crystalline acetic compound.

The author believes *tribromocamphor* to partake of the constitution of the two di-bromocamphors. Treated with nascent hydrogen in alkaline solution, it gives an oil resembling turpentine, boiling at 258—260°. Heated with fuming nitric acid, it gives a nitro-body melting at 175°. L. T. T.

Action of Nitric Acid on Oxycamphor from β-Dibromocamphor. By J. Kachler and F. V. Spitzer (*Ber.*, **15**, 2336—2337).—Oxycamphor (b. p. 259°), obtained by the action of sodium amalgam on an alcoholic solution of β-dibromocamphor, forms a crystalline barium salt, $Ba(C_{10}H_{15}O_2)_2$. When treated with nitric acid, oxycamphor yields a mixture of oxalic acid and nitroxycamphor, $C_{10}H_{15}NO_4$. This substance crystallises in colourless needles (m. p. 170°), which dissolve freely in hot alcohol. W. C. W.

Œnocyanin. By E. J. Maumené (*Compt. rend.*, **95**, 924).—Œnocyanin, the colouring-matter of black grapes and red wines, is of colourless origin, and becomes blue through oxidation, and probably hydration, which may be shown by placing a green grape picked from a bunch which is just beginning to turn red, in a vacuum of 1 to 2 mm. over boiled sulphuric acid for three or four days, or sufficient time to allow of the grape becoming hard and dry. The colour becomes yellow, but on admitting air, moisture and oxygen are rapidly absorbed, the colour changing to blue-black at the same time.

L. T. O'S.

The Poisonous Constituent of Andromeda Japonica. By J. F. Eykman (*Pharm. J. Trans.* [3], **13**, 365—367).—The aqueous extract of the leaves of this plant, which has long been considered as poisonous in Japan, contains a glucoside, "asebotoxin." It is a transparent brittle colourless substance, melting at 120°, and contains $C = 60{\cdot}48$, $H = 7{\cdot}405$, $O = 32{\cdot}115$ per cent.; it is only slightly soluble in cold water, but easily in ethyl and amyl alcohol, chloroform, &c. The aqueous solutions are unaffected by ferric, mercuric, or gold chloride, or by lead acetate; but they reduce alkaline copper solutions. The fatal dose for rabbits by hypodermic injection is 3 mgrms. for each kilogram of the animal; the symptoms are detailed.

Asebotoxin exhibits some fine colour-reactions, which are of importance toxicologically. If an alcoholic solution of the substance is poured into a watch-glass and strong hydrochloric acid added, a magnificent blue colour is gradually developed, and, at the same time, a peculiar odour resembling that of *Spiræa ulmaria.* On evaporating the blue solution on a water-bath, a fine violet-red tint develops itself at the edge of the liquid. If the blue solution be left to itself, it turns after some time to reddish-grey, and the liquid becomes turbid from the separation of a bluish-grey substance. Concentrated sulphuric acid dissolves asebotoxin with a red colour, which after some time becomes fine rose-red, while the liquid is rendered turbid from the separation of a bluish-grey substance. If asebotoxin is boiled with diluted hydrochloric acid, the liquid assumes a fine rose-red colour, and a brown resinous substance separates. The same effect is produced by diluted sulphuric acid. E. W. P.

Constituents of the Leaves of Fraxinus Excelsior. By W. Gintl and F. Reinitzer (*Monatsh. Chem.*, **3**, 745—762). — The aqueous decoction of the leaves of the ash-tree contains, as chief constituents, calcium malate and a tannin, designated *fraxitannic acid* by the authors, together with smaller quantities of mannitol and inosol, and still smaller quantities of quercitrin, dextrose, gummy matter, and free malic scid. To separate the fraxitannic acid, the aqueous extract was precipitated by normal lead acetate, and the precipitate, after being quickly washed with cold water, was treated two or three times at boiling heat with acetic acid of about 10 per cent., which dissolved nearly all the tannate of lead, leaving undissolved the greater part of the malate, together with other bodies. The resulting still impure acetic solution of the lead tannate was then precipitated by ammonia in nine separate fractions, of which the third, fourth, and fifth yielded the purest tannic acid, whereas the first and second contained also oxidised products, which, however, being less soluble in acetic acid than the pure lead tannate, could be separated by treating the precipitates with quantities of acetic acid not sufficient to dissolve the whole. The resulting solutions were then precipitated by ammonia, and the precipitates, as well as those previously obtained, were washed as quickly as possible by decantation with cold water, and decomposed by hydrogen sulphide; the solutions thus obtained were filtered into a flask previously filled with carbonic anhydride; the filtrates were freed from hydrogen sulphide by a stream of the same gas; and the solutions thus purified were evaporated to dryness in a vacuum over sulphuric acid. The first and second fractions thus obtained were but very slightly hygroscopic, and easily pulverisable; the third, fourth, and fifth also only slightly hygroscopic; whereas the sixth, which contained considerable quantities of malic acid, and the seventh, eighth, and ninth, were very hygroscopic, and formed syrupy strongly acid masses, the first two containing—together with small quantities of tannic acid—a moderate quantity of malic acid, a little inosol, a gummy substance, and a somewhat considerable quantity of amorphous silica, whilst the ninth fraction was destitute of tannic acid, contained only small quantities of malic acid and mannitol, and consisted mainly of the gummy substance just mentioned.

The first five fractions were next digested with absolute alcohol in closed flasks, filled with carbonic anhydride and kept in the dark, whereby the greater part of the tannic acid was dissolved to a yellow liquid, leaving only a small quantity of a blackish-brown substance, easily soluble in water. The united alcoholic filtrates were then freed from the greater part of the alcohol by distillation in a stream of carbonic anhydride; the residue was treated with water, which dissolved it all with the exception of a very small quantity of substance, probably an anhydride, formed by the prolonged boiling with alcohol; and lastly, the filtrate was evaporated to dryness. The substances thus obtained from the five fractions agreed so closely in composition, solubility, and reactions, that they may, without hesitation, be regarded as one and the same chemical compound.

This compound, *fraxitannic acid*, is an amorphous, yellow-brown, shining, brittle mass, yielding a golden-yellow powder, which, on exposure to moist air, gradually deliquesces to a yellow-brown shining tenacious mass. It dissolves in water, yielding, according to the degree of concentration, a golden-yellow to brown-red liquid, which has a rough, bitter taste, and reddens litmus slightly; alcohol, acetic acid, and ethyl acetate dissolve it readily, but it is quite insoluble in benzene, chloroform, and anhydrous ether, slightly soluble in ether containing water. The moderately concentrated aqueous solution is precipitated by sulphuric and hydrochloric acids, yielding a light-yellow precipitate, soluble in excess of the acids and on warming, and reappearing as the liquid cools. From its aqueous solution, unless very dilute, it is completely precipitated, like other tannins, on saturation with common salt. The aqueous solution is not precipitated by tartar emetic, but with normal lead acetate it gives a fine golden-yellow precipitate, easily soluble in acetic acid, becoming brown-green on exposure to the air, and at the same time less soluble in acetic acid. Ferric chloride imparts a fine dark-green colour to the aqueous and alcoholic solutions of the acid, forming a precipitate at the same time, the colour changing to blood-red on addition of an alkaline hydroxide, normal carbonate, or acid carbonate, these colours becoming dingy on exposure to the air. A small quantity of the tannin solution added to an alkaline cupric solution, throws down cuprous oxide on warming; with mercuric chloride, it forms a slight precipitate of calomel. Heated with dilute acids or with baryta-water, it does not yield glucose; with the latter reagent, it appears to yield protocatechuic acid.

Fraxitannic acid dried in a vacuum at ordinary temperature has the composition $C_{13}H_{16}O_7$, and when heated at 100° in a stream of carbonic anhydride, it gives off water and is converted into an anhydride, $C_{26}H_{30}O_{13} = 2C_{13}H_{16}O_7 - H_2O$, which is nearly insoluble in cold, and only slightly soluble in hot water.

The acid, if heated on the water-bath with acetic anhydride, is converted into an *acetyl-derivative*, $C_{17}H_{20}O_9 = C_{13}H_{14}(O\overline{Ac})_2O_5$, forming an amorphous yellowish mass, which gradually softens when heated to 100°, and melts at a slightly higher temperature; the liquid, after cooling, appears transparent with amber-yellow colour in thin layers, dark brown in thicker layers. It becomes very strongly electric on trituration. Its melting point is not determinable, as it passes into the liquid state by very slow degrees.

The corresponding *benzoyl-derivative*, $C_{27}H_{24}O_9 = C_{13}H_{14}(OBz)_2O_5$, is prepared by heating the tannic acid with fused benzoic anhydride for several hours in a paraffin-bath at about 130°; exhausting the mass which solidifies on cooling with ether, which leaves the whole of the benzoyl-derivative undissolved, then dissolving the residue in alcohol, and either evaporating on the water-bath, whereby a dark-brown residue is obtained yielding a light-brown powder, or precipitating the alcoholic solution with water, adding calcium chloride, and heating the liquid to cause the precipitate to settle down. The benzoyl-compound is thus obtained as a light-brown powder insoluble in water and in ether, but soluble in alcohol. It becomes electric by friction, though not so strongly as the acetyl-compound. Its alcoholic solution gives no coloration with ferric chloride.

On dropping bromine or fuming nitric acid into a well-cooled solution of acetylfraxitannic acid in glacial acetic acid, or, better, in acetic anhydride, then precipitating with water, washing the precipitate with cold water, and drying it in a vacuum over sulphuric acid, a light orange-yellow powder is obtained, which dissolves very sparingly in water or in ether, easily and with brown-red colour in alcohol. The nitro-compound, heated on platinum-foil, suddenly takes fire with slight detonation.

The *bromacetyl-compound* has the composition $C_{34}H_{37}Br_3O_{18} + 2H_2O$ or $C_{26}H_{25}(\overline{Ac}O)_4Br_3O_{10} + 2H_2O$.

The constitution of this body shows that fraxitannic acid contains four hydroxyl-groups, and that its molecular formula is the double of that above given, viz., $C_{26}H_{32}O_{14} = C_{26}H_{28}(OH)_4O_{10}$.

The acid, treated with manganese dioxide and sulphuric acid, gives off a strong odour of quinone. When heated in a stream of carbonic anhydride it liquefies at 120°, then becomes viscid and frothy, once more fluid at 180°, and between 220° and 260° yields a small quantity of yellowish-green oil, giving with ferric chloride a fine green colour, probably due to admixed catechol.

The insoluble residue left in small quantity in the purification of fraxitannic acid with absolute alcohol (p. 216), is a shining, brown-black, easily friable, non-hygroscopic substance, which dissolves in water to a yellowish-brown liquid, giving with lead acetate a brown-green precipitate, similar in colour to lead fraxitannate which has been exposed to the air. Dried in a vacuum, it has the composition $C_{13}H_{16}O_8$; after drying at 100°, $C_{26}H_{30}O_{15} = 2C_{13}H_{16}O_8 - H_2O$. It therefore bears to fraxitannic acid the relation of an ordinary acid to its aldehyde.

Another body is formed when a neutral or very slightly alkaline solution of fraxitannic acid is repeatedly evaporated on the water-bath in an open vessel, and remains, on drenching the residue with water, as a soft adhesive brown mass running together in a cake at the bottom. This substance, after being dried in a vacuum, forms a brown brittle resinous mass having the aspect of catechu. It is very slightly soluble in cold, somewhat more in hot water, and separates on cooling as a milky cloud, which gradually aggregates to a brown glutinous mass. For purification, it was dissolved in alcohol of 96 per cent. which left a residue, and separated by water into two portions, the portion thereby precipitated being treated with absolute alcohol to remove a small quantity of matter insoluble therein. When thus purified, it formed a brown powder perfectly soluble in absolute, and in not too much diluted alcohol, also in strong acetic acid and in ethyl acetate, but insoluble in water, ether, and benzene. Boiling water dissolves it in small quantity, and deposits it on cooling as a yellowish precipitate. It dissolves readily in alkalis with deep-yellow colour and a faint odour of tea. The alcoholic solution reacts with ferric chloride and an alkaline cupric solution, just like fraxitannic acid. This compound forms an acetyl- and a benzoyl-derivative, and is converted by fusion with potash into a substance which gives the reaction of protocatechuic acid with ferric chloride. Dried at 100° in a stream of carbonic anhydride, it gives by analysis numbers agreeing with the formula $C_7H_8O_3$. It appears, however, to be formed by separation of CO_2 and H_2O from several molecules of fraxitannic acid, as shown by the equation—

$$5C_{13}H_{16}O_7 - (2CO_2 + 4H_2O) = C_{63}H_{72}O_{27} = 9C_7H_8O_3,$$

Its *benzoyl-derivative*, $C_{105}H_{96}O_{33} = C_{63}H_{66}\overline{Bz}_6O_{27}$, is a light-brown powder insoluble in water, alcohol, and ether, soluble in chloroform; it begins to blacken, without fusing, at 120°.

Volatile Oil of Ash-leaves.—In preparing the aqueous decoction of the leaves, a pleasant smell of tea is given off, due to a very small quantity of a volatile oil, which may be separated by distilling the fresh leaves with water, shaking the aqueous distillate with pure ether, evaporating off the ether, dissolving the residue in alcohol, mixing the alcoholic solution with solution of common salt, separating the oily layer which rises to the surface, and rectifying it over calcium chloride. The oil thus rectified forms a colourless liquid having a strong and very pleasant odour like that of syringa flowers. It boils at 175°, and gives by analysis numbers leading to the formula $C_{10}H_{20}O_2$. It probably belongs to the class of terpenes, but has the formula of anhydrous terpin, although it is liquid. H. W.

Euxanthic Acid. By A. SPIEGEL (*Ber.*, **15**, 1964—1969).—Euxanthic acid has long been known as a conjugated compound, but the nature of the substance into which, together with euxanthone, it is resolved by the action of acids, has never yet been clearly ascertained. The author employed the action of 2 per cent. sulphuric acid in sealed tubes, and then found the product to be euxanthone and the anhydride of glycuronic acid. The identity of this latter with the glycuronic anhydride of Schmiedeberg and Meyer (*Jahrb. Chem.*, 1879, 986) was proved by a comparison of the crystallographic forms and chemical reactions of the two preparations. The author considers that the substance described by Erdmann as hamathionic acid was in reality a sulphate of glycuronic acid, the analysis given by Erdmann of a basic lead salt agreeing much better with the formula of the latter than with that assigned by him to hamathionic acid. In conclusion the author thinks that some light is thrown on the source of purree by these results; the view that it is a dried sediment from camels or elephants' urine has lately met with disbelief, but as conjugated glycuronic acids have lately been obtained several times from the urine of animals subjected to feeding experiments, it seems reasonable to conclude that euxanthic acid may have a similar origin. A. J. G.

Hydrates of Pyridic Bases derived from Cinchonine. By W. O. de Coninck (*Rec. Trav. Chim.*, **1**, 132).—The author finds that β-collidine (b. p. 195—196°) and β-lutidine (b. p. 165—166°), left for two months over a basin of water covered with a bell-jar, take up quantities of water, agreeing with the formulæ $C_8H_{11}N,H_2O$ and C_7H_9N,H_2O; he does not, however, regard the products thus obtained as well-defined hydrates. H. W.

Conine. By C. Schotten (*Ber.*, **15**, 1947—1951).—The only oxidation-product of conine at present known is normal butyric acid. As substances of pronounced acid or basic properties are frequently unsuitable for direct oxidation, the author first converted conine into its urethane, a completely neutral body.

Conylurethane, $C_8H_{16}N.COOEt$, is best prepared by the action of ethyl chlorocarbonate on conine in presence of aqueous potash. It is a colourless liquid (b. p. 245°) of agreeable ethereal odour, and is lighter than water. It is insoluble in water and in acids. It is not decomposed by boiling with concentrated potash or with hydrochloric acid, nor is it decomposed when heated with aqueous ammonia in sealed tubes at 200°. Hydrochloric acid in sealed tubes at 100° decomposes it into conine, carbonic anhydride, and ethyl chloride. On distillation with phosphoric acid, it yields, amongst other products, a hydrocarbon which is probably conylene. By the action of well-cooled nitric acid on conylurethane, a monobasic acid of the formula $C_7H_{14}O_2.COOEt$ is obtained as a nearly colourless heavy oil of well-marked acid properties. On heating this acid with hydrochloric acid in sealed tubes at 100°, the COOEt-group is eliminated (as ethyl chloride and carbonic anhydride), and on evaporating the solution, large crystals are obtained of a body having the formula $C_7H_{15}O_2N,HCl$. This body is readily soluble in water, has no poisonous properties, and gives a platinochloride crystallising in needles or prisms. The author regards it as the hydrochloride of an amido- or imido-acid, but he has not succeeded in isolating the acid. A. J. G.

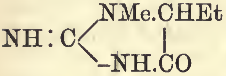
Conhydrine. By A. W. Hofmann (*Ber.*, **15**, 2313—2316).—When conhydrine, $C_8H_{17}NO$, is acted on by dehydrating agents, *e.g.*, phosphoric anhydride or concentrated hydrochloric acid, conine is not produced as stated by Wertheim (*Annalen*, **127**, 75), but an oily liquid is obtained which consists of a mixture of different compounds. W. C. W.

Compounds of the Creatinine-group. By E. Duvillier (*Compt. rend.*, **95**, 456—459).—*Methylamido-α-butyrocyamidine* or *α-butyric-creatinine*, $C_6H_{11}N_3O$, is obtained by the prolonged action of cyanamide in concentrated and slightly ammoniacal aqueous solution on methylamido-α-butyric acid. The substances are mixed in the proportion of equal molecules, and after about one month lamellar crystals begin to separate out, and continue to form for about four months. At the end of this time, the crystals are removed and about half the original quantity of cyanamide is added to the mother-liquor. A further crop of crystals is thus obtained. The crystals dissolve in boiling alcohol, and separate out on cooling in slender silky needles composed of small rectangular plates. The creatinine is not formed by the dehydrating action of the alcohol on the original crystals, for the latter contain no water of crystallisation and have sensibly the same composition as the purified product. This is the first instance of the formation of a creatinine without the intermediate formation of the corresponding creatine.

Methylamido-isovalerocyamidine or *Isovaleric Creatinine*, $C_7H_{13}N_3O$, is obtained in a similar manner by the action of cyanamide on methylamido-isovaleric acid. It forms slender needles, readily soluble in boiling alcohol.

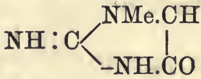
The formulæ of these compounds are—

Methylamido-α-butyrocyamidine.



$$\mathrm{NH{:}C}\begin{cases}\mathrm{NMe.CHEt}\\ \quad\quad\quad\ \ |\\ \mathrm{NH.CO}\end{cases}$$

Methylamido-isovalerocyamidine.



$$\mathrm{NH{:}C}\begin{cases}\mathrm{NMe.CH.CHMe_2}\\ \quad\quad\quad\ |\\ \mathrm{NH.CO}\end{cases}$$

, or

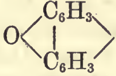
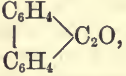
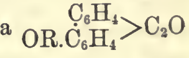
$NH:C:N.CO.CH,NH(Me).CH_2.Me$ $NH:C:N.CO.CH(NHMe).CHMe_2$

according as the view of Strecker and Erlenmeyer, or that of Kolbe, on the constitution of creatine and creatinine is accepted.

C. H. B.

Morphine. By E. v. Gerichten and H. Schrötter (*Ber.*, **15**, 2179—2183).—The object of this investigation was to examine the nature of the two non-nitrogenous bodies $C_{15}H_{10}O_2$ and $C_{15}H_9BrO_2$, which the authors obtained from codeïne and monobromocodeïne (Abstr., 1882, 1112). Their insolubility in dilute alkalis pointed to their still containing the methoxyl-group present in codeïne. An attempt to split off methyl from the compound $C_{15}H_{10}O_2$ by heating with hydrochloric acid, was unsuccessful. *Codethyline*, $C_{19}H_{21}NO_3$, treated by Hofmann's reaction (Abstr., 1882, 921), yielded a non-nitrogenous body, $C_{16}H_{12}O_2$, homologous with the above-cited codeïne derivative. Both these bodies yield phenanthrene—leaving no doubt of the presence of a methoxyl-group—when heated with zinc-dust, and may therefore probably be considered as phenanthrene derivatives. The following table shows the relationship of these compounds to the morphine alkaloïds:—

Alkaloïd.	Formula.	Non-nitrogenous derivative.	Hypothetical intermediate product between non-nitrogenous derivative and phenanthrene.	Phenanthrene.
Morphine	$C_{17}H_{17}NO{<}\substack{OH\\OH}$	$C_{14}H_7O.OH$.*	$C_{14}H_8O$.*	$C_{14}H_{10}$.
Codeïne (morphine monomethylether) .	$C_{17}H_{17}NO{<}\substack{OH\\OMe}$	$C_{14}H_7O.OMe$ m. p. 65°.		
Bromocodeïne	$C_{17}H_{16}BrNO{<}\substack{OH\\OMe}$	$C_{14}H_6BrO.OMe$ m. p. 121—122°		
Codethyline (morphine monoethyl ether) ..	$C_{17}H_{17}NO{<}\substack{OH\\OEt}$	$C_{14}H_7O.OEt$ m. p. 59°.		

The authors consider this hypothetical intermediate product to have either the formula (i)  $O{<}\substack{C_6H_3\\|\\C_6H_3}{>}C_2H_2$ or (ii)  $\substack{C_6H_4\\|\\C_6H_4}{>}C_2O$, and taking into account the ease with which it is reduced by zinc-dust, they consider (ii) as the more probable. The non-nitrogenous derivatives of codeïne and codethyline would then have the formula  $\substack{C_6H_4\\|\\OR.C_6H_4}{>}C_2O$ (where R = Me and Et respectively).

The non-nitrogenous derivative $C_{14}H_7O.OEt$, obtained from codethyline, is insoluble in water, but soluble in ether, alcohol, and acetic acid. It crystallises well, melts at 59°, and distils almost without decomposition. On heating it in sealed tubes with the calculated quantity of hydriodic or hydrochloric acid, ethyl iodide or chloride is produced, together with a resinous mass, from which a very small quantity of a body crystallising in white needles was extracted, insufficient for investigation. $C_{16}H_{12}O_2$ is soluble in strong sulphuric acid to a yellow liquid having a green fluorescence, and is reprecipitated unchanged on adding water. A nitro-derivative was obtained. $C_{16}H_{12}O_2$ is oxidised by chromic acid, and is easily reduced to phenanthrene by heating it with zinc-dust. L. T. T.

Cinchonine. By H. WEIDEL and K. HAZARA (*Monatsh. Chem.*, **3**, 770—788).—Cinchonine oxidised with chromic acid yields, as chief products, cinchoninic acid and an acid brownish syrup, together with small quantities of carbonic and formic acids.

The syrupy liquid freed from cinchoninic acid and other substances by a series of processes for which the original paper must be consulted, dried up in the exsiccator to a soft gummy mass, which showed

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* $C_{14}H_8O_2$ and $C_{14}H_8O$ have not yet been obtained.

no tendency to crystallise, even after standing for a year. Its aqueous solution decomposes carbonates at boiling heat, yielding deliquescent uncrystallisable salts. When neutralised with an alkali, it does not precipitate metallic salts. Heated with oxidising agents, it does not yield either cinchoninic or pyridine-tricarboxylic acid, whence the authors infer that the syrupy liquid obtained by the oxidation of cinchonine does not contain any portion of that half of the cinchonine molecule which yields cinchoninic acid.

The syrupy liquid treated for a day with nitric acid yielded a small quantity of *nitrohydroxyquinoline*, $C_9H_5(NO_2)(OH)N$, a compound which unites both with bases and with acids, the salts which it forms with the latter being however very unstable. Its platinochloride, $(C_9H_6N_2O_3,HCl)_2PtCl_4$, forms monoclinic crystals, in which $a : b : c = 0{\cdot}9705 : 1 : 0{\cdot}8806$; $\beta = 96° 20' 4''$. Optic axes nearly perpendicular to the base. Observed faces $\infty P \breve{\infty}$, $0P$, ∞P, $+P$, and $-P$.

When the residue left on evaporating the syrup over the water-bath is distilled with zinc-dust, a light-yellow oil passes over, and afterwards a brown viscid distillate, containing—together with ammonium carbonate, pyrroline, and bodies related thereto—the three following bases:—

Pyridine, C_5H_5N.	Ethyl-pyridine, C_7H_9N.	Quinoline, C_9H_7N.
b. p. 120°.	b. p. 161—164°	b. p. 233—237°

These bases are formed from that half of the cinchonine-molecule which is converted by oxidation into the syrupy product, and their formation shows that cinchonine must contain two hydrogenised quinoline-nuclei—a conclusion strengthened by the fact that tetrahydrocinchoninic acid, as shown by Weidel (*C. J.*, Abstr., 1882, 531), yields by oxidation, not cinchoninic acid, but a syrupy mass, which as the authors find by preliminary experiments, also yields by distillation over zinc-dust, bases of the pyridine séries, respecting which they promise a further communication. H. W.

Strychnine Sulphate. By Lextreit (*J. Pharm. Chim.* [5], 6, 259—266).—Regnault assigned to strychnine sulphate the formula $C_{21}H_{22}N_2O_2.H_2SO_4 + 7H_2O$, which was adopted by the Codex of 1866, but subsequent researches by Schabus, Des Cloizeaux, and Rammelsberg, who have described preparations containing from 5 to 6·5 mols. of H_2O, have failed to confirm this formula. Although a great number of samples used in pharmacy were analysed, not one satisfied the above formula.

To determine what hydrates exist, and the conditions under which they form, the following research was undertaken:—

When a neutral and saturated aqueous solution of strychnine sulphate is allowed to crystallise between 109° and 95°, a salt of the composition $C_{21}H_{22}N_2O_2 + H_2SO_4 + 5H_2O$ separates out, but if the temperature sinks below 95° some crystals containing 6 mols. H_2O are formed. When crystallised from alcohol it always crystallises with 5 mols. H_2O. To prepare this compound, 10 parts of strychnine and 1·27 parts sulphuric acid are mixed in a flask, and 50 parts strong alcohol added and gently warmed. When solution is complete, the mixture is left to cool, and the salt crystallises; a further crop of crystals may be obtained from the mother-liquors. If dilute alcohol is used, the crystals are very bulky, but its strength must not be less than 50°, otherwise square tables containing $6H_2O$ will be formed. The salt crystallises in slender needles from aqueous solutions, and from alcoholic in clinorhombic prisms identical with those described by Des Cloizeaux (*Ann. Mineral.*, 1858, **14**, 389), containing $6H_2O$, and by Rammelsberg containing $5H_2O$.

The hydrate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 6H_2O$, is obtained in long slender needles when a hot concentrated solution of the neutral sulphate is cooled between 95—50°; below 50° tabular crystals separate out. 10 parts of strychnine are dissolved in a mixture of 1·27 parts sulphuric acid and 35 parts water, the solution boiled, and allowed to crystallise at 70°; above 70° a mixture of this and the previous salt is obtained. This salt crystallises in octohedrons, which confirms the results of Rammelsberg (*Ber.*, 1882). Des Cloizeaux (*Compt. rend.*, **44**, 909) also obtained a salt crystallising in octohedrons, but found it to contain 6·5 H_2O. The crystals do not alter when exposed to the air, but slowly lose their water of crystallisation over sulphuric acid, and quickly at 100°. The anhydrous crystals reabsorb a portion only of the water they have lost.

The salt containing $7H_2O$, described by Regnault, is shown by the author from the analytical data of the former not to agree with the formula ascribed to it.

The *acid sulphate*, $C_{21}H_{22}N_2O_2H_2SO_4 + 2H_2O$, is prepared by treating 1 mol. of strychnine with 1 mol. of sulphuric acid, and crystallising either from alcohol or water. It forms short needles when crystallised at a high temperature, but when slowly formed at low temperatures they may be obtained several centimeters long. Their form could not be determined. L. T. O'S.

Preparation of Lupinine Hydrochloride from Lupinine Residues. By G. BAUMERT (*Ber.*, **15**, 1951—1952).—In the preparation of pure lupinine, a large amount of mother-liquors are obtained from the frequent recrystallisations; these contain considerable quantities of lupinine, whose crystallisation is prevented by the impurities present. The mother-liquors, after removal of ether, are shaken with an equal volume of cold water, and the emulsion heated for a few minutes on the water-bath, when it separates into two layers, the upper consisting of water containing lupinine in suspension. On cooling, the turbidity vanishes and the lupinine dissolves. The aqueous layer is poured off, and the residue treated several times with water in the same manner. The aqueous extracts are then neutralised with hydrochloric acid, evaporated, dissolved repeatedly in absolute alcohol, and evaporated to remove water, freed from a black syrup by pressure between filter-paper, and finally crystallised from absolute alcohol, when pure lupinine hydrochloride is obtained. A. J. G.

Putrid Fermentation, and the Alkaloïds produced by it. By A. GAUTIER and A. ÉTARD (*Compt. rend.*, **94**, 1598—1601).—The authors consider that the apparently complex phenomena of putrid fermentation may be explained by regarding putrefaction as a breaking up by hydration of the complex albuminoïd molecule into the simple nuclei which enter into its composition. As in the results Schützenberger obtained with barium hydroxide, so by the action of the bacteria, the albuminoïd molecule splits up first into two principal parts; one of these is relatively stable, giving rise to the glucoproteïns and leucines to which Schützenberger attributes the formula $C_nH_{2n-4}N_2O_2$, whilst the other is unstable, and decomposes rapidly, with formation of ammonia, carbonic anhydride, and formic, acetic, and oxalic acids. But whilst Schützenberger's method is incapable of hydrating the amides formed,—the leucines and leuceines,—bacteria slowly change them into ammoniacal salts, and also by the hydration of the crystalline body, $C_{11}H_{26}N_2O_6$, produced abundantly in the putrefaction of fish.

Putrefaction being essentially a process of hydration, it follows that the aromatic derivatives and the bases formed during the fermentation pre-exist as nuclei in the albuminoïd molecule. In order to obtain the bases, the liquid products of putrefaction of the skate are acidulated with sulphuric acid and evaporated in a vacuum, whereby indole, phenol, and other volatile products are removed; the residue is then treated with baryta and chloroform, which dissolves the bases. After purification, they are colourless oily liquids having all the characters of the bases described by Selmi. They have an odour like that of the carbylamines, recalling that of hawthorn and hydrocollidine, resinify rapidly, and give the reactions of the ptomaïnes. The hydrochlorides crystallise well, and yield sparingly soluble crystalline platinochlorides.

By fractionation, two bases were isolated, one having the formula of parvoline, $C_9H_{13}N$, and yielding a platinochloride which becomes rose-coloured on exposure to the air, the other an oil boiling at about 110°. The latter gives a hydrochloride crystallising in slender needles of bitter taste. The platinochloride is pale-yellow, and sparingly soluble; the aurochloride is very unstable. Although the analytical results agree better with the formula $C_8H_{11}N$, the author assigns to this base the formula $C_8H_{13}N$, as the boiling point, viscosity, and general properties so very closely resemble those of Cahours and Étard's hydrocollidine, with which he believes it to be isomeric.

From these considerations, the occurrence of indole and of pyridic and of hydropyridic bases amongst the products derived from albuminoïds by putrefactive hydration, the authors feel compelled to admit the existence of the homologous series C_5H_5N and C_5H_7N in the radicles of the proteïd molecule. C. E. G.

Invertin. By M. J. KJELDAHL (*Bied. Centr.*, 1882, 791).—Temperature has different effects on the action of invertin from surface and from bottom yeast. Bottom yeast acts best on saccharose at 52—53°, whilst surface yeast is most energetic at 56°. The action of the invertin also increases with the concentration until a certain limit (20 per cent.) is attained.

At the commencement, the action is proportional to the time of action, and also the amount of invertin, so long as not more than

40 per cent. of the whole sugar originally present has been converted. Alkalis and mercury salts cause the action to cease, whilst acids aid it at starting. On lævulose, dextrose, maltose, dextrin, and inulin, invertin has no effect.
E. W. P.

Physiological Chemistry.

Spontaneous Fermentation of Animal Matters. By A. Béchamp (*Compt. rend.*, **94**, 1533—1536).—The results already published by the author and others show that alcohol is produced in the spontaneous fermentation of animal matters, such as eggs, liver, horse-flesh, &c., thus raising the question as to whether alcohol is not produced in the tissues of the human organism itself; this has been answered in the affirmative, alcohol having been found in the urine of a subject who had abstained from taking alcoholic drinks, in freshly drawn milk, and in the muscles of animals recently killed.

The only histological elements in the organism which persist after death being the microzymas, it is natural to regard them as the organised ferments, producing alcohol, acetic acid, &c.; moreover, the presence of alcohol in the tissues indicates one of the causes of the disappearance of sugar. The fermentable matter which is the first to disappear after death is glucose or glycogen, and this change is caused by the microzymas from which the bacteria are evolved, since they never attack the albuminoïd matters until after the sugars have been completely destroyed, and it is then only under certain conditions, with free access of oxygen, that the animal matter is finally resolved into carbonic anhydride, water, and nitrogen, or nitrogenous compounds.

The author concludes by affirming that the microzymas are the active chemical and physiological agents, whereby the transformations in the organism are effected both when living and after death.
C. E. G.

Effect of Food on Sheep of Different Breeds. By H. Weiske, G. Kennepohl, and B. Schulze (*Bied. Centr.*, 1882, 743—745).—It is a well-known fact that the same quantity and quality of food given to sheep of different breeds does not produce like effects. To prove this fact experimentally, a sheep of the Rambouillet breed and a Southdown-merino were fed with like food. The digestive coefficients for each constituent of the food was found to be almost identical. Comparison of the amount of nitrogen retained by the two sheep showed that the Rambouillet sheep, which is well known as a bad "doer," retained the largest quantity, and this is probably due to the great amount of wool which grew. So far these experiments show no great difference between the races. A further set of experiments will be made to determine whether the difference lies in the laying on of fat, &c.
E. W. P.

Artificial and Natural Digestion of Nitrogenous Matter. By T. PFEIFFER (*Bied. Centr.*, 1882, 739—743).—Stutzer (Abstr., 1239) divides proteïd matter into albuminoïds (digestible) and nucleïn (indigestible), and considers that by means of artificial digestion a quantitative separation of the two can be accomplished. The author, however, judging from experiments on sheep, considers that Stutzer's conclusions are incorrect, as nucleïn does not pass through the system unaltered, and he finds that the nucleïn nitrogen excreted is 25—30 per cent. less than that given in the food. E. W. P.

Excretion of Nitrogen from the Skin. By J. B. POWER (*Proc. Roy. Soc.*, **33**, 354—360).—The results obtained by various experimenters on the excretion of nitrogen in the sweat have proved contradictory; Berzelius, Favre, Funke and others, have found nitrogen, whilst Voit, Ranke, and Parkes have denied its existence. The author takes exception to Funke's method of procedure, which presupposes an equality of secretive power, and identity of chemical composition of the sweat from the arm with that excreted from the rest of the body. The author by a suitable apparatus and a method whereby the sweat from the whole of the body is collected, finds, as a mean of 25 experiments, that 0·038 gram of nitrogen existing in some soluble form is excreted per hour. Healthy subjects were operated on, and also patients suffering from Bright's disease, catarrh, gout, acute rheumatism, and nephritis.

Several determinations were made of the quantities of nitrogen present in some insoluble form, *e.g.*, epithelium, and also of the sodium chloride in the sweat; the proportion of the latter to the nitrogen is about 10 : 1. The author concludes that the cutaneous excretion of nitrogen is so small, that it can never replace the renal excretion to any appreciable extent. V. H. V.

Milking of Cows Twice or Thrice Daily. By ERLENMEYER (*Bied. Centr.*, 1882, 785).—The amount of milk is dependent on the activity of the milk glands, as well as on the fodder supplied. Midday milk is the richest in fat, morning milk the poorest, because a longer time having elapsed since the evening milking, a greater quantity of milk is formed. Experimental data are given in support of these statements. E. W. P.

Nitrites in Human Saliva. By R. N. MUSGRAVE (*Chem. News*, **46**, 217).—By means of sulphanilic acid followed by naphthylamine hydrochloride, nitrites were detected in the saliva of numerous persons, the quantity varying between 0·4—2·0 parts nitrogen per million; the amount varied for the same person at different times, for example, the amount present before breakfast was 0·0, after breakfast (10—11 A.M.) 2·2, and between 1 and 2 P.M., 1·3 parts per million.
E. W. P.

Cause of the Evolution of Oxygen from Hydrogen Peroxide by Fibrin; Influence of Hydrocyanic Acid in Preventing the Activity of Fibrin. By A. BÉCHAMP (*Compt. rend.*, **95**, 925—926). Thénard believes that fibrin decomposes hydrogen peroxide in a manner similar to silver and platinum; he ascertained that oxygen was not absorbed, neither was carbonic anhydride evolved; and from the conditions of his experiments, he concludes that the fibrin does not lose weight, and suffers no modification. The liberation of oxygen from hydrogen dioxide by the red colouring matter of blood and by hæmatosin has been shown by the author to be accompanied with oxidation, and a change in the bodies themselves. The author is of opinion that Thénard was misled in his conclusions by the amount of oxygen absorbed, and the loss of weight being too small to be measured. The author shows that this property soon ceases, and with it that of rendering starch soluble.

30 grams of fibrin were treated three times with 60 c.c. of hydrogen peroxide (containing 10·5 c.c. oxygen per c.c.) free from acid. The first time, oxygen was rapidly evolved, the second time more slowly, and the third time after 24 hours no more gas was evolved. After ascertaining that the solution contained excess of hydrogen peroxide, the experiment was stopped. From 180 c.c. of hydrogen peroxide 1600 c.c. of oxygen were evolved by 30 grams fibrin in 48 hours. The solutions were separated from the fibrin which was finally pressed, and evaporated at about 90°; the residue dried at 100° amounted to 0·2 gram, of which 0·16 gram was organic matter. The fibrin remaining did not decompose hydrogen dioxide nor render starch soluble even after remaining in contact with it eight days, whilst fibrin from the same source previous to treatment with hydrogen peroxide rendered starch-paste fluid in six hours. Moreover, it gave rise to no bacteria.

The stoppage of the action of fibrin on hydrogen peroxide by hydrocyanic acid is thought to be due to the oxidation of the acid, since if sufficient hydrogen peroxide is present, the action is resumed after a certain time. L. T. O'S.

Lupine Sickness in Sheep. By HARMUTH and others (*Bied. Centr.*, 1882, 746—749).—Harmuth attributes an attack of lupine sickness which occurred to one of his flocks to dirt, &c., which was blown by a high wind and settled on the crop, whilst another crop which was not thus affected, produced no evil effects on sheep. Cream of tartar and sulphur readily cured the flock. It is quite possible that the dirt and sand thus taken in did do some harm, but Arnold refers the sickness to fungus. Arnold and Kuhn consider that in lupines there is a substance, ictrogen, which becomes more insoluble as the plant ages, so that if the crop be exposed to rain, ictrogen is more or less removed according to the age of the plant, but this ictrogen under the action of a ferment produces the poisonous compound. E. W. P.

Chemistry of Vegetable Physiology and Agriculture.

A New Milk Ferment. By E. KERN (*Bied. Centr.*, 1882, 789).—In the Caucasus "kephir," a thick acid drink, which on keeping changes into coumiss, is prepared from sweet milk by adding to it masses of a ferment; the ferment consists of yeast and schizomycetes cells, and these last seem to be allied to Bacillus, and have been named *Dispora caucasica;* drying has no effect on the activity of this ferment, and the *dispora* growing threadwise retains its life though dried hard as a stone. E. W. P.

Reduction of Sulphates by Living Organisms. By A. ÉTARD and L. OLIVIER (*Compt. rend.*, **95**, 846—849).—In the protoplasm of the cells of certain algæ, such as *Beggiatoa*, dark granules are found soluble in ether, chloroform, and especially in carbon bisulphide. These granules disappear when the algæ are placed in water free from sulphates, but on the contrary are formed when the organisms in question are cultivated in liquids rich in calcium sulphate. Hence the authors conclude that these granules consist of sulphur. These algæ flourish extremely well in liquids containing, in addition to sulphates, traces of selenium. At least three distinct kinds of algæ possess the power of reducing sulphates and disengaging sulphuretted hydrogen. Most authors in treating of mineral waters state that the organic matter exists *in solution* in the liquid, and becomes insoluble in contact with the air. The authors' experiments have led them to think that living organisms exercise an influence on the saline matters present in water, which could not be suspected, except by the light of the above experiments, and they think that sufficient notice of these facts is not taken in works on medicine.

E. H. R.

Reduction of Nitrates in the Soil. By DÉHÉRAIN and MAQUENNE (*Compt. rend.*, **95**, 691—693).—The reduction of nitrates takes place only in arable soils containing a considerable proportion of organic matter, and only when the atmosphere surrounding the soil is entirely free from oxygen. The proportion of gas evolved is influenced to a greater extent by the amount of organic matter present than by the amount of nitrate, but even when the proportion of organic matter is large, its volume never corresponds with the volume of gas in the nitrate. The gas given off consists of carbonic anhydride and nitrogen, but under certain special conditions nitrous oxide is evolved. In one experiment with 300 grams of garden earth containing 30 grams of potassium nitrate, the nitrous oxide amounted to 11·75 per cent. of the volume of gas evolved: and with 300 grams of earth and 10 grams of nitrate, it amounted to 9·35 per cent. C. H. B.

Reduction of Nitrates in Arable Soil. By DÉHÉRAIN and MAQUENNE (*Compt. rend.*, **95**, 732—734 and 854—856).—Schloesing and Müntz have shown that soil capable of producing nitrates loses that property if heated to 100°, or if treated with chloroform, but that soil rendered inactive by heat regains its activity if mixed with a little fresh active soil. The authors, following exactly the methods described by Pasteur, have shown that the same effects are produced by similar treatment on soils capable of *reducing* nitrates. The ferment capable of effecting the reduction of nitrates seems to be incapable of living in oxygen, since in no case did the authors find any action when oxygen was present. Since Schloesing has found that nitrification takes place, although with less energy, in an atmosphere poor in oxygen, whereas the converse action never takes place but in the complete absence of that gas, it seems highly improbable that reduction commonly happens in arable soils; but it is very likely that in many instances the loss of nitrogen observed is due to the formation of nitrates and their subsequent removal by drainage-water.

When soil capable of reducing nitrates in the absence of air is added to a 1 per cent. solution of sugar mixed with a small quantity of nitre, and the whole placed in a flask completely filled with the liquid and kept at about 35°, fermentation commences and gas is evolved, consisting of a mixture of carbonic anhydride, nitrous oxide, and nitrogen, and in some cases hydrogen. The composition of the gas varies with the energy of the fermentation. When hydrogen is evolved, the water from the flask smells of butyric acid. This led the authors to suspect the presence of the butyric ferment of Pasteur, described by Van Tieghem under the name *Bacillus amylobacter*, and large numbers of these organisms were detected by microscopic examination. Hence the authors attribute the reduction of nitrates to the action of this organism. E. H. R.

Fermentation of Nitrates. By GAYON and DUPETIT (*Compt. rend.*, **95**, 644—646).—If sewage-water is mixed with 0·02 gram of potassium nitrate per litre and some decomposed urine is added, the nitrate gradually disappears and the liquid becomes full of microscopic organisms. By successive cultivations, 0·1 and even 0·2 gram of potassium nitrate per litre can be reduced, but the reaction ceases at this limit. With fowl-broth neutralised with dilute potash, however, 5 per cent. potassium nitrate can be completely decomposed, and 10 per cent. partially. The denitrification is effected by the organisms which are developed; for if the liquid is sterilised by heat, or is mixed with chloroform or copper sulphate, the liquid remains clear and the nitrate is not altered. The temperature most favourable to the development of these organisms lies between 35° and 40°, and the presence of organic matter is essential. Sugar, ordinary alcohol, and especially propyl alcohol, give the best results. Phenol and salicylic acid, added in quantities even greater than those which are usually antiseptic, do not prevent fermentation, but, like other forms of organic matter, are decomposed together with the nitrate. In the process of fermentation, a large proportion of nitrogen is given off as gas, the remainder forming ammonia, and perhaps nitrogen-compounds derived from the organic matter; the oxygen is converted into carbonic anhydride, which remains in solution in the form of neutral or acid carbonate.

The organic matters cause the products of the fermentation of the nitrate to enter into new combinations. Sodium, ammonium, and calcium nitrate ferment in the same manner as the potassium salt.

C. H. B.

Absorption of Metallic Oxides by Plants. By F. C. Phillips (*Chem. News*, **46**, 224—226).—Freytag has always upheld that plants absorb oxides which are unnecessary for their growth, and poisonous; and as others have combatted this statement, the author grew several plants in soils to which had been added various oxides. Ageratums placed in soil containing 0·5 per cent. white lead matured and produced flowers; their roots were abundant, but the leaves were yellowish; lead was absorbed into the plant. Geraniums in soil containing 0·5 per cent. zinc carbonate grew normally, but contained zinc. Achyranthes in soil containing 0·5 per cent. copper carbonate grew at first normally, but the leaves soon darkened and the roots died; their ash contained copper in small quantities. Coleas in soil containing 0·5 per cent. calcium arsenate soon languished and died in two weeks. In another series, coleas growing in soil to which had been added 0·25 per cent. calcium arsenate, never matured, and the roots perished; only traces of arsenic were discovered in the ash. Although zinc was found in considerable quantities in the ashes of pansies growing in soil containing 0·5 per cent. zinc carbonate, yet the plants appeared healthy. The conclusions drawn from the experiments are—that plants may absorb small quantities of lead, copper, zinc, and arsenic; zinc and lead may enter into the tissues without causing any disturbance in the formation of the plant; compounds of copper and arsenic exert a distinctly poisonous effect.

E. W. P.

Composition of the Banana at Different Stages of Maturity. By L. Ricciardi (*Compt. rend.*, **95**, 393—395).—The pulp has the following composition:—

	Green.	Ripe.
Water (driven off at 110°)	70·92	66·78
Cellulose	0·36	0·17
Starch	12·06	traces
Tannin	6·53	0·34
Fat	0·21	0·58
Inverted sugar	0·08	20·07
Cane-sugar	1·34	4·50
Proteïd substances	3·04	4·92
Ash	1·04	0·95
Other substances	4·42	1·69
	100·00	100·00

The ash freed from carbon and carbonic anhydride contains—

SiO_2.	SO_3.	P_2O_5.	Cl.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	
5·77	3·06	23·18	traces	traces	6·13	9·79	6·79	45·23	= 99·95

The green fruit contains about 12 per cent. of starch, which disappears in the ripe fruit. The sugar in the fruit which ripens on the plant is almost entirely cane-sugar, but that in fruit cut and ripened by exposure to air consists of about 80 per cent. invert sugar and 20 per cent. cane-sugar; the organic acids and tannin in the green fruit disappear in the ripe fruit. The pulp of the fruit allowed to stay on the vine until the rind becomes almost black contains no ethyl alcohol. It is evident, therefore, that the carbonic anhydride given off by the banana in the third stage of its maturity is not produced by alcoholic fermentation. Neither can it be derived from the destruction of the tannin, since the latter has almost entirely disappeared in the ripe fruit. The evolution of carbonic anhydride is possibly the result of true eremacausis. C. H. B.

Oxalic Acid in Potatoes and in Malt. By M. Siewert (*Landw. Versuchs.-Stat.*, **28**, 263—270).—An incrustation found in the worm of an apparatus used for cooling the sweet wort, on being analysed, proved to be crystallised calcium oxalate; the mash usually employed consisting of potatoes and malt. In order to decide the question of the origin of this incrustation, samples were taken of the sweet uncooled, and the fermented wort, of the slime deposited from the mash, and of fresh potatoes and malt, and investigated with regard to their percentage of oxalic acid.

It was found unnecessary to filter the wort hot, as no oxalate separated on cooling. One litre of the cold filtered sweet wort contained 0·077 gram oxalic acid; the total amount in one litre of unfiltered wort being 0·134 gram, or 0·059 per cent. of the total acids. The fermented mash contained 0·155 gram oxalic acid per litre, or 0·189 per cent. of total solids; whilst in the deposit was found 0·196 gram per litre, or 0·4 per cent. of dry substance.

The amount of oxalic acid in potatoes was determined by boiling the pulp with sodium carbonate, precipitating the filtrate with calcium chloride and excess of acetic acid; the decomposition with soda and reprecipitation with calcium chloride being repeated until a tolerably pure product was obtained. The first sample of potatoes analysed contained 0·017 per cent., and the second 0·057 per cent. of acid. This was, however, not sufficient to account for the whole of the oxalic acid in the mash, and the malt used was therefore investigated. In this case, the starch was first made soluble by heating with tartaric acid at 145°; but this process was found to be attended by a considerable decomposition of oxalic acid. The starch was therefore converted into sugar by heating the malt for some time at 62°, and the oxalic acid then determined in the usual manner. The malt was found to contain only 0·0015 per cent., and germinated grain 0·064 per cent. oxalic acid. J. K. C.

Average Amount of Caffeïne in the Guarana of Commerce as compared with that in the Seeds, &c. By J. H. Feemster (*Pharm. J. Trans.* [3], **13**, 363).—From several samples of guarana seeds, 5·08 per cent. caffeïne was obtained. Using this as a basis of comparison with five samples of guarana, it was found that their average percentage amounted to 4·32. The best method of extracting the caffeïne was found to be Greene's (*Chem. J.*, 1877, **2**, 627). The best menstruum for the extraction was a solution containing 8 parts of alcohol, 4 of glycerol, made up with water to 20 parts. Dilute alcoholic extracts have a tendency to form a deposit.

E. W. P.

Researches on the Causes of Clover Sickness. By V. Kutzleb (*Bied. Centr.*, 1882, 728—735).—As the result of the examination of a special district affected with clover sickness, the author comes to the conclusion that this condition is due to want of potash in the soil, especially the want of soluble salts of potassium in the subsoil. The theory that clover sickness is due to decaying vegetable matter is incorrect, as is also that put forward by Linde, who attributes all to the presence of *Pleospora herbarum;* the reduction in the yield of clover may in part be due to the presence of parasites, such as *Peziza ciborioides*, or *Tylenchus devastatrix*, or *T. havensteinii;* but in the cases when these parasites were found, the general appearances did not resemble those presented by clover sickness. A form of *Phacidium medicaginis* has been found on clover; but as it is also to be found on other allied plants which do not suffer, the disease cannot be attributed to this parasite. E. W. P.

On Phylloxera. By P. de Lafitte and others (*Bied. Centr.*, 1882, 761).—Lafitte does not approve of V. Mayet's method of treating infected vineyards (Abstr., 1881, 1069). According to Boiteau, the winged insect was not produced in such great numbers as usual, owing to the dryness of July, August, and September, 1881; consequently, he concluded that winter eggs would be fewer in number, as also the galls in 1882. These conclusions have now been found to be correct. Pellicot and Jaubert recommend ferrous sulphate as destructive to phylloxera. Vannuccini considers that the natural and artificial moisture of sandy soils, together with the character of the vines themselves, is the only cause of the power of resisting the disease possessed by certain vines growing in such soils.

E. W. P.

Cure for Potato Disease. By J. L. Jensen (*Bied. Centr.*, 1882, 755—759).—It is recommended that, after the disease has attacked the leaves, the soil should be well ridged up, forming a ridge steep enough to induce the rain to run into the furrows; it should also be made so that the haulms should be bent over the furrow. All this is proposed so that the disease spores which fall off the leaf may not be washed down by rain into the soil and so attack the tubers. It is best not to lift the potatoes until 2—3 weeks have elapsed after the full ripening, as it appears that the germs retain vitality up to that date. E. W. P.

Atmospheric Nitrification. By A. Muntz and E. Aubin (*Compt. rend.*, **95**, 919—921).—The authors have examined six samples of rain, three of mist, and four of snow at the summit of the Pic du Midi for the presence of nitrates, but, with two exceptions, they failed to detect any; in these two cases the amount present was somewhat less than 0·1 mgram. per 10 litres. In the examination, 10 litres were used, and the rain gauge was of sufficient size to allow of that amount of water being collected in so short a time as to exclude the idea of the reduction of nitrates.* The results are at variance with those of Barral, Bence Jones, and Boussingault, who, with rare exceptions, always found nitrates present in rain, the experiments of Boussingault giving a mean of 0·5 mgram. per litre.

This absence of nitrates at an altitude of nearly 3000 meters would lead to the conclusion that the formation of nitrates in the atmosphere during thunderstorms takes place in regions below that height. Observations have shown that 184 thunderstorms have been observed from the Pic du Midi from August, 1873, to August, 1882, with an interruption from September, 1872, to June, 1874. Of these, only 23 took place at altitudes above 2300 meters. No observation is recorded of a storm taking place at a greater height than the summit of the Pic. It may therefore be concluded that in the Pyrenean region the violent electric disturbances which give rise to storms do not take place at an altitude of 3000 meters, and therefore the formation of nitrates under their influence takes place in lower regions.

Although these results are isolated, yet their concordance may lead to the following generalisation. Atmospheric nitrification is produced in the lower regions of the atmosphere in the zone between the levels of the earth and sea and the mean height of the clouds. The ammonium nitrate is in a state of powder, and does not rise to any great height. The observations confirm the opinion of Boussingault that the ammonium nitrate is not in a state of tension in the atmosphere, otherwise it would diffuse itself uniformly throughout the different atmospheric strata in a manner similar to the carbonic anhydride and ammonia. This absence of powdered nitrates at great altitudes accounts for the transparency of the atmosphere in them, and shows that the mountain vegetation and mountain soils can derive the nitrogenous matters which hthey contain only from the atmospheric ammonia. L. T. O'S.

Hailstorms and their Origin. By Rinicker and Dössekel (*Bied. Centr.*, 1882, 721).—The transformation of a thunderstorm into a hailstorm is caused by local peculiarities; the direction of these storms is from S.W., W., and N.W., and the fall of hail occurs only when after a succession of hot days thunder-clouds pass first over barren and thinly-wooded high land, and then, meeting with contrary or side-winds, are brought to rest over well-wooded and warm valleys. Hailstorms are never produced from thunderstorms which have passed over high-lying fir woods, for then the electricity has been sufficiently abstracted to prevent the formation of hailstones. The size of the stones is proportional to the height from which they fall, high localities receiving only small stones; stones of the size of hazel-nuts fall

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* During the evaporation of the water, access of air was prevented, thus avoiding contamination by the nitrates contained in the products of combustion of the source of heat, a source of error pointed out by Schönbein, and subsequently by Warington.

from a height of 100 m., while those as large as walnuts have fallen through a distance of 200 m. Storms descending into villages from the ridges of high mountains are the most severe. From all the observations made it is clear that by planting the higher mountainous regions with trees, the greater number of hailstorms which would otherwise occur may be prevented.

Dössekel in another district of Switzerland comes independently to the same conclusion as those mentioned above. E. W. P.

Cultivation of various Crops. By J. FITTBOGEN and others (*Bied. Centr.*, 1882, 745—752).—Fittbogen, comparing the crops obtained by sowing Hallett's Pedigree, Sheriff's Square-head, and New Zealand White Wheat, finds that Square-head produces the best yield in all respects, and that the amount of nutrients in all three sorts is the same. Oppenau grew three sorts of roots, and found that Champion Yellow Globe gave the highest yield and with the narrowest nutrient ratio. Hoffmann obtained a yield of prickly comfrey of 1200—3000 cm. per morgen, cutting it twice in the first year, but 4—5 times during each of the succeeding 20 years; it should be mixed with chaff, &c., as owing to its roughness it is at first somewhat distasteful to animals. E. W. P.

Soja Bean. By E. KINCH (*Bied. Centr.*, 1882, 753—755).—A number of analyses of the bean from various sources are given: 10 per cent. of the carbohydrates are analogous to mellitose, and of the albuminoïds 1 per cent. is as peptone, and 1—2 per cent. as amides; the high percentage of albuminoïds (37·8 per cent. in the Japanese) places this bean above all other leguminosæ—in fact the composition in this respect approximates to that of meat; moreover, the straw surpasses in value that of wheat and lentils and also hay as regards nitrogen. Tables of the composition of various Japanese foods made from soja are also given, as well as of the ash-constituents of the bean and straw. E. W. P.

Chemical Studies on the White Sugar-beet of Silesia. By H. LEPLAY (*Compt. rend.*, **95**, 760—763; 851—854).—These papers contain the results obtained by the analyses of the roots, stalks, and leaves of the beet in different stages of its growth, and the author gives an account, first, of the amounts of organic salts of potassium and calcium, taken as a whole, in different parts of the plant at different stages of vegetation; secondly, of the quantities of these salts in the soluble state in the juice, and in the insoluble state in the tissues; and, finally, of the condition of that portion of these salts which is found in the insoluble state in the tissues. The author discusses also to some extent the effect of different soils on the amounts of potassium and calcium to be found in the plant.

In continuation of his researches on this subject, the author has analysed the roots, leaves, and stalks of the beet, with especial reference to the richness of the roots in sugar. The quantity of sugar found appears to be closely connected with the quantity of calcium in the form of organic insoluble salts in all parts of the plant during growth.

Whenever the richness in sugar decreases, the quantity of organic insoluble calcium salts diminishes in all parts of the plant. These calcium salts have also an important influence in diminishing the rate of decrease of richness with increase of volume of the root.

The decrease of richness of the root under the influence of increase of volume and weight corresponds to a decrease in the quantity of calcium carbonate in the immediate neighbourhood of the root.

The means of diminishing the exhaustion of the soil and consequently the influence of that exhaustion on the richness of the root, consists in multiplying the points of contact of the rootlets with the soil by increasing the number of roots to a given surface of soil—that is, by growing the roots more closely together. This corresponds with the well-known fact that the yield of sugar is very much increased when the plants are grown close together. E. H. R.

Influence Exerted by the Weight of Potato "Sets." By Tobisch (*Bied. Centr.*, 1882, 759).—To the advantage gained by using heavy sets there is a limit beyond which the increase of yield is less than the weight of the sets employed; moreover, the number of diseased tubers increases with increased size of the sets.

E. W. P.

Amount of Gluten in Wheat. By Stumpf (*Bied. Centr.*, 1882, 786).—The best German and American summer wheats contain 24 per cent. of gluten; South Russian, 45 per cent.; Californian and Australian 23—24 per cent. Russian wheat is mixed with starchy English wheat, and sold under the name of "Mixed Danzig Wheat."

E. W. P.

Albuminoïd and Non-albuminoïd Nitrogen Compounds of certain Vegetables. By C. Böhmer (*Landw. Versuchs.-Stat.*, **28**, 247—262).—The vegetables examined were those ordinarily used for human food; they were grown in the garden of the Experimental Station at Münster, and cut and dried when fit for use. The samples were analysed with regard to total nitrogen, fibre, ash, &c.: the amount of total nitrogen varied from 1·9 in carrots, to 5·57 per cent. in broad beans, but ranged in all cases, except the former, between 4 and 5·5 per cent.: the percentage of water varied from 4·3 in the truffle to 96 in asparagus.

In splitting up the nitrogenous bodies into their various groups, the method of Stutzer was employed, together with precipitation by lead hydroxide, and the method by difference. Concordant results were obtained by all three methods. The ammonia was determined by means of milk of lime, as recommended by Schloesing and modified by Schulze and Emmerling, and estimated as platinochloride. To separate and determine the quantities of amido-acids and acid amides, the albuminoïds were precipitated with cupric hydroxide, and the filtrate was concentrated and divided into three equal parts, the first of which was treated at once with hypobromite, and the second after two hours' boiling with hydrochloric acid and neutralisation: the difference of the two gave the nitrogen of the carboxyl-groups, *i.e.*, of the amido-acid amides. The third portion, after being boiled first with hydrochloric acid and then with potash to drive off ammonia, was used for the determination of the pure amido-acids by means of nitrous acid, the nitric oxide formed being absorbed by a strong solution of permanganate.

As the following table shows, the above determinations do not exhaust the total quantity of nitrogen present; the remainder was found not to belong, in any considerable quantity, to the peptone-group, but must be classed under the heading of peptoïd bodies, substances which have a position intermediate between peptones and the crystalline final decomposition-products of albumin.

The appended table gives the percentages in the dried substance:—

	Total nitrogen.	N as albuminoids.	N as NH_3.	N as amido-acid amide.	N as amido-acid.
Spinach	4·56	3·51	0·021	0·123	0·068
Peas	4·69	3·56	0·020	0·052	0·361
Beans	5·57	4·39	0·013	0·027	0·059
Asparagus	4·13	3·33	?	—	—
Lettuce	4·85	2·97	0·024	0·155	0·154
Carrot	1·91	1·57	0·006	0·013	0·142
Turnip-cabbage	4·64	2·05	0·018	0·151	0·231
Cauliflower	5·11	2·60	0·017	0·104	0·566
French beans	4·32	2·67	0·010	0·061	0·442
Mushrooms	4·68	3·34	0·011	0·092	0·416
Truffles	4·50	3·63	0·008	0·072	0·202

J. K. C.

Fertility of a Soil as Dependent on the Action of Worms. By N. Hensen (*Bied. Centr.*, 1882, 723—727).—A portion of this paper is devoted to a short account of the work of others on the action of worms in the soil; the analyses of "worm earth" as compared with that of ordinary soil are given, and from these analyses it is evident that the composition of worm earth is not far removed from that of ordinary leaf mould. That the ordinary earthworm (*Lumbricus terrestris*) eats earth is undoubted, but it does so only for the purposes of forming its burrow, whilst for the purposes of nourishment it feeds on decayed vegetable matter. By its varied actions the worm causes an even distribution of natural manurial matter through the soil; by removing leaves and other loose particles from the wind the decay of matter is rendered more rapid, decayed matter is distributed through the soil, and the subsoil is rendered more open for the roots of plants. The worms as a rule live in the upper soil, descending only during very cold weather. The passages left by worms are of importance to rootlets, for there they always find moisture and an atmosphere rich in carbonic anhydride, and even during winter there is always moisture to be found in these passages, for moisture rising from below and unable to pass away from the surface owing to its frozen condition, is condensed like dew on the rootlets. E. W. P.

Effect on the Fertility of the Soil produced by Covering it with Farmyard Manure. By E. Wollny (*Bied. Centr.*, 1882, 735—738).—A not unimportant effect produced by spreading dung on a field is that the soil is kept warmer in winter and cooler in summer, and this action is intensified by a larger amount of enclosed air, as in the case of straw, which shelters the ground more than well-rotted dung. Again, this covering of manure lowers the evaporation of water, which results in a higher percentage of moisture in the soil, and a consequent increase in the amount of drainage-water. These actions are not always of use, so much depending on the character of the soil. Clover, sainfoin, and lucerne are all benefited by shelter, and are enabled to start growing earlier in the spring. But if a soil, such as clay, is highly retentive of moisture, then the quantity of water retained is too great, and the crops suffer in consequence. Further, close heavy soils which are benefited by frost, whereby they are lightened, remain heavy, and if the field is on a hill-side, and soaked with water, heavy rains will wash away all nourishment. The covering of manure raises the percentage of drainage-water running from light soils, and thus there is a loss of plant food; but on soils of medium texture this method of application cannot be too strongly recommended, and no loss of ammonia will occur, except perhaps during the very hottest weather.

E. W. P.

Manuring Sugar-beet with Dung. By BESELER (*Bied. Centr.*, 1882, 784).—Sheep-dung must not be applied alone, for the high percentage of nitrogen and potash is detrimental to the quality of the sugar-beet. Cow-dung must be applied in the late summer or autumn, and allowed to lie some time before ploughing in; thus the roots obtain the nitrates in the early stage of growth, for if nitrates are applied in the later stage the yield of sugar is reduced.

E. W. P.

Manuring Alpine Meadows. By M. MÄRCKER (*Bied. Centr.*, 1882, 783).—Meadows in the Alps are generally manured with liquid manure, farmyard manure mixed with water, also with superphosphate. In East Switzerland, no potash is added to the superphosphate, but in Western Switzerland, where the soil is more chalky, potash is added. The result of such manuring is that the hay crop is at least three weeks earlier than on the unmanured meadows; a second crop may also be taken. Observations have shown that the presence of chalk is necessary for the satisfactory action of potash, and that the atmospheric ammonia absorbed by the salts of potash is converted into nitrates by the agency of the lime, whilst nitrification does not occur when lime is absent. These facts account for the unsatisfactory results obtained when potash is added to unmarled sandy soils.

E. W. P.

Employment of Peat as Litter. By A. LENNÉ (*Bied. Centr.*, 1882, 785).—The following is the analysis of horse manure when peat was used as litter instead of straw. The use of the latter is the more expensive of the two.

In 1000 parts.	Peat manure.	Straw manure.
P_2O_5	2·23	1·18
K_2O	4·37	4·50
N	6·06	3·90
H_2O	705·81	750·00

E. W. P.

Transformation of Blood into a Solid and Inodorous Manure by Means of a new Ferric Sulphate. By P. DELACHARLONNY (*Compt. rend.*, 95, 841—843).—The author states that by use of an acid ferric sulphate having the composition

$$Fe_2O_3,4SO_3,12H_2O,$$

instead of the neutral sulphate as usually employed, a coagulum is obtained from the blood at the ordinary temperature, which loses half its water by simple drainage, whilst the remaining water can be expelled to a great extent by hydraulic pressure. Great expense is thus saved, as far less evaporation is necessary. The sulphate in question can easily be obtained by oxidising ferrous sulphate with nitric acid, sufficient sulphuric acid having been added to make up the quantity required for an acid sulphate of the above composition. On concentrating the solution sufficiently, the salt crystallises out.

E. H. R.

Analytical Chemistry.

Use of Diphenylamine and Aniline in Qualitative Analysis. By C. LAAR (*Ber.*, 15, 2086—2090).—The author recommends diphenylamine in preference to aniline as a qualitative reagent for detecting (more especially) chloric acid. A solution of the base in concentrated sulphuric acid gives with dilute chloric acid a beautiful blue coloration. The author finds, however, that other oxidising agents give a similar colour. E. H. R.

Sauer's Method of Estimating Sulphur, and some Modifications of it. By W. G. MIXTER (*Chem. News*, 46, 217).—Sauer's method of burning the compound in oxygen and oxidising the sulphurous anhydride by bromine is liable to error, by reason of the uncondensed fumes of sulphuric acid which are lost; these may, however, be retained, and the amount estimated, by passing the mixed gases into a large empty flask, when the fumes remain at the bottom and slowly condense. A hydrochloric acid solution of bromine is found to be no better than bromine-water as an oxidiser, and as there is a considerable loss of bromine if the mixed gases pass through saturated bromine-water, an ordinary two-bulb **U**-tube with a constriction at one end of the horizontal part just below the bulb is used. By using this apparatus a minimum of bromine is lost, and a constant supply of it is preserved for the purposes of oxidation. E. W. P.

Testing for Barium or Sulphuric Acid. By S. PICKERING (*Chem. News*, **46**, 223).—The smallest quantity of barium which can be detected is 1 part Ba in 833,000 parts H_2O; the reaction is not rendered more delicate by the use of alkaline ammonium sulphate. The light should fall vertically, there being a black background, allowing the light to fall on a portion only of the liquid.

E. W. P.

Estimation of Sulphuric Acid in Presence of Alkaline Chlorides. By B. SCHULZE (*Landw. Versuchs-Stat.*, **28**, 161—165).—The influence of nitrates on the precipitation of barium sulphate has already been studied by Fresenius, and he recommends warming the ignited precipitate with hydrochloric acid and washing with hot water. After filtration, the filtrate is evaporated to dryness to separate dissolved barium sulphate, the latter added to the rest of the precipitate, and the whole weighed. By this means, the nitrates are removed, but he does not enter into the question as to whether chlorides are also to be found in the precipitate. In the estimation of sulphur in organic substances by fusion with potash and saltpetre, excess of alkaline salts is always present: when they are in the form of nitrates, the precipitated barium sulphate will have to be purified by the above method; the author, however, prefers to convert the nitrates into chlorides by heating to dryness with hydrochloric acid. Upon re-dissolving and filtering, the sulphuric acid is precipitated by a little barium chloride, and the precipitate after filtration ignited alone, and finally with sulphuric acid, and weighed in the usual manner. A precipitate obtained this way was treated with a few drops of hydrochloric acid, and then with boiling water, and filtered. The filtrate showed quite a strong sulphuric acid reaction with barium chloride, which could only have arisen from the presence of alkaline sulphates in the precipitate, and was of course due originally to the co-precipitation of alkaline chlorides. In general, about 3 per cent. of the original precipitate was removed in this manner. To ascertain whether barium sulphate was also removed in any quantity by this process, so as to necessitate the evaporation of the wash-water, as in Fresenius's method, further portions were treated two or three times with hydrochloric acid, and the change of weight in each case noted. The loss by the second and third treatment was however found to be so small that it could be neglected; but one treatment with acid seems to be essential in all cases where excess of alkaline chlorides is present. J. K. C.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. By T. S. GLADDING (*Chem. News*, **46**, 213).—The processes at present in use for the estimation of phosphoric acid as magnesium phosphate are not sufficiently accurate, as an error of even 0·1 per cent. in the amount of phosphoric acid can affect the value of a cargo of phosphate to the amount of several pounds. Various modifications of the usual magnesium process have been tried, and it has been found that the following is the best to employ:—

To the solution of phosphate 75 c.c. in volume and strongly ammoniacal, add magnesia mixture from a burette at the rate of one drop per second, stirring meanwhile; after the addition of the magnesia, add

25 c.c. of strong ammonia, leave the whole at rest for three hours, and wash the precipitate with strong ammonia water (1 : 3), the important point being the gradual addition of the magnesia mixture. The errors then range from 0·05 per cent. without previous precipitation as molybdate to 0·1 per cent. with previous precipitation as molybdate.

E. W. P.

Estimation of Phosphoric Acid. By L. Mayer and E. v. Schmid (*Bied. Centr.*, 1882, 784).—The solution of any superphosphate is made according to the usual method, and is then freed from silica; to 50 c.c. of this solution, 5 c.c. ammonia is added until a permanent precipitate is formed, and then 50 c.c. of a solution of ammonium citrate (1 : 1), 25 c.c. of the usual magnesia mixture, and 100 c.c. concentrated ammonia solution are to be added. The mixture is to be thoroughly stirred every ten minutes, and after three hours filtered, the precipitate washed with ammonia water (1 : 3) and ignited. The presence of much alumina and lime is detrimental to the results, but the addition of 10—15 c.c. strong ammonium chloride solution counteracts the influence of the alumina; to remove the lime, the imperfectly washed precipitate is to be dissolved in a little dilute hydrochloric acid, and reprecipitated by 30 c.c. citrate, a few drops of magnesia mixture, and 60 c.c. ammonia solution. E. W. P.

Analysis of Potassium Thiocarbonate. By Guyot-Dannecy (*J. Pharm.* [5], **6**, 336—337).—A flask of two litres capacity containing 100 grams zinc chloride dissolved in a litre of water is fitted with a doubly perforated cork. In one perforation, a funnel tube is inserted which passes to within 1 cm. of the bottom, whilst in the other a tube bent at right angles is inserted, and by its means the flask is connected with a condenser, to which is attached a receiver immersed in ice. The flask is heated to 60° in a water-bath, and the potassium thiocarbonate added in small quantities at a time; a brisk effervescence takes place with evolution of carbon bisulphide, all effervescence is allowed to cease before a fresh quantity of the thiocarbonate is added. When all the thiocarbonate is added, the distillation is continued until all the carbon bisulphide has passed over to the receiver. From its weight the quantity of thiocarbonate present is obtained: the weight of the zinc sulphide gives the proportion of other substances.

Instead of using a water-bath for heating the flask, the author prefers to suspend the flask by means of a cord over a flame, whereby it is sheltered from the chance of breakage, and allows the flask to be gently shaken without disturbing the apparatus, and thus to prevent bumping. L. T. O'S.

Normal Solutions for the Volumetric Estimation of Iron. By B. Britton (*Chem. Centr.*, 1882, 733).—The author has examined a number of specimens of iron, such as are generally used for standardising, and found them much more impure than is generally supposed. The average percentage of iron found in a number of pianoforte wires was 98·76. The purest sample of bar iron from

Norway and Sweden contained, however, 99·6 per cent. iron. Iron salts were found to be still less trustworthy than metallic iron.

A. K. M.

Sources of Error in Estimating Iron in Ores by the Stannous Chloride Method. By K. F. Föhr (*Dingl. polyt. J.*, **246**, 236).—According to the author very appreciable quantities of ferric chloride are volatilised and lost whilst an iron ore is being heated with hydrochloric acid, especially when the operation is conducted in an open vessel. In the case of some ores, this source of error is, however, counterbalanced by another error, due to the presence of manganese dioxide. In this case, the liberated chlorine remains to a slight extent in solution, and may therefore make up for the loss of ferric chloride.

A. K. M.

Volumetric Estimation of Peroxides. By W. Diehl (*Dingl. polyt. J.*, **246**, 196—200).—The author has made direct comparisons between Bunsen's method of *distilling* the peroxide with hydrochloric acid, passing the liberated chlorine into solution of potassium iodide, &c., and Mohr's modification, according to which the peroxide is *digested* with the hydrochloric acid and potassium iodide. He has also tried the effect of substituting other acids for hydrochloric acid. The substances experimented with are potassium dichromate, the two oxides of manganese, Mn_3O_4 and MnO_2, and lead dioxide. His results show that the more simple method of Mohr can be relied on, and that in some cases other acids can be employed in place of hydrochloric acid. The same results are obtained with potassium dichromate, whether hydrochloric or oxalic acid is used, but with the oxides of manganese the latter acid cannot be employed. Acetic acid can be used in the case of manganese dioxide, and with advantage also in that of lead dioxide. The author also finds that the presence of iron does not interfere in estimating the available oxygen in pyrolusite by this method.

A. K. M.

A Colour-method for the Estimation of Manganese. By A. Ledebuhr (*Chem. Centr.*, 1882, 733).—This method depends on the conversion of manganese into permanganate, and is recommended by Goetz for the estimation of that metal in iron and steel. He dissolves 0·2 gram of the iron to be tested in nitric acid, and dilutes with distilled water to 100 c.c. To 10 c.c. of this solution 2 c.c. of nitric acid are added, the mixture heated to boiling, and then well shaken with an excess of lead dioxide. After again warming, the liquid is allowed to cool and is filtered through asbestos into a burette. Potassium permanganate solution of known strength is poured into a similar burette, and water added until the same tint is obtained as in the first burette. The strength of the solution is calculated from the amount of dilution necessary.

A. K. M.

Haswell's Method for the Volumetric Estimation of Mercury. By H. v. Jüptner (*Chem. Centr.*, 1882, 727).—To a solution containing mercuric chloride, standard solution of ferrous sulphate, acidulated with sulphuric acid, is added in excess. The solution is then made strongly alkaline with potash, and afterwards acidulated with a considerable excess of hydrochloric acid. On well shaking, the precipitate of mercurous chloride becomes quite white. The excess of ferrous salt in the solution is next oxidised by standard permanganate, and on then adding a few drops of stannic chloride solution and a further quantity of permanganate, the mercurous chloride becomes converted into mercuric chloride, the disappearance of the precipitate indicating the completion of the reaction. Each molecule of permanganate, added after oxidation of the excess of ferrous sulphate, corresponds with 1 atom of mercury. A. K. M.

Separation of Silver from Alloys. By SOLTHIEN (*Arch. Pharm.* [3], **20**, 201).—The author simplifies the process published by him in this Journal, 1880. The alloy is dissolved in the minimum quantity of crude nitric acid, and then decomposed by a strong excess of ammonia; in this liquid placed in cylinders is suspended strips of copper, upon which the silver will be deposited. E. W. P.

Use of Oxalic Acid as a Test for Arsenites in Alkaline Salts. By C. PATROUILLARD (*Pharm. J. Trans.* [3], **13**, 362).—An answer to a paper in this Journal by Naylor and Braithwaite, who affirmed that, contrary to the statement of the author, oxalic acid does not reduce arsenic acid. The author repeats his statement made in 1874, that oxalic acid does reduce arsenic acid in combination, and the more completely the more neutral the combination. In the original paper the uncombined acid was not referred to. E. W. P.

Detection of Iodoform, Naphthol, and Chloroform in the Fluids and Organs of the Animal Body. By S. LUSTGARTEN (*Monatsh. Chem.*, **3**, 715—722).—Iodoform and naphthol being now used, as well as chloroform, in medical practice, it becomes a matter of importance to be able to detect them in animal fluids and organs.

1. *Iodoform.*—The recognition of this substance by its saffron-like smell, and its peculiar crystallisation in six-rayed stellate groups, being often greatly hindered by the presence of other compounds occurring in animal liquids, the author directs attention to a new reaction not open to this objection. When iodoform is added by small quantities to a solution of phenol (20 grams) and sodium hydroxide (40 grams) in 70 c.c. water, heated on the water-bath or to 120° in a paraffin-bath, it quickly dissolves and colours the liquid red; and if the heating be continued till about 60 g. iodoform have been dissolved—which takes several days at the heat of the water-bath, or a shorter time in the paraffin-bath, and the solution be then acidulated with hydrochloric acid and distilled with steam—the excess of phenol will pass over, probably together with salicylic and parabenzoic aldehydes, while in the flask there will remain a resin, soft and black-brown while warm, brittle and red-brown after cooling. This resin dissolves easily in alcohol, with yellowish, and in alkalis with a fine crimson colour, which disappears on adding a slight excess of acid, but reappears on neutralisation; the alkaline solution is coloured dark-red by potassium ferrocyanide. The product of the above reaction, like that resulting from the action of an alkaline phenate on chloroform, doubtless consists of rosolic acid and allied bodies. To

exhibit the reaction on a small scale, an alkali phenate is placed at the bottom of a short test-tube, in very small quantity only, because the brown colour which these salts acquire when heated, would mask any slight red coloration that might afterwards be developed. An alcoholic solution (1—3 drops) of iodoform is then added, and the mixture is cautiously heated over a small flame; whereupon, after a few seconds, there appears at the bottom of the tube a red deposit, which dissolves with crimson colour in a few drops of dilute alcohol.

To detect iodoform in urine by this reaction, the liquid is distilled with steam till about 50 c.c. has passed over, and the distillate, mixed with a small quantity of potash-ley, is shaken with ether in a tap-funnel; the ethereal extract is evaporated to dryness; the residue treated with absolute alcohol; and the alcoholic solution tested with phenol as above.

For detection in blood, the liquid, diluted with 2 vols. water, is made alkaline and distilled with steam, and the distillate is treated in the manner just described, excepting that the ethereal extract separated from the aqueous alkaline solution is mixed with a little sulphuric acid to neutralise any amines that may have passed over in the distillation. The smallest quantity of iodoform that can thus be detected in blood is 4—5 mgrms.

In the reaction above described, the phenol may be replaced by resorcinol, but not by quinol or catechol.

2. *Naphthol.*—When chloroform is added to a solution of α- or β-naphthol in strong potash-ley, and the liquid is heated to about 50°, a fine Prussian-blue colour is developed, changing, in contact with the air, into blue-green, green, green-brown, and finally brown. The same reaction is produced by crystals of chloral hydrate, which, in presence of the alkali, is converted into formic acid and chloroform. To detect naphthol in urine by this reaction, the liquid is acidulated with hydrochloric acid and distilled with steam till about half has passed over; the distillate is shaken with ether; the ether evaporated; and the residue, dissolved in potash, is tested for naphthol as above. As, however, the alkaline solution is always brownish, the colour produced on adding the chloroform inclines more or less to green. The residue in the retort may also be tested for naphthol in a similar manner; but as its ether solution is always strongly coloured, it is necessary to evaporate this solution to dryness, dissolve the residue in alcohol, decolorise with animal charcoal, warm, filter, evaporate the filtrate to dryness, and test the residue as above.

3. *Chloroform.*—This compound may be detected in animal fluids exactly in the manner just described, with addition of naphthol instead of chloroform to the alkaline solution. H. W.

Reducing Power of Grape-sugar for Alkaline Copper Solutions. By F. ALLIHN (*Chem. Centr.*, 1882, 731).—Soxhlet and others have shown that the power of grape-sugar to reduce Fehling's copper solution is not constant, but varies under different conditions. The author has examined the method described by Degener (Abstr., 1882, 104), but finds it open to the same objection as Fehling's method. A. K. M.

Amount of Extract in Wines (Tyrolese). By E. Mach and C. Portele (*Bied. Centr.*, 1882, 773—775).—In thin sour wines, 0·1 per cent. sugar is perceptible by the taste, and in some cases as little as 0·05 per cent. can be detected. The factors influencing the percentage of extractive matter are many: continued dryness lowers extract and acidity; old wines are poorer in extract than new; as the quality of a red wine rises so does the percentage of extract, reaching even higher than 4 per cent. The lowest observed (but there may be lower) percentage of extract in pure white wine was 1·42 per cent.; in red, 1·76 per cent. E. W. P.

Rapid Method of Estimating Salicylic Acid in Wines, &c. By A. Remont (*Compt. rend.*, **95**, 786—788).—The author prepares a solution of salicylic acid to serve as a standard of comparison. 50 c.c. of a liquid analogous to that to be tested are taken, and into it is introduced the maximum amount of salicylic acid allowed by law. This is then shaken several times with 50 c.c. of ether, and the whole left at rest for a time. 25 c.c. of the ethereal solution are then taken and evaporated at a temperature below its boiling point in the presence of 10 c.c. of water, so that the latter dissolves the salicylic acid from the ether as it volatilises. The 10 c.c. of water are then made up to 25 c.c., and the liquid thus prepared is used as a standard of comparison.

In testing a wine, for example, 10 c.c. are treated with 10 c.c. of ether. 5 c.c. of the ethereal solution are then evaporated, as described above, with 1 c.c. of water, which is then made up to 5 c.c. This is placed with the wash-water in a glass vessel of 30 c.c. capacity and of 15 mm. internal diameter, the standard liquid being placed in an exactly similar vessel. A solution of ferric chloride, containing 10 grams to the litre, is then added drop by drop to both vessels, until the colour no longer deepens (three or four drops usually suffice). The comparison of the depth of tint is sufficient to decide whether the liquid tested contains more or less salicylic acid than the standard.

It is always advisable to take as a standard of comparison a liquid similar to that to be tested. The method is applicable, without modification, to fruits and syrups. E. H. R.

Occurrence of Myronic Acid and Estimation of the Corresponding Mustard Oil in the Seeds of Cruciferæ and in Oil-cakes. By V. Dircks (*Landw. Versuchs.-Stat.*, **28**, 179—200).—The amount of mustard oil is determined by oxidation with alkaline solution of permanganate, and precipitation with barium chloride. Test experiments were made with mustard oil, which was in some cases directly oxidised, and in others distilled into the oxidising solution. In the former method, a weighed quantity of oil was introduced into a thick flask with excess of alkaline permanganate solution, the flask sealed up, thoroughly shaken, and heated for some time on a water-bath, until the green colour had disappeared, and it was again red. It was then opened, the contents evaporated to dryness, and taken up with hydrochloric acid, again evaporated, dissolved, and precipitated hot with barium chloride. Comparative experiments with nitric acid as oxidising agent were fairly satisfactory. In the distillation method the oil was weighed out into a tubulated retort connected with a condensing apparatus and receiver with a doubly-bored cork, into the other bore of which a Will-Varrentrapp nitrogen apparatus bent at right angles was passed, connected at its other end with another of the same, and the whole apparatus communicated with an air-pump. The receiver and nitrogen bulbs were filled with permanganate solution, and after the oil was distilled over, were treated as before. Experiments showed that the sulphur determinations were rather too low; and this the author thinks is due to the excess of alkaline chlorides present, in which, as some test experiments show, barium sulphate is slightly soluble, 0·025 gram KCl and 0·175 gram NaCl representing about 5·5 mgrms. $BaSO_4$.

The mustard oil was determined by this method in cake and seeds of black mustard and rape, and in the seeds of *Sinapis arvensis.* The finely-powdered substance was mixed with ten times its weight of water, and allowed to stand nine hours at 50°, this being necessary to allow of the easy distillation of the oil. It was then steam-distilled, a current of air being drawn through at the same time to ensure thorough mixture, the sulphuric acid being estimated as before. By observing these precautions, constant and trustworthy results may be obtained. The thorough stirring of the contents of the retort is absolutely essential to expel the whole of the oil, and this is best done by a tube stopped up at the end and perforated with small holes, so that the current of air is well divided in passing through the liquid. The amount of fat present and the relative quantities of substance and water do not seem to have any effect. The following percentage quantities of mustard oil were found: Black mustard seed-cake, 1·39; rape seed from 0·018 to 0·037; rape seed cake, 0·020 to 0·109; yellow mustard seed cake, 0·018; turnip seed, 0·038; seeds of *Sinapis arvensis*, 0·006. In the case of rape seed cake, the quantity of oil decreases apparently with the age of the cake. Whether this is due to a decomposition of the myrosin or of the ferment, the author is still engaged in determining. As the seeds of the wild plant *Sinapsis arvensis* are used for adulterating rape seed, and as the former contain scarcely any mustard oil, the amount of the latter in rape seed may be almost taken as a standard of purity, if it should be found that the amount of oil does not greatly vary in samples from different localities.

J. K. C.

Estimation of Milk Fat. By R. EMMERICH (*Bied. Centr.*, 1882, 762).—Emmerich has compared the gravimetric estimation of milk fat with the processes of Soxhlet, Hoppe-Seyler, and Feser. Soxhlet's and Hoppe-Seyler's method gives a difference of 0—0·4 per cent., whilst the error of Feser's optical method is on the average 0·25 per cent. too high.

E. W. P.

Analysis of Butter. By A. v. BASTELAER (*Chem. Centr.*, 1882, 731).—A weighed quantity of butter is heated at 100—120°, the loss in weight indicating the amount of water present. The fat is then extracted by means of benzene, and its amount found on weighing the dried residue. This is finally ignited, the loss indicating the caseïn, and the ash the sodium chloride. The presence of oleomargarine can be detected by its odour when butter is heated to drive off the water, and also by the high percentage of caseïn due to the admixture of milk.

A. K. M.

Butter Testing. By J. Munier (*Chem. Centr.*, 1882, 730).—The author has examined a number of different sorts of butter in each month from October, 1880, to February, 1882. He adopted Reichert's modification of Hehner's method, and found that the proportion of volatile acids differed from time to time. It was lowest between October and January, increased from February to August, and afterwards again diminished. The author concludes, therefore, that in reporting upon a sample of butter it will be necessary to make allowance for the time of year at which the butter was made.

A. K. M.

Margarimeter of Leune and Harbulet. By D. Gäbel (*Bied. Centr.*, 1882, 766).—This instrument resembles a hydrometer, the zero of the instrument being that point to which it sinks when floating in butter heated by the vapour from boiling water; the other degrees are supposed to indicate the percentages of added fats; the results obtained by its use are very untrustworthy, for in one case it indicated 20 per cent. of foreign fats present in perfectly pure butter, moreover, a very slight variation in the temperature greatly affects the readings. E. W. P.

Albumin from Urine, coagulated by Nitric Acid and soluble in Alcohol. By L. Garnier (*J. Pharm.* [5], **6**, 339—340).—In examining for albumin the urine of persons to whom turpentine and balsams have been administered, it has been shown that nitric acid precipitates resins soluble in alcohol simultaneously with the albumin. In two cases of nephritis, the urine treated by Heller's process gave precipitates soluble in alcohol, although the patients had not taken turpentine or balsams. The reactions of the urines are as follows: The albumin is coagulated by boiling alcohol, nitric acid, trinitrophenol, and gives a red colour with Millon's reagent, but the precipitate with nitric acid is soluble in alcohol. It is necessary, therefore, to avoid confounding such precipitates with resinous matters.

L. T. O'S.

Estimation of Humus in Soils. By G. Loges (*Landw. Versuchs-Stat.*, **28**, 229—245).—Of the three methods usually employed for the estimation of humus, namely, loss on ignition, oxidation with chromic acid, and combustion with cupric oxide, the intermediate one is usually preferred, as being both rapid and safe. Later investigations, however, by Warington and Peake (this Journal, p. 617) have shown that lower results are obtained by oxidation with chromic acid than by ordinary combustion; the author was able to put this to the test in a long series of experiments. In employing the chromic acid method, the proportions given by Wolff were strictly followed out, and the carbonic anhydride was absorbed in a Pettenkofer's apparatus. For combustion, the weighed quantity of soil was treated with a dilute solution of phosphoric acid, and dried over a water-bath: it was then powdered, mixed with cupric oxide, and transferred to a combustion-tube open at both ends. The products of combustion were first passed through a Fresenius' drying tube, with moist wadding at the top, which was found quite sufficient for absorbing any oxides of nitrogen which might be formed: the carbonic anhydride being absorbed by a Pettenkofer apparatus. Samples of 40 different soils were analysed by both methods, as well as by loss on ignition, and the conclusions of Warington and Peake were confirmed; oxidation by chromic acid giving on the average only 84 per cent. of the carbonic anhydride yielded by combustion, the extreme limits being 96 and 64 per cent.

In nearly all the experiments, the estimation of humus by loss on ignition gave results very much too high, the only exceptions being in the cases of moor and certain sandy soils.

The deficit in carbon exhibited by the chromic acid method is attributable to two causes: either there are certain compounds in soil not attacked by chromic acid, or else the whole of their carbon cannot be converted into its ultimate oxidation-product. Experiments were therefore made with certain substances, of which presumably the humus is compounded, such as fibre, roots, &c.; the fibre was found to be fully oxidised, but not the roots; humic acid yielded 91 per cent. of its carbon by this method, but in this case the formation of 3 per cent. of acetic acid was observed, as well as the production of a higher carbon acid. In the insoluble residue also, a small proportion of unattacked carbon was found, which probably had existed in the form of brown coal. J. K. C.

Technical Chemistry.

Absorption and Utilisation of the Sulphurous Anhydride contained in Furnace Gases. (*Dingl. polyt. J.*, **246**, 228—236.) —According to Hasenclever, sulphurous anhydride and the vapours of sulphuric acid can be removed from a mixture of gases by sulphuric acid. Precht recommends cooling the gases to about 100°, and then passing them over moistened magnesium hydroxide previously mixed with 1 to 2 per cent. coal. The product consisting principally of magnesium sulphite is then heated, and the evolved sulphurous anhydride is used for the manufacture of sulphuric acid. The addition of the coal is to help the decomposition of a small quantity of sulphate which is formed on igniting the sulphite. Aluminium hydroxide can be substituted for magnesium hydroxide, but works more slowly. Schnabel employs zinc oxide and basic zinc carbonate for absorbing sulphurous anhydride. The zinc oxide must be kept continually moistened with water to prevent its becoming coated with a layer of sulphite. As in Precht's method, coal must be mixed with the zinc oxide, so that after a time the latter becomes contaminated with a very appreciable amount of ash. In order to remove this, the mixture is again exposed to furnace gases and the resulting zinc sulphite separated from the ash by solution in water. The solution is used instead of water for moistening the zinc oxide in the next operation. Fleitmann passes the furnace gases together with air through a furnace containing a mixture of oxide of iron and coal; ferrous sulphide being produced by the reducing action of the latter.

According to Kosmann's method, the gases are submitted to the action of steam and water, by which a part of the sulphurous anhydride becomes oxidised and converted into sulphuric acid. The remaining sulphurous anhydride is then decomposed by a solution of hydrogen calcium sulphide, thus:—

$$5SO_2 + 2H_2CaS_2 + 2H_2O = 7S + 2CaSO_4,2H_2O.$$

A. K. M.

Antiseptics. By A. MAYER (*Bied. Centr.*, 1882, 777).—Stuttgart "preservative salt" consists of a mixture of 2 parts boric acid and 3 of sodium chloride. "Septon," to preserve cheese from mould, &c., is only a mixture of equal parts of acetic acid and water. "Glacialin salt mixture" and "glacialin rose-extract" are both mixtures of boric acid with borax, the second mixture being intended to preserve meat without altering its colour. E. W. P.

Disinfectants. By R. KOCH (*Chem. Centr.*, 1882, 509—512).—The mode of action of individual disinfectants has not been sufficiently investigated, because of our incomplete knowledge of the infectious matter. An *efficient disinfectant* ought, in the author's opinion, to kill all living organisms and render all germs innoxious within twenty-four hours. To test a disinfectant thoroughly, its action must be tried on all disease-producing matter, and under conditions exactly similar to those in which it is used in practice. Thus a disinfectant which does not kill fungi would be of no use in contagious skin diseases, whilst one which did not destroy bacteria would be inefficient in diseases caused by these organisms. The author has investigated the action of disinfectants on bacteria. In these experiments, he has taken great care in the cultivation of bacteria, selecting those which are seldom found in the air. Experiments on the development of bacteria were made on solid nutritious substances. The chief points observed are—1. If all the organisms are killed. For this it is sufficient to note the action on the most persistent, viz., the bacilli spores. 2. The facility with which the development of micro-organisms in favourable nutritive solutions is prevented.

Carbolic acid is almost without action on spores of *Anthrax bacilli*, *e.g.*, the bacilli spores retained their vitality after being five days in a 2 per cent. solution, and in another experiment 15 days in a 1 per cent. It is, however, destructive to the living micro-organism, for 1 gram of pure carbolic acid can completely prevent the development of *Anthrax bacilli* in 850 c.c. of a nutritive solution, and even shows a marked effect in 1250 grams. Its action on other bacteria is less marked. Carbolic acid in the form of vapour does not affect the germinating power of bacilli spores at the ordinary temperature, even after being in contact with them $1\frac{1}{2}$ months; but at 55°, in half an hour many of the spores are destroyed, in three hours scarcely any germinating power is discernible, whilst after five or six hours their destruction is complete. Raising the temperature does not increase the activity. Carbolic acid vapour can only be conveniently used for small objects.

The above results are obtained with aqueous solutions of carbolic acid. Solutions in oil or alcohol do not show any antiseptic properties; this is also the case with other disinfectants, *e.g.*, salicylic acid, thymol, &c., except when they are used with substances containing water, such as flesh, &c., when some of the disinfectant becomes active.

Sulphurous acid, either alone or mixed with water or steam, does not disinfect dry objects. If, on the other hand, the object is first moistened with sulphurous acid and then treated, brisk action is observed; it does not, however, destroy all germs. Its disinfecting action is thus uncertain, and is not to be depended on.

Amongst many others, *zinc chloride* and *glycerol* are proved to be without effect. In fact the only *effective disinfectants* (see above) besides *chlorine*, *bromine*, and *iodine*, are *corrosive sublimate*, *osmic acid*, and *potassium permanganate*. The last-mentioned only acts in strong solutions (5 per cent.). Bromine and osmic acid are too expensive. Corrosive sublimate is very poisonous; its action, however, is so very quick that it could be used for solid substances, which could then be washed well with water.

Substances effective in checking the germination of spores are corrosive sublimate, some essential oils, thymol, and amyl alcohol.

D. A. L.

Effect of the Presence of Sheet Zinc in Boilers, and a Method for Preventing Explosions. By TRÈVE (*Compt. rend.*, **95**, 522—524).—When sheet zinc is placed in iron boilers, galvanic action is set up, and the water is slowly but continually decomposed. The oxide of zinc which is formed neutralises the fatty acids in the feed water, producing zinc soaps, which surround the boiler tubes and prevent the adherence of salts deposited by evaporation. The continuous evolution of hydrogen might be expected to assist ebullition and prevent superheating of the water. Since, however, it sometimes seems to fail in producing this effect, the author proposes to inject into the water in the boiler a stream of air or a non-oxidising gas, such as carbonic anhydride, in order to keep up ebullition and prevent superheating, which is undoubtedly the cause of many boiler explosions.

C. H. B.

Industrial Value of Crude Alunite. By P. GUYOT (*Compt. rend.*, **95**, 693—695).—The crystallised portions of the alunite from the Tolfa Mines contain as much as 32 per cent. of the base, but the average composition of the mineral is—

Al_2O_3.	SO_3.	K_2O.	H_2O.	Fe.	SiO_2.
27·60	29·74	7·55	11·20	1·20	22·71 = 100·00

When the mineral is gradually broken up, the fine powder is richer in alumina and potash than the coarser fragments. In the following table of analyses the numbers indicate the degree of fineness, the finest powder having the highest number:—

	First crushing.			
	1.	2.	3.	
Calcination	23·00	37·60	41·00	per cent.
Crude mineral.				
Alumina	17·81	25·40	31·00	,,
Potassium sulphate	8·40	12·20	15·30	,,
Calcined mineral.				
Alumina	23·13	40·70	44·90	,,
Potassium sulphate	10·91	19·50	22·17	,,

	Second crushing.				
	I.	II.	III.	IV.	
Calcination	22·40	24·40	33·90	34·60	,,
Crude mineral.					
Alumina	17·80	23·67	31·75	32·29	,,
Potassium sulphate	8·51	11·95	15·31	15·40	,,
Calcined mineral.					
Alumina	22·93	31·31	48·04	49·40	,,
Potassium sulphate	10·92	15·92	23·16	23·56	,,

C. H. B.

Gutzkoff's Process for the Separation of Gold in California. (*Chem. Centr.*, 1882, 508—509.)—The principal materials for separation are—1. Gold bar, containing 2 parts gold and 3 parts silver; this is granulated before being dissolved. 2. Silver plates with 2 to 10 per cent. of gold. 3. Silver plates mixed with copper; before dissolving, fine silver is added to these to reduce the percentage of copper to 12 to 8.

The alloys are treated with boiling sulphuric acid in covered vessels of cast iron (containing 2 to 4 per cent. of phosphorus, so as to better resist the action of the acid), capable of holding a charge of 100 to 150 kilos. of alloy. The pots being partially filled with acid (the acid reservoirs are so arranged that the pots can be easily filled) and boiled, the charge is put in; after 15 minutes the necessary additional quantity of acid is added, and the whole boiled for three to four hours. The hot liquid is then syphoned off by means of a vacuum arrangement into shallow iron tanks, capable of holding five charges, in which there is sulphuric acid of 58° B. in the proportion of 0·5 c.m. for every 100 kilos. of alloy at 110° C.; here the liquid remains at this temperature until clear. The gold remains behind in the pots; there is also some deposited along with graphite and lead sulphate in the tanks. The hot clear liquid containing silver, copper, and iron sulphates is run into vessels and cooled to 30—40° by means of a current of water, when silver sulphate crystallises out; the copper sulphate is syphoned back into the tank. The silver sulphate crystals when drained are ladled into wooden vats lined with lead, having a false bottom with a tap underneath. A hot saturated neutral solution of ferrous sulphate is poured over the crystals, and ultimately run out by the tap. The copper sulphate is dissolved first; the liquid is therefore blue; the silver sulphate is then reduced, the liquid becoming brown, and at the end of the operation it is green; the reduction occupies 3—4 hours. The liquids are separated; the brown one holds in solution $2\frac{1}{2}$ per cent. of silver; the (green) ferric solution is treated with scrap iron, and is returned to the ferrous sulphate store tank. The gases and vapours given off during the dissolving are condensed in leaden chambers, towers, and shafts. A figure is necessary for an efficient and clear description of the apparatus employed.

D. A. L.

Deplastering of Wines. By Blarez (*J. Pharm. Chim.* [5], **6**, 267—270).—The author confirms the opinions of Calles (Abstr., 1882, 1336) on the deplastering of wines, maintaining that from a hygienic point of view the deplastering is more injurious than the plastering—(1) owing to the use of poisonous barium salts, and (2) because in the decomposition of the potassium sulphate by the barium chloride the potassium chloride is injurious. L. T. O'S.

Application of Strontium Chloride in Purifying Syrups. By G. Kottman (*Dingl. polyt. J.*, **245**, 395).—The juice obtained by diffusion or pressure is treated with calcium chloride until the acids forming insoluble calcium salts have been precipitated. The filtrate is then saturated with lime and again filtered. To the solution a sufficient quantity of strontium chloride is added, when a further separation of acids in the form of insoluble strontium compounds is effected. The author recommends to precipitate with calcium chloride in the first place, add strontium chloride after removing the calcium precipitate, and finally saturate the mixture with lime. Strontium chloride may be employed also for the purification of syrups.

D. B.

Recovery of Sugar from Molasses by means of Strontium Hydroxide. By C. Scheibler (*Ding. polyt. J.*, **245**, 430—433, 465—469, and 506—508).—The author has recently patented an improved process for the recovery of sugar from molasses by means of strontium hydroxide, according to which molasses is diluted with water, the degree of dilution depending on the composition and the percentage of sugar contained in the solutions, and mixed with strontium hydroxide in the proportion of 3 mols. to 1 of sugar. The solution is then heated, and the strontium saccharate separated in the form of a heavy sandy precipitate. By diffusing this through warm water it splits up into a less basic saccharate and strontium hydroxide. The filtrate from the saccharate precipitate contains only from 0·3 to 0·8 per cent. of sugar. The composition of the saccharate is represented by the following formula: $C_{12}H_{22}O_{11},2SrO,xH_2O$. On throwing it into water it suffers the following decomposition:—

$$3C_{12}H_{22}O_{11},2SrO,xH_2O = 4H_2SrO_2,8H_2O + 3C_{12}H_{22}O_{11},2SrO + (x-9)H_2O.$$

The paper, which is of considerable length, gives full particulars relating to the entire method of working, and describes in detail the preparation of the strontium hydroxide. D. B.

Preparation of Brown and White Cellulose. (*Dingl. polyt. J.*, **245**, 520.)—According to Rasch and Kirchner, the steamed blocks of wood are broken up into pieces of the size of a pea by means of a chopping machine; they are then crushed between rollers, and the fibres disintegrated in a centrifugal rag-engine. The product thus obtained is used for the preparation of pasteboard and coarse kinds of paper. D. B.

Preparation of the Homologues of Phenol, Naphthol, and Resorcinol. (*Dingl. polyt. J.*, **246**, 201.)—Equivalent quantities of a phenol and an alcohol are heated with zinc chloride until two layers form, and the oil is then rectified. The reaction takes place thus:—

$$C_6H_5.OH + Et.OH = C_6H_4Et.OH + H_2O.$$

A. K. M.

Becker's Creaming Process. By W. Fleischmann and R. Sachtleben (*Bied. Centr.*, 1882, 770).—The authors find that no special advantage is gained by employing the above process, as the amount of cream removed is no greater than that obtained by the older methods, and moreover it is uncertain and of long duration. One advantage is, however, gained—that the coagulum formed by the rennet is not in thick lumps, but in fine flocks, which is the more digestible form of caseïn. E. W. P.

Jakobsen's Testing-churn. By W. Fleischmann and R. Sachtleben (*Bied. Centr.*, 1882, 763).—The results obtained by the use of this apparatus (*ibid.*, 1876, 400, and 1877, 224) are not trustworthy, as the percentage of butter yielded falls with the weight of milk experimented on, and the greatest yield is obtained by the more rapid rotation of the apparatus. Sour milk gave the most trustworthy results. E. W. P.

On Creaming. By D. Gäbel (*Bied. Centr.*, 1882, 626).—The author adheres to his opinion, previously expressed, that it is quite unnecessary to cool milk before creaming. E. W. P.

Preservation of Milk, &c. By Barff and others (*Bied. Centr.*, 1882, 627—630).—Barff preserves milk, &c., by the addition of a solution of boroglyceride in water (1 : 20—60). Le Bon employs a calcium and sodium compound of boroglyceride. Mayer and Portele find that salicylic acid must not be added to milk or butter, as it imparts an unpleasant taste. To preserve milk for transport, A. Meyer keeps it at 50° by steam for three hours, introducing sodium benzoate (0·8 gram per litre), or half as much boric acid with or without sodium chloride. He believes the benzoate to be harmless, but cannot say as much for the boric acid, which, however, only costs a sixth as much as the benzoate. E. W. P.

Preservation of Milk. By B. DIETZELL (*Bied. Centr.*, 1882, 789).—The method proposed is almost identical with that proposed by Scherff (Abstr., 1882, 1016). E. W. P.

Preservation of Milk. By BUSSE (*Bied. Centr.*, 1882, 789).—To every litre of milk 1—2 teaspoonfuls of hydrogen peroxide is to be added. Butter made from milk containing hydrogen peroxide remains for a long time without becoming rancid. E. W. P.

Preserved Milk, &c. By W. FLEISCHMANN (*Bied. Centr.*, 1882, 771—773).—In this report from the Experimental Station in Raden, the composition of milk is reported as follows:—

	Morning.	Evening.	Mid-day.
Dry matter	11·332—12·852	11·203—12·694	11·376—12·557
Fat............	2·816— 4·015	2·276— 3·858	2·820— 3·790

The composition of two samples of Swiss condensed milk without added sugar, but with added benzoic acid, was:—Water, 52·315; fat, 13·090; albumin, 12·130; lactose, 17·434; ash, 2·788; benzoic acid, 1·740. Loss, 0·503.

Comparisons of estimation of milk by the gravimetric process with those obtained by the use of Soxhlet's method and the lactobutyrometer (Schmöger's modification) yielded good results, but Mittelstrass' optical method gave results varying between +0·37 and −0·26. Pepsin causes caseïn to separate more rapidly from milk than when rennet is used, but there is no perceptible difference in the appearance of the curds thus formed. E. W. P.

On Milk. By M. SCHRODT and others (*Bied. Centr.*, 1882, 625).—Schrodt finds that the addition of saltpetre to milk which tastes of turnips does not remove that unpleasantness, as has been stated. Lézé placed milk in contact with several odorous gases, which communicated their taste to the milk; ammonia rendered milk gelatinous and thick. It occasionally happens that butter during churning appears as a flocculent coagulum. H. Schultze's analyses show that it consists of 12 per cent. water, 11 per cent. caseïn, and 75 per cent. fat; the cause is probably the presence of excess of acid in the cream, due to carelessness, &c. E. W. P.

Preservation of Butter. By W. HAGEMANN (*Landw. Versuchs.-Stat.*, **28**, 201—227).—The peculiar smell and taste of rancid butter is generally assumed to be due to the presence of free butyric acid, of which only a very small quantity is required to give fresh butter similar properties to those of rancid. In approaching the question as to the origin of the free acid, two theories present themselves: either it arises from a butyric fermentation at the expense of the lactose or glycerol, or else is the product of chemical changes, and is set free from certain glycerides in the butter. In carrying out experiments suggested by the former of these views, bacteria were obtained from a mass of cane-sugar undergoing butyric fermentation; these were introduced into quantities of pure butter fat which had been washed and freed from water, salts, and lactose: nutriment was added in the form of lactose, and ammonium and other salts necessary for the growth of the cells. The conditions of experiment were varied greatly, but in no instance was the fat turned rancid, even after standing many weeks: and the addition of a small quantity of rancid to fresh butter did not appear to accelerate the process. Analysis also showed that the quantity of glycerol in fresh and rancid butter was as nearly as possible the same, hence the presence of free acid could not arise from a decomposition of the glycerol. From these facts the author concludes that the rancidity of butter is not due to butyric fermentation.

In testing the reaction of fresh and rancid butter with litmus-paper, it was noticed that the former gave reddish spots in all cases when the cream from which it was prepared had become sour owing to lactic fermentation of the milk-sugar: rancid butter, however, gave in all cases a most powerful reaction. About half a per cent. of undecomposed lactose is contained in fresh butter, and its fermentation appears to proceed further as the butter becomes rancid: the question then suggested itself whether this rancidity was not actually due indirectly to the lactic acid formed, and the action of this on fresh butter was therefore studied. Experiments made at the close of autumn showed that fresh butter when mixed with lactic acid becomes rancid very quickly, and at a temperature too low for the growth of bacteria. Pure butter fat was dissolved in ether, a few drops of lactic acid were added, and the whole allowed to stand over night: the ether was then driven off at a low temperature, and the residual fat proved to be strongly rancid. In order rightly to comprehend these results, the action of lactic acid on mono- and tri-butyrin was studied; and it was found that butyric acid was in every case set free, as shown by its smell and reaction with litmus-paper: the amount varying with the temperature, and being greater with tri- than mono-butyrin; these results indicate that the rancidity of butter is due to the formation of lactic acid by a process of fermentation from the milk-sugar contained in the butter.

The liability of butter to become rancid might be prevented either by removing the glycerides of the volatile acids, by creaming milk fresh from the cow with the addition of a small quantity of caustic soda, or by removing the milk-sugar itself; but at present no successful practical methods of performing either separation have been described: washing with water gives a tolerably stable product, but, if pushed too far, the aroma is lost. The ferment which acts on the lactose appears to be organic, and not a chemical ferment such as diastase, myrosin, &c., as its activity is entirely restrained by chloroform; the amount also of acid formed does not vary with the quantity of the ferment, and increases instead of diminishing the longer the ferment remains in the lactose solution. This behaviour can only be due to the presence of some organised bodies which increase in numbers as the fermentation proceeds, the amount of acid increasing in like proportion. J. K. C.

Cheese, Oleomargarin-cheese, &c. By P. VIETH and others (*Bied. Centr.*, 1882, 764).—The following is the composition of spurious American cheeses made from grease and oleomargarin :—

	Grease.	Oleomargarin.
Water	38·26	37·99
Fat..............	21·07	23·70
Caseïn, &c.	35·55	34·65
Ash..............	5·12	3·66
	100·00	100·00
The extracted fat contained—		
Insoluble fatty acids	90·46	91·82
Butter fat	63·00	46·00
Foreign fat	37·00	54·00

Schmöger reports that some cheeses made from milk that has passed through a centrifugal machine become blue throughout the whole mass. Gäbel has noticed the same appearance, and attributes it to unclean vessels which retain some organisms to which the production of the blue colour is due. E. W. P.

Injurious Action of a Cupriferous Oil used in Turkey-red Dyeing. By E. SCHAAL (*Dingl. polyt. J.*, **245**, 516).—In dyeing vegetable fibres with alizarin, the yarn is subjected to a preliminary mordanting process, consisting in treating it with soda or soluble glass, drying, and bringing it into a bath of Turkey-red oil (*huile tournante*), potash-ley, and sheep's dung. After drying, the yarn showed a number of places full of holes. On examination, it was found that the destruction was due to the presence of copper in the oil, the iron tank used for storing the warm oil being fitted with a gun-metal cock. When this was replaced by an iron stopcock these appearances were no longer visible. D. B.

Fixation of certain Artificial Colouring Matters by means of Metallic Mordants. By M. H. KOECHLIN (*Chem. News*, **46**, 179).—A long list of colouring matters is given which have been fixed by aluminium, magnesium, calcium, and chromium acetates, or a mixture of these. It is frequently necessary to use a mixture in order that the colour produced shall be "fast," and compound mordants have a greater resisting power as regards acids and alkalis, and are therefore suitable for colours which are either acid or alkaline. A short historical account of the introduction of compound mordants is also given.
E. W. P.

Preparation of Aluminium Thiocyanate. (*Dingl. polyt. J.*, **245**, 306.)—Lauber and Haussman obtain aluminium thiocyanate in the following manner :—In the preparation of thiocyanates by means of carbon bisulphide and sulphuretted hydrogen, there is obtained in the first place a ley containing ammonium thiocyanate and sulphuretted hydrogen; if after driving off the latter, the ley is decomposed in suitable vessels by a definite quantity of lime, a solution of calcium thiocyanate is obtained, which is free from iron, and sufficiently pure for the manufacture of aluminium thiocyanate. The latter is prepared as follows:—5 k. aluminium sulphate are dissolved in 5 l. boiling water, 250 g. chalk added, then 11·5 l. calcium thiocyanate solution of 20° B. The mixture is stirred well, allowed to settle, filtered, and the clear solution used. D. B.

Application of Baeyer's Artificial Indigo. By H. Schmid (*Dingl. polyt. J.*, **245**, 302—305).—Orthonitrophenylpropiolic acid is brought into commerce in the form of a yellow paste containing 25 per cent. dry matter. A weak reducing agent, when allowed to act in an alkaline solution at a temperature of 31°, develops the blue, and fixes it on the fibre. The receipt originally given by the Baden Aniline and Soda Works consists of 40 g. propiolic acid in the form of paste, 10 g. finely pulverised borax, 70 g. starch thickening, to which 15 g. sodium xanthate are added immediately before the printing. After being printed, the goods are dried and hung in a warm place. The rapidity with which the colour is developed differs in accordance with the degree of heat. A passage through Mather and Platt's continuous fixing machines suffices to produce the blue, whilst if hung in the cold, 48 hours' time is necessary to effect the same result. In order to remove the unpleasant smell resembling mercaptan accompanying the printing colour, the pieces are treated with a boiling solution of 10 g. sodium carbonate per litre, and soaped at 30—40°. For the production of lighter shades, a thickening is used containing 100 g. sodium xanthate. The quantity of borax is calculated to form the neutral sodium salt of orthonitrophenylpropiolic acid; in its place an equivalent amount of sodium carbonate or acetate may be used, whilst the starch thickening may be replaced by gum tragacanth; burnt starch and gum Senegal weaken the colour, although borax coagulates the former. At a price of 44*s*. per kilo. of propiolic acid in 25 per cent. paste, 1 kilo. of indigo blue fixed on the cloth costs 70·4*s*., it being assumed that the conversion into blue is theoretical. Sodium xanthate acts at a low temperature without steaming, in fact the latter is injurious. It is obtained by the action of sulphuretted hydrogen on alcoholic soda-ley, and forms a yellow crystalline powder. Its principal products of decomposition are carbonic anhydride, alcohol, and sulphuretted hydrogen. The nitrophenylpropiolic acid is therefore exposed to this weak reducing action, which is frequently used for reducing aromatic nitro-compounds in alcoholic or alcoholic ammoniacal solutions by means of sulphuretted hydrogen. The author finds that when thiocarbamide is used a higher temperature is needful, which has the advantage that the printing colour keeps better, besides being free from smell. The printing colour prepared with sodium xanthate is decomposed in a very short time, hence it is necessary to add the xanthate immediately before printing, or the cloth may be prepared with it, in which case it is padded in a solution containing from 100—300 g. sodium xanthate. The blue obtained from the propiolic acid gives brighter colours than the blue dyed with natural indigo, and resists rubbing and soaping better. It can be printed in conjunction with aniline-black and all colours which are developed by means of oxidation. Owing to its reducing action, sodium xanthate may be used as resist for aniline-black. The acid contained in the black liberates xanthic acid, which readily decomposes into alcohol and carbon bisulphide. The author used this reaction to reserve indigo-blue under aniline-black. Sodium xanthate forms a yellow precipitate with copper salts, so that it is possible to produce a green colour. By adding an excess of sodium xanthate to the propiolic acid blue, and passing the goods through a solution of copper after full development of the blue, a bluish-green is obtained, owing to the mixture of the yellow with the blue. The yellow produced with copper xanthate withstands acids and dilute alkalis, whilst the green resists soaping extremely well. D. B.

Chemical Theory of Gunpowder. By H. DEBUS (*Proc. Roy. Soc.*, **33**, 361—370).—The author at the outset draws attention to the fact that notwithstanding the antiquity of the use of gunpowder, no theory has hitherto been propounded by which the quantities of the chief products of combustion can be calculated from the known composition of a given weight of gunpowder, or of the amount of heat generated during its metamorphosis.

The potassium nitrate, charcoal, and sulphur are transformed during the combustion into potassium carbonate, sulphate, bisulphide, and thiocyanate, carbonic oxide and anhydride, nitrogen, hydrogen sulphide, methane, ammonia, hydrogen, and water. Of these substances, the hydrogen and its compounds, together with potassium thiocyanate amounting to about 2 per cent. of the original weight of the powder, are merely secondary products, and not direct results of the explosion of the powder; potassium thiosulphate has also been found, but is formed from the sulphide during the analysis by Bunsen and Schischkoff's method. With regard to the remaining products, the author proposes to solve the following problems (1) to determine the reactions which cause their formation and the order in which they succeed one another, and to represent the *complete* combustion of gunpowder by one equation; (2) to calculate from the known composition of a given weight of powder the volume of the gases, the amount of heat generated, and the relative energies of powders of different composition.

The experiments of Noble and Abel (*Phil. Trans.*, 1875, 137) have shown that the proportions of the several constituents of the solid residue are dependent upon accidental variations of the conditions of the explosion, and therefore any attempt to express by a single equation the metamorphosis in question would be apt to convey an erroneous idea, and would lead to no important elucidation of the theory of the explosion of gunpowder. But the author shows that the differences in the composition of samples of powder of the same nature, together with the inevitable errors attached to the analytical operation, are quite sufficient to explain the variations in the proportions of the product of combustion. For instance, 1st, a portion of the potassium bisulphide is partly converted into the sulphate and thiosulphate, and thus the quantities of these salts vary in different experiments; 2nd, the potassium bisulphide gives up readily a portion of the sulphur to the steel of the vessel in which the explosion is effected, and the quantity of ferrous sulphide so produced is dependent upon the conditions of the explosions.

If the sources of error be taken into consideration, the explosion of powders in a confined space may be expressed with some degree of accuracy by the equation $16KNO_3 + 21C + 5S = 5K_2CO_3 + K_2SO_4 + 2K_2S_2 + 13CO_2 + 3CO + 8H_2O$, whereas the composition of the powder calculated from the mean results of the analyses of Noble and Abel can be represented by the symbols $16KNO_3 + 21{\cdot}18C + 6{\cdot}63S$.

The author by the light of the results obtained by Karolyi and those of Noble and Abel has been enabled to develop a theory of the explosion of gunpower competent to explain the observations of former experimenters, and in harmony with the thermochemical relations of the reacting substances. According to this theory, gunpowders which differ considerably in their composition are transformed during the first stage according to the equation—

$$10KNO_3 + 8C + 3S = 2K_2CO_3 + 3K_2SO_4 + 6CO_2 + 5N_2 \ (1),$$

but as carbonic oxide is produced, the following equation more nearly represents the nature of the change:—

$$16KNO_3 + 13C + 5S = 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2 \ (2).$$

The oxygen contained in the potassium carbonate and sulphate, and the carbonic anhydride in equation (1) stand in the ratio 1 : 2 : 2, whereas the heat developed by the formation of the potassium carbonate to the sulphate and carbonic anhydride in equation (2) stand in the relation 1 : 2·05 : 1·04.

But, as a rule, gunpowder contains more carbon and sulphur than is required by the equations above, so that, in the second stage of the explosion, the carbon reacts on the potassium sulphate, and the sulphur on the carbonate, thus: $4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2$ and $4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2$, while some of the free carbon reduces carbonic anhydride to carbonic oxide. These latter reactions are endothermic, are not of an explosive nature, and in practice are seldom complete.

If x, y, z be positive numbers, and a represents the molecules of carbonic oxide formed by the complete combustion of a given weight of powder, we have the following general equation as representing the complete combustion of gunpowder: $xKNO_3 + yC + zS = \frac{1}{28}(4x + 8y - 16z - 4a)(K_2CO_3) + \frac{1}{28}(20x - 16y + 4z + 8a)(K_2SO_4) + \frac{1}{28}(-10x + 8y + 12z - 4a)(K_2S_2) + \frac{1}{28}(-4x + 20y + 16z - 24a)(CO_2) + \alpha CO + \frac{1}{2}xN_2$. The correctness of the equation is proved by the agreement of the calculated numbers with those observed by Bunsen and Schischkoff, Noble and Abel, and others. But if in this equation $x = 16$ and $a = 0$ (and this latter value does not materially affect the main result), we obtain $16KNO_3 + yC + zS = \frac{1}{28}(64 + 8y - 16z)(K_2CO_3) + \frac{1}{28}(320 - 16y + 4z)(K_2SO_4) + \frac{1}{28}(-160 + 8y + 12z)(K_2S_2) + \frac{1}{28}(-64 + 20y + 16z)(CO_2) + 8N_2$.

If the coefficients of the potassium carbonate, sulphate, and bisulphide be taken as 0, the equation (α) $64 + 8y - 16z = 0$, and (β) $320 - 16y + 4z = 0$, and (γ) $- 160 + 8y + 12z = 0$, represent three sides of a triangle, of which the two sides represented by equations (α) and (γ) intersect at points $y = 8$ and $z = 8$, and these values introduced into the equation above give $16KNO_3 + 8C + 8S = 8K_2SO_4 + 8CO_2 + 8N_2$, and finally the two sides represented by equations (β) and (γ) intersect in points $y = 24$ and $z = 16$, hence

$$16KNO_3 + 24C + 16S = 8K_2S_2 + 24CO_2 + 8N_2.$$

Again, if V represent the volume of gas evolved by the combustion of a powder containing 16 mols. KNO_3, y atoms of carbon and z atoms of sulphur, and W the units of heat developed, then, on the assumption that $a = 0$, $V = \frac{160 + 20y + 16z}{14}$, and $W = 1000[1827{\cdot}154 - 16{\cdot}925y - 8{\cdot}788z]$. Thus the volume of gas becomes *greater*, and amount of heat *less* when y and z are increased, and *vice versâ;* quantities of KNO_2, C, and S, represented by the symbols $16KNO_3 + 8C + 8S$, produce the greatest amount of heat and the smallest volume of gas, while those corresponding to $16KNO_3 + 24C + 16S$ produce the largest volume of gas and the smallest amount of heat. The products of the equations for V and W divided by $2 \times 1000 = \frac{V \times W}{2000} = 10440{\cdot}88 - 12{\cdot}09y^2 + 1208{\cdot}39y - 15{\cdot}95yz + 993{\cdot}867z - 5{\cdot}022z^2 = E$, which may be taken as the relative energies of powder of different composition. The difference of the values for E is very small if the powders contain from 21—24 atoms of carbon, and from 8—16 atoms of sulphur for every 16 mols. of potassium nitrate.

Equal weights of the mixtures $16KNO_3 + 22C + 8S$ and $16KNO_3 + 24C + 16S$ give for E the values 16·84 and 16·95 respectively. If therefore a powder is required which shall possess nearly the greatest amount of energy, and at the same time contain the smallest amount of sulphur and carbon compatible with this condition, theory points to a mixture, $16KNO_3 + 22C + 8S$, whereas the gunpowders of most nations fluctuate about $16KNO_3 + 21{\cdot}2C + 6{\cdot}8S$.

The author finally draws attention to the advantage of the geometrical demonstration above for illustrating the qualitative nature, and the quantitative relations of the products of combustion, the volumes of the gases, and the amount of heat developed. V. H. V.

Cause of the Acid Reaction Exhibited by some Kinds of Paper. By HAERLING (*Dingl. polyt. J.*, **246**, 195).—It has been stated by Feichtinger (Abstr., 1882, 1339) that paper sized with resin exhibits an acid reaction, which he attributes to the presence of free sulphuric acid. According to the author, the acid reaction is not due to free acid, but to the presence of aluminium sulphate, which is used for fixing the size. A. K. M.

General and Physical Chemistry.

The Light emitted by Comets. By BERTHELOT (*Ann. Chim. Phys.* [5], **27**, 232—233).—Arguing from the presence of hydrogen, carbon, and nitrogen detected by Huggins in the spectra (corresponding to those given by acetylene and hydrocyanic acid) of the light emitted by comets, the author suggests electrical disturbance as a more probable cause of luminosity than combustion. L. T. T.

Telluric Rays and the Spectrum of Water Vapour. By J. JANSSEN (*Compt. rend.*, **95**, 885—890).—An historical summary.

Spectra of Carbon and its Compounds. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **34**, 123—130).—The authors, in former experiments, have traced a fluted band spectrum, which occurs when carbon poles transmit the arc or spark current in air to the compound cyanogen (Abstr., 1882, 252—253). The present paper is a continuation of the investigations, which have received fresh interest from the discovery by Huggins of cyanogen bands in the comet of 1881.

The arc discharge between graphite poles in carbonic anhydride shows the cyanogen triple set beginning about λ 4380, with traces of the fluted bands at 4218 and 3883; if the carbonic anhydride is displaced by air, the triple set is weakened, whilst the fluted series is strengthened. The spark discharge in carbonic anhydride does not show the cyanogen series; but it appears when the discharge is taken in nitrogen. With the arc discharge in hydrogen, the triple set is well marked, while the series at 4218 disappears, but the hydrocarbon-group at 4310 comes out strong. When the pressure in different gases was reduced to 1 inch, the arc in air showed the hydrocarbon set, the cyanogen series, and the nitrogen series near H. But in carbonic anhydride, the triple set alone was strongly marked: in hydrogen, the triple set disappears, but the hydrocarbon-group comes out strong. The authors give a list of carbon arc-lines from λ 2434·8 to λ 2881·1, when a continuous Siemens current is used; these seem to prove that carbon-vapour of a low tension exists in the arc discharge, which would account for the combination of carbon with hydrogen or nitrogen under these conditions.

When the spectrum of a magnified image of the electric arc is examined, all the more refrangible cyanogen-groups are seen near the positive pole, together with a series of channellings in the red; the cyanogen-group is also visible at the negative pole. But if puffs of air or carbonic anhydride are passed into the arc, the hydrocarbon lines are produced; the same result obtains if one of the poles is moistened.

The De Meritens arc in water shows the hydrocarbon spectrum alone, but if a little nitrobenzene in glycerol be substituted the cyanogen triplet about 4380 appears.

The authors have repeated their experiments with vacuum tubes, using those of capillary glass; the tubes containing benzene or a solution of naphthalene in benzene, show no trace of the cyanogen spectrum, until, after continued use, there is a leak or crack at the point where the platinum is sealed into the glass.

In observations by the eye of flames of coal-gas which had passed through ammonia, no cyanogen spectrum could be observed; similarly, hydrogen mixed with carbonic anhydride and ammonia gave no result, but cyanogen can be detected if the ammonia is mixed with chloroform and other carbon compounds.

As a result of their experiments, the authors consider that hydrocyanic acid can always be separated from reducing flames, in which the free carbon or dense hydrocarbon vapours favour its formation.

In photographs taken by means of a quartz and calcspar train, the authors could detect in a flame of coal-gas well supplied with oxygen only the hydrocarbon-groups; but if the coal-gas is passed through ammonia, photographs reveal the characteristic cyanogen-groups at λ 3803 and λ 4218. Spectrum analysis can then detect the presence of cyanogen under widely different conditions. In photographs of the ultra-violet spectrum of a cyanogen flame fed with oxygen, the authors succeeded in detecting the carbon line λ 2478·3, which proves that carbon-vapour does exist in flames of cyanogen, although to a smaller extent than in the arc discharge. V. H. V.

The Ultra-violet Spectra of Elements. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **34**, 122—123).—From photographs taken with a Rutherford grating, the authors have determined the wave-lengths of 91 of the principal lines in the spark spectrum of iron between λ 2948, the termination of Cornu's map of the solar spectrum, and λ 2327; and 14 of the strongest lines of the spark spectrum of copper up to λ 2135. With these lines as lines of reference, they have deduced the wave-lengths of 584 more lines in the arc and spark spectra of iron within those limits.

The authors have further mapped out the ultra-violet lines of the arc spectra of sodium, lithium, barium, strontium, calcium, zinc, mercury, gold, thallium, aluminium, lead, tin, antimony, bismuth, and carbon. They consider that in several cases harmonic relationships exist similar to those noticed in the visible lines of the spectra of the alkalis and magnesium. V. H. V.

An Arrangement of the Electric Arc for the Study of Radiation of Vapours. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **34**, 119—122).—The authors have constructed a form of apparatus suitable for a study of the reversal of metallic lines; it consists of a block of lime, perforated by two holes in planes at right angles to one another, and through which pass the carbon rods connected with a Siemens dynamo-machine. One of these rods is perforated, and observations are made by projecting with a lens the light issuing from the tube on the slit of the spectroscope. By introducing a small rod of carbon into the perforation from the further end, a luminous background can be obtained, and as the walls of the tube are hotter than the metallic vapours, the metallic lines are reversed; an alteration of the position of the carbon rod causes the lines to disappear, reappear, or show reversal. Using commercial carbons, the first lines seen were the potassium lines λ 4044—6, next the two aluminium lines between H and K, then the manganese triple about λ 4034, a calcium line λ 4226, then the calcium lines near M, the iron line M, and then gradually many conspicuous lines between O and *h*. In the higher region, the continuous spectrum extends beyond the solar spectrum. The calcium lines H and K were often absent, and not even brought out reversed when calcium or its chloride was introduced into the tube. The lithium lines λ 4603 and λ 4131 are relatively difficult of reversal. If ammonia is passed into the tube, most of the lines attributed to cyanogen by the authors appear. As it is known that ammonia reacts on carbon at a white heat to produce ammonium cyanide and hydrogen, the appearance of the cyanogen lines offers an independent confirmation of the author's views. The two indium lines λ 4101 and λ 4509 are always reversed; tin gives flutings in the highly refrangible portions of the spectrum, and silver gives a fluted spectrum in the blue. Calcium chloride gives six or seven bands between L and M; these are sometimes bright and sometimes reversed. V. H. V.

Reversal of Metallic Lines in Over-exposed Photographs of Spectra. By W. N. HARTLEY (*Proc. Roy. Soc.*, **34**, 84—86).—The author has made a series of comparative experiments in order to ascertain the exact period of exposure of the sensitive plate to the rays, in order to bring out the most characteristic lines, without the diffused rays of the air spectrum. Over-exposure causes strong lines to be reversed without materially altering the appearance of the rest of the spectrum; this is particularly the case with lines of the metals magnesium, aluminium, and indium: thus in two over-exposed photographs the magnesium triplet *b′* between K and L became a quadruple group by reason of the most refrangible line being split into two by a reversal. The author considers that the method of comparative exposures should be employed to confirm the accuracy of observations based entirely on photographic representations of spectra. V. H. V.

Researches on Spectrum Photography. By W. N. HARTLEY (*Proc. Roy. Soc.*, **34**, 81—84).—The author has made an experimental comparison of the spectra of various compounds in solution with those of the elements they contain. In order to eliminate lines foreign to the substances examined, the arc spectrum between graphite poles was chosen, as producing about 12 insignificant lines due to carbon, and about 66 easily recognisable lines and bands due to air. On comparing the spectra of solutions of salts with those from metallic electrodes, it was found that the same lines, with the same graphic character, were produced in both cases, but their continuity was altered. Thus discontinuous but long lines, or, in certain cases, even short lines, appear as long lines in the solution-spectra. Zinc offers an exceptional instance of this variation, for the pure metal exhibits a series of short lines or dots, which are absent from photographs of the spectra from its solutions. Certain discontinuous lines in the spectrum of iridium become continuous when moistened with calcium chloride solution.

The author considers that only the method of solution is available for the estimation of the relative proportions of the constituents of an alloy or mineral; for most alloys are not homogeneous, whereas the composition of a solution represents throughout the composition of the mass dissolved.

Experiments were made in order to examine the sensitiveness of the spectrum reaction under various conditions, as the nature of the element, time of exposure, and intensity of the spark; it was found that $\frac{1}{1000}$ per cent. of calcium, silver, copper, and $\frac{1}{10000}$ per cent. of manganese, were recognisable quantities. V. H. V.

Atomic Refraction of Sulphur. By R. NASINI (*Ber.*, **15**, 2878 2892).—The author, at the outset, alludes to the dependence of the atomic refraction of an element on the nature of its combination with other elements, which has been established by the researches of Brühl. As the specific refraction of only a few sulphur compounds has been determined, the author has made a minute examination of several organic and inorganic compounds, in order to ascertain whether the atomic refraction of sulphur varies with its valency.

The refractive indices were determined for the hydrogen lines α, β, and γ, and the sodium line D, and the specific refraction calculated according to the empirical formula $\frac{n-1}{d}$, and the formula $\frac{n^2-1}{(n^2+2)d}$; on the basis of these formulæ, the index of refraction A for a ray of infinite wave-length is calculated by the aid of Cauchy's dispersion formula $(\mu\lambda = A + \frac{B}{\lambda_2} + \frac{C}{\lambda_4} + \ldots)$. The sp. gr. of the liquid used was taken at 20°, and reduced to that of water at 4°.

The following table embodies the author's results :—

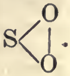
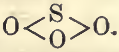
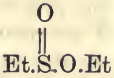
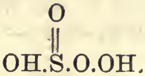
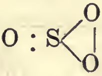
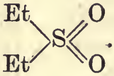
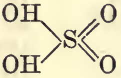
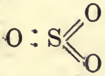
Substance.	d^{20}_4	μ_α	μ_D	μ_β
Ethyl mercaptan, EtSH…………	0·89307	1·42769	1·43055	1·43788
Ethyl sulphide, Et_2S ……………	0·83676	1·4396	1·44233	1·44929
Ethyl bisulphide, Et_2S_2…………	0·99267	1·50306	1·50633	1·51604
Isobutyl mercaptan, C_4H_9SH ….	0·83573	1·43575	1·43859	1·44547
Isoamyl sulphide, $(C_5H_{11})_2S$ ……	0·84314	1·44966	1·45238	1·45889
Carbon bisulphide, CS_2 ……….	1·2634	1·61847	1·62037	1·65268
	d^{22}_4.			
Ethyl ethylsulphonate, $Et.SO_3Et$..	1·14517	1·41733	1·41959	1·4242
	d^{23}_4.			
Sulphuric acid…………………	1·8273	1·42659	1·42922	1·43353
	d^{20}_4.			
Sulphuric anhydride …………	1·9365	1·4077	1·40965	1·41484

Substance.	μ_{γ}.	A.	B.
Ethyl mercaptan, EtSH	1·4445	1·41805	0·34979
Ethyl sulphide, Et_2S	1·45522	1·42746	0·52362
Ethyl bisulphide, Et_2S_2	1·52407	1·4067	0·70431
Isobutyl mercaptan, C_4H_9SH	1·4511	1·42382	0·51456
Isoamyl sulphide, $(C_5H_{11})_2S$	1·46447	1·43813	0·49646
Carbon bisulphide, CS_2	1·67515	1·5864	1·16098
Ethyl ethylsulphonate, $Et.SO_3Et$	1·42595	1·41065	0·28896
Sulphuric acid	1·43745	1·41826	0·36202
Sulphuric anhydride	—	1·39922	0·36924

From the values obtained for the line α in the above table, together with a few others obtained by Wiedemann, the author has calculated the atomic refraction r_a and r_A, $\mathfrak{r}_\alpha$ and $\mathfrak{r}_A$, for the line α, and deduced from the constant A, according to the old and new formulæ. The results are contained in the table below:—

	$\frac{n-1}{a}$		$\frac{n^2-1}{(n^2+2)d}$	
Substance.	r_a.	r_A.	$\mathfrak{r}_\alpha$.	$\mathfrak{r}_A$.
Ethyl mercaptan	13·8	13·43	7·8	7·64
Ethyl sulphide	14·28	13·63	8	7·72
Ethyl bisulphide	14·41	13·7	8	7·68
Isobutyl mercaptan	13·93	13·31	7·82	7·53
Isoamyl mercaptan	14	13·34	7·84	7·55
Isoamyl sulphide	14·2	13·47	7·74	7·46
Diethyl monothiocarbonate	—	13·65	—	7·89
Diethyl dithiocarbonate	—	13·78	—	7·78
Mean	14·10	13·53	7·87	7·65
Carbon bisulphide	15·61	15·20	9·02	8·88
Diethyl thiocarbonate, $CS(OEt)_2$	—	14·98	—	8·80
Mean	15·6	15·09	9·02	8·84

From this table it is evident that the atomic refraction of sulphur varies according as it is combined with two different groupings, by one affinity each, or with both of its affinities to one carbon-atom; and further, the values for r_α and $\mathfrak{r}_\alpha$ are concordant among themselves, and stand in relation to one another, similar to that existing between the values for r_A and $\mathfrak{r}_A$. As far as regards the other sulphur compounds examined, the values for the atomic refraction of sulphur are in accordance with one another, but differ in a most marked way from the values above; they vary according to the hypothesis adopted to express their constitution, *i.e.*, whether the oxygen-atom is combined with the sulphur-atom by one or two bands.

		Atom. refraction. $\frac{n-1}{d}$. r_A.	$\frac{n^2-1}{(n^2+2)d}$. r_A.
Diatomic sulphur	Et.S.O.O.O.Et....	8·91	5·25
	OH.S.O.O.OH ..	9·01	5·24
		8·10	6·37
	 $\mathrm{O}<^{\mathrm{S}}_{\mathrm{O}}>\mathrm{O}$........	8·37	5·82
Tetratomic sulphur ..	 $\mathrm{Et.}\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{S}}\mathrm{.O.Et}$	8·33	4·52
	 $\mathrm{OH.}\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{S}}\mathrm{.O.OH}$......	84·3	4·51
	O : S : O	6·94	4·91
		7·79	4·59
Hexatomic sulphur ..		7·75	3·79
		7·85	3·78
		6·63	3·13

These variations in the atomic refraction of sulphur may arise from one of two causes, *i.e.*, alteration of valency, or the direct combination of sulphur with oxygen instead of carbon; a further examination of other sulphur compounds alone can decide the question, and the author proposes to carry on researches for this purpose.

V. H. V.

Electric Discharge in Rarefied Gases. By E. GOLDSTEIN (*Phil. Mag.* [5], **14**, 366—387).—The author has previously shown that the electrical discharge in rarefied gases cannot be effected by the actual projection of gas particles, and for the same reasons it cannot be propagated by particles torn off from the tube, electrodes, &c. A system of pores in an insulator, or a single aperture of relatively small diameter, sends out rays with properties precisely similar to those from a metallic kathode. It is known also that at sufficiently high exhaustions the positive light has the property of rectilinear propagation and the power of exciting phosphorescence, and hence it would not be reasonable to adopt an explanation of the kathode light, the principle of which is not applicable to the positive light.

If two wires, *a* and *b*, are inserted in the end of a cylindrical tube, parallel with its axis, and both are made kathodes of the same discharge, each repels those rays from the other which pass near it, thus producing two sharply defined surfaces, one of which receives no rays from *a*, whilst the other receives no rays from *b*. If one of the electrodes is platinum, it is found that that part of the tube on which no rays from the platinum kathode fall, is just as thickly covered with a deposit of platinum as is any other part of the tube. In other words, the rays of the kathode light are deflected, whilst the particles projected from the electrode are not deflected. It follows, therefore, that, contrary to the usual supposition, recently defended by Gintl and by Puluj, the two cannot be essentially connected. The objections to the supposition that the discharge is effected through the medium of particles torn from the electrodes, apply equally well in the case of particles torn from the walls of the tube.

Since the discharge cannot be explained by the motion of ponderable particles, it follows that it must be a process which takes place in the free ether.

Hittorf found that the resistance of the positive light decreases as the exhaustion increases, and that changes in the form and magnitude of the anode are without influence. He also concluded that the resistance of the kathode light, and at the surface of the kathode, increases as the exhaustion increases, and hence the resistance to the discharge at very high exhaustions is exerted at the surface of the kathode and in the space filled by the kathode light. The author finds, however, that the resistance of the kathode light at very low pressures becomes comparatively small with respect to the total resistance to the discharge. Hence it appears that the resistance at very low pressures is exerted entirely at the surface of the kathode. The experiments on this point were made with a spark micrometer, included in a second circuit connecting the electrodes of the discharge tube. It was found that the discharge did not pass exclusively through the tube up to a certain distance between the balls of the micrometer, and then with a certain small decrease in this distance exclusively through the air space between the balls; but that there are certain positions in which the spark sometimes takes one path, sometimes the other, and the one path the less frequently, the closer the approach to the point at which the other alone is taken. This phenomenon did not affect the accuracy of the measurements. If the micrometer is included in the branch circuit of tubes which transmit the discharge at both make and break, it is found that if the distance between the balls of the micrometer is gradually diminished, a point is reached at which the current at break completely leaves the tube and passes only across the air space between the balls, whilst the current at make continues to pass through the tube with undiminished luminosity. This phenomenon may depend on different maximum tension of the current on making and breaking contact. From these experiments, it is evident that when the discharge takes place in gases, the division of the current cannot be calculated by means of Ohm's law. If two similar tubes are placed side by side, opposite to each other, in the same induced current, then at a certain pressure the current does not divide itself between the two tubes in any definite ratio to the resistance of the tubes, but passes exclusively through one of them, leaving the other entirely dark. These observations will slightly, but not materially, affect the accuracy of some results given in the author's book on a "New Form of Electrical Repulsion."

By means of a vacuum tube of special form, in which the anode was placed close and parallel to the plane of a kathode of large surface, and in which the length of the tube could be altered by sliding an enclosed closely-fitting glass cylinder, the author was able, at very low pressures, to increase the expansion of the kathode light in the ratio 1 : 30, without causing the resistance to vary as much as 1 : 1·05; hence the resistance of the kathode light is a vanishing quantity in comparison with the resistance at the surface of the kathode. It is also evident that the resistance of the gas in the discharge tube becomes less as the quantity of gas decreases, and it follows that the tube would have the greatest conductivity when the whole of the gas is removed and the tube is filled only with free ether, which the author regards as the true medium of the discharge. The motion of the ether cannot be regarded as progressive, but is best regarded as radiant. Every particle of ether in a pencil of negative light assumes that form of motion which is excited at the point of origin of the pencil.

Experiments with a tube filled partly with nitrogen and partly with sodium vapour, show that the positive light can be displaced without any corresponding displacement of the gas itself, and experiments with two tubes connected by a capillary tube furnished with a stop-cock, show that when the discharge is powerfully deflected by a magnet against the side of one tube, the stop-cock being open, there was no actual transport of gas from one tube to the other, or, rather, that the difference in pressure caused by such transport, if it did take place, was less than 0·01 mm. of mercury, a difference which could have been recognised by alteration in the distance between two consecutive striæ. It has been argued in opposition to the theory that the ether is the vehicle of the discharge, that if such were the case all gases would give the same spectrum, which is contrary to fact. But the ether itself has not the power of emitting light. The luminosity of gas subjected to an electric discharge depends on the molecules of the gas having a form and period of oscillation necessary for the emission of visible rays. The phenomena of phosphorescence and fluorescence show that molecules of matter can take up invisible vibrations of free ether, and thus become luminous. The author considers that the discharge takes place in free ether, but is itself non-luminous. The motion of the ether is, however, communicated to the molecules of gas in the tube, and these then vibrate according to their particular structure and conditions of elasticity, and in their turn communicate to the ether transverse vibrations which produce the sensation of light. In fact, the luminosity of gases traversed by the electric discharge is a phenomenon closely analogous to resonance. It differs from fluorescence and phosphorescence in that, in both these cases, the vibrations of the ether are transferred to the atoms or molecules of matter, and back again to the ether, without changing their character as transverse vibrations, whilst in the luminous discharge a motion of the ether, which does not consist of transverse vibrations, is converted into such vibrations. Moreover, a temperature-condition is always associated with phosphorescence, which does not obtain in the case of the luminous discharge in gases. The assumption that a vacuum conducts electricity is of the highest importance in cosmical physics. The author considers that certain terrestrial electric and magnetic phenomena may be due to currents of electricity radiated from the sun through interplanetary space. Experiments show that there is no limit to the expansion of the kathode light, and that it streams out into space without reference to the position of the anode. It is therefore not necessary to assume that the earth is one pole of the solar current, for discharges, both poles of which were on the sun, might produce negative rays radiating from the sun into space.

II. Two processes are essential to the production of an electric discharge: a change in the condition of the ether preceding the discharge, which produces a certain condition of unstable equilibrium in the arrangement of its parts (this condition may be called the *tension* of the ether) and the restoration of stable equilibrium, *i.e.*, the discharge itself. The tension preceding the discharge is not equally great at all cross sections of the discharge-tube, even when the tube is of equal section throughout; in certain parts of the tube it may even be zero: it has either finite or maximum values at the surfaces of the metal poles, and at those points which appear as points of issue of the separate positive layers or of secondary negative pencils. The so-called ether-envelopes surrounding the atoms or molecules of a gas undoubtedly play an important part in the emission of light produced by the discharge, but their exact function cannot at present be determined. The forces which are exerted by the particles of matter in the production of the ether-envelopes tend to produce an arrangement of the ether different from that produced by the electrical forces alone, and consequently the more gas molecules in a given space, the greater will be the electrical forces necessary to bring about that arrangement of the ether which must precede discharge: hence the resistance of the space in which the discharge takes place is less the more completely the gas is removed. The author cannot accept Wiedemann's view that the ether-envelopes are the real medium of discharge. If the envelopes suffer deformation without the free ether taking part in the discharge, then there must be a pure distance-action between the envelopes.

From the results of the following experiments, the author concludes that the direction of the negative current from the kathode is the direction in which the electric discharge is propagated in the kathode light and also in the negative pencils and in the positive stratifications. If a solid body is placed in the path of a pencil of kathode light, or of secondary negative light, the shadow is cast on that side farthest away from the kathode, and the shadows formed in the phosphorescent surfaces excited by the positive light exhibit similar behaviour. The properties of secondary negative rays, even for a considerable distance, correspond with the conditions which exist at that boundary of the negative rays which is nearest the kathode. With higher and higher degrees of exhaustion, the pencils radiate continually more and more from the mouth of a narrow tube opening into a wider tube, a phenomenon which would not occur if the pencil had its origin in the wider tube and was propagated from it into the narrower tube. If a sufficiently weak magnet is allowed to act on the end of a long kathode pencil remote from the kathode, only the end of the pencil is affected by the magnet, the rest of the pencil remaining unaltered. If, however, the magnet is brought close to the kathode, so as to act on the rays nearest the kathode, then the whole of the pencil is deflected even to its furthest point, although the distance of the latter from the magnet is so great that the magnet could not produce any direct effect. Precisely similar phenomena are exhibited by secondary negative pencils, and also by the rays of separate positive stratifications. It is evident, therefore, that in each separate stratification the discharge is propagated from the bounding surface on the kathode side to the bounding surface on the side nearest the anode. The usual phenomena of deflection may be explained in a similar manner.

III. It is necessary to distinguish between the velocity and direction of the discharge of a pencil of electrical rays and the velocity and direction with which the tension preceding the discharge is propagated. All the observed phenomena indicate that the tension is propagated in the direction of the negative current; the tension of separate positive stratifications is developed in the same order of time as that in which they follow one another in space from the kathode to the anode. The position and character of separate complete stratifications, especially the position of the points from which the separate discharges formed by the stratifications issue, depend, not on the conditions of the anode, but on the position and character of the kathode. With high exhaustion and a sufficiently powerful and regular induction current, stratifications can be obtained which are perfectly stationary and equal in thickness to the diameter of the tube. In a tube arranged so that the electrodes can be moved along the axis of the tube, any motion of *the anode* produces no displacement of the stratification. The layers passed over by the anode as it approaches the kathode disappear one by one as if absorbed by the anode. If the anode is moved away from the kathode, all the previously existing layers retain their original positions, and new layers appear in the space left by the anode, each new layer after its formation being perfectly independent of any subsequent motion of the anode in the same direction. If, however, *the kathode* is moved towards the anode all the layers in the tube move at once through exactly the same distance and exactly in the same direction as the kathode moves. As the distance between the electrodes is diminished, the number of layers possible is diminished also, and each layer disappears as soon as it is pushed up against the anode. If the kathode is moved away from the anode, all the layers follow the kathode and new layers appear in the space left between the last layer and the anode, each layer after its formation following the motion of the kathode. The interval between every two layers in a tube is *practically* the same, so that at a given density of gas and intensity of discharge we may speak simply of the *stratification interval.* The number of layers in a tube is evidently the quotient of the length of the column by the stratification interval. When, as frequently happens, this quotient is not a whole number, it is found that the layer nearest the kathode is at the same distance from it for every distance between the two electrodes, whilst the incomplete layer is in contact with the anode and shortens or lengthens in proportion to the excess of the quotient above a whole number. Moreover, consecutive layers in a column of positive light may show distinct differences in colour although of the same form and magnitude, a phenomenon especially marked in the case of hydrogen. The colour of each layer depends entirely on its position with respect to the kathode, and not at all on its relation to the anode. Further, variations in the size of the anode have no effect on the position of the layers, but a variation in the size of the kathode changes the position of all the positive layers. Other conditions being the same, the smaller the kathode the greater the distance between the kathode and the first positive layer; the intervals between the successive positive layers are not altered.

It must not be assumed, however, that the conditions of tension and discharge of the whole stratified column are determined by the kathode, or the physical conditions at the kathode. The position and properties of each layer depend mainly, if not entirely, on the position and properties of the layer preceding it on the side next the kathode. The influence of the kathode on the entire stratified column is therefore only indirect. The conditions at the kathode determine the properties of the kathode light; this determines the position and properties of the first positive layer; this the position, &c., of the second layer, and so on. This view is based on the results of experiments with secondary negative light. A cylindrical tube provided with a movable kathode, K, and fixed anode, A, contained a closely-fitting short glass tube, R, with a small aperture, x, which could be moved along the larger tube; the small aperture, x, acting as a secondary negative pole. Any movement of K affected all the layers between K and x, but had no effect on the layers between x and A. If K remains stationary while x is moved, the movement affects all the layers between x and A, just as if x were a metallic kathode. Then, too, the colours between K and x depend on the position of K, whilst those between x and A depend only on the position of x, and are independent of K. The magnitude of the secondary pole affects all the layers between it and the anode, just as the magnitude of the kathode affects all the layers between it and the secondary pole. With a tube containing two secondary negative poles it was found that the position of each layer depends on the position and character of that secondary negative pole or pencil of secondary negative light which is nearest to it on the side towards the kathode.

As a matter of fact, the interval between two consecutive layers in a simple cylindrical tube diminishes slightly from the kathode to the anode. If a secondary pole is introduced, the distances diminish from the kathode up to this secondary pole, then the distance suddenly increases, and a new series of diminishing intervals is commenced. With infinitely small changes in the section when the secondary negative pencil passes into a positive layer, the distance between any two layers depends on the properties of that component of the pair which is nearest the kathode. The conditions existing at the point of origin of each layer always influence the layer following next to it on the side of the anode, but have no effect on the preceding layer on the side of the kathode. The conditions of formation of the *n*th layer stand to the properties of the $(n + 1)$ layer in the relation of cause to effect. In other words, the propagation of electrical tension or the production of separate layers, is effected in the direction from the kathode to the anode. C. H. B.

The Leclanché Cell, and the Reactions of Manganese Oxides with Ammonium Chloride. By E. DIVERS (*Chem. News*, **46**, 259—260).—Longi doubts Priwoznik's statement that zinc acts on ammonium chloride and forms zinco-diammonium chloride, $Zn(NH_3Cl)_2$; the author has, however, obtained this same substance, and describes its properties; in solution it probably exists as a double salt with ammonium chloride, for when the liquid is heated, much ammonia appears and a double chloride of zinc and ammonium is formed. The zinco-diammonium chloride is decomposed by water into a soluble salt, $(ClH_4N)_2,Zn(NH_3Cl)_2$, and an insoluble compound, $HO.Zn.NH_3Cl$, which latter is probably the same as that found by Davis, and to which he assigned the formula $Zn(OH)_2,NH_4Cl$.

Manganese dioxide is not affected by digestion with ammonium chloride; the monoxide, however, is attacked, a portion passing into solution accompanied by evolution of ammonia and the formation of a light-coloured body, presumably manganous hydroxychloride, HOMnCl, as treatment with water gives rise to the formation of manganous hydroxide. Intermediate oxides are also attacked in a similar manner. Zinco-diammonium chloride, in presence of ammonium chloride, acts gradually on hydrogen manganite, $Mn_2H_2O_4$, manganese passing into solution, and zinc being precipitated as manganite, but this action does not occur with native manganite. Solid manganese dioxide is attacked by zinc in presence of ammonium chloride, both zinc and manganese going into solution, whilst ammonia is set free. From these observed facts, a theory of the action of the Leclanché cell is deduced.

Primary action—

$$Mn_2O_4 + 2HNH_3Cl + Zn = Mn_2O_4H_2 + (NH_3Cl)_2Zn.$$

This zinc compound remains in solution until the liquid is saturated, and then crystallises out in the usual manner.

Secondary reaction causing polarisation—

$$Mn_2O_4 + Zn(NH_3Cl)_2 + Zn = Mn_2O_4Zn + (NH_3Cl)_2Zn.$$

The zinc manganite thus formed coats over the manganic oxide, protecting it from the action of the ammonium chloride.

Secondary reaction causing depolarisation—

$$Mn_2O_4Zn + 4NH_4Cl = MnO_2 + 2H_2O + MnCl_2 + Zn(NH_3Cl)_2 + 2NH_3.$$

From this equation we see that the manganese dioxide becomes active again, but as this action is slower than that which occurs during polarisation, it is necessary to leave the cell uncircuited for a time in order that it may recover its full power after being used.

E. W. P.

Currents Produced by Fused Nitrates in Contact with Incandescent Carbon. By BRARD (*Compt. rend.*, **95**, 890—892).—Becquerel has shown that when incandescent gas-carbon is plunged into a bath of a fused nitrate, a powerful current is produced which passes from the bath to the carbon in the exterior circuit. The author finds that this takes place with all forms of carbon. The current rapidly becomes weaker, in consequence of the deposition on the surface of the carbon of a very compact strongly adhering crust of salts which protects the carbon from the action of the nitrate. The fused nitrates become very fluid, and acquire the property of moistening for a considerable distance the surfaces of heated bodies with which they are brought into contact. In consequence of this property it is not necessary to plunge the ignited end of the carbon into the fused nitrate, but the cool end may be placed in the bath, and the other end then made incandescent. If a capsule, containing some grains of fused nitrate, is left for a few minutes on the surface of glowing coals, a current is produced which flows from the bath to the coals in the exterior circuit, and remains sensibly constant in intensity so long as the coals continue to glow or any nitrate remains in the capsule. In this experiment the fused nitrate creeps over the edge of the vessel and flows down the outside on to the hot coals on which the capsule rests. The gradual flow of the thin layer of fused nitrate produces regular chemical action, and thus the current remains sensibly constant. The current passes through the fire the more easily the higher the temperature. When a metallic capsule containing the fused salts is suspended freely above an active fire, a current still passes from the nitrate to the exterior of the capsule. These currents are more feeble than those obtained by the preceding methods, but they may be increased by surrounding the outside of the capsule with a layer of black-lead and encasing the whole in metallic gauze. The best effect is obtained by covering the outside of the capsule with a layer of asbestos-paper, covering the latter with black-lead, and then putting on the coarse metallic gauze. The metallic gauze forms the negative pole of the element, and the capsule the positive pole. A couple of this kind heated over a Bunsen flame gives a remarkably constant current of 6 to 7 milliampères. It is important to place the capsule just in the point of the flame where the number of incandescent carbon particles is greatest, for it is these incandescent particles which, coming in contact with the fused nitrate absorbed by the asbestos, produce the current: the constancy of the current is due to the fact that with a properly regulated lamp the temperature and the proportion of carbonaceous products remain practically constant for a long time. The nitrates which melt at about 200° are very stable, and only decompose at about 1000° or 1200°. Up to this point they not only do not attack the vessels in which they are contained but, on the contrary, appear to prevent or to retard considerably the oxidising action of the fire. C. H. B.

Determination of High Temperatures. (*Chem. Centr.* [3], **13**, 666—667.)—Gold and platinum alloys are recommended for this purpose. The alloy used is made into balls of 1 to 2 grams; these are hammered out to plates about the size of sixpenny-pieces, bent in the form of an arch, and placed in rows in cupels, which are then arranged in the furnace so that they can be seen through a peep-hole. The temperature is reckoned from the melting point, which may vary from the melting point of silver to that of steel (nearly). The same alloy may be used over and over again. D. A. L.

Specific Heat and Heat of Transformation of Silver Iodide, and its Alloys with Cuprous and Lead Iodides. By H. Bellati and R. Romanese (*Proc. Roy. Soc.*, **34**, 104—105).—The authors have made a series of calorimetric investigations on these substances, the expression and contraction of which Rodwell has studied (Abstr., 1881, 495, 465). In the table below θ_1 and θ_2 are the temperatures between which the structural change occurs, c the mean specific heat between t and T for temperatures below θ_1, c_1 the mean specific heat for temperatures above θ_2, and λ the heat absorbed by unit weight of the substance in consequence of modification of structure:—

Formula of substance.	θ_1.	θ_2.	c.	c_1.	λ.	
AgI........	142	156·5	0·054389	+ 0·0000372 (T + t)	0·0577	6·25
Cu_2I_2 + 2AgI	95	228	0·05882	+ (from 16 to 89)	0·058	8·31
Cu_2I_2 + 4AgI	180	282	0·056526	+ 0·000041 (T + t)	0·0702	7·95
Cu_2I_2 + 3AgI	194	280	0·059624	+ 0·000028 (T + t)	0·0726	7·74
Cu_2I_2 + 2AgI	221	298	0 061035	+ 0·0000295 (T + t)	—	7·88
Cu_2I_2 + AgI.	256	324	0·063099	+ 0·000026 (T + t)	—	8·67
PbI_2 + AgI.	118	144	0·47458	+ 0·000026 (T + t)	0·0567	2·556

V. H. V.

Direct Determination of the Heat of Combination of Certain Gases. By F. W. Raabe (*Rec. Trav. Chim.*, **1**, 158—166). —*Ammonium Carbonate.*—Lecher (*Wien. Akad. Ber.*, October, 1878) determined by an indirect method the heat of combination of carbonic anhydride and ammonia, and obtained the numbers 38,817 and 36,642 heat-units (gram-degrees); mean 37,700. The difference between these numbers being rather wide, the author has endeavoured to obtain a more exact result by direct combination of the gases, bringing them together in a modified form of Bunsen's calorimeter. The mean value found for the heat evolved when 44 g. CO_2 and 34 g. NH_3 unite to form 78 g. ammonium carbamate, $(NH_3)_2CO_2$ or $NH_2.CO.ONH_4$, was 39,300 units. Thomsen by an indirect method found 42,500, and Berthelot 38,100.

Ammonium Chloride.—The heat of combination of NH_3 and HCl has been determined indirectly by Thomsen, by Berthelot, and by Favre and Silbermann, with the following results:—

Thomsen.	Berthelot.	Favre and Silbermann.
41,899	42,700	43,240

Favre and Silbermann by an indirect method obtained the number 39,970, but regard this result as less exact than that found indirectly. The author of the present paper obtained by the method above indicated the value 44,460. H. W.

Lead Iodide. By BERTHELOT (*Compt. rend.*, **95**, 952—955).—If lead iodide is dissolved in a hot concentrated aqueous solution of potassium iodide, the liquid on cooling deposits a pale-yellow crystalline salt, of the composition $PbI_2,2KI,2H_2O$. At a lower temperature, or by the gradual evaporation of the mother-liquor in the cold, long pale-yellow needles are obtained, of the composition

$$4KI,3PbI_2,6H_2O.$$

These salts combine together, forming intermediate compounds. The heat of formation of these double salts was determined by treating them with a large quantity of water. The following results were obtained:—

		Develops.
$2KI,PbI_2 + 2H_2O$ liquid $= 2KI,PbI_2,2H_2O$,	crystallised.	+ 4·62 cal.
,, ,, solid = ,, ,,	,, ..	+ 1·76 ,,
$2KI + PbI_2 + 2H_2O$ solid $= 2KI,PbI_2,2H_2O$	,, ..	+ 2·58 ,,
$2KI + PbI_2 = 2KI,PbI_2$ anhydrous	,, ..	+ 0·84 ,,
$4KI,3PbI_2 + 6H_2O$ liquid $= 4KI,3PbI_2,6H_2O$	,, ..	+ 12·36 ,,
,, ,, solid = ,, ,,	,, ..	+ 3·8 ,,
$4KI + 3PbI_2 + 6H_2O$ solid $= 4KI,3PbI_2,6H_2O$	,, ..	+ 2·8 ,,
$4KI + 3PbI_2 = 4KI,3PbI_2$	,, ..	− 1·0 ,,

The formation of the first salt is exothermic in both the hydrated and anhydrous condition, whereas the formation of the second salt is exothermic in the hydrated condition only.

A cold saturated solution of lead iodide yields an immediate precipitate on addition of a few drops of a dilute solution of potassium iodide or hydriodic acid. Solution of lead bromide, on the other hand, is precipitated by hydrobromic acid, but not by soluble bromides, and solution of lead chloride is precipitated by hydrochloric acid, but not by soluble chlorides. C. H. B.

Ethylene Oxide. By BERTHELOT (*Bull. Soc. Chim.*, **39**, 484—487).—The following heat determinations of ethylene oxide were made by the author:—Heat of combustion, $C_2H_4O + O_5 = 2CO_2 + 2H_2O$ (liquid) $= 307·5$ cal. at constant volume, 308·4 at constant pressure; heat of vaporisation, 6·1 cal.; heat of solution, 1·5 cal.; heat of formation from its elements, C_2 (diamond) $+ H_4 + O = C_2H_4O$ (gas) $= 17·7$ cal; heat of formation from ethylene, $C_2H_4 + O = C_2H_4O$ (gas) $= 33$ cal. This last number is practically the half of the heat of formation of aldehyde from the same constituents, which may account for the fact that the formation of ethylene oxide directly from ethylene has not been observed, aldehyde being formed in preference.

From the data of the heat of solution of glycol, the following number is deduced:—C_2H_4O (liquid + H_2O (liquid) = $C_2H_6O_2$ (liquid) = 19·1, a result comparable with the heat of hydration of sulphur trioxide (20·4 cal.) and barium oxide (17·6 cal.).

On heating ethylene oxide to redness the volume is doubled, with formation of carbonic oxide and marsh-gas, $C_2H_4O = CO + CH_4$, a reaction which disengages 26·4 cal. A very volatile liquid, probably aldehyde, is formed as an intermediate product.

The author draws attention to the differences of the heat of formation of gaseous aldehyde and ethylene oxide, for C_2 (diamond) + $H_4 + O = C_2H_4O$

In forming gaseous ethylene oxide evolves 17·7 cal.
„ „ aldehyde evolves .... 50·1 „

Thus ethylene oxide has a greater potential energy than aldehyde, which explains its ready polymerisation and direct combination with water and acids. The conversion of ethylene oxide into aldehyde disengages 32·8 cal., this isomeric change being accompanied with a loss of energy. Inasmuch as glycol on dehydration with zinc chloride furnishes not ethylene oxide, but aldehyde, conclusions as to the constitution of compounds drawn from their products of dehydration by zinc chloride must not be accepted as final without an appeal to the thermochemistry of the compounds in question. V. H. V.

Critical Temperatures of Alkyl Salts. By B. PAWLEWSKI (*Ber.*, **15**, 2460—2464).—The author has made a series of determinations of the critical temperatures and boiling points of the alkyl salts of the $C_nH_{2m}O_2$ series, the results of which are embodied in the following table. In the first column are the several boiling points, t; in the second the difference of boiling point $(t - t_1)$ of two consecutive salts; in the third the critical temperature, T; in the fourth the difference of critical temperature, $T - T_1$, of two consecutive salts; in the fifth the difference between the boiling point and critical temperature.

Ethereal salt.	(t).	$(t - t_1)$.	(T).	$(T - T_1)$.	$(T - t)$.
Ethyl formate	55·7	—	238·6	—	182·9
Propyl formate	85·1	29·4	267·4	28·8	182·3
Isoamyl formate	121·8	36·7	304·6	37·2	182·8
Methyl acetate	57·1	—	239·8	—	182·7
Ethyl acetate	75·0	17·9	256·5	16·7	181·5
Propyl acetate	100·3	25·3	282·4	25·9	182·1
Normal butyl acetate ..	123·7	23·4	305·9	23·5	182·2
Isobutyl acetate	114·6	—	295·8	—	181·2
Methyl propionate......	80·0	—	262·7	—	182·7
Ethyl propionate	98·5	18·5	280·6	17·9	182·1
Propyl propionate......	122·3	23·8	304·8	24·8	182·5
Isobutyl propionate	135·8	—	318·7	—	182·9
Ethyl butyrate	121·7	—	304·3	—	182·6
Propyl butyrate........	144·3	22·5	326·6	22·3	182·3

Ethereal salt.	(t).	($t-t_1$).	(T).	(T$-$T$_1$).	(T$-t$).
Methyl isobutyrate	91·7	—	273·6	—	181·7
Ethyl isobutyrate	108·6	16·9	290·4	16·8	181·8
Propyl isobtyrate	133·4	24·8	316·0	25·6	182·6

The following relations are rendered evident by the tabulated results:—

(1.) The difference between the boiling point and the critical temperature is a constant = 182·3.

(2.) Alkyl salts of the same formula and analogous structure have approximately the same critical temperature.

(3.) The difference between the critical temperatures of two consecutive alkyl salts is equal to the difference between their boiling points.

(4.) The difference between the critical temperatures of two salts of the same acid and alcohol-radicals (alkyls) is equal to the difference between their boiling points.

The author considers that the determination of the critical temperature can be used as a control for the boiling point.

V. H. V.

Critical Point of Mixed Gases. By G. Ansdell (*Proc. Roy. Soc.*, **34**, 113—119).—The author, in continuation of his researches on the physical constants of liquid acetylene and hydrochloric acid (Abstr., 1882, 266), has investigated the behaviour of two gases in presence of one another as regards the alteration of the critical point. Carbonic anhydride and hydrochloric acid were chosen as offering examples of gases which are easily prepared, and whose critical points are accurately known; and further the results are probably not modified by their mutual decomposition or by the formation of an addition compound. The author used a Cailletet pump and the same method of experiment which he adopted in his former researches. The critical point of the mixture was determined, and then the tensions of the saturated vapour at different temperatures, together with the fractional volume to which the gas was reduced at the point of liquefaction, and also the relation between the liquid and gaseous volumes at different heights in the Cailletet tube. Some of the results are appended below.

	Temp. of mixed gases.	Pressure.		Temp. of mixed gases.	Pressure.
P. c. of CO_2 in mixture 17·18	0	27·84	P. c. of CO_2 in mixture 19·37	0	28·86
	15	40·66		13·8	39·86
	27	54·22		25·5	52·77
	37·5	70·28		38	67·36
	46	82·26		44	76·23
Critical point	47·2	92·21	Critical point	45·5	80·52
P. c. of CO_2 in mixture 25·48	0	33·17	P. c. of CO_2 in mixture 45·67	0	32·72
	16·3	50·09		17·5	50·73
	25·4	63·98		26·6	63·31
	34	77·02		35	76·64
	43·2	90·03		37·6	79·14
Critical point	45·1	—	Critical point	38	81·35

Pawlewski, from his experiments on the ethers and alcohols, arrives at the result that the critical point of mixed bodies is directly proportional to the percentage composition of the mixture when the co-ordinate origin of temperature taken is that of the body having the lowest critical point. He infers that the same rule would hold good in the case of liquid substances which are gaseous at ordinary temperatures; but as the physical constants of liquefied gases are so exaggerated as regards their compression and expansion, and as the variation of their critical points is materially affected by traces of impurity, it would appear probable that mixtures of such liquefied gases would not follow Pawlewski's rule. This view is confirmed by the results of the author's experiments. V. H. V.

Law of Freezing of Solvents. By F. M. RAOULT (*Compt. rend.*, **95**, 1030—1033).—If A represents the reduction of freezing point caused by the solution of 1 gram of the substance in 100 grams of the solvent, M the molecular weight of the dissolved substance (anhydrous), and T the molecular reduction of freezing point, *i.e.*, the reduction caused by the solution of a gram-molecule in 100 grams of liquid, then, if the solution is dilute,

$$MA = T.$$

The author has examined solutions of a large number of inorganic and organic bodies in water, benzene, nitrobenzene, ethylene dibromide, formic acid, and acetic acid, all of which, with the exception of water, contract on solidification.

Acetic Acid.—All organic and many inorganic bodies produce a molecular reduction of freezing point between 36 and 40, generally about 39. Certain inorganic compounds, sulphuric and hydrochloric acid, calcium nitrate, and magnesium acetate produce a molecular reduction of about 19, nearly half the ordinary number.

Formic acid behaves in a similar manner; the normal molecular reduction is 28, the abnormal 14.

Benzene.—Almost all organic compounds and all non-metallic chlorides produce a molecular reduction between 47 and 51, mean 49. Methyl and ethyl alcohols, formic, acetic, valeric, and benzoic acids, produce a mean reduction of 25, or half the normal reduction.

Nitrobenzene and *ethylene dibromide* behave in a similar manner, the mean molecular reductions with the first-named being 68 and 34, and with the second 117 and 58. The different reductions are produced by the same compounds as in the case of benzene.

Water.—The results are not so concordant. The majority of the inorganic acids, alkaline bases, salts of the alkalis and alkaline earths produce a molecular reduction between 33 and 43. Barium and strontium chlorides give about 50. With the greater number of more than 60 inorganic substances the reduction is about 37. On the other hand, magnesium sulphate, metaphosphoric acid, hydrogen sulphide, and all organic bodies without exception give a much more constant molecular reduction, lying between 17 and 20, mean 18·5. Here, as in the other cases, one reduction is just double the other.

From the results of experiments with more than 200 compounds dissolved in these six different liquids, the author draws the following conclusions:—

All bodies when dissolved in a liquid compound which can solidify, lower its freezing point. In all liquids, the molecular reduction of the freezing point due to different compounds approaches two values, invariable for each liquid, and of which one is double the other. The greater value is most frequently met with, and is the normal molecular reduction; the lower value is the abnormal reduction. This lower value corresponds with those cases in which the molecules of the dissolved substance are united in pairs.

The normal molecular reduction of freezing point varies with the nature of the liquid, but if each of the molecular reductions is divided by the molecular weight of the particular solvent, which reduces the results to the case of a molecule of the substance dissolved in 100 mols. of the solvent; the quotients, except in the case of water, are practically the same.

Water	37 : 18 = 2·050	Benzene	49 : 78 = 0·628
Formic acid	28 : 46 = 0·608	Nitrobenzene	70·5 : 123 = 0·600
Acetic acid.	39 : 60 = 0·650	Ethylene dibromide	117 : 188 = 0·623

Water obeys the general law if it is assumed that the physical molecule, at least near the freezing point, is composed of three chemical molecules, for 37 : 18 × 3 = 0·685. It follows that a molecule of any compound whatever, when dissolved in 100 mols. of any liquid whatever of a different nature, lowers the freezing point of the liquid by a quantity which is almost constant, and which is about 0·62. This law is general if it is admitted that physical molecules may be composed of two, or in rare cases of three, chemical molecules. C. H. B.

Report to the R. Accademia dei Lincei on a Memoir by R. Schiff "On the Molecular Volumes of Liquids." By P. Blaserna and S. Cannizzaro (*Gazzetta*, **12**, 488—494).—A theoretical paper, not admitting of abstraction.

Passage of Alcoholic Liquids through Porous Vessels. By H. Gal (*Compt. rend.*, **95**, 844—846).—The author has studied the alteration in composition of aqueous alcohol when placed in bladders under different conditions. It is generally taught that alcohol placed in bladders becomes stronger with lapse of time, but the author shows that this is not always true. When the bladders are exposed to a comparatively high temperature and dry atmosphere, the alcohol increases regularly in strength, but when placed in an atmosphere saturated with moisture and at low temperatures, the liquid *loses* strength regularly. The author thinks that those who have previously studied this subject have assigned too much importance to the part taken by the *membrane* used, and have not taken sufficient account of the effect of the surrounding atmosphere. E. H. R.

Lecture Experiments. By A. W. Hofmann (*Ber.*, **15**, 2656—2677).—A continuation of experiments previously described.

Electrolysis of Hydrochloric Acid.—The acid is decomposed in the closed limb of a **U**-tube, and the liberated chlorine is absorbed by a solution of potassium iodide, which is admitted through the open end of the second limb, the volume of the gas being reduced to one-half.

To show that by the union of chlorine with hydrogen no change of volume takes place, a glass bulb containing the mixed gases is introduced into a large wide-mouthed globe containing dry air. The gaseous mixture is exploded by means of the magnesium light, the pressure in the globe before and after explosion being indicated by a manometer.

For showing that the weight of a body is increased by combustion, magnesium or phosphorus is burned in a globe, the globe and metal being weighed before the experiment, and the globe together with the product of combustion after the experiment.

To show that carbonic anhydride has the same volume as the oxygen it contains, a glass globe fitted with a mercury safety tube is filled with oxygen. A piece of glowing carbon is then introduced, and the opening immediately closed. After the combustion of the carbon, the globe is allowed to cool, when the mercury regains its original level.

Combustion of Oxygen in Hydrogen.—The hydrogen is passed *upwards* into a glass globe, and the jet supplying the oxygen is introduced from *above*, both ends being closed by corks, through which the supply tubes pass. In this way the cracking of the globe is avoided which so frequently took place when, as in the older form of the experiment, the hydrogen was allowed to burn below it in contact with the air.

To show that aqueous vapour is lighter than air, water is boiled in a flask, the vapour being made to pass through a horizontal tube, in connection with which are two vertical tubes, one directed upwards, and the other downwards. The steam escapes by the upper tube, and at the end of the horizontal tube, but does not escape by the lower tube.

Relative Volumes of Water in the Liquid and Gaseous State.—A rapid current of steam is passed through a globe connected above and below with narrow glass tubes. When full of vapour the upper end is closed, and the lower end dipped under mercury. The latter rises and fills the globe, while the condensed water is forced into the capillary tube.

Maximum Density of Water.—In a glass tube containing distilled water a coloured glass float is placed, the density of which is such that the body just floats when the temperature of the water is 4°. The tube is sealed, so that when once adjusted it cannot get out of order.

Decomposition of Water by Sodium.—By placing the sodium on the end of a long packing needle, and introducing it quickly into the water under the inverted gas jar, the explosions which sometimes occur when gauze is used, are avoided.

Alternate Decomposition and Reproduction of Water.—A **U**-tube, closed at one end, is arranged with wires for passing the electric spark, and lower down with electrodes for decomposing water. The lower part of the **U**-tube contains mercury, and above this in the closed limb is acidulated water. A cork is inserted in the open end, and mercury is run out below, so as to diminish the pressure in the tube. The decomposition of the water is then started by the current, and as soon as the evolved gases surround the upper wires, they are caused to combine again by the passage of the electric spark.

Volumetric Analysis of Ammonia.—One limb (which can be closed at both ends by stopcocks) of a **U**-tube is filled with chlorine. Ammonia solution is poured into the other limb, and about 10 c.c. admitted into the chlorine. The tube is well shaken, and the excess of ammonia replaced by dilute sulphuric acid, which is then admitted into the closed limb. The liquid rises until the volume of the gas (nitrogen) is seen to have diminished to one-third of the original chlorine.

Volumetric Relation of Ammonia to the Nitrogen it contains.—The apparatus described in the last experiment is filled with dry ammonia. On shaking with a solution of bromine in dilute soda, the nitrogen is set free, and occupies half the original volume of the ammonia.

For showing quantitatively *the production of sulphuric acid*, the author employs a **U**-tube, one limb of which is provided at its upper extremity with a three-way stopcock, the other limb being open. After filling the tube with mercury, nitric oxide (40 c.c.), sulphurous anhydride (60 c.c.), and dry oxygen (30 c.c.) are introduced. On finally admitting steam, the temporary formation of the characteristic white crystals may be observed. At the end of the experiment nearly the original volume of the nitric oxide remains, whilst the sulphuric acid forms a layer above the mercury.

Demonstration of Dulong and Petit's Law.—The apparatus employed consists of two similar thermometers, the bulbs of which are double cylinders of glass, so that there is a hollow space in the centre of each bulb, into which the metal experimented with can be inserted. In conducting an experiment, the two metals whose specific heats are to be compared are heated to a given temperature, and quickly dropped into the cavities of the two thermometers.

The equivalent weights of lead and zinc can be shown by suspending a weighed cylinder of zinc in a solution of lead acetate, and comparing the weight of the precipitated lead with that lost by the zinc.

Leidenfrost's Experiment Reversed.—A platinum flask is maintained at a white heat by a current of oxygen and hydrogen passing into it. It is then made to dip under water, when the platinum will continue to glow for some seconds. A. K. M.

Inorganic Chemistry.

Oxygen prepared from Potassium Chlorate. By A. WAGNER (*Zeits. Anal. Chem.*, **21**, 507—510).—It is well known that oxygen prepared from potassium chlorate frequently contains appreciable traces of chlorine. The author finds that whilst the absolutely pure salt yields pure oxygen, the commercial salt never does, owing to traces of organic matter present in it. Carbonic anhydride decomposes even pure chlorate, with formation of chlorine. O. H.

Formation of Ozone and Hydrogen Peroxide. By S. KAPPEL (*Arch. Pharm.* [3], **20**, 574—577).—The author, having previously experimented on the nitrification of ammonia in presence of metals (p. 286), made experiments of a similar kind with fixed alkalis and copper in the presence of air, thinking that the nitrogen of the air would be oxidised to nitrous acid; he was, however, unsuccessful as regards the end sought. The test papers which he suspended in the flasks certainly became blue, but were immediately decolorised, and the fluid, on the termination of the experiment, gave no nitrous reaction.

The results indicate the simultaneous production of ozone and hydrogen peroxide; the latter probably decomposes the former, which is again formed, and a continuous process of the kind appears to go on. The fluid, if tested with potassium dichromate and sulphuric acid and shaken with ether, does not show the hydrogen peroxide reaction, but if left for a long time in an open flask, or if a current of air is passed through it to remove the ozone, the reaction is easily obtained.

J. F.

Activity of Oxygen. By M. TRAUBE (*Ber.*, **15**, 2421—2443).—A continuation of the author's researches (Abstr., 1882, 795).

PART I.—In this paper the author criticises the theory of Hoppe-Seyler, which supposes the dependence of the life functions of animal organisms on a process of fermentation whereby hydrogen is evolved, and the oxygen molecule separated into its constituent atoms, these at the moment of liberation assuming the active character of ozone, and effecting the oxidation processes necessary for the continuation of life. According to the author, this theory fails both on physiological and chemical grounds, for in the first place the evolution of hydrogen has only been observed in the alimentary canal, where fermentation processes are undoubtedly effected by bacteria: further, if the fermentation and life processes were identical, then those organs of the body, such as the blood and muscles, on which the function of life is dependent, would soon after death show an evolution of hydrogen (in the absence of oxygen); but this is directly contradicted by the researches of Broech (*Annalen*, **115**, 78) and those of the author, for fresh muscle does not reduce dilute nitric acid. Again fermentation bacteria convert nitrogenous into ammoniacal compounds, but the animal organs in the absence of such bacteria effect no such change. Secondly, Hoppe-Seyler based the chemical part of this theory on experiments which showed that petroleum shaken up with sodium in the presence of air absorbed oxygen with formation of volatile acids. Hoppe-Seyler did not however examine whether this result was not due to the inevitable moisture of the air; and the experiments of Fudakowski, Schönbein, and others have shown that a number of organic compounds, as benzene, ether, turpentine, gradually darken in the air with absorption of oxygen, without the intervention of sodium or of active hydrogen at the moment of its liberation. Such experiments cannot serve as examples of the conversion of oxygen into ozone by nascent hydrogen. The author made some experiments directly bearing on the point. Dilute sulphuric acid and zinc were shaken up with air, but no ozone could be detected even by indigo sulphate. Again, zinc and concentrated ammonia solution, or a mixture of ammonia and soda, shaken up with air, caused no conversion of oxygen into ozone, for the ammonia was not converted into nitrous or nitric acids; therefore nascent hydrogen cannot separate from the oxygen molecule active atoms, which combine together to form ozone. Further, nascent hydrogen cannot form hydrogen peroxide with oxygen in the presence of water; for although zinc and dilute sulphuric acid shaken up with air cause a formation of hydrogen peroxide, yet this must be attributed solely to the water present in the sulphuric acid, for if concentrated acid be used, no hydrogen peroxide is formed, and nascent hydrogen by itself reduces hydrogen peroxide.

Schönbein observed that various metals, which with dilute acids do not cause the formation of hydrogen peroxide, possess this property when amalgamated with mercury; this the author explains by supposing that the amalgams of these metals have a more feeble reducing action than the metals themselves, and so do not destroy the molecules of the hydrogen peroxide. This view receives support from the fact that the evolution of hydrogen from zinc and sulphuric acid is considerably modified by the amalgamation of the metal.

Again, Hoppe-Seyler attributes the oxidising action of hydrogen palladium in presence of water and oxygen to the liberated or nascent hydrogen, but he completely overlooks the formation of hydrogen peroxide, which is produced according to the equation—

$$\begin{array}{l}\mathrm{Pd}_2\\\mathrm{Pd}_2\end{array}\boxed{\begin{array}{lcl|lcl}\mathrm{H} & & \mathrm{OH} & \mathrm{H} & & \\ & + & & & + & \mathrm{O}_2\\\mathrm{H} & & \mathrm{OH} & \mathrm{H} & & \end{array}} = 4\mathrm{Pd} + 2\mathrm{H}_2\mathrm{O} + \mathrm{H}_2\mathrm{O}_2.$$

The presence of water is necessary for this change, for palladium hydrogen shaken up with ether in the air, forms no hydrogen peroxide, but its presence becomes manifest directly a little water is added.

Substituting palladium hydrogen for zinc, the author repeated the experiments described in his former paper (*vide supra*), and with the same results. Palladium-hydrogen must then be classed among those substances, which like zinc, lead, pyrogallol, &c. (which the author proposes to name *autoxidisable*), possess the property of attracting oxygen, so as to combine with the hydrogen of water to form hydrogen peroxide. In conclusion, the author remarks that this property of such substances is neither identical nor intimately associated with the more rare property possessed by some substances of rendering oxygen active by converting it into ozone.

PART II.—The author, to examine his theory that hydrogen peroxide is not oxidised water but reduced oxygen, has studied the electrolysis of acidulated water, the platinum electrodes being separated by a cylinder of some porous material. No hydrogen peroxide is formed at the positive pole, but only at the negative pole, when the oxygen liberated from the opposite pole can come in contact with the hydrogen. It is thus probable that the hydrogen peroxide is formed by the direct combination of the nascent hydrogen with the oxygen molecule, thus: $\mathrm{H} + \mathrm{H} + \mathrm{O}_2 = \mathrm{H}_2\mathrm{O}_2$; in this case, hydrogen peroxide differs in its chemical character from the peroxides of the heavy metals, which are formed by oxidation processes at the positive pole. The quantity of hydrogen peroxide is increased when the electrodes are of palladium, but decreased with electrodes of mercury, silver, gold, and the heavy metals, and it is *nil* when the negative pole is of carbon. As a general result, it is found that those metals which, with dilute sulphuric acid and air readily form hydrogen peroxide, form this substance the less readily when they are made the electrodes for the decomposition of water. Conversely those metals, which form no hydrogen peroxide in presence of acid and air, but which possess the property of retaining hydrogen like palladium, form hydrogen peroxide in the larger quantities during the electrolysis of water; but if the palladium-hydrogen is made the negative electrode, the hydrogen is completely burnt to water: $2Pd_2H + O = 4Pd + H_2O$.

Thus the formation of hydrogen peroxide is not caused by active oxygen, as hitherto believed, but is prevented by it. V. H. V.

Ozone in Presence of Platinum-black. By E. MULDER and H. G. L. VAN DER MEULEN (*Rec. Trav. Chim.*, 1, 167—172).—By passing ozonised oxygen over platinum-black at the ordinary temperature, the authors have obtained results from which, they say, it appears highly probable that the ozone is thereby converted into ordinary oxygen; and they regard this result as the first known instance of the transformation of an element into an allotropic modification under the influence of another element, without the occurrence of chemical action between the two. For the theoretical speculations as to the manner in which this transformation may be supposed to take place, we must refer to the original. H. W.

Variations of the Amount of Oxygen in the Atmosphere. By C. A. VOGLER (*Chem. Centr.* [3], **13**, 556—558).—The author makes some remarks in support of his theory against the attack on it by Morley. Both agree as to the fact that the atmosphere varies in composition vertically and not latitudinally, and therefore that the variation in the quantity of oxygen is due to vertical air-currents. Morley is of opinion that the air which sinks down when the barometer is high is poor in oxygen, and would thus lower the amount of that element; and that when the barometer is low, the lower layers of air are rich in oxygen. The author thinks that when the barometer is low the air is well mixed by currents, and that therefore there is no difference in the amount of oxygen found above or below a certain point; and that when the barometer is high, the air, being in a state of rest, resolves itself into bands according to Dalton's law, which would cause a greater quantity of oxygen to be found in the lower bands. He urges this by arguments and calculations. Finally, he welcomes the idea of analysing air from various places under similar circumstances, for it will settle the point whether the variation in the quantity of oxygen in the atmosphere is really a regular phenomenon or simply local. D. A. L.

Carbonic Anhydride in the Atmosphere. By E. H. COOK (*Phil. Mag.* [5], **14**, 387—395).—Taking the polar diameter of the earth as 7899 miles, the equatorial diameter as 7925·5 miles, and the height of the homogeneous atmosphere as 26,214 feet (nearly 5 miles), the cubical content of the homogeneous atmosphere is found to be 591,647,337 cubic miles, or in round numbers 592,000,000 cubic miles. If the average amount of carbonic anhydride in the atmosphere is taken as 4 vols. in 10,000, the total volume of the carbonic anhydride is 236,800 cubic miles, and the total weight 4287 billions of pounds, or 1,913,685,908,480,000 kilos. These numbers differ considerably from those given by Dumas and Boussingault, and from that given in Roscoe and Schorlemmer's chemistry. The first of these is nearly 40 per cent. and the second about 33 per cent. too high. Recent investigations, however, show that the proportion of carbonic anhydride in the atmosphere is not so high as 4 vols. in 10,000. If the mean of these (Fittbogen and Hasselbarth, 3·4 vols. in 10,000, Farsky 3·4 vols., and Reiset 2·942 vols.) is taken, the total weight of the carbonic anhydride is nearly 1545 billions of kilograms. The average amount of coal raised annually in the world during the last three years is about 280,000,000 tons. Assuming that this contains 75 per cent. of carbon, 10 per cent. of which is thrown away with the ash, 182,000,000 tons of carbon are annually converted into carbonic anhydride, which gives a daily production of 1,800,000 tons, or nearly 1,800,000,000 kilos. Assuming that one-third more is produced by the combustion of wood, peat, oil, &c., the total daily production by combustion is 2,400,000,000 kilos. The present population of the world is about 1,500,000,000, and each individual produces on an average a kilogram of carbonic anhydride in 24 hours. Assuming that twice as much carbonic anhydride is produced by the respiration of lower animals as by that of man, the total amount produced by respiration is 4,500,000,000 kilos. per day. The amount produced by the decay of animal and vegetable matter may be taken as equal to that produced by the respiration of man, and the amount sent into the air from subterranean sources may be fairly assumed to be five times as great as the total amount derived from all the other sources together. This gives about 40,000,000,000 kilos. per day. Adding all these quantities together, it is found that the total amount of carbonic anhydride daily added to the atmosphere is at least 50,000,000,000 kilos., from which it follows that if no compensating influences were at work the proportion of carbonic anhydride would be doubled in about 100 years.

The causes which remove carbonic anhydride from the air are fixation of carbon by plants, removal of the anhydride by zoophytes, and absorption of the anhydride by inorganic chemical action. In the first case alone is oxygen returned to the atmosphere; in the other two cases the carbonic anhydride is absorbed as a whole. The total area of the land-surface of the globe is 57,600,000 square miles (Saunders). Of this 8,200,000 square miles are in arctic and antarctic regions, thus leaving 49,400,000 square miles on which vegetation might flourish. A considerable portion of this area is, however, occupied by barren mountains, cities, and rivers. Estimating the total area of leaf-surface as 50 per cent. of the area of plant-bearing land, it follows that 24,700,000 square miles or 63,973,000,000,000 square meters of leaf-surface are engaged in the work of removing carbonic anhydride. Since each square meter of leaf-surface decomposes about 1 litre of carbonic anhydride per hour, it follows that 63,973,000,000,000 litres of the gas are decomposed every hour. Taking into account the fact that sunlight on the average lasts only ten hours each day, and allowing 25 per cent. for diminution of the action in winter, the average amount of carbonic anhydride decomposed per day is 479,000,000,000 kilolitres, or more than 900,000,000,000 kilos. A considerable proportion of the carbon thus removed is, however, returned to the air when the leaves decompose in the autumn, and allowance must also be made for the fact that some plants give off carbonic anhydride in the dark. On this point, however, there are no data on which to base any calculation, and the evolution of carbonic anhydride by the nocturnal respiration of plants may be much greater than is usually supposed. From the numbers given it would appear that the vegetable life on the globe is of itself sufficient to maintain the purity of the atmosphere. This conclusion is, however, based on incomplete data.

The removal of carbonic anhydride from sea-water by low forms of animal life takes place on a gigantic scale, but the carbonic anhydride thus removed exists in the sea and not in the atmosphere, and a very large proportion of it must be derived from submarine volcanic eruptions. In all probability the influence of this action is felt only after many years, and so far as the atmosphere is concerned, it cannot be compared to plant life in point of activity. Large quantities of carbonic anhydride are removed by inorganic chemical changes, as, for example, in the conversion of orthoclase into kaolin (Sterry Hunt, *Am. J. Sci.*, May 1880), but any estimate of the rate of this action is impossible.

These calculations seem to show that the causes which remove carbonic anhydride from the air are more powerful than those which add this gas to the air. Its proportion must therefore be gradually decreasing, but there are no trustworthy data on which to base any conclusions on this point. As to the source of the enormous quantities of carbonic anhydride already fixed in the form of limestone, we have no knowledge. Either at one time the atmosphere surrounding the earth must have been much richer in carbonic anhydride than it is at present, or, as Sterry Hunt supposes, there must be a universal atmosphere similar to our own from which the carbonic anhydride now fixed in the earth's crust has been derived. C. H. B.

Nitrification in Presence of Copper and other Metals. By S. KAPPEL (*Arch. Pharm.* [3], **26**, 567—573).—The author was accustomed to show his pupils, as a class experiment, the production of nitric reactions when ammonia was left in contact with metallic copper. Some flasks used in his experiments were left with their contents, corked, for about a year; on examination he then found that the fluid had lost its ammoniacal smell, and contained both nitrites and nitrates, and induced by this observation he made the experiments reported in the present paper:—

1. A quantity of copper cuttings were placed in a flask connected with a drying apparatus—a bulb tube containing copper oxide, and an

aspirator—the flask was placed on a sand-bath, and air drawn through the arrangement for 14 days, at the end of which time the fluid gave strong reactions of nitrites and nitrates, and the copper oxide was not reduced; a second experiment exactly similar, except that it was made in the cold, gave the reactions plainly, but not so strongly.

2. Copper clippings and ammonia were placed in a flask through which carbonic acid was passed, and when as nearly as possible free from atmospheric air, the mouth was closed by fusion. After six hours the fluid became intensely blue; it then gradually waned, and became colourless. When the flask was opened, nitrites and nitrates were distinctly present.

3. The arrangement in this experiment was similar to the last, but the fluid was heated to 60—70° during the process; the reactions were similar but sharper.

Other experiments were made in which a current of hydrogen was passed through the arrangement during the process. The results were variable and inconclusive.

Similar experiments were made with iron and zinc, and it was found that in all cases nitrification took place, but not with as much activity; possibly, the author says, the nascent hydrogen had a reducing effect on the nitrites at the moment of their formation, a continuous process of oxidation and reduction proceeding simultaneously. The author's opinion is that the presence of air is necessary to this process of nitrification, and that although it proceeds in the cold, it is facilitated by heat, and he thinks metals other than those mentioned are capable of producing similar results. J. F.

Conversion of Tricalcium Phosphate into Chlorine Compounds of Phosphorus. By J. Riban (*Compt. rend.*, **95**, 1160—1163; and *Bull. Soc. Chim.*, **39**, 14).—When chlorine is passed over a mixture of tricalcium phosphate and carbon, or when chlorine and carbonic oxide are passed over tricalcium phosphate alone heated to incipient redness, a small quantity of calcium chloride and metaphosphate is formed, but no further change takes place. If, however, a mixture of chlorine and carbonic oxide is passed over an intimate mixture of calcium phosphate and carbon (*e.g.*, bone-black), heated in a glass tube to 330—340° in an oil-bath, phosphorus oxychloride, calcium chloride, and carbonic anhydride are produced. After some time, the calcium chloride formed interferes with the reaction, but if it is removed by washing, the phosphate can be completely decomposed. The carbon plays no chemical part in the reaction, and is found practically unaltered at the end of the experiment. It is essential to the production of the reaction, and probably acts by condensing the gases in its pores. The reaction takes place in two stages, thus: (1) $Ca_3P_2O_8 + 2CO + 2Cl_2 = CaP_2O_6 + 2CO_2 + 2CaCl_2$, and (2) $CaP_2O_6 + 4CO + 4Cl_2 = 2POCl_3 + 4CO_2 + CaCl_2$. The reaction takes place slowly at 180°, and proceeds rapidly between 330° and 340°. When carbonic oxide and chlorine are passed over bone-black at this temperature, no phosphorus oxychloride is at first obtained, the gases being used up in converting the phosphate into metaphosphate, which is afterwards decomposed in accordance with the second equation. The phosphorus oxychloride thus obtained is almost pure.

When phosphorus oxychloride is passed over a long column of wood charcoal heated to redness in a glass tube, phosphorus trichloride is formed, and carbonic oxide, or a mixture of carbonic oxide and carbonic anhydride, according to the length and temperature of the column of carbon, is given off.

This method of reduction by means of a mixture of chlorine and carbonic oxide in presence of carbon, will doubtless prove valuable in many other cases. It answers very well for the production of aluminium chloride from alumina, the change taking place easily at the temperature of an oil-bath. It may also serve for the production of phosphorus oxychloride from calcium phosphate on a large scale.

C. H. B.

Volume-weight of Sulphuric Acid. By A. SCHERTEL (*J. pr. Chem.* [2], **26**, 246—249).—If concentrated sulphuric acid is boiled down to about half its volume, the residue contains 80·40 per cent. SO_3 = 98·50 per cent. H_2SO_4: sp. gr. at 0° (compared with water at 0°) = 1·857. If the same acid is distilled until acid of constant composition passes over, and the last portions of this are collected, they have the composition 80·54 of SO_3 = 98·66 per cent. H_2SO_4, and are of sp. gr. 1·8575 at 0°. If these acids are mixed with dry or fuming sulphuric acid, a fall in the volume-weight takes place until the composition of normal hydrogen sulphate, H_2SO_4, is reached. On the other hand, by the addition of anhydride, the volume-weight increases again, as seen from following table:—

Percentage of SO_3.	Corresponding with	Parts. H_2SO_4.	Volume-weight at 0°.
80·40		98·50	1·8570
80·54		98·66	1·8575
81·00		99·23	1·8558
81·10		99·35	1·8550
81·63		100·00	1·8540
81·86		100·28	1·8548
82·10		100·57	1·8577
82·55		101·13	1·8640
82·97		101·64	1·8722

The acid obtained by distillation with constant composition is the most concentrated, and has the highest sp. gr. The liquid normal acid undergoes dissociation even at 0°.

The tables of the volume-weights and composition of sulphuric acid edited by Bineau, Kolb, and Otto, show a continual increase in sp. gr.

D. A. L.

Argentous Oxide. By W. PILLITZ (*Zeitsch. Anal. Chem.*, **21**, 496—506).—In continuation of his investigation (*ibid.*, **21**, 27), the author has examined the precipitates obtained by the action of alkaline solutions of antimony trichloride, stannous oxide, or stannous chloride on silver nitrate. The product obtained by means of the antimony solution was proved to consist of a mixture of disodiodihydric pyroantimonate ($Na_2H_2Sb_2O_7 + 6H_2O$), metallic antimony, metallic silver, and silver chloride, whilst the alkaline tin solutions furnished a mixture of metallic silver and stannic acid. The precipitates were quite free from argentous oxide. O. H.

Aluminates and Basic Haloïd Salts of Barium: Notes on Barium Hydroxide and Haloïd Salts. By E. BECKMAN (*J. pr. Chem.*, **26**, 385—421).—This paper, the first instalment of the research, gives a description of the barium aluminates.

Action of Baryta-water on Aluminium Compounds.—The result of this action is the production of a soluble aluminate having the composition Al_2O_3,BaO,Aq, and if the solution of this compound is digested with excess of aluminium hydroxide, an insoluble aluminate is formed. The result of mixing baryta-water with aluminum chloride is a precipitate of aluminium hydroxide, but a small percentage of barium is found in the precipitate, and this is probably due to the formation of barium carbonate. The solvent action of baryta-water on metallic aluminium cannot be stated with certainty, as only metal having a small percentage of silica was obtainable, but at the ordinary temperature aluminium hydroxide was formed as insoluble crystalline powder, whilst BaO,Al_2O_3 was present in solution. At high temperatures aluminium foil is attacked by water, but not readily, whilst wire remains unaltered; but with baryta-water under like circumstances, a solution of monobarium aluminate is formed. It appears then that barium forms definite compounds with aluminium, and the author carefully describes the method of preparation, the analytical results, &c., and shows that $Al_2O_3,BaO,6H_2O$; $Al_2O_3,2BaO,5H_2O$, and $Al_2O_3,3BaO,11H_2O$, exist. The dibarium aluminate is prepared by boiling together the requisite quantities of baryta-water and freshly prepared aluminium hydroxide, filtering while hot, and then boiling the filtrate; when this liquid is reduced to eight times the amount of compound present, colourless crystals begin to be deposited, and can be washed with hot water; these have the composition of dibarium aluminate; the crystals are well formed, asymmetrical with an axial proportion of 0·8545 : 1 : 0·9888, and amongst other faces, have the following as principal: $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $0P$, $2'\breve{P}2$. Dibarium aluminate is a tasteless powder scarcely soluble in cold water, and is precipitated from its solutions by alcohol; when heated, the crystals decrepitate, slowly losing water, but not their form, and do not fuse at the highest temperature; as regards the crystalline water, some is lost up to 125°; at 155°, 2 mols. H_2O are slowly lost, and a third more slowly still; a rise of temperature to 250° removes a further quantity, but the whole of the fourth mol. is not got rid of below 300°, and the last or 5th mol. only at a red heat. It is probable that this last mol. is retained by the barium hydroxide, because in the case of the tribarium aluminate a mol. of water corresponding to each mol. of BaO is firmly retained up to the last. When dibarium aluminate is heated in a current of dry gas, the water is rapidly and suddenly removed, and when it is fused with acid potassium chromate, the removal is irregular; this is exactly opposite to what occurs in the case of barium hydroxide under like conditions.

A crystalline precipitate consisting of aluminium and barium hydroxides, is produced when carbonic anhydride is passed into a solution of the dibarium aluminate, and baryta-water removes the alumina from this precipitate; but if the gas be passed into the boiling solution, short acicular crystals are formed, and baryta-water removes only alumina from this at a high temperature. Dry carbonic anhydride does not act on cold solid dibarium aluminate, but if this compound is ignited, then every mol. absorbs 1 mol. CO_2.

Monobarium Aluminate.—The solution of this compound is obtained by boiling the result of the last-mentioned reaction with water; the solution is stable, but if much concentrated deposits the dibarium compound.

The solid compound is prepared (1) by precipitation from the last-named solution by means of alcohol; (2) by allowing the solution of the monobarium aluminate, whose percentage of alumina corresponds with that of a concentrated dibarium aluminate solution $(1 = 8)$ to form spontaneously a granular non-crystalline deposit; (3) the dibarium solution will also deposit crystals of the monobarium compound, and will decompose the more rapidly the more concentrated the solution. All the preparations of this compound are loose white tasteless powders, but slightly soluble in cold water, and by boiling with water form an opaque alkaline liquid. No alteration in appearance is noticeable when this compound is heated, although it loses crystalline water. When heated at 110°, nearly 3 mols. H_2O remain, analogous to those present in dibarium aluminate; of these, 1 mol. is removed at 130°, another at 220°, the last remaining until a red heat is reached: heated with acid potassium chromate, all the water passes away at once. Carbonic anhydride causes all barium and alumina to be precipitated as needles from hot solutions, but the dry monobarium aluminate only absorbs this gas if an excess of the barium oxide is present.

Tribarium Aluminate.—When 1 part of dibarium aluminate is boiled in 30 parts of water with 10 parts of barium hydroxide, the solution filtered hot, and concentrated to 28 parts, colourless crystals of the tribarium compound are deposited; if the concentration is effected over a lamp, there will be $7\frac{1}{2}$ mols. H_2O present, but when an oil-bath is employed, 11 mols. are found. This substance may also be prepared by mixing hot dibarium aluminate solution with barium hydroxide dissolved in its own water of crystallisation. The crystals are opaque and brittle, taste alkaline, and dissolve in 15 parts boiling water; this solution decomposes when boiled, the dibarium compound being formed. The first mol. of water of crystallisation is lost by heating at 115°, 5 mols. are lost at 165°, and 6 mols. at 255°, the remaining $1\frac{1}{2}$ mol. making up the whole $7\frac{1}{2}$ mols., is only lost at a red heat. Fused potassium dichromate removes that amount of water corresponding to its own temperature, 2 mols. remaining even after complete fusion. Microscopic needles containing barium and aluminium are separated from hot solutions by carbonic anhydride, but the gas is only absorbed by the solid at incipient redness, every molecule absorbing 2 mols. CO_2. Oxygen is not absorbed by this compound. E. W. P.

Beryllium Hydroxides. By J. M. v. BEMMELEN (*J. pr. Chem.* [2], **26**, 227—246).—From previous researches the author concluded that those hydroxides which separate from their solutions in a colloid form, such as those of silicon, iron, &c., never have a constant composition, and are scarcely ever homogeneous. He, however, thinks it probable that under certain conditions they ought to be obtained as chemical compounds, and remain constant within a wide range of changes of temperature. For illustration of this hypothesis the hydroxides of beryllium seemed well adapted. Of these the author has distinguished two, α, granular, and β, gelatinous. The *β-hydroxide* is precipitated by ammonia from pure beryllium sulphate, it is washed out of contact with the air with cold water, dried in a stream of air free from carbonic anhydride and powdered; its constitution is then represented by: $BeO,1\cdot61(H_2O),0\cdot025(CO_2)$. When washed and dried in the air, its constitution is $BeO,2\cdot63(H_2O),0\cdot05(CO_2)$. To prepare the *$\alpha$-hydroxide*, the solution of the β-hydroxide in sulphuric acid is precipitated with potash and redissolved by excess of the precipitant; it is then diluted with much water and boiled. The granular deposit of the hydroxide is washed with boiling-hot water, excluding air; it forms a fine white powder, is free from carbonic anhydride, and has the constitution BeO,H_2O, which remains constant up to 200°; dissociation now commences and reaches a maximum at 215°, and after two hours' heating at 215—220°, the oxide loses half a mol. H_2O, whilst after ten hours' heating $BeO,0\cdot18H_2O$ remains; the last $\frac{1}{10}$th mol. H_2O is only entirely driven off at a strong red heat. From air saturated with moisture, the α-hydrate will absorb as much as $\frac{1}{4}$—$\frac{1}{2}$ mol. H_2O, which, however, is given off again in the ordinary air. After losing $\frac{1}{2}$ mol. H_2O at 200°, its constitution is definitely changed, for although it absorbs 1 mol. of water from moist air at 15°, it gives it up again in dry air. Heated at 280°, the water is reduced to 0·13 mol., now again it absorbs 1 mol. H_2O, but gives it up only till the residue is reduced to 0·18 mol. After being heated to redness, it behaves in the same way; but a strong red heat changes it altogether; it then loses all power of absorbing water, and is only soluble in boiling sulphuric acid.

The β-hydroxide is a fine powder; at the ordinary temperature it absorbs a considerable amount of water from moist air, even when it has been previously heated at 100°. It has no constant composition. When heated it gradually and constantly loses weight (water); between 150 and 180°, the compound BeO,H_2O is attained, and remains constant between 180 and 200°; above this temperature at about 215° it undergoes changes similar to the α-hydroxide. When tested with regard to the power of absorbing salts from aqueous solutions, the β-hydroxide shows this property, the α- does not. Comparative experiments with hydrated magnesium oxide confirm the results of previous investigators (Ditte and Rose); it retains the composition MgO,H_2O even when heated above 350°, and does not even undergo molecular change below this temperature; it loses water of hydration between 350° and red heat. The author comes to the conclusion that beryllium α-hydroxide resembles those of magnesium and calcium, whilst beryllium β-hydroxide resembles those of aluminium, &c.

Thus the former can be represented by a definite and simple formula, and is constant within a certain range of changes of temperature, but smaller than that of magnesia. The changes which the β-compound undergoes during heating are similar to those observed by Berthelot in ferric hydroxide, for he found that from the time it was precipitated, it constantly changed molecularly, and at no period could be represented by a simple formula. The author considers this peculiarity of the gelatinous hydroxide to be due to the fact that it is a mixture of hydroxides, which behave differently at the same temperature, that is, that each one requires a different temperature to convert it into the lower hydroxide or anhydride. This view is supported by some observations which the author has made on the hydroxide freshly precipitated from aluminium chloride by ammonia. 1. After boiling for 24 hours with water it has the composition $Al_2O_3,1\cdot6H_2O$. 2. Washed for some time with cold water it is $Al_2O_3,1\cdot9H_2O$. 3. Precipitated from diluted solution and quickly washed with water it is $Al_2O_3,2\cdot6H_2O$. 4. After half a year in contact with water it is $Al_2O_3,3\cdot1H_2O$. The last-mentioned is quite constant between 15 and 100°, and even above. Nos. 1, 2, and 3 are mixtures of this with a lower hydroxide. D. A. L.

Atomic Weight of Yttrium. By P. T. CLEVE (*Compt. rend.*, **95**, 1225—1226).—The determinations of the atomic weight of yttrium made in 1872 are inexact, since no precautions were taken to separate terbium, which at that time was not definitely known to exist. By fractional precipitation with oxalic acid, the author has obtained from 3 to 4 grams of yttria with a constant molecular weight. The mean of twelve determinations of the amount of yttria in the sulphate prepared from this pure oxide is $48\cdot503 \pm 0\cdot00029$ per cent. It follows, therefore, that the atomic weight of yttrium is $89\cdot02$ if $O = 16$ and $S = 32$, or $88\cdot9 \pm 0\cdot027$ if $O = 15\cdot9633$ and $S = 31\cdot984$. Pure yttria is perfectly white, the yellow colour which it sometimes has being due to the presence of very small quantities of terbia.

C. H. B.

Lecture Experiments illustrating the Combination of Zinc with Sulphur. By H. SCHWARZ (*Ber.*, **15**, 2505—2508).—After alluding to the common method of illustrating chemical combination by heating flowers of sulphur with copper or iron filings, the author suggests the following experiment. Two parts of zinc-dust and one part flowers of sulphur are intimately and carefully mixed; on applying a light the mixture ignites and burns with a green flame, and the zinc sulphide is deposited on surrounding objects; the mixture can also be ignited by percussion, and in an explosion apparatus the author found that the detonating power of the mixture was about an eighth of that of blasting powder.

The author explains the fact that sulphur does not mix directly with molten zinc, as a form of Leidenfrost's phenomenon, as the sulphur vapour prevents the metal coming in contact with the molten sulphur; or perhaps a thin layer of zinc oxide or sulphide is formed between the sulphur and the metal.

If carbon bisulphide vapour, either by itself or mixed with hydrogen sulphide, be passed over heated zinc-dust, zinc sulphide is formed with formation of methane and hydrogen. Similarly, if carbon bisulphide and ammonia is led over zinc-dust, ammonium cyanide is formed according to the reaction $CS_2 + 2NH_3 + 2Zn = 2ZnS + NH_4.CN + H_2$.

The author also calls attention to the use of zinc-dust for removing sulphur from compounds, and adduces as examples the decomposition of thiocarbanilide into aniline and phenylnitrile [$CS.NHPh_2 + Zn = ZnS + NH_2Ph + PhCN$], of thiocarboparatoluidide into paratoluidine and tolylnitrile, and the conversion of allylthiocarbimide into allylnitrile. V. H. V.

Separation of Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, **95**, 1192—1194 and 1332—1334; see also this vol., p. 21, and Abstr., 1882, pp. 897 and 1323).—*From Bismuth.*—(1.) The moderately acid solution of the chlorides is saturated with hydrogen sulphide; the precipitated bismuth sulphide is free from gallium. (2.) The bismuth is reduced by means of zinc, or much better, by finely divided copper in a slightly acid solution at a gentle heat. (3.) The gallium is precipitated by means of potassium ferrocyanide in a solution containing one-third its volume of strong hydrochloric acid: contrary to the general statement, the precipitate produced by potassium ferrocyanide in solutions of bismuth chloride is soluble even in dilute hydrochloric acid. Bismuth and gallium cannot be separated by means of potassium hydroxide, since the alkaline solution retains notable quantities of bismuth.

From Copper.—(1.) The copper is precipitated in an acid solution by means of hydrogen sulphide; the precipitate is washed with acidulated water containing hydrogen sulphide. (2.) The copper is precipitated with excess of potassium hydroxide, and the liquid boiled for some minutes. (3.) The copper is precipitated by metallic zinc or, much better, by electrolysis. (4.) The solution is made strongly alkaline with ammonia, and boiled for some time. If much copper is present, the precipitate must be redissolved, and the operation repeated several times. The liquid should contain a moderate quantity of ammonium chloride. All four methods are good, but the first is preferable where it can be applied.

From Mercury.—(1.) The solution is strongly acidified with hydrochloric acid and saturated with hydrogen sulphide. This method is rapid and exact, and is to be strongly recommended. (2.) The mercury is reduced by zinc or, better, by copper. (3.) The gallium is precipitated as ferrocyanide in presence of a considerable quantity of free hydrochloric acid, and the precipitate is washed with dilute hydrochloric acid. Mercury cannot be separated from gallium by means of potassium hydroxide, as contrary to the usual statement, the alkaline liquid retains notable quantities of mercury. The precipitated mercuric oxide is, however, free from gallium.

From Silver.—The silver is precipitated by a slight excess of hydrochloric acid in presence of a considerable quantity of nitric acid, or the silver is precipitated by hydrogen sulphide in a moderately acid (hydrochloric or nitric) solution.

From Gold.—(1.) The distinctly acid solution is saturated with hydrogen sulphide. (2.) The gold is reduced by sulphurous acid, and the precipitated metal washed with water containing a little hydrochloric acid. (3.) The solution is made distinctly acid with hydrochloric acid, and the gold reduced by finely divided copper at the ordinary temperature, or at a gentle heat.

From Palladium.—(1.) The solution is strongly acidified with hydrochloric acid, submitted to long treatment with hydrogen sulphide, and then heated at 70° for two hours. The solution should be somewhat concentrated, and the greater part of the free acid should be expelled by evaporation before the last treatment with hydrogen sulphide. (2.) The palladium is reduced by copper in a distinctly acid solution at 80°, the precipitated metal never containing more than an insignificant trace of gallium. If zinc is used instead of copper the precipitated palladium obstinately retains notable quantities of gallium. Precipitation of the palladium as potassium palladiochloride is inexact, since the double chloride is slightly soluble in alcohol, and the precipitate retains distinct traces of gallium.

From Platinum.—The only exact method is to saturate the distinctly acid solution with hydrogen sulphide, heat to 70°, and continue the passage of hydrogen sulphide for several hours. The wash-water is mixed with the filtrate, evaporated to expel the greater part of the acid, and again treated with hydrogen sulphide. An approximate separation is effected by adding ammonium chloride to the solution made distinctly acid with hydrochloric acid, and mixed with alcohol. The precipitate appears to be free from gallium, but the liquid contains small quantities of platinum. Platinum is reduced with great difficulty by copper, even in a hot solution. It is completely precipitated by zinc, but the metal retains gallium even more obstinately than does palladium. C. H. B.

Stannous Oxide and some of its Compounds. By A. DITTE (*Ann. Chim. Phys.* [5], **28**, 145—182).—When a solution of stannous chloride is treated with potassium or sodium hydroxide, stannous hydroxide separates as a compact precipitate, which may be easily washed by decantation as long as an excess of the alkaline chloride formed in the reaction is present. When the washing approaches completeness, however, the solution becomes turbid, and the precipitate needs days to settle. The author has made a careful investigation of the behaviour of stannous hydroxide and stannous chloride in the presence of various reagents. From the results of these experiments, he draws the following conclusions:—

(i.) Stannous hydroxide is transformed into the crystalline anhydrous oxide by traces of any acid which is capable of forming a stannous salt, decomposable by boiling water into free acid and oxide. (ii.) The same change takes place in the presence of salts (such as stannous chloride, ammonium chloride, &c.) which are partially decomposed by water, with liberation of small quantities of an acid coming under head (i). (iii.) This conversion of the hydroxide into the oxide is not effected by acids forming stable stannous salts (such as nitric acid), nor by those (such as sulphuric acid) giving stable basic salts in the presence of water. (iv.) Potassium and sodium hydroxides act on stannous hydroxide both in the cold and on heating, but the reaction is complicated, and the resulting product varies according to the concentration and temperature of the solution. According to circumstances, an alkaline stannate, a mixture of this latter with stannous oxide, or a mixture of the stannate with metallic tin, may be obtained. (v.) Contrary to the statements usually given in text-books, ammonia not only does not cause the dehydration of the hydroxide, but prevents it taking place: the author shows that if the anhydrous oxide is formed, it is only after the ammonia has been expelled by boiling, and that if care be taken to replace this, and the solution be kept alkaline, no dehydration will take place, however long the boiling may be continued. (vi.) Anhydrous stannous oxide may be obtained in several slightly modified forms, but these modifications are not definite enough to be termed allotropic. (vii.) At a red heat, stannous oxide partially decomposes into stannic oxide and tin, the former uniting with unchanged stannous oxide to form Sn_3O_4. (viii.) The salts of silver, palladium, and platinum form with stannous salts, stannates or meta-stannates, according to the relative proportions of the two reagents. From the decided colours of these compounds, they are very good tests for distinguishing stannous from stannic salts. L. T. T.

A Higher Oxide of Titanium. By A. Weller (*Ber.*, **15**, 2599—2600).—A higher oxide of titanium, probably TiO_3, is produced when freshly precipitated titanic hydroxide is treated with hydrogen peroxide or when ammonia is added to a solution of titanic acid and hydrogen peroxide. This oxide has a yellow colour. It is decomposed by heat, yielding oxygen, water, and titanic oxide. It dissolves in strong acids, forming a reddish-yellow solution, from which the oxide is reprecipitated by alkalis; if an excess of alkali is used, titanic oxide is thrown down. On heating the hydrochloric acid solution, chlorine is evolved.

W. C. W.

Arsenious Sulphide in Aqueous Solution. By H. Schulze (*J. pr. Chem.*, **25**, 431—452).—It is well known that sulphuretted hydrogen does not precipitate, or only partially precipitates, a pure aqueous solution of arsenious anhydride. The author has experimented on this fact, and concludes that the water contains arsenious sulphide in solution. In one experiment, he dissolved 10 grams of pure arsenious anhydride in 1 litre, and passed sulphuretted hydrogen into the solution, which became yellow and turbid, forming very thin golden-yellow flakes on the surface, which, on agitation, were thrown down and sank to the bottom in a flocculent state. The remaining solution was slightly turbid and of a reddish-yellow tint. This turbidity could not, however, be removed by filtration, and on examination under the microscope no traces of solid matters could be detected, the solution being clear and yellow. When the solution was rendered turbid by addition of an acid or salt insufficient to produce complete precipitation, solid particles in a yellow menstruum were seen under the microscope. The solution moreover was not turbid when viewed by transmitted light (*e.g.*, in thin layers between parallel plates of glass), but only in reflected light, an effect which the author attributes to fluorescence. Carbonic anhydride was passed through the above solution to remove excess of sulphuretted hydrogen, and the arsenic and sulphur were determined in a portion, and found to be in the ratio of $As_2 : S_3$. This solution of arsenious sulphide is a colloïd, and cannot be dialysed, although any added arsenious anhydride can be readily removed from it by dialysis. On evaporation to dryness, an amount of arsenious sulphide remains proportional to the amount of arsenious anhydride taken, this solid sulphide being no longer soluble in water.

There is a limit to the strength of the solutions of arsenious sulphide prepared by passing sulphuretted hydrogen through aqueous solutions of arsenious anhydride on account of the sparing solubility of the latter, but by passing sulphuretted hydrogen and then dissolving fresh arsenious anhydride and so on, the author succeeded in obtaining a 37·46 per cent. solution of As_2S_3 (1 pt. As_2S_3 in 1·67 pts. water); it was like an intensely yellow milk, but perfectly transparent under the microscope. The stronger solutions deposit a small quantity of solid matter on prolonged standing; the dilute solutions are more permanent, a solution of 1 in 500 being quite unchanged after standing for three months.

Dilute solutions of arsenious sulphide prepared from stronger solutions by dilution are more turbid than dilute solutions of the same strength prepared directly, and have a yellow rather than a reddish-yellow tint.

These solutions are only very slightly influenced by high temperatures; but finely divided animal and vegetable charcoal, acids, and soluble salts have the power of precipitating the solid sulphide. In the case of soluble salts, it is found that there is a certain state of dilution for each salt, at which it ceases to precipitate, and further the precipitating power of the various salts depends on the metals, and only slightly on the acids in those salts. The salts of the alkalis have the least precipitating power; the ferric, chromic, and aluminium salts the greatest.

The author infers that we have to deal with a colloïdal modification of arsenious sulphide comparable with the colloïdal ferric and aluminium hydroxides, soluble silicic acid, and soluble albumin.

F. L. T.

Formation of Crystallised Uranates in the Dry Way. By A. Ditte (*Compt. rend.*, **95**, 988—991).—If uranoso-uranic oxide, U_3O_8, is fused with sodium chloride in a platinum crucible, the bottom of which is kept considerably hotter than the upper portions, a ring is formed round the sides of the crucible at the surface of the fused mass, consisting of a mixture of sodium chloride and brilliant greenish-yellow plates of sodium uranate, $Na_2U_2O_7$, insoluble in water, but easily soluble in dilute acids. If the heating is continued after the removal of the first ring, a second ring is obtained, smaller than the first, but soon the fused mass ceases to yield a crystalline deposit no matter how long the fusion may be continued. The mass is allowed to cool, and the sodium chloride removed by washing, when a deep green crystalline residue is left, which dissolves partially in dilute hydrochloric and sulphuric acids, leaving a black crystalline residue of uranous oxide. The portion soluble in acids consists of crystals of the intermediate oxide, U_2O_5. When the sodium chloride is heated with the uranoso-uranic oxide, the latter is decomposed into oxygen which unites with the uranic oxide, forming sodium uranate, and into uranous oxide, part of which combines with uranic oxide forming the intermediate oxide, UO_3,UO_2, whilst the remainder crystallises. The chlorine of the sodium chloride is liberated, but at high temperatures, attacks neither the uranium oxides nor the platinum of the crucible.

If the sodium chloride is mixed with a little sodium carbonate the same products are obtained; but if the chloride and carbonate are in about equal proportions, sodium uranate is the sole product. If the uranoso-uranic oxide is fused with pure sodium chloride, and sodium chlorate is added in small portions so that the crucible is always filled with an atmosphere of oxygen, the uranium is entirely, although slowly, converted into crystalline uranate. If the uranium oxide is mixed with sodium chlorate, decomposition is accompanied by deflagration, and the uranium oxide is almost instantly converted into amorphous sodium uranate. The reaction is moderated by the presence of sodium carbonate, but the product is the same. The amorphous uranate can be obtained in crystals by fusing it with sodium chloride.

Any of the alkaline uranates can be obtained in greenish-yellow plates, insoluble in water, and infusible at a bright red heat, by any of these three general methods. Sodium uranate is more readily formed than the corresponding potassium salt. If the green uranium oxide is fused with sodium and potassium chlorides mixed in equivalent proportions, the crystals deposited are almost pure sodium uranate. The potassium, rubidium, lithium, and magnesium uranates have been obtained in crystals by these methods.

When uranoso-uranic oxide is fused in the same way with calcium, barium, and strontium chlorides, the corresponding uranates are obtained, CaU_2O_7, BaU_2O_7, SrU_2O_7. If the uranium oxide is heated with the chlorates of the alkaline earths, it is entirely converted into amorphous uranates, but the latter, when fused with sodium chloride, yield a ring very slowly, and the greenish-yellow plates thus obtained have the composition respectively CaU_4O_{12}, BaU_4O_{12}, SrU_4O_{12}. The strontium salts crystallise more slowly than those of calcium, whilst those of barium, on the other hand, form very rapidly. These uranates form greenish-yellow plates, insoluble in water, but soluble in dilute acids. If heated for some time to bright redness, they acquire a deeper colour, and become less soluble in dilute acids.

C. H. B.

Nitrososulphides and Nitrosocyanides. By O. PAVEL (*Ber.*, **15**, 2600—2606).—*Potassium ferronitrososulphide*, $K_2Fe_8(NO)_{14}S_6$, is best obtained by adding 400 c.c. of potassium sulphide, prepared from 44 grams potash, to a boiling solution of 35 grams of sodium nitrite in 400 c.c. water. After the addition of a few drops of dilute sulphuric acid, 159 grams of ferrous sulphate dissolved in 1200 c.c. water are slowly poured into the hot mixture. The liquid is heated in a water-bath for about half an hour, until a deposit begins to settle on the sides of the flask. It is then quickly filtered, and dilute potash is added to the filtrate. After 48 hours potassium ferronitrososulphide crystallises out. It is purified by recrystallisation from water at 70°, containing a small quantity of potassium hydroxide. The potassium and ammonium salts contain 2 mols. H_2O. The ammonium salt is less soluble than the potassium salt, and the rubidium salt is less soluble than the ammonium salt. The cæsium compound is insoluble in cold water, and sparingly soluble in alcohol and ether. The easily soluble sodium, lithium, magnesium, calcium, and barium salts are unstable. $TlFe_4(NO)_7S_3 + H_2O$ is sparingly soluble. The salt obtained by the action of ferrous sulphate on a mixture of sodium thiocarbonate and sodium nitrite, is sodio-ferrous nitrosulphide, and not ferrous nitrosothiocarbonate, $Fe_4S(NO)_6CS_2$, as stated by O. Löw. These nitrososulphides are decomposed by heat in presence of air, with formation of ammonium sulphate, ferrous sulphide, and other products; if air is excluded, no ammonium sulphate is produced. The free acid, $Fe_4(NO)_7S_3H$, is precipitated by dilute sulphuric acid from an aqueous solution of the sodium salt. It is an amorphous unstable compound, insoluble in water, alcohol, and ether, but soluble in chloroform and carbon bisulphide. Sodium ferronitrososulphide is completely decomposed by hot strong sulphuric acid, by silver oxide or sulphate, by hydrochloric acid, and by iodine.

A second series of nitrososulphides is obtained by treating the preceding salts with a warm dilute solution of potash. These salts are unstable; they are, with the exception of the iron compound, insoluble in ether, chloroform, and carbon bisulphide. They are decomposed by potassium ferricyanide, which does not attack the first class of nitrososulphides. The composition of the potassium and sodium salts is represented by the formulæ—

$$K_2Fe_2(NO)_4S_2 + 4H_2O \text{ and } Na_2Fe_2(NO)_4S_2 + 8H_2O.$$

Ethyl ferronitrososulphide, $Et_2Fe_2(NO)_4S_2$, prepared by the action of ethyl iodide on an alcoholic solution of the potassium salt, forms large monoclinic crystals melting at 78°. The dark glistening crystals dissolve freely in ether, chloroform, benzene, ethyl iodide, and carbon bisulphide. This compound is not attacked by potash or by sulphuric or hydrochloric acids, but it is completely decomposed by nitric acid. The author considers that the formation of sodium nitro-prusside, *i.e.*, sodium nitrosoferricyanide, by the action of nitric acid on sodium ferrocyanide, takes place in the following stages:—

$$\left\{\begin{matrix}FeCy_2 4NaCy\\ FeCy_2 4NaCy\end{matrix}\right. \left\{\begin{matrix}FeCy_4 2NaCy\\ FeCy_2 4NaCy\end{matrix}\right. \left\{\begin{matrix}FeCy_4 2NaCy\\ FeCy_4 2NaCy\end{matrix}\right. \left\{\begin{matrix}Fe(NO)_2Cy_2 2NaCy\\ FeCy_4 2NaCy\end{matrix}\right.$$

W. C. W.

Artificial Production of Iridosmin. By H. Debray (*Compt. rend.*, **95**, 878—880).—If iridium is fused with iron pyrites at a high temperature a regulus is obtained, which, when treated with dilute hydrochloric acid, leaves a residue of crystallised iridium, mixed with a light black amorphous sulphide easily soluble in dilute nitric acid. The iridium retains from 1 to 2 per cent. of iron, and crystallises in octohedrons, although some flattened crystals have the appearance of regular hexahedrons. Osmium behaves in a precisely similar manner, but the crystals obtained retain no sensible traces of iron, and have all the characteristics of the metal obtained by the action of hydrochloric acid on alloys of osmium with zinc or tin.

When a mixture of one part amorphous osmium with 1, 2, or 3 parts amorphous iridium, is fused with a large excess of iron pyrites, and the fused mass treated successively with hydrochloric and nitric acids, a crystalline residue is obtained, which consists of regular octohedrons mixed with hexagonal plates, closely resembling certain natural varieties of iridosmin. The crystals have not the composition of the mixture from which they are prepared, owing to the partial conversion of the metals into sulphides; the relative proportion of osmium and iridium does not depend on the relative quantities of the two metals employed, but varies with the temperature to which the mixture is heated. Three specimens obtained had the following composition:—

	1.	2.	3.
Iridium	50	59	62·5
Osmium	50	41	37·5
	100	100	100·0

In appearance and properties, these alloys are identical with the natural iridosmin. Since osmium and iridium are isomorphous, and can crystallise together in all proportions, it is possible that natural iridosmin may be a true isomorphous mixture belonging to the regular system, notwithstanding the hexagonal appearance of some of the crystals. The composition of natural iridosmin is, however, much more complex than that of the artificial crystals. C. H. B.

Mineralogical Chemistry.

Analysis of the Coal of the Muaraze. By P. Guyot (*J. Pharm.* [5], 6, 474—475).—This is a short paper, containing an account of thin beds of coal found in the valley of the River Muaraze, a tributary of the Zambesi. The volatile matter varies in different specimens from 20 to 22 per cent., and the coke from about 50 to 55 per cent. E. H. R.

The Thorite of Arendal. By L. F. Nilson (*Compt. rend.*, **95**, 784—786).—Nordenskiöld found, near Arendal, in 1876, a crystalline silicate containing 50 per cent. of oxide of thorium, and 10 per cent. of uranous oxide. He regards the mineral as a variety of thorite. Later, the same mineral was discovered at Hitterö (Norway) by Lindström, and at Champlain (U.S.A.) by Collier, who called it *uranothorite*.

The mineral is interesting as containing *uranous oxide*. Zimmerman has shown that uranous oxide has the formula UO_2, and the oxide of thorium having probably the formula ThO_2, it is to be presumed that the two oxides are capable of replacing one another in thorite in variable proportions. The molecular volumes of the oxides in question confirm this hypothesis.

The author has obtained pure sulphate of thorium by a new and simple method. He finds that by saturating 5 parts of water at 0° with 1 part of crude anhydrous sulphate and then warming to 20°, thorium sulphate is precipitated as a heavy white crystalline powder, amounting to two-thirds of the sulphate dissolved. The precipitate is washed with cold water, the mother-liquors are evaporated to dryness, and the product is subjected to the same treatment. Proceeding in this way a solution is finally obtained which, saturated at zero, precipitates nothing more when warmed to 20°. The solution contains principally thorium sulphate, and gives, with potassium sulphate, insoluble double sulphates, while certain double sulphates remain in solution. The insoluble double sulphates contain thorium, cerium, and didymium, whilst the others include all the metals contained in the old "erbia," and are characterised by their absorption-bands. In examining the earths precipitated as double sulphates, the author has observed the following peculiarity:—The anhydrous sulphates of the earths, from which the didymium has been separated by repeated partial decomposition of the nitrates, are of a yellow colour. Their solution is also yellow, but is decolorised by sulphurous anhydride. When the decolorised solution is evaporated, and the excess of sulphuric acid expelled, the sulphates reassume the yellow colour, and this can be repeated as often as desired. The author finds that a mixture of pure thorium sulphate and *cerous* sulphate behaves in the same manner. The yellow colour indicates the presence of *ceric* sulphate. Hence the author concludes that the presence of thorium oxide determines the conversion of the *cerous* into *ceric* sulphate by means of the excess of sulphuric acid.

The author finds that four precipitations of thorium sulphate, in the manner described above, are sufficient to obtain it in a perfectly pure state. E. H. R.

Study of "Longrain" and Measure of the Foliation in Schistose Rocks by Means of their Thermic Properties. By E. JANNETTAZ (*Compt. rend.*, **95**, 996—999).—The law that heat is conducted more easily along the plane of foliation than along the perpendicular direction, holds good in all cases. By means of experiments made in the manner previously described (*Compt. rend.*, **78** and **81**), the author has constructed the isothermal surfaces characteristic of schistose rocks. The isothermal surface of these rocks is an ellipsoid, the three principal sections of which are the plane of foliation, containing the major and the minor axes, and two others perpendicular to this and to one another, the one containing the major and the minor axes, the other the mean and the minor axes. Sometimes the two axes in the plane of foliation are equal, in which case the ellipsoid is a figure of revolution.

In slate quarries the workmen split up the rock into slabs, by taking advantage of the ease with which it cleaves in the plane of foliation, or, as the author terms it, *first cleavage*, and then cut these up into smaller slabs along a somewhat more difficult plane of cleavage, which is locally termed the "longrain," "long," or "fil," and which the author terms *second cleavage.* By experiments on a large number of schistose rocks from different localities and of different composition, it is found that the intersection of these two planes is parallel with the major axis of the ellipsoid, and the plane of foliation is perpendicular to the least axis. In other words, the major axis of the isothermal surface is parallel with the *longrain* or second cleavage, and the minor axis is perpendicular to the plane of foliation or first cleavage. The author has applied this method to the contorted schistose beds in the lias in the neighbourhood of La Pauté and Vénosc. The following table shows the percentages of calcium carbonate and clay in these beds, with the ratio of the axes of the isothermal surface on sections perpendicular to the plane of foliation.

	Calcium carbonate.	Clay.	Ratio of axes.
La Pauté	90	10	1·07
"	65	35	1·30
"	50	50	1·42
Vénosc	25	75	2·00

C. H. B.

Lithium, Strontium, and Boric Acid, in the Mineral Waters of Contrexeville and Schinznach (Switzerland). By DIEULAFAIT (*Compt. rend.*, **95**, 999—1001).—The author's previous researches have led to the conclusion that the salts existing in different strata have been derived directly or indirectly from the evaporation of ancient seas. He also concludes that mineral waters derive their saline matter from the salt-bearing strata of the permian, triassic, and tertiary formations, this saline matter itself being derived from ancient seas. If this conclusion is correct, all the substances which existed in these seas should be found in the mineral waters. Amongst the most characteristic are lithium, strontium, and boric acid, and it follows from the author's investigations of sea water that these substances should exist in mineral waters in relatively considerable proportions. The lithium spectrum ought to be obtained with the residue left by the evaporation of 1 c.c., or often even from a single drop, the strontium spectrum with the residue from 5 c.c., and the boric acid reaction with the residue from not more than 100 c.c.

Water of Contrexeville.—Lithium exists in relatively considerable proportion, and the strontium spectrum is obtained distinctly with the residue from 5 c.c. Deboul failed to find strontium in this water, because he looked for it in the precipitate produced by boiling, on the assumption that the strontium is present as bicarbonate, whereas it really exists as sulphate.

Water of Schinznach.—This water derives its saline matter from the trias. Contrary to the statement of Grandeau, lithium can be detected in a single drop, strontium in 4 c.c., and boric acid in 25 c.c. of this water.

These two waters are therefore not exceptions to the author's law, but, on the contrary, afford further proof of its accuracy.

C. H. B.

Presence of Arsenic in the Waters of Barèges. By M. SCHLAGDENHAUFFEN (*J. Pharm.* [5], **6**, 475—480).—The author has detected arsenic in these waters from the different springs. The quantities vary from 0·000016 to 0·00022 gram per litre. The source of the metal is the rock through which the water runs. The residue on evaporation yields only part of its arsenic to hydrochloric acid: hence the author concludes that the metal is partly present as a sulpharsenate which is converted by the acid into insoluble sulphide.

E. H. R.

Origin of Arsenic and Lithium in Waters containing Calcium Sulphate. By M. SCHLAGDENHAUFFEN (*J. Pharm.* [5], **6**, 457—463).—The author has established the presence of arsenic in the mineral waters of Schinznach and Baden in Switzerland. According to Orfila and Walchner, the arsenic is present in all similar mineral waters in combination with iron, but it is shown in this paper that the quantity of arsenic bears no relation to the proportion of iron, and that the former is often present when the latter is entirely absent. Hence the arsenic probably exists in these waters in combination with calcium. The origin of arsenic is without doubt the sulphide of that element contained in marls associated with the gypsum, from which it is dissolved by waters charged with calcium carbonate, being first converted into sulpharsenate and finally into arsenate of calcium.

The author shows that these marls also contain lithium, and that this metal can easily be detected by the spectroscope in these mineral waters.

E. H. R.

Glairin or Baregin. By N. JOLY (*Compt. rend.*, **95**, 1194—1195).—The *glairin* or *baregin* found in almost all the hot sulphuretted waters of the Pyrenees, is a very complex substance, consisting of the remains of animal and vegetable matter, together with various inorganic substances, such as crystals of sulphur, iron pyrites, silica, &c. The nitrogenous organic matter which exists in solution in these waters is apparently derived from the ultimate decomposition of the various animal and vegetable organisms which live in the waters. The complex glairin of Luchon is derived almost entirely from the decomposition of the dead bodies of *naïs*, *cyclops*, *infusoria*, and *sulfurairia*. The author has been able actually to watch the gradual formation of glairin from the decomposition of these organisms. There can be no doubt that true glairin is an animal product.

C. H. B.

Organic Chemistry.

Relation between Boiling Points and Specific Volumes. By W. STAEDEL (*Ber.*, **15**, 2559—2572).—An examination of the chlorinated derivatives of ethane shows that the boiling point (under the normal pressure) is raised 56·22° when one atom of hydrogen is replaced by chlorine in the group CH_3, *e.g.*, $CH_3.CHCl_2$ (b. p. 57·7°), and $CH_2Cl.CHCl_2$ (b. p. 113·7°). The introduction of a second chlorine-atom into the methyl group raises the boiling point 31·3°, *e.g.*, $CH_2Cl.CCl_3$ boils at 130·5°, and $CHCl_2.CCl_3$ boils at 161·7°. The conversion of the group $CHCl_2$ into CCl_3 raises the boiling point 16·04°. The specific volume of these compounds at their boiling points is increased 14·2 by the introduction of the first chlorine-atom in the methyl group, 16·37 for the second, and 19·16 for the introduction of the third chlorine-atom. Hence it appears that an atom of chlorine can possess different specific volumes. W. C. W.

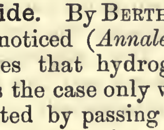
Conversion of Organic Chlorides into Iodides by means of Calcium Iodide. By P. v. ROMBURGH (*Rec. Trav. Chim.*, **1**, 151—153). —The transformation of organic chlorides into iodides cannot conveniently be effected by heating them with potassium iodide, as the action is too slow; aluminium iodide, on the other hand, acts too rapidly. Hydrogen iodide can be used only at ordinary temperatures, since at higher temperatures it acts as a reducing agent. Calcium iodide, on the other hand, appears to be available in all cases, and effects the conversion more rapidly than potassium iodide, inasmuch as the difference between the heats of formation of chloride and iodide of calcium is greater than that which is found to exist in the case of any of the other metals except aluminium.—*Allyl chloride*, heated with calcium iodide in a sealed tube at 100° for six hours, is completely converted into allyl iodide (b. p. 100—101°; sp. gr. 1·846 at 15°).—*Amyl chloride* (b. p. 112°), heated with CaI_2 for 24 hours at 100°, is almost wholly converted into iodide (b. p. 147°; sp. gr. 1·499 at 15°).—*Ethylene chloride*, heated with CaI_2 at 100° for three hours, yields a small quantity of a crystalline body, melting at 82°, subliming without alteration, decomposed at a stronger heat with separation of iodine vapour, and in fact exhibiting all the characters of ethylene iodide.—*Benzyl chloride* similarly treated at 100°, yielded a red-brown liquid, which was decolorised by washing first with water, then with aqueous potash; and on distilling the colourless liquid thus obtained, the temperature soon rose above the boiling point of benzyl chloride, and at 215° decomposition took place, with separation of iodine-vapour, the greater part of the product solidifying at the same time. In another experiment white crystals were obtained, melting at the heat of the hand. These characters, together with the irritating odour of the product, pointed to the presence of benzyl iodide, but the author intends to examine it further. H. W.

Decomposition of Cyanogen. By BERTHELOT (*Compt. rend.*, **95**, 955—956).—Cyanogen decomposes with explosion under the influence of a discharge of mercury fulminate. This effect is due to the high temperature developed by the destruction of the first layers of cyanogen by the detonation, the conditions being favourable to the production and propagation of an explosive wave. On the other hand the gas is but slowly decomposed when passed through a red hot tube. Perfectly dry cyanogen is completely decomposed into nitrogen and carbon after about three hours by the continuous passage of induction sparks. In presence of the least trace of moisture small quantities of hydrocyanic acid and acetylene are formed. Decomposition under these conditions remains slow, and has no explosive characteristics. The gas is very rapidly decomposed by the electric arc, the carbon being partly deposited in a flocculent condition round the negative pole. It would appear that decomposition under these conditions approaches the point at which it becomes explosive. In presence of hydrogen or a hydrogen compound, some hydrocyanic acid is formed.

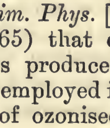
C. H. B.

Properties of Normal Cyanic Acid. By E. MULDER (*Rec. Trav. Chim.*, **1**, 191—222).—From the experiments detailed in this paper, and from previous researches, the author draws the following conclusions:—1. The existence of normal cyanic acid as potassium salt, CN.O.K, appears to be impossible under ordinary circumstances.—2. *Cyanetholine* (corps de M. Cloez) is conveniently prepared by the action of cyanogen bromide on absolutely anhydrous alcohol (easily obtained by decomposition of a solution of sodium ethylate in ordinary absolute alcohol).—3. By the action of cyanogen bromide dissolved in ether upon sodium ethylate in presence of alcohol and ether, and subsequent filtration and evaporation of the volatile parts of the filtrate, a crude product is obtained, which dissolves for the most part in water, leaving a small residue of cyanetholine, and appears to consist chiefly of $x(CN.OEt,C_2H_6O)$.—The wash-water treated with ether yields urethane, formed according to the equation $CN.OEt + H_2O = NH_2.COOEt$. This water likewise contains normal ethyl cyanurate, and a very small quantity of ethyl monamidoyanurate, and perhaps also ethyl diamidocyanurate. It is remarkable that cyanogen bromide, acting on sodium ethylate in presence of alcohol and ether, gives rise to normal ethyl cyanurate, even in presence of water, to the amount of $5H_2O$ to EtONa, a result which seems to imply the existence of EtONa in alcoholic solution, in presence of a relatively large quantity of water, much larger, indeed, than that which would be necessary to decompose EtONa into Et.OH and NaOH.—4. Cyanetholine, after drying for some time in the exsiccator, gives by analysis numbers agreeing pretty nearly with the formula CN.OEt; it probably always contains small quantities of ethylic monamidocyanurate and diamidocyanurate.—5. This body, after remaining at rest for some time, gradually deposits crystals, consisting chiefly of normal ethyl cyanurate, sometimes in well-formed prisms. The crystals deposited from aqueous solution at low temperatures contain a large proportion of crystal-water, which is given off with efflorescence at 6°. This compound melts at about 29°, remaining liquid for some hours, and then solidifying. Normal ethyl cyanurate may be distilled under diminished pressure, without being converted into isocyanurate. It is very slightly soluble in water, and its saturated or nearly saturated solution becomes thickly clouded when heated nearly to the melting point of the compound.—6. Normal ethyl cyanurate is soluble in bromine, and on evaporating the excess of bromine at a sufficiently low temperature, there remains an orange-red compound, apparently consisting of 3CNOEt,6Br, which undergoes dissociation. The same is the case with an addition-product, which separates in yellow needles on adding bromine-water to an aqueous solution of ethyl cyanurate. Neither isocyanuric acid, nor its methylic or ethylic ether, forms an addition-product with bromine, so that the formation of such a product may be regarded as a reaction characteristic of the normal cyanurates.—7. Cyanetholine is very slightly soluble in water; its solution becomes very turbid when heated, and in presence of bromine-water behaves for the most part like that of normal ethyl cyanurate. Ethyl isocyanurate, on the contrary, differs from cyanetholine in its behaviour with bromine-water; the same is the case also with the aqueous solutions of these bodies at low temperatures.—8. Ammonia-gas passed through the alcohol-etheric filtrate of the preparation does not appear to form either cyanamide or dicyanamide, which might be expected to form in presence of N⋮C.OEt, if cyanamide were regarded as the amide of normal cyanic acid, N⋮C.NH_2. Cyanamide, moreover, does not combine either with bromine or with cyanogen, whence it is probably a derivative of isocyanic acid, its constitutional formula being that of carbodiimide, HN⁚C⁚NH. H. W.

A Reaction of the Compounds of Normal Cyanuric Acid and Cyanetholine (corps de M. Cloez). By E. MULDER (*Rec. Trav. Chim.*, **1**, 41).—The compounds of normal cyanuric acid (the free acid is not known) and cyanetholine (isomeric with ethyl cyanate) form addition-products with bromine, whereby they may readily be distinguished from isocyanuric acid and its compounds, which do not form such addition-products. For example, an aqueous solution of normal ethyl cyanurate forms with bromine-water a crystalline addition-product $(CN)_3O_3Et_3,Br_2$, very soluble in water, which is not the case either with ethyl isocyanurate or with isocyanuric acid. Hence the author infers that the two isomeric acids may probably be represented by the following formulæ:—



Normal cyanuric acid.



Isocyanuric acid.

H. W.

Ethyl Peroxide. By BERTHELOT (*Ann. Chim. Phys.* [5], **27**, 229—232).—v. Babo noticed (*Annalen*, Suppl. **2**, 165) that ozone acts on ether, and states that hydrogen peroxide is produced. Berthelot finds that this is the case only when the ether employed is wet. If dry ether is evaporated by passing a dry current of ozonised oxygen over its surface, a small quantity of a dense syrupy liquid is left. This liquid is miscible with water, does not solidify when cooled to −40°, and when subjected to heat, explodes violently as soon as a small portion has distilled over. It acts as an oxidising agent in a manner similar to hydrogen peroxide, and gives up 10—11 per cent. of oxygen when treated in the cold with permanganic or chromic acids. The author ascribes the formula $(C_2H_5)_4O_3$ to this body, and gives it the name of *ethyl peroxide*. L. T. T.

Second Anhydride of Mannitol. By A. FAUCONNIER (*Compt. rend.*, **95**, 991—993).—When mannitol is subjected to dry distillation in a vacuum, it yields a brownish-yellow liquid mixed with empyreumatic substances. The liquid is filtered through a moistened filter and distilled. It begins to boil at 60° under ordinary pressure. The fraction which passes over between 160° and 190° under a pressure of 0·03 m., consists partly of the second anhydride of mannitol, $C_6H_{10}O_4$. When freshly distilled, this compound is a colourless syrup which, if perfectly pure, forms bulky crystals melting at 87°, and apparently belonging to the monoclinic system. It boils without decomposition at 176° under a pressure of 0·03 m., and with partial decomposition at 274° under ordinary pressure. It is very soluble in water and alcohol, but insoluble in ether, and possesses in a high degree the properties of remaining in superfusion, and of forming supersaturated solutions.

This second anhydride of mannitol does not combine directly with either cold or hot water, and is not affected by nascent hydrogen. It is not attacked by bromine in the cold; but if the two bodies are heated together alone or in presence of water, hydrobromic acid is given off, and black resinous products are formed, but cannot be distilled. When boiled for eight hours with three times its weight of acetic anhydride, the mannitol anhydride yields a diacetic derivative, $C_6H_8O_4\overline{Ac}_2$, an almost colourless viscid liquid, which is not altered by the prolonged action of acetic anhydride; it boils at 197—198° under a pressure of 28 mm.

The mannitol anhydride is not attacked by phosphorus oxychloride, but with phosphorus pentachloride it yields a dichlorhydric derivative, $C_6H_8O_2Cl_2$, which forms hexagonal lamellæ, very soluble in ether, somewhat soluble in alcohol and benzene, insoluble in water. It melts at 49°, boils at 143° under a pressure of 43 mm., and can be distilled in the vapour of water. Not more than two atoms of chlorine can be introduced into the molecule by the action of phosphorus pentachloride. When heated in sealed tubes at 120° for four hours with ethyl iodide and concentrated potash, the anhydride yields a monethyl derivative, $C_6H_9O_4Et$, a colourless somewhat mobile liquid, soluble in water, alcohol, and ether: it boils at 165° under a pressure of 17 mm. From these facts it is evident that the second anhydride of mannitol is a saturated compound containing two alcoholic hydroxyl-groups, and that there are no double bonds between the carbon-atoms. Its formula is therefore $C_6H_8O_2(OH)_2$. The primary, secondary, or tertiary character of the hydroxyl-groups, and the function of the two other oxygen-atoms, has yet to be established. C. H. B.

Influence of Mass and Time on the Inversion of Sugar. By F. Urech (*Ber.*, **15**, 2457—2460).—The author has observed that the inversion of cane-sugar in the case of a mixture of 16·35 grams cane-sugar and 11·40 grams hydrochloric acid in 100 c.c. water, is an exothermic reaction.

Therefore, as the velocity increases with the temperature, no constant can be deduced from the laws of mass action, but only approximate values for short intervals of time.

In the first half of the reaction more heat is evolved than in the second, during which smaller quantities of cane-sugar enter into the reaction. The author has, notwithstanding the experimental difficulties, made a series of observations on the velocity of the reaction by the polariscope and by a titration method with Fehling's solution. The experimental tube of the polariscope was kept cool by a current of water; and in the titration method quantities of the inversion mixture were taken out at given intervals of time, run into excess of alkali to stop the reaction, and then titrated.

From the results obtained by these two methods, the author concludes that generally in equal intervals of time, equal quantities of cane-sugar disappear, while the hydrochloric acid plus water increases in direct proportion to the decrease of cane-sugar. Large quantities of hydrochloric acid and water invert more quickly than smaller quantities of the same concentration. V. H. V.

Formula of Starch. By T. Pfeiffer, B. Tollens, and F. Salomon (*Bied. Centr.*, 1882, 775—777).—Sachsse and Nägeli attribute to starch the formula $C_{36}H_{62}O_{31} + 5H_2O = 6C_6H_{12}O_6$, and ground this formula on the amount of sugar obtained by the action of acid. Pfeiffer and Tollens, however, consider that the formula should be $C_{24}H_{40}O_{20}$, or $C_{24}H_{42}O_{21}$, deducing this from the composition of the sodium and potassium compounds, which contain 3·44 per cent. Na and 5·25 per cent. K; they also think that inulin and dextrin should be represented by $C_{12}H_{20}O_{10}$ or $C_{12}H_{22}O_{11}$, and that the molecules of starch and inulin are not of the same size. Salomon repeated Sachsse's experiments, and proceeding further claims $xC_6H_{10}O_5$ as the formula which more closely represents the composition of starch, for he obtained 111 per cent. dextrin from starch. Combining these two formulæ as suggested by Pfeiffer, Tollens, and Salomon, it appears that we must adopt $4C_6H_{10}O_5$. E. W. P.

Action of Triethylamine on Symmetrical Trichlorhydrin and on the Two Dichloropropylenes. By E. Reboul (*Compt. rend.*, 95, 993—996).—When trichlorhydrin is heated with three vols. triethylamine in sealed tubes for some hours at 100°, the product becomes almost entirely solid on cooling; no gas is given off. The contents of the tube are dissolved in water and evaporated on a water-bath in order to expel all unaltered triethylamine.

The syrupy mass thus obtained is a mixture of triethylamine hydrochloride and the two isomeric chlorides, α-chlorallyltriethylammonium chloride, $ClNEt_3.CH_2.CCl \colon CH_2$, and β-chlorallyltriethylammonium chloride, $ClNEt_3.CHCl.CH \colon CH_2$.

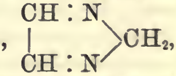
The triethylamine hydrochloride may be separated from the mixture by means of boiling alcohol, from which it separates in silky needles on cooling. If platinum tetrachloride is added in slight excess to an aqueous solution of the mixture, an abundant precipitate is formed, readily soluble on warming. The solution on cooling deposits *α-chlorallyltriethylammonium platinochloride* in nodular groups of long thin orange-red needles, only slightly soluble in cold water. On further concentration and cooling, the orange-red needles are succeeded by orange-yellow crystals (not needles) of *β-chlorallyltriethylammonium platinochloride*, more soluble in cold water than is the first compound. On further concentration the mother-liquor yields triethylamineplatinochloride.

When triethylamine acts on trichlorhydrin, it first removes hydrochloric acid, producing a mixture of the two isomeric dichloropropylenes, which then unite with the excess of triethylamine, forming the compounds just described.

If triethylamine is heated with an excess of trichlorhydrin, the product is a mixture of the two isomeric dichloropropylenes. α-Dichloropropylene, $CH_2 \colon CCl.CH_2Cl$ (b. p. 94°) attacks triethylamine in the cold; the action proceeds rapidly at 100°, and after some hours the whole mass becomes solid. No gas is given off, and the product consists of α-chlorallyltriethylammonium, without any of the β-compound, and with only slight traces of triethylamine hydrochloride. When the mixture of the two dichloropropylenes obtained by the action of potash on trichlorhydrin is heated with triethylamine, it yields a mixture of the two ammoniums already described, with mere traces of triethylamine hydrochloride.

It is evident that symmetrical trichlorhydrin does not simply fix two molecules of triethylamine, as would be supposed from the existence of two CH_2Cl groups, but loses hydrochloric acid, the chlorine of which is derived partly from a CH_2Cl group, and partly from the middle group, CHCl. The two isomeric dichloropropylenes thus produced obey the same law as the chlorine derivatives of the primary monhydric alcohols, and simply fix triethylamine. The two tetrammonium hydrochlorides thus formed are easily decomposed by freshly precipitated silver oxide, and yield the corresponding ammonium hydroxides, which precipitate calcium hydroxide from a solution of calcium chloride. C. H. B.

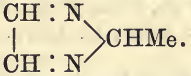
Glyoxaline and its Homologues. By B. Radziszewski (*Ber.*, **15**, 2706—2708).—In a previous communication (Abstr., 1882, 1064) the author expressed his opinion that glyoxaline has a constitution analogous to that assigned by him to lophine, viz.,



$$\left.\begin{array}{l}CH \colon N\\ |\\ CH \colon N\end{array}\right\rangle CH_2,$$

basing this formula on the synthesis of glyoxaline by the action of ammonia on glyoxal and formaldehyde, just as lophine is formed from benzil, benzaldehyde, and ammonia. Its solubility in alkalis and its passive behaviour to nascent hydrogen again suggest an analogy to lophine. Against Wyss's formula, the author urges its neutral behaviour towards the acid chlorides and anhydrides, and also the fact that it forms no nitroso-derivative. In order to further test the correctness of his views, the author has substituted other aldehydes for formaldehyde in the above-mentioned reaction, and has succeeded in obtaining homologues of glyoxaline.

With acetaldehyde he obtained a body melting at 137°, and boiling at 266—268°. It crystallises in needles which readily dissolve in water, alcohol, and boiling benzene. It is represented by the formula $C_4H_6N_2$, and is in fact identical with Wallach and Schulze's paroxalmethyline (*Ber.*, **14**, 426). With bromine it forms the compound $C_4H_3Br_3N_2$ (m. p. 258°). The properties of paroxalmethyline show that it is a true homologue of glyoxaline, and from its synthesis from glyoxal, &c., the author assigns to it the constitution—



A. K. M.

Decomposition of Tertiary Amyl Acetate by Heat. By N. Menschutkin (*Ber.*, **15**, 2512—2518).—Tertiary amyl acetate, prepared by the action of acetic anhydride on ethyl dimethyl carbinol, is slowly decomposed by heat at 125°, according to the equation—

$$C_2H_3(C_5H_{11})O_2 = C_5H_{10} + C_2H_4O_2.$$

In six days 2·06 per cent. of the acetate is decomposed. At a higher temperature decomposition proceeds more rapidly. At 155° signs of decomposition make their appearance two hours after the commencement of the experiment.

The rate of decomposition is at first slow, it then accelerates until it reaches a maximum point, when it gradually diminishes to zero.

W. C. W.

Tetrasubstituted Propionic Acids. By H. B. Hill and C. F. Mabery (*Amer. Chem. J.*, **4**, 263—272).—*Tetrabromopropionic acid*, $C_3H_2Br_4O_2$, is easily prepared by adding the calculated quantity of bromine to a solution of tribromopropionic acid in chloroform at ordinary temperatures, and gradually separates in large well-defined prisms, the yield being about 90 p. c. of the theoretical amount. The crystals are triclinic, having the axial ratio $a : b : c = 1·507 : 1 : 0·934$, and angle $ab = 94° 50'$; $ac = 104° 28'$; $bc = 74° 20'$. Observed forms $\infty P\breve{\infty}$, $\infty P\bar{\infty}$, $0P$, $P\bar{\infty}$, $\infty P'$. The acid melts at 125—126°; dissolves very readily in alcohol or ether, readily also in hot chloroform, carbon bisulphide, and benzene, and separates in crystals on cooling; it is sparingly soluble in light petroleum. Under water it melts at a very low temperature to a colourless oil, which dissolves freely on heating.

The *silver salt*, $C_3HBr_4O_2Ag$, separates on adding silver nitrate to a solution of the acid in dilute alcohol in clusters of needles, the quantity of which may be increased by cautious addition of ammonia. It is extremely unstable, yielding silver bromide when warmed, and blackening rapidly on exposure to light. The *barium salt*,

$$(C_3HBr_4O_2)_2Ba,2H_2O,$$

obtained by saturation, separates on spontaneous evaporation in groups of flattened needles, which give off their crystal-water over sulphuric acid. The *calcium salt*, $(C_3HBr_4O_2)_2Ca$, prepared in like manner, crystallises in anhydrous needles.

The barium salt in aqueous solution is resolved by heat into barium bromide, carbonic anhydride, and tribromethylene: $(C_3HBr_4O_2)_2 Ba = BaBr_2 + 2CO_2 + 2C_2HBr_3$. The acid heated with alcoholic potash is resolved into hydrobromic acid and tribromacrylic acid, $C_3HBr_3O_2$, melting at 118° (Abstr., 1881, 1125).

α-Dichlorodibromopropionic acid, $C_3H_2Cl_2Br_2O_2$, is prepared by heating dichloracrylic acid (m. p. 85—86°) with 1 mol. bromine for several hours at 100°, and may be purified by pressing it between paper and crystallising it, first from carbon bisulphide and finally from chloroform. It crystallises in well-formed triclinic crystals, exhibiting the faces $\infty P\breve{\infty}$, $\infty P\bar{\infty}$, $0P$, $P^{|}_{|}\breve{\infty}$, $P^{|}_{|}\bar{\infty}$, ${}_{|}P^{|}\breve{\infty}$, ${}_{|}P^{|}\bar{\infty}$; frequently also $\infty P^{|}_{|}$ and $\infty{}^{|}_{|}P$. Axes $a : b : c = 1·02 : 1 : 1·052$. Angles $ab = 91°$; $ac = 70° 31\frac{1}{2}'$; $bc = 108° 52'$.

The *silver salt*, $C_3HCl_2Br_2O_2Ag$, is obtained by precipitation in flattened jagged needles, easily decomposed by heat. The *barium salt*, $(C_3HCl_2Br_2O_2)_2Ba$, obtained by neutralisation, crystallises in long branching anhydrous needles. It is decomposed by heat, yielding products similar to those obtained from the tetrabromopropionate.

β-Dichlorodibromopropionic Acid.—Chlorine gas passed into dibromacrylic acid in ordinary daylight is slowly taken up, and dichlorodibromopropionic acid is formed, but so contaminated with oily products that its purification is somewhat difficult. If, however, the action be made to take place in direct sunshine at 100°, it goes on rapidly, and the process may be stopped when the melted acid becomes solid, from separating crystals of the addition-product. This product purified by crystallisation, first from carbon bisulphide and then from chloroform, forms oblique prisms melting at 118—120°, easily soluble in water, alcohol, and ether, somewhat less easily in carbon bisulphide, chloroform, and benzene. The solution in carbon bisulphide deposits well-defined monoclinic crystals having the axes $a : b : c = 2·393 : 1 : 1·731$, and the angle $ac = 46° 9'$. Observed faces $\infty P\bar{\infty}$, ∞P, $+ P$, $+ \frac{1}{2}P\bar{\infty}$. The *silver salt* of this acid is precipitated in short thick pointed prisms on adding silver nitrate to the aqueous acid; it is easily decomposed by heat. The *barium salt*, $(C_3HBr_2Cl_2O_2)_2Ba + 2H_2O$, is obtained by neutralisation, and crystallises by slow evaporation in long radiating needles, very soluble in cold water. H. W.

Constitution of the Substituted Acrylic and Propionic Acids. By H. B. HILL (*Amer. Chem. J.*, **4**, 273—276).—*α*-Monobromacrylic acid can be made from *α*- and from *αβ*-dibromopropionic acid, and must therefore have the structure $CH_2 \colon CBr.COOH$; the tribromopropionic acid made from it by addition of bromine will have the corresponding form, $CH_2Br.CBr_2.COOH$, and the dibromacrylic acid obtained from the latter will be represented by the formula $CHBr \colon CBr.COOH$. The dibromacrylic acid of Fittig and Petri, which, as shown by Mabery and Hill, can be made from bromopropiolic acid, must have the form $CBr_2 \colon CH.COOH$, and the acids made in like manner, containing two halogens, will be represented by the corresponding formulæ—

$$CBrI \colon CH.COOH \text{ and } CBrCl \colon CH.COOH.$$

The tribromopropionic acid melting at 118° must be represented by the formula $CHBr_2.CHBr.COOH$, and tetrabromopropionic acid by $CHBr_2.CBr_2.COOH$. H. W.

Crystalline Form of Tribromacrylic Acid. By W. H. MELVILLE (*Amer. Chem. J.*, **4**, 277).—This acid forms monoclinic crystals exhibiting the forms $\infty P\breve{\infty}$, ∞P, $+P\bar{\infty}$, $-P\bar{\infty}$, $\frac{1}{2}P\bar{\infty}$, the last three however occurring but rarely. $a : b : c = 0{\cdot}502 : 1 : 0{\cdot}559$; Angle $ac = 64° 29\frac{1}{2}'$. H. W.

Addition of Hypochlorous Acid to β-Crotonic Acid. By P. Melikoff (*Ber.*, **12**, 2586—2588).—β-Crotonic acid unites directly with hypochlorous acid, forming chloroxybutyric acid. On treating an alcoholic solution of chloroxybutyric acid with alcoholic potash, potassium chloride is deposited, and potassium butylglycidate remains in solution; the excess of potash is precipitated by a current of carbonic acid, and ether added to the filtrate, when potassium butylglycidate is deposited in oily drops.

Butylglycidic acid, $C_4H_6O_3$, is a mobile liquid forming viscous salts. It combines with hydrochloric acid, yielding chloroxybutyric acid, $C_4H_7ClO_3$, which crystallises in prisms melting at 98°, and forms a zinc salt crystallising in rhombic plates containing 1 mol. H_2O. Butylglycidic acid also unites directly with water, forming butylglyceric acid, which has been described by Hanriot (*Ann. Chim. Phys.* [5], **17**, 104). W. C. W.

Ethyl Acetoacetate. By A. E. Matthews and W. R. Hodgkinson (*Ber.*, **15**, 2679).—By the action of potassium cyanide on monochloracetone, $Me.CO.CH_2Cl$, the corresponding cyanide $Me.CO.CH_2.CN$ is obtained, and on decomposing this with hydrochloric acid, it yields ethyl acetoacetate. A. K. M.

Preparation of Methyl Chlorocarbonate. By A. Klepl (*J. pr. Chem.*, **26**, 447).—In preparing the chlorocarbonate by passing chlorocarbonic oxide into methyl alcohol in the ordinary way, a considerable quantity of methyl carbonate is formed at the same time, and can only be separated with difficulty. This may be avoided by diluting the alcohol with ready-formed methyl chlorocarbonate, and employing chlorocarbonic oxide free from chlorine; for this purpose the gas is first passed over a mixture of metallic antimony with fragments of glass, kept at a temperature of 100° to absorb the free chlorine, and then into a mixture of methyl chlorocarbonate with less than one-third of its bulk of methyl alcohol surrounded by ice-cold water. As soon as the chlorocarbonic oxide is no longer perceptibly absorbed, a fresh quantity of methyl alcohol is added, and the operation repeated, taking care that the alcohol added always bears about the same ratio to the chlorocarbonate already formed. When successive additions of alcohol have brought up the total quantity of liquid to about 150 c.c., the operation is stopped, the product washed with water at 0°, dried over calcium chloride, and distilled; almost the whole passes over between 70° and 72°, and one or two fractionations with a Linnemann's tube, render it perfectly pure (b. p. 71—71·5°). The same process may be employed with advantage in the preparation of ethyl chlorocarbonate. C. E. G.

Action of Chloroform on Sodium Ethylmalonate. By M. Conrad and M. Guthzeit (*Ber.*, **15**, 2841—2844).—Oppenheim and Pfaff have observed that by the action of chloroform and other chlorine derivatives of methane on sodium acetoacetate, the ethyl salt of hydroxyuvitic acid is formed; a reaction which they explain by the intermediate formation of an ethyl salt of an unsaturated acid of formula $C_5H_6O_4$, thus:—

$$2(CH_2\overline{Ac}.COOEt) + CHCl_3 = 3HCl + COOEt.C\overline{Ac} : CH.CH\overline{Ac}.COOEt.$$

The authors have studied a similar reaction in the case of sodium ethylmalonate, and obtained in the first place a sodium compound, $C_{15}H_{20}O_8Na$, crystallising in glistening prisms, whose aqueous solution gives crystalline precipitates with the chlorides of the alkaline earths and the acetates of the heavy metals, and a violet coloration with ferric chloride. On decomposing the sodium compound with hydrochloric acid, a substance of the formula $C_{15}H_{22}O_8$ is found. It is a colourless oil (b. p. 270—280°, sp. gr. 1·131) which gives off carbonic anhydride when heated with hydrochloric acid, and is converted into a crystalline acid (m. p. 133°) of composition $C_5H_6O_4$, which the authors propose to name *glutonic acid*, in that it yields glutaric acid on hydrogenation. The changes described above may be explained by the following reactions:—

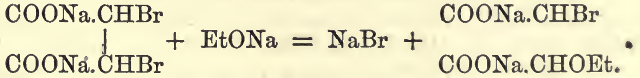
$$2CNa_2(COOEt)_2 + CHCl_3 = (COOEt)_2CNa.CH : C(COOEt)_2 + 3NaCl$$

and

$$(COOEt)_2CH.CH : C(COOEt)_2 + 4H_2O = COOH.CH_2.CH : CH.COOH + 2CO_2 + 4EtOH.$$

V. H. V.

Action of Sodium Ethylate on the Sodium Salt of Symmetric Dibromosuccinic Acid. By E. MULDER and G. HAMBURGER (*Rec. Trav. Chim.*, **1**, 54—55).—Sodium dibromosuccinate (1 g.), treated with absolute alcohol containing in solution 0·2875 g. sodium, *i.e.*, with four times the quantity required by the following equation, yields a gelatinous mass; and on treating this mass with a small quantity of water, filtering, and mixing the filtrate with alcohol, a gelatinous precipitate is obtained, which when washed with alcohol to remove sodium bromide, and dried under a bell-jar, forms a bulky hygroscopic mass consisting of sodium monobromethylmalate, $C_6H_7BrO_5Na_2$, formed according to the equation—



$$\begin{array}{l} COONa.CHBr \\ \quad | \\ COONa.CHBr \end{array} + EtONa = NaBr + \begin{array}{l} COONa.CHBr \\ COONa.CHOEt. \end{array}$$

The formation of this compound in presence of an excess of sodium shows that the second bromine-atom in the dibromosuccinate is difficult to replace; but by acting on the bromethylmalate with sodium ethylate, the authors hope to obtain the sodium salt of diethyltartaric acid, $C_8H_{14}O_6 = C_4H_4Et_2O_6$.

H. W.

Derivatives of Citraconic Acid. By G. L. CIAMICIAN and M. DENNSTEDT (*Gazzetta*, **12**, 500—502).—Gottlieb (*Annalen*, **77**, 274), by evaporating to dryness a mixture of citraconic acid with excess of ammonia, and heating the residue to 180°, obtained an amorphous resinous mass, which he regarded as citraconimide; and the authors of the present paper, by exactly following Gottlieb's directions, have obtained an amorphous mass of similar character; but on heating this substance to a higher temperature, they find that it gives off large quantities of ammonia, together with a yellow oily distillate solidifying on cooling to a mass of crystals; and at a still higher temperature a small quantity of a brown oil which does not solidify, and whose vapour exhibits the characteristic reaction of pyrroline with a deal shaving moistened with hydrochloric acid; finally there remains in the retort a quantity of shining friable charcoal.

The crystalline body above-mentioned may be freed from adhering oil by pressure between paper, and further purified by repeated crystallisation from boiling water with addition of animal charcoal, the solution on cooling depositing groups of splendid colourless needles which give by analysis 53·90 per cent. carbon, 4·72 hydrogen, and 12·92 nitrogen, agreeing very nearly with the formula of citraconimide, $C_5H_5NO_2$, which requires 54·05 C, 4·50 H, and 12·61 N. This body melts at 109—110°, is volatile and sublimable, slightly soluble in cold, freely in hot water and alcohol, sparingly in ether. It has a neutral reaction, and gives with ammoniacal silver nitrate a compound sparingly soluble in water. Heated with phosphorus pentachloride at 105—110°, it yields a dark brown liquid, which dissolves partially in water, forming a solution from which ether extracts a chlorinated body melting at 144—145° and subliming in colourless leaflets. This and other derivatives of citraconimide will form the subject of a future communication. H. W.

Acetylenedicarboxylic Acid. By E. Baudrowski (*Ber.*, **15**, 2694—2698).—Anhydrous acetylenedicarboxylic acid crystallises from ether in well-formed four-sided plates, melting with decomposition at 175°. Dimethylacetylenedicarboxylate, $C_4O_4Me_2$, is a colourless liquid (b. p. 195—198°) of aromatic but pungent odour.

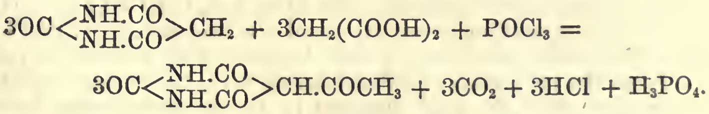
Chlorofumaric acid, $C_4H_3ClO_4$, obtained by the action of hydrochloric acid on acetylenedicarboxylic acid, melts at 178°. It dissolves very readily in water, alcohol, and ether, and crystallises in microscopic needles. Hydrogen potassium chlorofumarate, $C_4H_2ClO_4K$, crystallises in sparingly soluble prisms. The silver salt, $C_4HClO_4Ag_2 + H_2O$, forms a white crystalline precipitate, and the lead salt, $C_4HClO_4Pb + 2H_2O$, a flocculent precipitate which, however, soon becomes crystalline. From the properties of chlorofumaric acid, the author considers it as identical with the acid obtained by Perkin and Duppa by the action of phosphorus pentachloride on tartaric acid (*Annalen*, **115**, 105). Caius's acid, obtained by the action of hypochlorous acid on benzene (*Annalen*, **142**, 139), appears, however, to be an isomeride. Bromofumaric acid, prepared by dissolving acetylenedicarboxylic acid in fuming hydrobromic acid, agrees in all its properties with the acid described by Kekulé and Fittig (*Annalen*, **195**, 63). Iodofumaric acid obtained by the action of hydriodic on acetylenedicarboxylic acid, is readily soluble in water, alcohol, and ether. It melts at 182—184°. The hydrogen potassium salt, $C_4H_2IKO_4$, forms small well-formed crystals, sparingly soluble in water. The lead salt, $C_4HIO_4Pb +$

$2H_2O$, and the silver salt, $C_4HIO_4Ag_2$, are precipitated amorphous, but soon become crystalline. A. K. M.

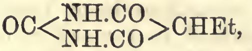
Propargylic Acid. By E. BAUDROWSKI (*Ber.*, **15**, 2698—2704).—The potassium salt of propargylic acid has been previously described by the author (*Ber.*, **13**, 2340). To prepare the free acid, $C_3H_2O_2$, a solution of hydrogen potassium acetylenedicarboxylate is treated with dilute sulphuric acid and shaken with ether. After standing for some hours, the ethereal extract is separated, dried, and evaporated on a water-bath. On distilling the residue, the principal fractions obtained are one at 100—125°, which after repeated fractioning yields ethyl propargylate boiling at 117—119°, and another at 125—154°. The greater part of this fraction distils at 140—145°, but as it decomposes at the same time, a constant boiling point cannot be obtained. Analysis showed this body to be propargylic acid. The residue in the flask became partly solid on cooling, apparently from separation of anhydrous acetylenedicarboxylic acid. Propargylic acid is a colourless liquid, which solidifies at about 4°, forming long silky crystals which melt at 6°. It is soluble in water, alcohol, ether, and chloroform. Its odour resembles that of acetic acid, but is more powerful. The salts of mercury, silver, and platinum are readily reduced by this acid. With the alkalis and alkaline earths, it forms salts very readily soluble in water. On reduction it yields propionic acid, and by the action of the halogen acids substituted acrylic acids. Bromine converts it into dibromacrylic acid melting at 85—86°.

A. K. M.

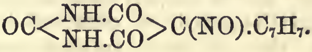
Derivatives of Barbituric Acid. By M. CONRAD and M. GUTHZEIT (*Ber.*, **15**, 2844—2850).—The author alludes to the interest attached to the chemistry of barbituric acid as the central point of the alloxan group, and the starting point for the synthesis of uric acid. In the course of preparation of barbituric acid from malonic acid, carbamide, and phosphorus oxychloride, the authors obtained as a bye-product a golden powder of empirical formula $C_3H_3NO_2$. As this substance gives dibromobarbituric acid by the action of bromine, it is most probably acetobarbituric acid, formed according to the equation—



$$3OC{<}\begin{matrix}NH.CO\\NH.CO\end{matrix}{>}CH_2 + 3CH_2(COOH)_2 + POCl_3 =$$
$$3OC{<}\begin{matrix}NH.CO\\NH.CO\end{matrix}{>}CH.COCH_3 + 3CO_2 + 3HCl + H_3PO_4.$$

Ethylbarbituric acid,  $OC{<}\begin{matrix}NH.CO\\NH.CO\end{matrix}{>}CHEt$, prepared from ethylmalonic acid, carbamide, and phosphorus oxychloride, crystallises in vitreous prisms melting at 190°; with bromine it forms a white crystalline monobrom-derivative. *Benzylbarbituric acid* from benzylmalonic acid forms prismatic crystals (m. p. 206°) soluble in hot water. The researches of the authors and others have established that one hydrogen-atom is replaceable by metals, the halogens and the nitrosyl group. In the present paper the silver salt is described. It is obtained as a reddish flocculent precipitate by the addition of silver nitrate to the acid ammonium barbiturate. *Dimethylbarbituric acid*, prepared by heating silver barbiturate with methyl iodide, was obtained as a red precipitate. The corresponding diethyl compound is a crystalline compound melting at 182°.

On mixing an aqueous solution of barbituric acid with potassium nitrite and adding silver nitrate, the silver salt of purpuric acid is formed. Benzylpurpuric acid, obtained by the action of benzyl chloride on this silver salt, forms glistening crystals (m. p. 226°). On saponifying benzylpurpuric acid, benzylnitromalonic acid is obtained, which shows that the benzyl group (and therefore the silver-atom) is directly combined to a carbon-atom, thus—



$$OC<\begin{matrix}NH.CO\\NH.CO\end{matrix}>C(NO).C_7H_7.$$

V. H. V.

Extraction of Asparagine from Liquids. By E. SCHULZE (*Ber.*, **15**, 2855—2856).—The author proposes to separate asparagine from plant-extracts by precipitation with mercuric nitrate, and decomposition of the white precipitate by sulphuretted hydrogen. This method is useful when the presence of soluble carbohydrates prevents the crystallisation of the asparagine.

V. H. V.

Benzene from Various Sources. By V. MEYER (*Ber.*, **15**, 2893—2894).—Baeyer has shown that benzene and isatin combine, when shaken with concentrated sulphuric acid, to form the deep-blue indophenine ($C_8H_5NO_2 + 2C_6H_6 = H_2O + C_{20}H_{15}NO$). In the present communication the author points out that the purest benzene (b. p. 78·8°) from coal-tar oil undergoes this reaction, whereas benzene of the same boiling point prepared from benzoic acid remains unaltered. The same result obtains whatever be the source of the benzoic acid, but if the purest benzene from coal-tar be heated for ten hours with concentrated sulphuric acid, and the unattacked portion separated and purified, the benzene so obtained (b. p. 78·8°) will not react with isatin. This difference in property the author considers to be due to a minute impurity in the benzene from coal-tar, which assists the reaction, or of an impurity in the benzene from benzoic acid, which prevents the reaction, or finally the presence of two modifications of benzene in the liquid obtained from coal-tar.

V. H. V.

Trinitro-derivatives of Benzene and Toluene. By P. HEPP (*Annalen*, **215**, 344—375).—To prepare trinitrobenzene, metadinitrobenzene (4 parts) is dissolved in a mixture of concentrated nitric acid (12 parts) and pyrosulphuric acid (30 parts); the mixture is then heated for two days at 80° and two days at 120°; the resulting product is poured into water, filtered, washed with water and with dilute sodium carbonate solution, and then crystallised from alcohol. The first crystallisation consists nearly exclusively of trinitrobenzene, which can be obtained quite pure by a single recrystallisation from water. The trinitrobenzene remaining in the alcoholic mother-liquor is best recovered by precipitation with aniline and decomposition of the resulting compound with dilute hydrochloric acid. The yield is about 50 per cent. of the dinitrobenzene employed.

Trinitrobenzene crystallises from warm alcohol in silky plates or needles; by slow evaporation of the cold saturated solution, small rhombic tables are obtained, giving the axial relations $a : b : c = 0{\cdot}954 : 1 : 0{\cdot}733$, and showing combinations of P, $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, ∞P, and, seldom and very small, $2\breve{P}2$ and $\infty\breve{P}2$. It melts at 121—122°, can be sublimed in small quantities by careful heating, explodes when quickly heated, and does not distil with water vapour.

By the action of ammonium sulphide on trinitrobenzene, only a very small quantity of a dinitraniline (?) was obtained, which resinified on attempting to purify it. With tin and hydrochloric acid the double salt $C_6H_3(NH_2)_3(HCl)_3,SnCl_2$ is obtained in brilliant white crystals. By removing the tin with sulphuretted hydrogen, the triamidobenzene hydrochloride may be obtained as a white crystalline mass. It does not give a blue coloration with ferric chloride, whilst the triamidophenol of Heintzel and the triamidobenzene prepared from picric acid (which should be identical with that from trinitrobenzene) both yield a deep-blue colour with this reagent.

On oxidation with potassium ferricyanide in weak alkaline solution, trinitrobenzene yields picric acid, the reaction occurring with great readiness. In order to ascertain what influence the accumulation of NO_2 groups had in accelerating oxidation, the author investigated the action of the same oxidising mixture on di- and mono-nitrobenzene. With metadinitrobenzene the reaction was very slow; after one hour's boiling, the greater part of the metadinitrobenzene was unaltered; the products of oxidation were β-dinitrophenol and a small quantity of α-dinitrophenol. Mononitrobenzene was not attacked by this oxidising mixture.

Addition-products of Trinitrobenzene and Aromatic Amines.—Trinitrobenzene-aniline, $C_6H_3(NO_2)_3,NH_2Ph$, is precipitated on adding aniline to an alcoholic solution of trinitrobenzene. It crystallises in long brilliant orange-red needles which melt at 123—124°. It is resolved into its constituents on long exposure to air, or by treatment with dilute acids. *Trinitrobenzene-dimethylaniline*, $C_6H_3(NO_2)_3,NMe_2Ph$, crystallises in dark-violet needles melting at 106—108°. Compounds were also prepared with ortho- and para-toluidine, both crystallising in long red needles, and forming violet-black granules with metaphenylene diamine.

Picramide, on reduction with tin and hydrochloric acid, gave the hydrochloride $C_6H_2(NH_2,HCl)_3.OH$, crystallising in brilliant white needles. The corresponding sulphate was obtained by the addition of sulphuric acid to an alcoholic solution of the hydrochloride. Picramide also unites with amines (Mertens, Abstr., 1878, 725). The *aniline* compound (m. p. 123—125°) forms dark-red crystals, the *dimethylaniline* compound (m. p. 139—141°) brilliant dark-blue crystals.

Picryl chloride reacts with potassium iodide in alcoholic solution, giving a substance crystallising in golden-yellow needles (m. p. 164°), decomposed by potash into potassium iodide and potassium picrate, and is therefore *trinitro-iodobenzene.*

By the nitration of paradinitrobenzene, 1 : 2 : 4 trinitrobenzene should be obtained; but all attempts to separate it from the unaltered dinitro-body were unsuccessful. Its presence was, however, conclusively proved by the formation from the product of the reaction of α-dinitraniline [1 : 2 : 4] by treatment with alcoholic ammonia, of dinitrodiphenylamine (m. p. 153°) by boiling in alcoholic solution with aniline, and of α-dinitrophenol by boiling with dilute soda solution.

TRINITROTOLUENES.—Two trinitrotoluenes have been described, α-trinitrotoluene by Wilbrand (*Annalen*, **133**, 178) and Tiemann (*Ber.*, **3**, 217 and 213), and γ-trinitrotoluene, prepared from γ-nitrotoluene by Beilstein and Kuhlberg (*Annalen*, **155**, 26). The author's researches add a third, β-trinitrotoluene.

α-Trinitrotoluene, $C_6H_2Me(NO_2)_3$, closely resembles trinitrobenzene. It crystallises in the rhombic system, $a : b : c = 0{\cdot}7586 : 1 : 0{\cdot}597$, and shows the faces ∞P, $\infty P\infty$, $\infty\bar{P}2$, $\breve{P}\infty$. It unites with amines, and these compounds may be prepared in a manner similar to those of trinitrobenzene, which they closely resemble. *α-Trinitrotolueneaniline* crystallises in long brilliant red needles melting at 83—84°. The dimethylaniline compound forms violet needles.

γ-Trinitrotoluene is obtained by the nitration of metanitrotoluene. It crystallises in six-sided yellow rhombic tables; axial relations, $a : b : c = 0{\cdot}9373 : 1 : 0{\cdot}6724$; observed forms, $\infty\breve{P}\infty$, P, $\infty\bar{P}2$, $2\bar{P}\infty$, $0P$. It is sparingly soluble in cold alcohol, moderately soluble in hot alcohol or hot glacial acetic acid, readily soluble in ether, benzene, and acetone. The last solvent yields the best formed crystals. It does not yield simple additive products with aromatic amines.

γ-Dinitrotoluidine, $C_6H_2Me(NO_2)_2.NH_2$, is prepared by the action of concentrated alcoholic ammonia on γ-trinitrotoluene. It crystallises in small, hard, well-formed, golden-yellow crystals, apparently of the rhombic system. It melts at 192—193°, and is sparingly soluble in nearly all solvents, dissolving most readily in acetone.

γ-Dinitrotolylphenylamine, $C_6H_2Me(NO_2)_2.NHPh$, is obtained by the action of aniline on a hot alcoholic solution of γ-trinitrotoluene. It crystallises in orange-coloured needles (m. p. 142°), sparingly soluble in alcohol.

β-Trinitrotoluene is formed, together with γ-trinitrotoluene, by the nitration of metanitrotoluene. It is obtained in less quantity than the γ-body, from which it can be separated by its greater solubility. It crystallises in colourless thick prisms of the triclinic system; axial relations, $a : b : c = 0{\cdot}6657 : 1 : 0{\cdot}6228$; observed faces, $\infty P'$, $\infty{}'P$, $\breve{P}\infty'$, $'\bar{P}'\infty$, $'\breve{P}_{,}\infty$, $\bar{P}$, $\infty\breve{P}\infty$, $0P$. It is sparingly soluble in cold alcohol, moderately in hot alcohol and glacial acetic acid, readily soluble in ether, benzene, and acetone; with ammonia and aniline it behaves like γ-trinitrotoluene.

β-Dinitrotoluidine, $C_6H_2Me(NO_2)_2.NH_2$, is prepared by heating β-trinitrotoluene with alcoholic ammonia for four or five hours in sealed tubes at 100°. It crystallises in short golden-yellow needles melting at 94°, and is more readily soluble than the corresponding γ-derivative. A. J. G.

Addition-products of the Nitro-derivatives with Hydrocarbons. By P. HEPP (*Annalen*, **215**, 375—380).—*Trinitrobenzene-*

benzene, $C_6H_3(NO_2)_3,C_6H_6$.—Trinitrobenzene is readily soluble in benzene, crystals of it deliquescing rapidly in benzene vapour; these solutions, on slow evaporation in the cold, yield hard, compact, brilliant, well-formed crystals of the new compound. They only retain their brilliancy whilst preserved in an atmosphere of benzene vapour, and are completely resolved into their components by a few hours' exposure to air.

Trinitrobenzene-naphthalene, $C_6H_3(NO_2)_3,C_{10}H_8$, separates on mixing cold saturated solutions of trinitrobenzene and naphthalene; it crystallises in long white needles which melt at 152°, and can only be recrystallised from alcohol containing naphthalene. Anthracene and trinitrobenzene yield a red additive compound.

α-Trinitrotoluene-naphthalene, $C_6H_2Me(NO_2)_3,C_{10}H_8$, crystallises in needles (m. p. 97—98°) closely resembling the trinitrobenzene compound. *Trinitrotoluene-anthracene* crystallises from benzene in red needles. A benzene-compound could not be obtained.

β-Trinitrotoluene-naphthalene crystallises in yellowish-white needles which melt at 100°. *γ-Trinitrotoluene-naphthalene* forms fine yellowish-white needles melting at 88—89°.

Metadinitrobenzene-naphthalene, $C_6H_4(NO_2)_2,C_{10}H_8$, prepared by mixing solutions of its components in benzene, crystallises in long thick prismatic needles melting at 52—53°. *Paradinitrobenzene-naphthalene* forms long white needles melting at 118—119°, and is distinguished from the last by its ready solubility in alcohol.

Dinitrotoluene-naphthalene, $C_6H_3(NO_2)_2Me,C_{10}H_8$, closely resembles the metadinitrobenzene-compound, and melts at 60—61°.

A. J. G.

Paradiethylbenzene. By H. ASCHENBRANDT (*Annalen*, **216**, 211—223).—This compound is best prepared by mixing dibromobenzene (25 g.) with ethyl iodide (50 g.), sodium (15 g.), and benzene (20 g.), and leaving the mixture to itself for about a day and a half, by which time the reaction comes to an end. 15 g. ethyl iodide are then added, whereupon further action takes place, and the decomposition is completed by adding 10 g. more, and heating the mixture in a paraffin-bath for two or three hours at about 150°. The product still contains small quantities of bromine-compounds, from which it may be freed by boiling it in a reflux apparatus with 3 or 4 grams of sodium cut up into small pieces. 150 g. *p*-dibromobenzene thus treated yielded 15 to 16 grams of pure *p*-diethylbenzene boiling at 181—182°.

p-Diethylbenzenesulphonic acid, $C_6H_3Et_2.SO_3H$.—The author, by heating 5 g. diethylbenzene with 20 g. fuming sulphuric acid on the water-bath, neutralising with lead carbonate, and decomposing the resulting lead salt with hydrogen sulphide, obtained this sulphonic acid as a brown rather viscid liquid which could not be brought to crystallise even by prolonged exposure to freezing mixtures. Fittig and König (*Annalen*, **144**, 277), on the other hand, describe the same acid as crystallising in colourless deliquescent laminæ.

The salts of this acid are, for the most part, easily soluble in water, and (excepting the alkali-salts) are prepared by heating the acid with the corresponding carbonates. The *barium salt*, $(C_{10}H_{13}SO_3)_2Ba,4H_2O$, separates by rapid crystallisation in brilliant nacreous laminæ; by slower crystallisation in fine rosettes of crystals; it is but sparingly soluble in alcohol. The *strontium salt* (+ $4H_2O$) separates from a highly concentrated solution in large shining laminæ; by slower crystallisation in very fine compact monoclinic crystals. The *calcium salt* (+ $5H_2O$) crystallises in small laminæ, more soluble than either of the preceding salts. The *magnesium salt*, $(C_{10}H_{13}SO_3)_2Mg$, is less soluble than the salts of the alkaline earths, and separates from dilute solution in fine prismatic crystals. The *nickel salt* (+ $5H_2O$) is but sparingly soluble, and separates from a concentrated solution in fine green laminæ. The *cobalt salt* (+ $5H_2O$) crystallises from dilute solutions in cruciform groups of red tablets, which, when cautiously heated on platinum foil, change to a splendid blue, and melt to a deep blue liquid.

Mercuric Salts.—On boiling the acid with mercuric oxide and concentrating the solution, shining yellow crusts separate, probably consisting of a basic salt, whilst the mother-liquor yields the normal salt, $(C_{10}H_{13}SO_3)_2Hg$, in small laminæ, which, when once separated no longer dissolve in water. The *potassium salt*,

$$C_{10}H_{13}SO_3K + 3\tfrac{1}{2}H_2O,$$

obtained by precipitating the barium salt with potassium sulphate, is very soluble in water, and crystallises therefrom in large nacreous laminæ, or by slower separation in thick tablets. The *sodium salt*,

$$C_{10}H_{13}SO_3Na,$$

prepared in like manner from the *strontium salt*, is somewhat less soluble than the potassium salt, and crystallises in large laminæ. The *ammonium salt* is extremely soluble in water, and crystallises in flat well-defined plates. The *silver salt*, $C_{10}H_{13}SO_3Ag$, obtained by heating the acid with silver oxide, is even more soluble than the potassium salt, and separates from concentrated solutions in beautiful shining tablets, which decompose on exposure to the air, with blackening and separation of silver oxide.

p-Ethylbenzoic acid, $C_6H_4Et.COOH$, is obtained by heating *p*-di-ethylbenzene with dilute nitric acid, and may be purified by steam-distilling the product which separates on cooling, then converting it into the sodium salt, decomposing the latter with hydrochloric acid, and digesting the precipitate with tin and hydrochloric acid to remove traces of a nitro-acid. The acid thus prepared is identical with that which Fittig and König obtained from a mixture of *o*- and *p*-diethylbenzene, and crystallises from hot aqueous solution in bright shining laminæ; it melts at 112—113°, and sublimes in laminæ. The residue of the steam-distillation above mentioned consists of a mixture of mono- and dinitro-ethylbenzoic acids, together with terephthalic and nitroterephthalic acids.

p-Ethylbenzoic acid is easily soluble in ether, alcohol, benzene, and chloroform, and separates from these solutions in rhombic tablets and prisms. The *calcium salt*, $(C_9H_9O_2)_2Ca + 3H_2O$, obtained by prolonged boiling of the acid with calcium carbonate in a flask with upright condensing tube, is slightly soluble in cold water, and crystallises in colourless needles. The *barium salt* (+ $2H_2O$) obtained by gentle boiling of the acid with barium carbonate, forms thin nacreous laminæ, easily soluble in water. The *strontium salt*, prepared in like manner, is very soluble, and crystallises in small laminæ.

Nitro-p-ethylbenzoic acid, $C_6H_3Et(NO_2).COOH$, is obtained by dissolving *p*-ethylbenzoic acid in cooled fuming nitric acid, and pouring the resulting solution into cold water, as a crystalline precipitate which may be purified by filtering, washing, and recrystallisation from boiling water, and then separates in long shining needles, which turn yellow when exposed to light, and on keeping split up into small needle-shaped fragments. It melts at 155—156°, dissolves readily in alcohol, ether, benzene, and chloroform, and separates therefrom in needles or prisms. Its *barium salt*, $[C_9H_9(NO_2)O_2]_2Ba$, crystallises in tufts of needles only slightly soluble in water. The *calcium salt* ($+ 2H_2O$) is sparingly soluble, and crystallises in broad tufts of needles. The *strontium salt* ($+ 4H_2O$) is also sparingly soluble, and forms small, shining, faintly yellowish laminæ. The *sodium salt*,

$$C_9H_8(NO_2)O_2Na + 2H_2O,$$

crystallises in shining laminæ, very soluble in water. The potassium salt, $C_9H_8(NO_2)K + H_2O$, is much more soluble than the sodium salt, and separates from a highly concentrated solution in long silky needles.

p - Bromethylbenzene, $C_6H_4Et.Br$, was once obtained, in consequence of using an insufficient quantity of sodium for the preparation of *p*-diethylbenzene from *p*-dibromobenzene by the process above described (p. 318), in the form of a heavy liquid, boiling after careful fractionation at 204°. It remains quite colourless on keeping, refracts light very strongly, has a strong smell of anise, and does not solidify in freezing mixtures. H. W.

Camphor-cymene, and the So-called Second Sulphonic Acid of Paracymene. By P. SPICA (*Gazzetta*, **12**, 482—488).—The statements respecting the sulphonic acids obtained from camphor-cymene do not quite agree (see Abstr., 1880, 878, 890; 1881, 174, 594, 602; 1882, 196). Paternò, in preparing the barium salt of ordinary camphocymenesulphonic acid, obtained also a small quantity of a *less soluble salt*, which crystallised in white scales containing 1 or 1½ mols. water. Subsequently Paternò and Spica obtained, together with the ordinary barium cymenesulphonate, a *more soluble salt* containing 12·02 p.c. crystal-water. Jacobsen obtained from "isocymene" two sulphonic acids, the barium salt of one of which, containing 12 p.c. water, was regarded by Paternò and Spica as identical with the more soluble salt which they obtained from camphor-cymene. Claus also obtained from paracymene two sulphonic acids, one yielding a barium salt *more soluble* than ordinary barium cymenesulphonate, and containing 3 mols. H_2O like the ordinary salt. The sulphonic acid from this salt melted at 130—131°, and yielded a lead salt containing $3H_2O$, and a calcium salt containing $2H_2O$, like the ordinary calcium sulphonate; also sodium, potassium, and copper salts crystallising with 1 mol. H_2O. To throw further light on the constitution of these acids, the author has made experiments upon a large quantity of cymene prepared by the action of sulphur and red phosphorus on camphor, carefully purified, and boiling at 175—178°. This was converted into sulphonic acids; these acids into barium salts; the barium salt containing 1 mol. H_2O was converted into a sodium salt; and from this latter, by heating it in sealed tubes at 190—200° with strong hydrochloric acid, the corresponding hydrocarbon was obtained. The examination of this hydrocarbon and its products of oxidation—details respecting which the author will communicate in a subsequent paper—showed clearly that the hydrocarbon in question consisted of *meta*-cymene. Hence it appears that when cymene is prepared from camphor by the action of sulphur and red phosphorus, the paracymene which forms the chief product is accompanied by metacymene; and that the mono-hydrated barium cymenesulphonate prepared from camphor-cymene, is derived, not from *para*- but from *meta*-cymene.

H. W.

Paradipropylbenzene, $C_{12}H_{18} = \overset{1}{Pr^{\alpha}}.C_6H_4.\overset{4}{Pr^{\alpha}}$. By H. KÖRNER (*Annalen*, **216**, 223—232).—This hydrocarbon, obtained by the action of sodium and propyl bromide on *p*-dibromobenzene, is a colourless strongly refracting liquid, having an aromatic odour like that of sassafras oil, and not solidifying in freezing mixtures. It floats on water, boils at 218—220°, volatilises with aqueous vapour, and burns with a very smoky flame.

p-Dipropylbenzenesulphonic acid, $C_{12}H_{18}SO_3 = C_6H_3(C_3H_7)_2.SO_3H$, is obtained by gently heating the hydrocarbon with a quantity of fuming sulphuric acid sufficient to form a compound soluble in water. On diluting the solution with water, supersaturating with lead carbonate, precipitating the lead from the filtered solution with hydrogen sulphide, evaporating the filtrate on the water-bath, and then leaving it to evaporate in the exsiccator, the sulphonic acid is obtained in thin colourless needles having a nacreous lustre; they absorb water rapidly from the air, and soon deliquesce. The *lead salt*,

$$[C_6H_2(C_3H_7)_2.SO_3]_2Pb + H_2O,$$

obtained as above, crystallises in concentric groups of silky needles. The *barium salt* ($+ \frac{1}{2}H_2O$) forms slender colourless needles which slowly give off their water in the exsiccator, and may be heated to 180° without decomposition. The *calcium salt* ($+ 9H_2O$) crystallises in large, colourless, highly lustrous, orthorhombic prisms, terminated by two dome-faces. On exposure to the air it effloresces, and quickly loses its lustre. The *sodium salt*, $C_6H_3(C_3H_7)_2.SO_3Na + 4H_2O$, forms colourless very soluble laminæ.

Dinitro-p-dipropylbenzene, $C_{12}H_{16}(NO_2)_2 = C_6H_2Pr_2^{\alpha}(NO_2)_2$.—When *p*-dipropylbenzene is added, with stirring, to cooled fuming nitric acid, and the resulting solution is poured into cold water, two nitro-compounds separate, both volatilising with steam, one solid at ordinary temperatures, the other liquid. The quantity of the liquid compound was too small for analysis; the solid body, after washing with water, repeated pressure between bibulous paper, drying, and several recrystallisations from alcohol, exhibited the composition of dinitrodipropylbenzene. The crystals of this nitro-compound are large, colourless, nacreous, rectangular tablets, usually with truncated summits. It melts at 65°, volatilises with aqueous vapour, turns yellow in the air, and dissolves with yellow colour in alcohol.

Dibromo-p-dipropylbenzene, $C_6H_2Pr_2{}^aBr_2$, is prepared by dropping the hydrocarbon into excess of bromine, and removing hydrobromic acid and excess of bromine by agitation with potash-lye, whereupon it separates in white flocks which may be purified by washing with water, pressing, drying, and solution in alcohol, from which the compound separates in shining needles or rectangular plates melting at about 48°.

p-Propylbenzoic acid, $C_{10}H_{12}O_2 = C_6H_4Pr^a.COOH$, is prepared by boiling *p*-dipropylbenzene with a mixture of 1 vol. nitric acid (sp. gr. 1·3), and 3 vols. water, and separates, after some hours' boiling, in loose masses of crystals. To purify it, the product is diluted with 3 vols. water, and distilled, with renewal of the water which passes over; the distillate, after saturation with sodium carbonate, is distilled with steam to remove any unaltered nitro-dipropylbenzene; the residue of the distillation is then evaporated over the water-bath to a small bulk; the propylbenzoic acid, somewhat contaminated with nitro-acid, is precipitated with hydrochloric acid; and the precipitate, after being dried and pressed, is treated with tin and hydrochloric acid to remove the last traces of nitro-acid, and again distilled in a stream of aqueous vapour.

p-Propylbenzoic acid crystallises from boiling water in small brilliant, six-sided, monoclinic prisms. It is insoluble in cold, and only slightly soluble in boiling water, but dissolves readily in alcohol, ether, benzene, chloroform, and carbon bisulphide, and separates from these solvents in long broad needles resembling benzoic acid. It sublimes undecomposed, volatilises readily with steam, and melts at 140°.

Barium propylbenzoate, $(C_3H_7.C_6H_4.COO)_2Ba + 2H_2O$, obtained by saturating the acid with barium carbonate, crystallises in large colourless laminæ or tablets having a satiny lustre, and less soluble than benzoate or ethylbenzoate of barium. The *calcium salt* ($+ 3H_2O$) forms moss-like groups of fine satiny needles, more soluble than the barium salt. The *strontium salt* ($2\frac{1}{2}H_2O$) forms colourless shining laminæ, somewhat sparingly soluble in water. The *lead salt* ($2H_2O$) forms druses of slender needles, nearly insoluble in cold, and only slightly soluble in boiling water.

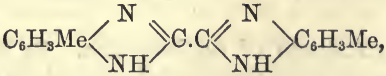
From the preceding facts, it appears that the *p*-propylbenzoic acid prepared by oxidation of *p*-dipropylbenzene is identical with that which Paternò and Spica obtained from isopropyl-propylbenzene (Abstr., 1880, 296). By this coincidence, the constitution of the latter acid is established, supposing that the reaction by which it was formed was not attended with any molecular transformation of normal propyl into isopropyl.

Nitro-p-propylbenzoic acid, $C_6H_3Pr^a(NO_2).COOH$, separates in yellow flocks on adding propylbenzoic acid to fuming nitric acid, and pouring the acid solution into a large quantity of water. It is very soluble in alcohol, ether, chloroform, and benzene, and crystallises from alcohol in large, broad, colourless needles. It is nearly insoluble in cold water, but melts in hot water to small oily drops, then dissolves in moderate quantity, and crystallises on cooling in small, colourless, shining needles. The *barium salt*, $[C_9H_{10}(NO_2).COO]_2Ba,4H_2O$, crystallises in colourless rectangular plates, sparingly soluble in cold, easily in hot water. The *strontium salt* ($5H_2O$) is sparingly soluble in cold water, and crystallises in tufts of colourless needles. H. W.

A New Hydrocarbon. By E. LOUISE (*Compt. rend.*, **95**, 1163—1164).—120 grams of mesitylene are mixed with 20 grams benzyl chloride, heated at 100°, and aluminium chloride gradually added until evolution of hydrochloric acid ceases. The black product is gradually added to water, and the yellow liquid which separates out is distilled. When the fraction boiling between 295° and 305° is purified it yields a liquid which boils at 300—303°. This new hydrocarbon, *benzyl-mesitylene*, $C_6H_2Me_3.C_7H_7$, forms a white crystalline mass with a slightly yellow tinge, easily soluble in benzene, light petroleum, alcohol, ether, acetic acid, acetone, &c., from which it separates in small white needles. Benzyl-mesitylene melts at 31°, and will remain in a superfused condition for several days, even if cooled repeatedly to $-25°$. When benzyl-mesitylene is dissolved in warm alcohol saturated with picric acid in the cold, the liquid deposits on cooling small citron-yellow needles, probably analogous in composition to the compounds of hydrocarbons with picric acid described by Berthelot.
C. H. B.

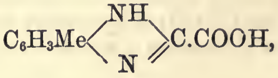
The History of the Metanitrils. By W. STAEDEL (*Ber.*, **15**, 2864—2865).—A purely controversial paper.

Oxalic Acid Derivatives of Metanitro-paratoluidine and 3—4 Diamidotoluene. By O. HINSBERG (*Ber.*, **15**, 2690—2694).—On heating metanitro-paratoluidine with oxalic acid at 110—130°, the two bodies, oxalylnitrotoluidide, $C_2O_2(NH.C_6H_3Me.NO_2)_2$, and nitrotolyloxamic acid, $COOH.CO.NH.C_6H_3Me.NO_2 + H_2O$, are formed. The former has been described by Rudolph (*Annalen*, **209**, 371). The latter crystallises from dilute alcohol in yellowish-red plates, which lose their water of crystallisation at 100°. Its ethyl-derivative (m. p. 127—128°) splits up when boiled with alkalis, yielding nitrotoluidine, oxalic acid, and alcohol. The sodium salt, $C_9H_7N_2O_5Na + H_2O$, and the barium salt, $C_{18}H_{14}N_4O_{10}Ba + 3H_2O$, both crystallise in yellow needles. The amido-compound, $C_2O_2(NH.C_6H_3Me.NH_2)_2$, obtained on reducing oxalylnitrotoluide, crystallises in small colourless needles. Heated to 130°, it loses one mol. H_2O, and the compound $C_{16}H_{16}N_4O$ is formed. At 300° a second mol. water is given off, with formation of the anhydro-base—

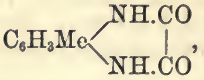


$$C_6H_3Me\begin{matrix}N\\ \\ NH\end{matrix}C.C\begin{matrix}N\\ \\ NH\end{matrix}C_6H_3Me,$$

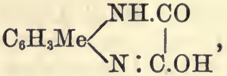
which in its properties closely resembles the diamido-compound. On reducing nitrotolyloxamic acid, water is eliminated and the body $2C_9H_8N_2O_2 + H_2O$ is produced; this is feebly acid and readily soluble in alcohol, sparingly in water, from which it crystallises in colourless needles, melting above 300° with slight decomposition. Its salts are decomposed by carbonic anhydride. The author suggests three formulæ for this body, viz.:—

I. 

$C_6H_3Me\langle{}^{NH}_{N}\rangle C.COOH$,

II. 

$C_6H_3Me\langle{}^{NH.CO}_{NH.CO}$,

III. 

$C_6H_3Me\langle{}^{NH.CO}_{N:C.OH}$,

but from its feebly acid properties he considers the last formula as the most probable. A. K. M.

Crystalline Cumidine. By A. W. HOFMANN (*Ber.*, **15**, 2895—2897).—The author at the outset alludes to the industrial application of the method devised by Martius and himself for the introduction of the methyl-group into a phenyl residue (*Ber.*, **4**, 742). In the present paper, the author describes a cumidine obtained by the action of methyl alcohol on xylidine hydrochloride. This base agrees in chemical and physical properties (m. p. 62°, b. p. 234°) with a cumidine obtained by Schäfer from pseudocumene. By the methylation of cumidine, mono- and di-methyl cumidine are formed together with the tetralcoholic ammonium iodide. *Monomethylcumidine*, $C_9H_{11}.NHMe$, melts at 44°, and boils at 237°; its platinochloride crystallises in needles. *Dimethylcumidine*, $C_9H_{11}NMe_2$, is a fragrant oil boiling at 222°; the methiodide, $C_9H_{11}NMe_3$, crystallises in prisms. These compounds when heated yield the last member of the series of methylated anilines, viz., pentamethyl-aniline, $C_6Me_5.NH_2$, the properties of which the author proposes to study. V. H. V.

The Three Isomeric Phenylenediamines. By E. LELLMANN (*Ber.*, **15**, 2839—2840).—The researches of Hübner and Ladenburg have established various differences in the chemical behaviour of the three isomeric phenylenediamines. In the present communication the author shows that under similar conditions the dithiocyanates of these compounds undergo a dissimilar decomposition, for the orthocompound gives orthophenylenethiocarbamide, but the meta- and para-compounds give the corresponding dithiocarbamides. *Orthophenylenethiocarbamide* crystallises in glistening leaflets (m. p. 290°), having an intensely bitter taste. *Metaphenylenedithiocarbamide* crystallises from alkaline solutions in microscopic leaflets melting at 215°. *Paraphenylenedithiocarbamide* crystallises from aqueous ammonia in small colourless needles (m. p. 218°), sparingly soluble in alcohol.

V. H. V.

Substitution-products of Azobenzene. By H. JANOVSKY (*Ber.*, **15**, 2575—2579).—*Azobenzenemonosulphonic acid*, formed by the action of fuming sulphuric acid on azobenzene at 130°, yields aniline and amidobenzeneparasulphonic acid on reduction with iron and hydrochloric acid. When azobenzene is treated at 150° with Nordhausen acid containing 25 per cent. SO_3, a mixture of three acids is obtained. On diluting the acid liquid with water, the mixture of the α- and β-disulphonic acids solidifies to a crystalline mass. They can be separated by fractional crystallisation of the free acids or of their barium salts.

α-Azobenzenedisulphonic acid, $SO_3H.C_6H_4.N\colon N.C_6H_4.SO_3H$ [4 : 1 : 1 : 4], crystallises in ruby-coloured needles containing 3 mols. H_2O. It is identical with the acid obtained from [1 : 4] benzenenitrosulphonic acid. The *β-disulphonic acid* [3 : 1 : 1 : 3] forms yellow plates, which are freely soluble in water. Its salts are more soluble than those of the α-acid. On reduction with tin and hydrochloric acid, the β-acid yields amidobenzenemetasulphonic acid. The third acid, found in small quantities in the mother-liquor of the α- and β-acids, yields aniline and amidobenzenedisulphonic acid on reduction. Its formula is probably $Ph.N_2.C_6H_3(SO_3)_2$ [1 : 2 : 4].

Two mononitro-derivatives are obtained by treating azobenzeneparasulphonic acid with nitric acid (sp. gr. 1·41). The α-acid, $C_6H_4(NO_2).N_2.C_6H_4.SO_3H$, resembles azobenzenesulphonic acid in appearance. It crystallises in golden scales belonging to the rhombic system. The crystals are sparingly soluble in water, but dissolve freely in dilute nitric acid. The salts of this acid are colourless. On reduction, it yields an amidosulphonic acid which crystallises in pale yellow monoclinic plates. The potassium salt forms rhombic plates. β-nitrazobenzenesulphonic acid, $C_6H_4(NO_2).N_2.C_6H_4.SO_3H$ [3 : 1 : 1 : 4], is very deliquescent. Its salts have a yellow colour. *Dinitrazobenzeneparasulphonic acid*, prepared by the action of nitric acid (sp. gr. 1·45) on azobenzenesulphonic acid, crystallises in microscopic needles. The potassium salt explodes on heating. A *trinitro-acid* is formed when nitric acid (sp. gr. 1·5) is employed. Its salts are very explosive.

W. C. W.

Formation of Anilides. By G. TOBIAS (*Ber.*, **15**, 2866—2876).—This paper consists of a series of observations on the conditions attending the formation of the anilides. The author has confirmed the results of Willm and Girard as regards the formation and properties of the formyl-derivatives of diphenylamine; he finds further that ethylaniline reacts with formic acid, but the resultant anilide cannot be obtained in the pure state. Attention is also drawn to the fact that formic acid acts more readily than acetic acid to form the anilide. Thus 15·7 per cent. formic acid heated with the equivalent quantity of aniline for four hours gave 79 per cent. of the theoretical yield of the anilide, but 15 per cent. acetic acid under the same conditions gave only 18 per cent. after 36 hours.

The author also criticises the observations of Menschutkin on the decomposition of acetanilide by water containing a trace of acetic acid; he considers that the change is effected by the acetic acid, and is inclined to maintain the view that pure acetanilide is unaffected by pure water, and that the same result would hold good with pure formanilide.

V. H. V.

Formanilide and its Homologues. By G. TOBIAS (*Ber.*, **15**, 2443—2452).—The author has made a series of experiments to prove that aniline reacts more completely and more rapidly with formic than with acetic acid to form the anilide. Thus, under similar conditions, 90 per cent. of the theoretical quantity of the formanilide, but only 35 per cent. of the acetanilide was obtained. Traces of mineral acids and the presence of large quantities of water exert a material influence on the preparation of the formanilide. When 1 mol. anhydrous formic acid acts on 1 mol. aniline, the reaction limit reaches 98 per cent. of the theoretical quantity.

Formorthotoluide, $H.CONH.C_6H_4Me$, from orthotoluidine and formic acid, crystallises in white glistening leaflets melting at 58°; *formoparatoluide*, from paratoluidine, crystallises in compact crystals, melting at 52°; *α-naphthylformamide*, from α-naphthylamine, crystallises in white silky needles, melting at 138·5°; β-naphthyl formamide, from β-naphthylamine, crystallises in glistening leaflets, melting at 128°. By the action of metaphenylenediamine on formic acid, a substance was obtained in refractive crystals melting at 155°, soluble in hot water and alcohol, and giving no reaction with the nitrites of the alkali-metals unless previously heated with hydrochloric acid. The substance in question was probably *diformylmetaphenylenediamine*, although the results of the analyses showed that it was not quite pure.

On passing dry hydrochloric acid through formanilide, methenyldiphenyldiamine was obtained (a result in accordance with the researches of Hofmann and others), with considerable evolution of carbonic oxide. Methenyldiphenyldiamine easily reverts to its two components, aniline and formanilide. The sodium salts of formortho- and para-toluide crystallise in glistening leaflets, which rapidly absorb carbonic anhydride from the air. V. H. V.

Decomposition of Acetanilide by Water. By N. MENSCHUTKIN (*Ber.*, **15**, 2502—2505).—After some remarks on the general concordance of his quantitative results with L. Meyer's qualitative experiments on the decomposition of acetanilide with water (this vol., p. 56), the author takes exception to the observation that acetanilide is not decomposed by water. Although, when pure water is heated with acetanilide, no reaction occurs even after an interval of 150 hours, yet if a trace ($\frac{1}{1000}$) of acetic acid is added, a different result is obtained; about 19·75 per cent. of the acetanilide being decomposed when a mixture of 1 mol. acetanilide with 1·103 mols. of water is heated for some hours. Experiments were also made to determine the effect on the limit of the reaction, caused by altering the proportion of water, and the following were the results:—

Proportion of acetanilide to water.	Limit of reaction.
1 : 0·87	86·50 per cent.
1 : 0·88	84·41 ,,
1 : 0·9	81·31 ,,

These experiments show that acetanilide is decomposed by water, and that the reactions between aniline and acetic acid on the one hand, and acetanilide and water on the other, are reversible according to the conditions of the experiment. The author further shows that an increase in the proportion of acetic acid is favourable to the production of the acetanilide—a result which is in accordance with the observation of Berthelot, that an increase of acetic acid favours its etherification by alcohol. V. H. V.

Aromatic Arsenic- and Antimony-compounds. By A. MICHAELIS and A. REESE (*Ber.*, **15**, 2876—2877).—The authors show that triphenylarsine is best prepared by the action of sodium on a mixture of arsenic trichloride, monobromobenzene, and ether. On filtration and evaporation of the ethereal solution, the compound separates out as a solid mass, which can be readily purified by crystallisation from alcohol. By a similar process the corresponding antimony-compound may be obtained in the form of golden leaflets melting at 48°, soluble in ether and benzene, insoluble in water and hydrochloric acid. If the sodium is not in excess, crystalline bromo- and chloro-addition products, $SbPh_3Br_2$ and $SbPh_3Cl_2$, are formed, but cannot be separated from the free stibine. The author suggests the above process for the preparation of the aromatic silicon, boron, and metallic derivatives.

V. H. V.

New Nitro-derivatives of Phenol. By R. HENRIQUÉS (*Annalen*, **215**, 321—344).—So far no isomerides of picric acid have been obtained; Bantlin (this Journal, 1875, 640) stated that he had prepared isopicric acid by boiling the dinitrophenols obtained from metanitrophenol with nitric acid; but he found later (this Journal, 1877, ii, 475) that the substance was trinitroresorcinol (styphnic acid). The author has re-investigated this reaction, and succeeded in obtaining two new trinitrophenols.

γ-Dinitrophenol is dissolved in three times its weight of concentrated nitric acid in the cold, and the solution, after standing for 36 to 48 hours, is poured into water, when an oily mixture separates; the free nitric acid is neutralised with ammonia, and the nitrophenols are extracted with ether. The ethereal solution is evaporated to dryness and treated with steam to remove unaltered dinitrophenol; the residue is dissolved in water, treated with barium carbonate, and evaporated to dryness; and the barium derivatives are treated with absolute alcohol. The residue then consists of barium styphnate, together with a small quantity of the barium salt of a tetranitrodihydroxybenzene (see later). The alcoholic solution contains the barium salts of β- and γ-trinitrophenol, which can be separated by fractional crystallisation. The yield of the trinitrophenols is only about one-sixth of the dinitrophenol employed.

Bantlin concluded that γ-dinitrophenol had the constitution $[OH : NO_2 : NO_2 = 1 : 3 : 5]$. As this, however, is in contradiction to its ready conversion into trinitroresorcinol, in which the two OH-groups are known to be in the meta-position, the author has re-investigated the question. γ-Dinitrophenol was heated for a short time at 100° with methyl iodide and methyl alcohol, when the anisoïl of melting point 96° was obtained. This was heated with alcoholic ammonia at 200—210°; the resulting dinitraniline, on treatment with ethyl nitrite, gave a readily sublimable mass of m. p. 170°. (Paradinitrobenzene melts at 171—172°, whilst metadinitrobenzene, which should have been formed according to Bantlin's hypothesis, melts at 90°.) From this, it is evident that the constitution of γ-dinitrophenol would be [1 : 3 : 6] (OH in 1).

The nitration of ϵ-dinitrophenol [1 : 2 : 3] is best effected by adding it to well-cooled nitric acid, and, after two or three hours, pouring into water, the subsequent treatment being similar to that given for the γ-compound. It yields trinitroresorcinol and γ-trinitrophenol.

δ-Dinitrophenol [1 : 3 : 4] yields on nitration trinitroresorcinol, β-trinitrophenol, and possibly another trinitrophenol in small quantity, as after the treatment with ammonia, the aqueous solution was found to contain a dinitramidophenol, apparently not derived from β-trinitrophenol.

The new trinitrophenols closely resemble picric acid; they have a bitter taste, readily decompose carbonates, detonate on heating, yield explosive salts, and give crystalline compounds with some hydrocarbons.

β-Trinitrophenol, $C_6H_2(NO_2)_3.OH$ (m. p. 96° uncorr.), being derived from both δ- and γ-dinitrophenols, must have the constitution [1 : 3 : 4 : 6] (OH in 1). It crystallises in white satiny needles or plates, is very readily soluble in alcohol, ether, and benzene, moderately soluble in hot water, sparingly in cold water and dilute acids. The *barium* derivative, $[C_6H_2(NO_2)_3O]_2Ba + 4H_2O$, crystallises in reddish-brown prisms, and only completely loses its water on long heating at 150°; it is moderately soluble in water and alcohol. The *potassium* derivative forms anhydrous, brilliant, clear-red crystals of violet reflex; it is sparingly soluble in water, nearly insoluble in alcohol. Solutions of the salts of β-trinitrophenol give a yellow precipitate with lead salts, which can be obtained crystallised in needles, and a reddish-brown flocculent precipitate with silver salts. On gently heating it with nitric acid, β-trinitrophenol is converted into trinitroresorcinol.

Naphthalene unites with β-trinitrophenol, giving a compound of the formula $C_{10}H_8,C_6H_2(NO)_3.OH$; it crystallises in yellow needles, which melt at 72—73°, and are readily soluble in alcohol. Phenanthrene does not yield a similar compound.

γ-Trinitrophenol is obtained from γ- and ϵ-dinitrophenol, and therefore has the constitution [1 : 2 : 3 : 6]. It crystallises in white needles (m. p. 117—118°), behaves towards solvents like β-trinitrophenol, and is also converted into trinitroresorcinol on oxidation with nitric acid. The *barium* derivative, $[C_6H_2(NO_2)_3O]_2Ba$, crystallises in clear brown to golden-yellow scales, frequently united in rosettes; it is not very soluble in water or alcohol. (In the preparation of γ-trinitrophenol from ϵ-dinitrophenol, barium salts were obtained in small quantity, crystallising with 1 and 3 mols. H_2O, but all attempts to prepare such hydrates from the anhydrous barium salt were unsuccessful.) The potassium salt crystallises in deep-red anhydrous needles, readily soluble in water with red colour, nearly insoluble in alcohol; the aqueous solution dyes wool and silk of an orange colour. Solutions of γ-trinitrophenol salts give a dark-yellow precipitate with lead salts; a reddish-brown flocculent precipitate with silver salts, and no precipitate with copper or mercuric salts. With naphthalene, a compound of the formula $C_{10}H_8,C_6H_2(NO_2)_3.OH$ is obtained in golden-yellow needles, which melt at 100°.

β-Dinitroamidophenol, $C_6H_2(NO_2)_2(NH_2).OH$, isomeric with picramic acid, is obtained, as previously described, by treating the trinitrophenols from δ-dinitrophenol with aqueous ammonia; it crystallises in

brilliant red needles, melting at 202°, and subliming readily. It is nearly insoluble in ether, water, and mineral acids, sparingly soluble in absolute alcohol, but dissolves readily in solutions of alkalis or alkaline earths with formation of salts. The *potassium* derivative crystallises in clear yellow needles, readily soluble in water; it explodes feebly on heating.

Tetranitrodihydroxybenzene, $C_6(NO_2)_4(OH)_2$, obtained in small quantity in the nitration of γ-dinitrophenol, crystallises in yellowish or colourless needles, which melt at 166°, and are readily soluble in alcohol and ether, sparingly in water. The barium derivative, $C_6(NO_2)_4O_2Ba + 6H_2O$, crystallises in golden-yellow silky needles; when anhydrous, it acquires a cherry-red colour. It is sparingly soluble in water, insoluble in alcohol.

The constitution of styphnic acid is also settled by these experiments. It has long been known to be a resorcinol derivative, and being formed by the oxidation of both β- and γ-trinitrophenol, it must have the constitution $[OH : NO_2 : OH : NO_2 : NO_2 = 1 : 2 : 3 : 4 : 5]$.

A. J. G.

Conversion of Tolylenediamine into an Amidocresol and γ-Orcinol. By O. WALLACH (*Ber.*, **15**, 2831—2835).—In order to determine the constitution of the monacetotolylenediamine already described by the author, with a view of deciding between the formulæ $NH_2.C_6H_3Me.NH\overline{Ac}$ $[Me : NH_2 : NH\overline{Ac} = 1 : 2 : 4]$ or $[Me : NH\overline{Ac} : NH_2 = 1 : 2 : 4]$, the author converted it into an amidocresol, and compared it with the amidocresol obtained by Knecht from nitrotoluidine (Abstr., 1882, 728). By the action of nitrous acid on monacetotolylenediamine, an acetamidocresol, $OH.C_6H_3Me.NH\overline{Ac}$, is formed; it crystallises in large leaflets (m. p. 224)°, sparingly soluble in cold water, soluble in alcohol. When the acetamidocresyl is boiled with hydrochloric acid, it is converted into amidocresol chloride, which crystallises in leaflets, soluble in water and alcohol. The free amidocresol is obtained by precipitating an aqueous solution of the hydrochloride with potassium hydrogen carbonate; it forms needles melting at 159°, sparingly soluble in cold water. This amidocresol is not identical, but isomeric with the amidocresol obtained by Knecht from nitrotoluidine, which has the constitution $[Me : NO_2 : OH = 1 : 2 : 4]$; it is therefore a derivative of orthocresol, and has the constitution $[Me : OH : NO_2 = 1 : 2 : 4]$. The author has re-examined the former amidocresol, and finds that its hydrochloride gives no colour reaction with ammonia as described by Knecht; it crystallises in leaflets melting at 138°, sparingly soluble in cold water.

The amidocresol melting at 159° is converted by the diazo reaction into γ-orcinol, $C_6H_3Me(OH)_2$ $[Me : OH : OH = 1 : 2 : 4]$, identical with the cresorcinol of Knecht.

V. H. V.

Synthesis of Indole from Cuminol. By O. WIDMAN (*Ber.*, **15**, 2547—2553).—Nitrocumic acid can be prepared by the action of a glacial acetic acid solution of chromic acid on nitrocuminol. When an alkaline solution of this acid is treated with a concentrated solution of potassium permanganate, it is converted into nitrohydroxypropylbenzoic acid, $CMe_2(OH).C_6H_3(NO_2).COOH$, which is obtained as a crystalline precipitate on acidifying the cold solution with hydrochloric acid. A good yield of *nitrohydroxypropylbenzoic acid* can also be obtained by the direct action of potassium permanganate on nitrocuminol. This acid is deposited from a hot aqueous solution in colourless needles melting at 190°, freely soluble in alcohol and ether.

The ammonium salt crystallises in needles, and the silver salt in rhombic prisms or plates. The ethylic salt forms rhombic plates, melting at 96°. It is freely soluble in the usual solvents, with the exception of light petroleum. It is decomposed by warm hydrochloric acid, forming nitropropenylbenzoic acid. *Sodium azoxypropylbenzoate*, $(C_{10}H_{10}NO_3Na)_2 + 10H_2O$, is obtained by the action of sodium amalgam on an aqueous solution of nitrohydroxypropylbenzoic acid, in rectangular plates, exhibiting a brilliant red colour. The free acid crystallises in yellow plates, insoluble in alcohol, ether, and benzene. It is not decomposed by hot hydrochloric acid.

Nitropropenylbenzoic acid, $C_{10}H_9NO_4$, prepared by boiling nitrohydroxypropylbenzoic acid with hydrochloric acid (sp. gr. 1·10), crystallises in colourless needles (m. p. 154°), which dissolve freely in alcohol and ether, but are sparingly soluble in water. The ammonium and silver salts of this acid crystallise in needles. The methyl and ethyl salts are uncrystallisable oils.

On distillation with lime, nitropropenylbenzoic acid yields indole, $C_{10}H_9NO_4 + CaO = C_8H_7N + CaCO_3 + H_2O + CO$. W. C. W.

Brominated Derivatives of Toluquinone. By F. Canzoneri and P. Spica (*Gazzetta*, **12**, 469—475).—*Tribromotoluquinone*,

$$C_7H_3Br_3O_2 = C_6MeBr_3O_2,$$

is obtained, as chief product, on agitating toluquinone, in presence of a little water, with a quantity of bromine rather more than sufficient to form the monobromo-derivative, the liquid becoming warm and yielding as it cools a brown viscid mass, from which alcohol removes a resinous portion, leaving undissolved a yellow crystalline substance obtainable by repeated crystallisation from alcohol in broad golden-yellow laminæ which melt with slight blackening at 223°. The substance thus prepared has nearly the composition of tribromotoluquinone, but contains only 66·06 to 66·32 per cent. bromine, whereas the formula of that compound requires 66·85 per cent., the deficiency being due to the presence of less highly brominated compounds formed at the same time and very difficult to separate. The pure tribromo-derivative may however be obtained by oxidising tribromotoluquinol (next page) with ferric chloride, in which case it separates in rather smaller laminæ having the same crystalline form, a bright golden-yellow colour, and melting at 235—236°. It is insoluble in water, but very freely soluble in ether and in benzene, very sparingly in cold alcohol; it dissolves with partial resinification in potash, also in sulphuric acid, from which it is precipitated by water.

The same tribromotoluquinone is also formed by the action of sulphuric acid, manganese dioxide, and potassium bromide on commercial cresol, and lastly, together with a more highly brominated compound, by subjecting cresol to the simultaneous action of bromine and iodine. Being thus obtained by three different processes, it may be regarded as the one of the three possible tribromotoluquinones, which is most easy of formation.

With regard to its constitution, it may be observed that the toluquinone from which it was prepared, having been formed from orthotoluidine, must have the constitution $C_6.Me.O.H.H.O.H$, and therefore its tribromo-derivative must be represented by the formula—

$$C_6.Me.O.Br.Br.O.Br;$$

and this view is in accordance with its formation from commercial cresol which, although it contains the three isomeric cresols, is capable of yielding only one tribromotoluquinone, inasmuch as para-cresol cannot furnish a quinone at all, and ortho- and meta-cresol must necessarily yield the same tribromotoluquinone.

Tribromotoluquinol, $C_7H_3Br_3(OH)_2 = C_6MeBr_3(OH)_2$, is formed by the prolonged action of sulphurous anhydride on tribromotoluquinone suspended in water, the colour of the substance changing from yellow to white. On filtering and treating the residue with cold alcohol, the tribromoquinol dissolves, the solution when mixed with water depositing a flocculent precipitate, which when purified by successive crystallisation from water and from alcohol, yields the tribromotoluquinol in white or faintly reddish needles melting at 201—202°. The same product is obtained by reducing tribromotoluquinone with tin and hydrochloric acid. Its alcoholic solution, treated with excess of ferric chloride, yields a precipitate of tribromotoluquinone.

The *anilide of tribromotoluquinone*,

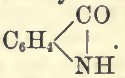
$$C_{19}H_{15}Br_3O_2 = C_6MeBr_3O_2 : (NHPh)_2,$$

appears to be formed, together with other anilides, on boiling an alcoholic solution of the tribromoquinone with excess of aniline, the product separating on cooling in black shining crystals, infusible and nearly insoluble in alcohol.

Dibromotoluquinone, $C_6HMeBr_2O_2$.—The alcohol which had been used for washing the tribromoquinone yielded on fractional evaporation an additional quantity of the latter, together with products of lower melting point mixed with resinous matter; and the remaining mother-liquor, when filtered and left at rest, deposited yellow crystals (m. p. about 100°) which, after repeated crystallisation from dilute acetic acid, yielded, as the constituent most soluble in that liquid, yellow crystals melting at 85°, and having the composition of dibromotoluquinone; the same substance, mixed with traces of the tribromoquinone, is also found in the alcohol which has been used for crystallising the latter, and separates in small quantity on adding water. The same products were obtained by the use of ether instead of alcohol, the proportion of dibromotoluquinone thereby produced being however somewhat larger. H. W.

Orthamidobenzaldehyde. By P. FRIEDLAENDER (*Ber.*, **15**, 2572—2575).—Orthamidobenzaldehyde is best prepared from anthranil, which is obtained from crude nitrobenzaldehyde by the process previously described by the author (*Ber.*, **15**, 2105). A mixture of pure anthranil, ferrous sulphate, and ammonia is gently heated until the odour of anthranil is no longer perceptible. On distillation in a current of steam, orthamidobenzaldehyde is found in the distillate in shining scales melting at 39°. The crystals are freely soluble in alcohol, ether, benzene, and chloroform. Amidobenzaldehyde forms a crystalline compound with mercuric chloride and with hydrogen sodium sulphite. Acetorthamidobenzaldehyde crystallises in long needles melting at 71°. When this compound is heated with acetic anhydride and sodium acetate, carbostyril is produced. Attempts to prepare salts of amidobenzaldehyde were unsuccessful.

Quinoline is produced on warming a mixture of this aldehyde with acetaldehyde and soda solution.

The ready conversion of anthranil into amidobenzaldehyde is in favour of the view that the constitution of anthranil is  $C_6H_4\left\langle\begin{array}{l}CO\\ \vert\\ NH\end{array}\right.$.

W. C. W.

Bromacetophenone. By R. MÖHLAU (*Ber.*, **15**, 2464—2466).—After a description of the numerous difficulties which attend the formation of bromacetophenone by dropping bromine into a solution of acetophenone in carbon bisulphide, the author proposes the substitution of acetic acid for the carbon bisulphide, as being a better solvent of the water and hydrobromic acid formed in the reaction. Adopting this change, the author, in a test experiment, obtained 80 per cent. of the theoretical quantity of bromacetophenone. V. H. V.

Action of Bromacetophenone on Phenol. By R. MÖHLAU (*Ber.*, **15**, 2497—2500).—The intoduction of the benzoyl-group into the molecule of methyl bromide, and the readiness with which the resultant bromacetophenone reacts with the primary amine, points to bromacetophenone as possessing the character of an acid bromide. In order to examine this hypothesis, the author has studied the action of phenol on bromacetophenone, and finds that no action occurs unless the hydrogen of the phenol is previously replaced by a metal, when *acetophenone phenyl ether*, $COPh.CH_2.OPh$, is produced. This substance crystallises in colourless prisms, melting at 72°, soluble in alcohol, and decomposed by fusion with potash into phenol and phenylmethylketone.

Acetophenone paranitrophenyl ether,

$$COPh.CH_2.O.C_6H_4.NO_2\ [O : NO_2 = 1 : 4],$$

formed by the action of sodium paranitrophenol and bromacetophenone, crystallises in golden prisms melting at 144°, sparingly soluble in alcohol, insoluble in water, decomposed by molten alkali into paranitrophenol and phenyl-methyl ketone. Orthonitrophenol does not undergo a similar reaction. These results show that bromacetophenone possesses the character rather of an alcoholic than of an acid bromide. V. H. V.

Acetophenoneanilide. By R. MÖHLAU (*Ber.*, **15**, 2466—2480; compare Abstracts, 1881, 262).—The *hydrochloride of acetophenone-*

anilide, $COPh.CH_2.NHPh,HCl$, is obtained by passing hydrochloric acid into an ethereal solution of the anilide; it forms glistening prismatic crystals, decomposible by water into its constituents. The hydrobromide forms polysynthetic prisms.

Acetylacetophenoneanilide, $COPh.CH_2.NPh\overline{Ac}$, crystallises in rhombic prisms melting at 126°, insoluble in water, sparingly soluble in alcohol and ether. *Benzoylbromacetophenoneanilide*, $COPh.CH_2.NPh\overline{Bz}$, crystallises in glistening prisms melting at 145°, insoluble in water, soluble in alcohol and ether.

The product of the action of nitrous acid on acetophenoneanilide is dependent on the conditions of the reaction; in presence of alcohol *nitroacetophenoneanilide* is formed; in presence of glacial acetic acid, *nitrosoacetophenonenitranilide.* Nitrosoacetophenoneanilide crystallises in golden prismatic needles melting at 73°, insoluble in water, easily soluble in alcohol, ether, &c.; soluble in potash, with formation of a red colour. It readily gives Liebermann's reaction for nitroso-compounds. Nitrosoacetophenonenitranilide crystallises in glistening leaflets, insoluble in water, easily soluble in ether; soluble in potash with a red colour. On boiling an alcoholic solution of this compound with concentrated hydrochloric acid, it is converted into *acetophenonenitranilide*, $COPh.CH_2.NH.C_6H_4.NO_2$, which forms glistening golden needles, melting at 167°; it can readily be reconverted into the nitroso-derivatives by nitrous acid. On oxidation it yields benzoic acid, and on reduction acetophenone and paraphenylenediamine; these results show that the nitro-group is in the anilide radical, and that the nitro-group is in the para-position to the imido-group.

By the action of fuming nitric acid on acetophenoneanilide, a *dinitro-derivative*, $COPh.CH_2.NH.C_6H_3(NO_2)_2$, is obtained, which crystallises in golden prisms, melting at 171°; on oxidation it yields benzoic acid, and on reduction, acetophenone and Will's triamidobenzene

$$[NH_2 : NH_2 : NH_2 = 1 : 2 : 4],$$

and therefore the constitution of the acetophenonedinitranilide is $[NH : NO_2 : NO_2 = 1 : 2 : 4]$. V. H. V.

Oxidation of Durene by Chromic Acid.—Dinitrodurylic Acid. By R. GISSMANN (*Annalen*, **216**, 200—211).—When durene, $C_6H_2Me_4$ [1 : 2 : 4 : 5], is subjected to the action of chromic acid or other powerful oxidising agents, only one of its methyl-groups is converted into a carboxyl-group, the greater part of the substance being completely broken up. The oxidation is best effected by treating durene with the calculated quantity of chromic acid, both dissolved in glacial acid. On pouring the resulting green liquid into water, part of the oxidised product separates as a white flocculent precipitate, and a further quantity may be obtained by precipitating the chromium from the hot filtered liquid with caustic soda, filtering again, and supersaturating with hydrochloric acid. The product thus obtained is *durylic acid*, $C_{10}H_{12}O_2 = C_6H_2Me.COOH$ [formerly called cumylic acid]. It dissolves very sparingly in cold, more readily in hot water, from which it crystallises in needles; with moderate facility in alcohol, ether, and benzene, and separates from the latter in long thick transparent strongly refracting prisms; it sublimes between watch-glasses in long needles, volatilises completely with aqueous vapour, and melts at 150°.

Jannasch (*Zeits. f. Chem.*, **6**, 449), by oxidising durene with dilute nitric acid, obtained, in addition to durylic (cumylic) acid, a bibasic acid, $C_6H_2Me_2(COOH)_2$, which he called *cumidic acid.* The oxidation of durene by chromic acid in acetic acid solution does not appear to yield a bibasic, or any more highly basic acid.

Dinitro-durylic acid, $CMe_3(NO_2)_2.COOH$, is obtained by gradually adding durylic acid (1 pt.) to strong nitric acid (10 pts.), in which it dissolves immediately, with copious evolution of red vapours. On pouring the cooled solution into water, a flocculent precipitate separates; and on distilling this with steam, there passes over, together with unaltered durylic acid, a small quantity of a yellowish low-melting compound, insoluble in alkalis, which the author regards as probably consisting of nitrotrimethylbenzene, formed by exchange of one of the carboxyl-groups for a nitro-group.

The non-volatile part of the product separates on cooling as a finely divided precipitate; and on boiling this with water and pounded calcspar, a calcium salt is obtained, which, when purified by recrystallisation and treated with hydrochloric acid, yields dinitrodurylic acid as a yellowish powder, melting at 205°, slightly soluble in cold, more readily in hot water, and always separating therefrom as an amorphous deposit. It dissolves very readily in ether, chloroform, and benzene, but does not separate from either of these solvents in characteristic crystals. On dissolving it in alcohol, adding just sufficient water to produce turbidity, and boiling the liquid till it becomes clear again, this clear solution yields large transparent prisms, which before redissolving melt to a transparent oil. The same compound was once obtained in very well-defined prisms from a solution of the dinitro-acid in alcoholic ether. The crystals quickly become cloudy when dried in the air, and when left over sulphuric acid they entirely lose their crystalline form, and are reconverted into dinitrodurylic acid. They probably consist of an unstable compound of this acid with alcohol of crystallisation. Their formation affords a ready means of obtaining the acid in great purity.

Calcium dinitrodurylate, $[C_6Me_3(NO_2).COO]Ca,3H_2O$, obtained by neutralisation, crystallises from a highly concentrated solution in radiate groups of shining needles, easily soluble in hot, sparingly in cold water. It explodes violently when heated on platinum foil. The *barium salt* forms slender silky peach-blossom-coloured needles, likewise containing $3H_2O$, and dissolving in water with moderate facility.

Monobromodurene, C_6HBrMe_4, is formed, together with the dibromo-compound, on gradually adding bromine (2 mols.) to durene (1 mol.), both dissolved in glacial acetic acid; and on pouring the contents of the flask, which are nearly colourless after 12 hours' action, into a considerable quantity of cold water, a white flocculent precipitate is obtained, consisting of a mixture of mono- and di-bromodurene, easily separable by distillation with steam, the monobromo-compound passing over much more readily than the other. The solution of the distillate in boiling alcohol yields monobromodurene in thin shining laminæ, which after several recrystallisations melt at 61°, while the mother-liquor deposits a small quantity of another bromine-compound in needles melting at 199°. This latter, which is obtained in larger quantity by repeated crystallisation of the residue of the distillate, bears considerable resemblance in external aspect to monobromopseudocumene.

Bromodurene, obtained as above, crystallises in thin nacreous laminæ, sparingly soluble in cold, readily in hot alcohol, also in ether and benzene. It volatilises with aqueous vapour, and melts at 61°. It is the fourth crystalline monobromo-derivative of a benzene-homologue, the previously known members of the series being parabromotoluene (m. p. 28·8°), bromoparaxylene (9—10°), and bromopseudocumene (73°). H. W.

Protocatechutannic Acid and Anhydrides of Aromatic Hydroxycarboxylic Acids. By H. SCHIFF (*Ber.*, **15**, 2588—2592). When a mixture of phosphorus oxychloride and parahydroxybenzoic acid is gently warmed at a temperature not exceeding 50°, *tetraparoxybenzoid*, $C_{28}H_{18}O_9$, is produced. It is a white insoluble powder, which is decomposed by heat without melting. Under similar treatment metahydroxybenzoic acid yields *dimetoxybenzoid*, $C_{14}H_{10}O_5$, and *octometoxybenzoid*, $C_{56}H_{34}O_{17}$. The former compound melts between 130° and 135°, and is soluble in hot alcohol; the latter is an amorphous powder melting at 160—165°, insoluble in alcohol, but freely soluble in chloroform. These condensation-products do not give a coloration with ferric chloride.

When ether is added to an aqueous solution of protocatechuic acid, which has been boiled for some hours with arsenic acid, the liquid separates into three layers, and on evaporating the middle layer, *diprotocatechuic acid*, $C_{14}H_{10}O_7$ remains as a hygroscopic vitreous mass, soluble in water and alcohol. This compound produces a green coloration in a solution of ferric chloride, but it resembles tannin in its other reactions. *Tetraprotocatechutannic acid*, $C_{28}H_{18}O_3$, obtained by the action of phosphorus oxychloride on an ethereal solution of protocatechuic acid, dissolves slowly in water. It gives a green coloration with ferric chloride, and bright red with alkalis.

Katellagic acid, $C_{14}H_{10}O_7$, is formed when a mixture of dry arsenic and protocatechuic acids is heated at 160°. It dissolves in nitric acid, yielding an orange-coloured liquid. *Gallamide*, $C_7H_7NO_4 + 1\frac{1}{2}H_2O$, prepared by the action of ammonia on digallic acid, forms large colourless crystals. Gallanilide is deposited as a crystalline mass when digallic acid is dissolved in aniline. W. C. W.

Allyloxybenzoic Acids. By S. SCICHILONE (*Gazzetta*, **12**, 449—454).—The methylic and ethylic salts of these acids are prepared by a reaction analogous to that which yields the corresponding alkyl salts of methoxybenzoic acid and its homologues, viz., by heating the methylic or ethylic salts of the three hydroxybenzoic acids in sealed tubes with molecular proportions of allyl iodide and potassium hydroxide in alcoholic solution, methylic allylsalicylate, for example, by heating methyl salicylate (Gaultheria oil) with allyl iodide and alcoholic potash for nine hours at 120°, the reaction being represented by the equation $C_6H_4(\overset{1}{O}H).\overset{2}{C}OOMe + C_3H_5I + KOH = H_2O + KI + C_6H_4(\overset{1}{O}C_3H_5).\overset{2}{C}OOMe$.

Methylic allylsalicylate thus prepared, and purified by treatment with water, drying with calcium chloride, and repeated fractional distillation, is a colourless or faintly yellow liquid, having a fragrant aromatic odour, and boiling at 245°. By saponifying it with excess of aqueous potash, and treating the product with excess of hydrochloric acid, allylsalicylic acid, $C_6H_4(OC_3H_5).COOH$, is obtained as a mass of transparent needles, which after purification by repeated crystallisation, melt at 113°. This acid crystallises well from very weak spirit, but from stronger alcohol it separates as an oily liquid, and retains that form even on evaporating the solvent, or leaving it in a vacuum. It may however be made to crystallise readily by dissolving it in alcohol, even at ordinary temperature, and quickly diluting the solution with a large quantity of water, whereupon the liquid becomes milky, but recovers its transparency after a few hours, and then yields very beautiful needles of allylsalicylic acid. The author has in several instances found this method of crystallisation very useful for purifying substances, which, in presence of foreign matters, tend to assume an oily consistence.

Allylsalicylic acid is tasteless and inodorous, very soluble in alcohol, ether, benzene, and chloroform, moderately soluble in water. Its silver salt, $C_6H_4(OC_3H_5).COOAg$, is crystalline.

Para-allyloxybenzoic acid, $C_6H_4(\overset{1}{O}C_3H_5).\overset{4}{C}OOH$.—The ethylic salt of this acid, prepared from ethyl *p*-hydroxybenzoate, allyl iodide, and alcoholic potash, and purified by distillation, boils at 260°, condenses to a dense, transparent, nearly colourless liquid, having an odour somewhat like that of acroleïn, but not so repulsive, and solidifies on cooling to a mass of colourless transparent needles, melting at 109°. The acid obtained from it by saponification crystallises in transparent laminæ, melts at 123°, dissolves very easily in alcohol, ether, benzene, and chloroform, slightly also in water.

Meta-allyoxylbenzoic acid, $C_6H_4(\overset{1}{O}C_3H_5).\overset{3}{C}OOH$.—The ethylic salt of this acid, prepared like that of the para-compound, passes over, after fractional distillation between 283° and 285°, as a heavy fragrant oil, which after 15 or 16 hours solidifies to a crystalline mass. By the action of potash it is converted into meta-allyloxybenzoic acid, which crystallises in colourless laminæ, soluble in alcohol and ether, slightly soluble in water, melting at 118°. H. W.

Benzoylacetic Acid (Preliminary Notice). By A. BAEYER (*Ber.*, **15**, 2705).—On dissolving ethyl propiolate in sulphuric acid and pouring the solution upon ice, an oil separates which is ethyl benzoylacetate. The reaction may be thus expressed:—

$$CPh \vdots C.COOEt + H_2O = COPh.CH_2.COOEt.$$

The free acid is crystalline, and is obtained by the saponification of its ethyl derivative. A. K. M.

Synthesis of some Acids Analogous in Constitution to Hippuric Acid. By T. CURTIUS (*J. pr. Chem.* [2], **26**, 145—208).—Kolbe considered that hippuric acid might be regarded as "amidacetobenzoic acid," but as it has been prepared synthetically by Dessaignes from glycocine and benzoic acid, and by Jasukowitsch from monochloracetic acid and benzamide, it is now generally looked upon as "benzoylamidacetic acid."

Kolbe, however, is of opinion that this benzoylamidacetic acid is isomeric and not identical with the natural hippuric acid, and the author has undertaken the present research with the object of settling this point. The crude natural hippuric acid is readily purified by treating the boiling solution with chlorine until it smells distinctly of that gas and the colour becomes pale yellow. On cooling, the hippuric acid deposited is recrystallised with aid of animal charcoal, whereby it is obtained quite pure.

To prepare pure glycocine, hippuric acid is decomposed by boiling it for 12 hours with four times its weight of strong sulphuric acid (1 of acid to 2 of water), and after 24 hours the benzoic acid is filtered off, and the benzoic acid still in solution is removed by agitation with ether. The solution of glycocine sulphate thus obtained is neutralised with barium hydroxide or with chalk, filtered, and the excess of barium removed from the solution by carbonic anhydride (or the calcium by oxalic acid). On evaporation glycocine is deposited in beautiful crystals, generally short monoclinic prisms; the form of crystallisation, however, is greatly affected by the presence of inorganic matter; thus a trace of soda produces rhombohedrons, and with a trace of baryta the crystals are long. Amidacetic acid has a sp. gr. 1·1607, turns brown at 228°, and melts at 232—236° with evolution of gas, and becomes purple coloured: it does not polarise. Its basic are more prominent than its acid properties. It does not combine with barium, sodium, or thallium hydroxides (strong bases capable of attacking the amido-group), to form salts. With zinc oxide, however, it forms two salts,

$$(NH_2.CH_2.COO)_2Zn + H_2O, \text{ and } (NH_2.CH_2COO)_2Zn + CH_2(NH_2)COOH.$$

The solution of the former deposits zinc oxide on adding water or on boiling, the latter salt being left in solution. In the same way sodium carbonate precipitates zinc carbonate readily from the first salt, but not from the second. Sulphuretted hydrogen precipitates both salts. *Silver amidacetate*:—A concentrated solution (containing 100 grams) of amidoacetic acid is poured on 38 grams of freshly precipitated silver oxide; the whole is well stirred and heated nearly to boiling, filtered, and the filtrate allowed to cool in the dark, when crystals of the salt are deposited; the unused silver oxide is again treated with the mother-liquor, and so on until all the oxide along with 38 grams more is taken up. The crystals are generally small transparent prisms, but sometimes form large tablets: they soon become grey and opaque on exposure to light. This salt is not hygroscopic, does not contain water of crystallisation, and does not decompose below 100°.

Action of Benzoic Chloride on Amidacetic Acid.—When silver amidacetate or free amidacetic acid is heated with benzoic chloride, a large quantity of resinous matter and benzoic acid are obtained, but very little of the desired compound, as the silver salt or acid decomposes below the boiling point of the benzoic chloride.

On diluting the mixture with benzene, however, reaction soon sets in with deposition of silver chloride: the whole is kept gently boiling until hydrochloric acid commences to come off. The benzene is then distilled off, and the residue after being washed with ether to remove benzoic acid, is extracted with 30 per cent. alcohol. The alcoholic extract is concentrated, neutralised with soda, acidified with strong hydrochloric acid, and the crystals formed are purified with the aid of animal charcoal.

The crystalline product is a mixture of three acids, (α) containing one, (β) containing two, and (γ) containing three atoms of nitrogen.

1. The α-acid, synthetical hippuric acid, is identical with the hippuric acid from the urine of Graminivora. It is separated from the mixed product by extraction with chloroform, in which the other acids are practically insoluble. If the silver amidacetate and benzoic chloride are mixed according to the equation, $AgC_2H_4O_2N + C_7H_5OCl = C_9H_9NO_3$, then only small quantities of the β- and γ-acids are obtained; if, however, 2 equivalents of silver amidacetate are mixed with 1 equivalent of benzoic chloride, and the 2nd equivalent of the latter added afterwards, then the chief products are the β- and γ-acids. The mixed product is treated with absolute alcohol, in which the γ-acid is almost insoluble. The α-acid is nearly all separated from the alcoholic extract by chloroform, and finally, the β-acid is purified by fractional crystallisation from absolute alcohol; 1st fraction contains α- and β-acids, 2nd pure β, 3rd β and γ.

When the aqueous solution of the β-acid is cooled slowly, it is deposited in small transparent colourless rhombic tablets, with satin lustre, greasy to the touch; when, however, the solution is cooled quickly it forms tufts of sharp-pointed microscopic needles. It melts at 206·5°, and at this temperature decomposes and becomes red. It is insoluble in cold ether, chloroform, benzene, and carbon bisulphide. It is sparingly soluble in cold absolute alcohol, somewhat more so when hot. It is very soluble in 30 per cent. alcohol. Ammonia dissolves it immediately, forming a salt. Cold mineral acids have no action on the β-acid, but when boiled with them it is decomposed into 1 mol. benzoic acid and 2 mols. amidacetic acid, taking up 2 mols. water—hippuric acid under similar circumstances produces 1 mol. benzoic acid and 1 mol. amidacetic acid, taking up 1 mol. H_2O. If, however, the decomposition with warm acid be conducted very carefully, avoiding excess of acid, then the β-acid takes up only 1 mol. H_2O, and breaks up into 1 mol. hippuric acid and 1 mol. amidacetic acid. From these decompositions, coupled with its method of formation, the author concludes that this acid is analogous to hippuric acid,

$NH\overline{Bz}.CH_2.COOH$, being amidacetic acid in which one of the hydrogens is replaced by the radical of hippuric acid, "hippuryl,

$$NH\overline{Bz}.CH_2.CO,"$$

It is therefore called *hippuramidacetic acid*,

$$NH\overline{Bz}.CH_2.CONH.CH_2.COOH.$$

With alkalis it behaves in a similar manner: in the cold, salts are formed, and the acid can be reprecipitated unaltered, but they are decomposed when warmed, with formation of hippuric acid and glycocine, and finally of benzoic acid and glycocine. It has no basic properties, but is a strong monobasic acid; it does not dissolve metallic zinc with evolution of hydrogen, but forms crystalline soluble salts with most of the metals. *Silver hippurylamidacetate*,

$$C_{11}H_{11}N_2O_4Ag,$$

forms nodular groups of microscopic needles, insoluble in cold, soluble in hot water and in ammoniacal liquids. In the moist state it is blackened by light, but when dry it is not perceptibly coloured, and is perfectly stable at 105°. The *thallium salt*, $C_{11}H_{11}N_2O_4Tl$, crystallises in small hexagonal monosymmetrical tablets. The *barium salt*, $(C_{11}H_{11}N_2O_4)_2Ba + 5H_2O$ (?), can be obtained in four-sided leaflets, or in fine hair-like needles, easily soluble in cold water and ordinary alcohol, sparingly in absolute alcohol. The *copper salt*,

$$(C_{11}H_{11}N_2O_4)_2Cu + 3\tfrac{1}{2}H_2O,$$

forms brilliant transparent dark-blue rhombic prisms terminating at each end in short pyramids. It loses its water of crystallisation at 110°, becoming bright green. The *zinc salt* crystallises in drusy groups of small transparent needles or tablets, with $1\tfrac{1}{2}H_2O$, which are driven off at 110°.

Ethyl hippuramidacetate, $C_{10}H_{11}N_2O_2.COOEt$, prepared either by the action of dry hydrochloric acid gas on a solution of hippuramidacetic acid in absolute alcohol, or by the action of ethyl iodide on the silver salt suspended in absolute alcohol. It crystallises from ether in transparent tablets, from water in large white needles with satin-like lustre, melting at 117° (ethyl hippurate melts at 60·5°). It is moderately soluble in cold chloroform and cold water, and easily in cold absolute alcohol spirit, and in boiling chloroform and ether and in warm water. Ethyl hippurate is insoluble in cold water, and very easily soluble in ether; this difference can be used to advantage in separating hippuric and hippuramidacetic acid. On warming it with aqueous ammonia, ethyl hippuramidacetate is dissolved, and a somewhat violent reaction takes place resulting in the formation of *hippuryl glycollamide*, $C_{10}H_{11}N_2O_2.CONH_2$, which crystallises in transparent sharp-edged leaflets melting at 202° (hippuramide melts at 183°), easily soluble in warm absolute alcohol and hot water, sparingly in ether and cold water, and insoluble in chloroform and benzene. *Hippurylglycollamide hydrochloride* crystallises in yellow quadrangular leaflets; it is resolved into its components by the action of water. It does not form a platinochloride. Monochlorobenzoic acid is formed by the action of chlorine on hippuramidacetic acid. The γ-acid, $C_{10}H_{12}N_3O_4$, is deposited from boiling water in brilliant semi-transparent films, which under a powerful microscope are seen to consist of stellate groups of needles; when it is dried at 100°, it turns yellow. Heated at 230°, it becomes gradually brown, and at a little above 240° it melts with complete decomposition. It is almost insoluble in cold water and absolute alcohol, and quite so in other solvents. It is more soluble in 30 per cent. spirit, in ammonia, alkalis, and concentrated mineral acids. On heating it with soda, ammonia is evolved.

This (γ-) acid is decomposed on heating it with hydrochloric acid in sealed tubes. The products are a nitrogenous substance, $C_9H_9NO_3$, and benzoic and amidacetic acids. A quantitative experiment showed the radical $\overline{Bz}$ to be contained only once in the molecule of the γ-acid. With dilute Fehling's solution it gives rise to a carmine coloration, with strong solution a purple-violet. With phenol and sodium hypochlorite it is coloured dark green-blue, whilst hippuramidacetic acid is coloured very slightly greenish-yellow, and hippuric acid is not coloured at all. This acid has a strongly acid reaction, but does not form simple salts. The *silver salt* forms a white precipitate soluble in ammonia, from which it is deposited in small transparent irregular granules. The author suggests the probable isomerism of this γ-acid with Griess's uramidohippuric acid. D. A. L.

Triphenyl Orthoformate. By F. Tiemann (*Ber.*, **15**, 2685—2687).—On heating an alkaline solution of phenol with chloroform, and extracting with ether, a neutral oil is obtained which becomes crystalline after purification. It is triphenyl formate, $CH(OPh)_3$. It crystallises in long white needles (m. p. 71·5°) which are insoluble in water, but soluble in ether, chloroform, boiling alcohol, and hot benzene, less soluble in light petroleum. It decomposes when distilled at the ordinary pressure, but passes over unchanged under a pressure of 50—55 mm. Acids readily decompose it into phenol and formic acid, but alkalis do not affect it. A. K. M.

Tribasic Nitrophenyl Orthoformate. By A. Weddige (*J. pr. Chem.*, **26**, 444—446).—The action of the alkali salts of ortho- and para-nitrophenol on chloroform results in the formation of a nitro-derivative of the tribasic phenyl orthoformate. This substance, $CH(O.C_6H_4.NO_2)_3$, is produced by heating 2 mols. chloroform with 3 mols. potassium nitrophenol and 4 to 6 parts of alcohol at 140—150° for 10 hours. After purification by crystallisation from alcohol, it forms white needles, which melt at 182°. They are not decomposed by boiling potash or soda, but are destroyed by distillation. The ethereal salt prepared in a similar way from para-nitrophenol melts at 232°. Reduction by tin and hydrochloric acid produces a crystalline base, $CH(O.C_6H_4.NH_2)_3$.

It will be interesting to see whether this compound yields a dye under the influence of oxidising agents in a manner analogous to triamidotriphenylmethane, $CH(C_6H_4.NH_2)_3$. E. W. P.

Paradichlorazobenzene-monosulphonic Acid. By A. CALM (*Ber.*, **15**, 2558—2559).—The following salts of paradichlorazobenzene-monosulphonate (*Ber.*, **13**, 1183) have been prepared:—

The *potassium salt*, $C_6H_4Cl.N_2.C_6H_3Cl.SO_3K$, forms glistening orange-coloured plates, soluble in alcohol and in hot water. The *silver salt*, $C_{12}H_7Cl_2N_2.SO_3Ag$, a pale-orange amorphous precipitate. The *barium salt*, $(C_{12}H_7Cl_2N_2.SO_3)_2Ba$, and the *lead salt* are obtained as crystalline precipitates soluble in hot water. The *calcium salt*, $(C_{12}H_7Cl_2N_2.SO_3)_2Ca$, forms lustrous golden scales. The *sulphochloride*, $C_6H_4Cl.N_2.C_6H_3Cl.SO_2Cl$, is deposited from an ethereal solution in orange-coloured needles melting at 161°. W. C. W.

Preparation of Indigo-blue from Orthonitrobenzaldehyde. By A. BAEYER and V. DREWSEN (*Ber.*, **15**, 2856—2864).—By the action of alkalis on a solution of orthonitrobenzaldehyde in acetone, a condensation-product is formed, a dilute solution of which yields indigo if acted on by excess of alkali. This intermediate product is orthonitro-β-phenyllactyl methyl ketone. It crystallises in monoclinic prisms (m. p. 68°), soluble in ether and alcohol, insoluble in petroleum. On boiling its aqueous solution, it decomposes with formation of indigo. This substance is a direct addition-product of nitrobenzaldehyde and acetone, and probably stands in the same relation to orthonitrocinnamyl ketone that aldol does to crotonaldehyde. Its formation may be expressed thus:—$NO_2.C_6H_4.CHO + (CH_3)_2CO = NO_2.C_6H_4.CH(OH).CH_2.COMe$. On boiling one part of this condensation-product with acetic anhydride, *orthonitrocinnamyl methyl ketone* is formed thus:—

$$NO_2.C_6H_4.CH(OH).CH_2.COMe = H_2O + NO_2.C_6H_4.CH\colon CH.COMe.$$

This ketone crystallises in long flat needles melting at 58°, soluble in ether and alcohol, insoluble in petroleum; it is identical with one of the nitro-compounds obtained by the direct nitration of cinnamyl methyl ketone; and the identity is further established by the formation of indigo from both under similar conditions. In order to obtain indigo from orthonitro-β-phenyllactyl methyl ketone, soda is added to its aqueous solution, and the precipitated indigo washed with alcohol and water. The indigo so obtained is perfectly free from indirubin; the change may be represented thus:—

$$2C_{10}H_{11}NO_4 = C_{16}H_{10}N_2O_2 + 2C_2H_4O_2 + 2H_2O.$$

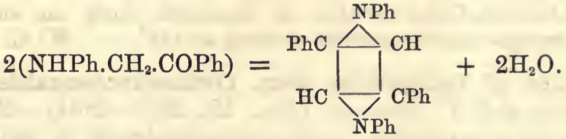
If aldehyde be substituted for acetone, a similar condensation-product is formed, which with excess of alkali yields indigo. This substance is probably analogous to aldol, and is the alcohol of orthonitro-β-phenyllactic acid, $NO_2.C_6H_4.CH(OH).CH_2.CH_2.OH$. It crystallises in needles melting at 108°; it is converted by silver oxide into an acid (probably orthonitro-β-phenyllactic acid), which crystallises in monoclinic prisms, melting at 127°.

On saturating a solution of orthonitrobenzaldehyde in pyrotartaric acid with hydrochloric acid, orthonitrocinnamyl formic acid,

$$NO_2.C_6H_4.CH\colon CH.COOH,$$

is obtained in the crystalline form (m. p. 135°), soluble in alcohol and ether. Its barium salt crystallises in leaflets. Orthonitrocinnamyl formic acid is easily decomposed by alkalis, with formation of indigo and oxalic acid. V. H. V.

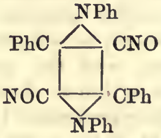
Diphenyldiisoindole. By R. Möhlau (*Ber.*, **15**, 2480—2490).—If bromacetophenone is added gradually to boiling aniline, a violent reaction occurs, and from the crude product diphenyldiisoindole is obtained. This substance, $C_{28}H_{32}N_2$, is derived from the condensation of 2 mols. of acetophenone anilide and loss of 2 mols. of water, a change which may be represented thus:—



It offers the first example of a nitrogen-atom combined with three different hydrocarbon radicals, belonging to the class of substances which the author proposes to call *paranitriles.*

Diphenyldiisoindole crystallises in colourless glistening scales (m. p. 181°, b. p. over 360°), soluble in alcohol and ether, insoluble in water. It shows some points of resemblance to dimethylaniline in forming a blue-green colouring matter when heated with benzotrichloride and zinc chloride, and in giving azo-dyes.

The picrate crystallises in vermillion-coloured prisms melting at 127°, easily soluble in alcohol, ether, and benzene. The nitroso-derivative, $C_{28}H_{20}N_2(NO)_2$ crystallises in rhombic leaflets melting at 244°. It combines directly with mineral acids to form salts, of which the hydrochloride, $C_{28}H_{20}N_2(NO)_2,2HCl$, crystallises in prisms, the nitrate, $C_{28}H_{20}N_2(NO)_2,2HNO_3$, in needles. The nitroso-derivative does not give Liebermann's reaction. From the analogy of nitrosodiphenyldiisoindole to nitrosodimethylaniline in forming azo colouring matters, the author suggests for it the following formula:—



V. H. V.

Azo-Colouring Substances from Diphenyldiisoindole. By R. Möhlau (*Ber.*, **15**, 2490—2497).—*Diphenyldiisoindolazotribrombenzene hydrochloride*, $C_{40}H_{24}N_6Br_6,2HCl$, prepared from diphenyldiisoindole and tribromodiazobenzene hydrochloride, crystallises in fine golden needles, insoluble in water and alcohol. On warming it with sodium carbonate, the corresponding base is obtained, which crystallises in orange-golden prisms melting at 150°. Its alcoholic solution absorbs all the rays from the green to the violet.

Diphenyldiisoindolazodibromophenol, $C_{40}H_{26}N_6Br_4O_2$.—The hydrochloride of this base is obtained by heating an alcoholic solution of diphenyldiisoindole and paradiazodibromophenol with hydrochloric acid. It crystallises in glistening olive-coloured prisms, insoluble in water, and decomposed by alkalis with formation of the free azo-colouring substance, which crystallises in golden-green prisms melting at 198°. An aqueous solution of its sodium salt dyes wools of an orange, and silk of a yellow colour, and absorbs all lines of the green, beginning from E, and all the blue and violet rays. As the paradiazodibromophenol is convertible into the [6 : 1 : 2] dibromophenol, the diphenyldiisoindolazodibromophenol can be represented by the formula $(C_6H_4.N_2.C_6H_2Br_2.OH)_2(N_2C_4)H_2Ph_2$, in which the nitrogen-atoms and the phenyl-groups are in the para-position to each other, and [Br : OH : Br = 6 : 1 : 2].

Diphenyldiisoindolazobenzene-sulphonic acid, $C_{40}H_{30}N_6S_2O_6$, from diisoindole and diazosulphanilic acid, crystallises in red-brown metallic glistening scales. Its sodium salt forms golden leaflets, its silver salt vermillion-red prisms. On reduction, the acid is converted into diphenyldiisoindole-sulphanilic acid, together with a basic substance crystallising in colourless prisms, but which was not obtained in a sufficiently large quantity for a minute examination. V. H. V.

Derivatives of Diphenyl. By E. LELLMANN (*Ber.*, **15**, 2837—2838).—*Mononitrodibromodiphenyl*, $C_6H_4Br.C_6H_3Br.NO_2$.—The author alludes to the difficulty experienced in introducing one nitro-group into Fittig's dibromodiphenyl (m. p. 164°), for either no nitro-derivative is formed or else a dinitro-compound. In order to obtain a mononitro-compound the dibromodiphenyl is dissolved in acetic acid, and an equal volume of nitric acid of sp. gr. 1·52 added. After purification by alcohol, the compound is obtained as a golden crystalline mass melting at 127°, easily soluble in alcohol and benzene.

Trinitrodibromodiphenyl, $NO_2.C_6H_3Br.C_6H_2Br(NO_2)_2$, obtained by dissolving dibromodiphenyl in fuming nitric acid, crystallises in small colourless needles melting at 177°, sparingly soluble in alcohol, easily soluble in benzene.

Dibenzoyldiamidodibromophenyl, $(C_6H_3Br.NH\overline{Bz})_2$, is formed by the action of benzoic chloride on the corresponding diamidodibromophenyl. V. H. V.

A Case of Physical Isomerism. By E. LELLMANN (*Ber.*, **15**, 2835—2837).—The dibenzoyldiamidodibromophenyl mentioned in the preceding abstract crystallises in colourless needles, which melt at 195°; but if the melting-point tube be suddenly taken out of the hot bath, the contents solidify as a glassy mass, which melts at 99°, solidifies in crystals at 125—130°, and finally melts again at 195°. This series of changes can be repeated frequently. If the substance of lower melting point be dissolved in alcohol, the modification of high melting point crystallises out. The former could be obtained only as a vitreous mass, whilst the latter formed distinct crystals.

V. H. V.

Nitro-derivatives of Naphthalene. By V. MERZ and W. WEITH (*Ber.*, **15**, 2708—2731).—By the action of fuming nitric acid on bromonaphthalene, two isomeric bromodinitronaphthalenes are formed. One of these, called by the author α-bromodinitronaphthalene, melts at 170·5°, and the other, β-bromodinitronaphthalene, at 143°. The former crystallises from benzene in groups of slender needles, and the latter in plates (from benzene) or needles (from alcohol). Both dissolve readily in alcohol, benzene, and glacial acetic acid. Boiling with soda-solution does not decompose them. To obtain more highly nitrated compounds, the dinitro-derivatives are treated with a mixture of fuming nitric and concentrated sulphuric acids, when the α-derivative yields bromotetranitronaphthalene, melting at 189—189·5°, and the β-derivative a tetranitro-compound melting at 245°.

On dissolving α-bromotetranitronaphthalene in sodic carbonate solution, and then acidulating, *tetranitronaphthol* (m. p. 180°) is precipitated. It forms coloured metallic derivatives, which crystallise well. They explode slightly on heating. The sodium salt, $C_{10}H_3(NO_2)_4.ONa + 2H_2O$, crystallises in reddish-yellow scales, the potassium salt, $C_{10}H_3(NO_2)_4.OK + 1\frac{1}{2}H_2O$, in dark-red prisms. The barium salt, $[C_{10}H_3(NO_2)_4O]_2Ba + 3H_2O$, forms yellowish-red crystalline flocks, the calcium salt, $[C_{10}H_3(NO_2)_4O]_2Ca + 2H_2O$, yellowish-red needles, and the silver salt, $C_{10}H_3(NO_2)_4.OAg + 3H_2O$, dark-coloured needles. By the action of aniline and ammonia on α-bromotetranitronaphthalene, tetranitronaphthylphenylamine, $C_{10}H_3(NO_2)_4.NHPh$, melting at 162·5°, and tetranitronaphthylamine, $C_{10}H_3(NO_2)_4.NH_2$, melting at 194°, are produced.

From β-bromotetranitronaphthalene the corresponding tetranitronaphthol could not be obtained pure. β-Tetranitronaphthylphenylamine (m. p. 253°), and β-tetranitronaphthylamine (m. p. 202°) were, however, prepared. When oxidised with dilute nitric acid, both α- and β- bromodinitronaphthalene yield ordinary α-mononitrophthalic acid melting at 212°. By the oxidation of α-bromotetranitronaphthalene, a dinitrophthalic acid (m. p. 227°) is obtained, which by reduction and subsequent distillation with soda-lime yields metadiamidobenzene. β-Bromotetranitronaphthalene yields a dinitrophthalic acid (m. p. 200°), from which para-diamidobenzene may be obtained. The formulæ for the two dinitrophthalic acids are therefore

$$NO_2 : COOH : COOH : NO_2] = (\alpha)\ [1:2:3:5] \text{ and } (\beta)\ [1:2:3:4].$$

From the oxidation-products, it is evident that both in the dinitro- and tetranitro-bromonaphthalenes the nitro-groups are equally divided between the two benzene nuclei. The fact that both bromodinitronaphthalenes yield α-nitrophthalic acid shows that in both dinitro-derivatives one nitro-group must have the position 1′, and since it has been ascertained that in bromomononitrophthalene (from bromonaphthalene) the bromine and the nitro-group are in the 1 : 4 position to one another, it is highly probable that the two dinitro-compounds are represented by the following formula :—$[NO_2 : Br : NO_2 = 1' : 1 : 4$ and $4' : 1 : 4]$.
A. K. M.

Picrates of α- and β-Naphthol. By C. Marchetti (*Gazzetta*, **12**, 502—504).—These compounds are prepared by dissolving the naphthol in a small quantity of 85 per cent. alcohol, and the picric acid in a quantity of the same alcohol sufficient to form a solution saturated at ordinary temperature, pouring the boiling picric acid solution into that of the naphthol, then agitating, and cooling. The liquid then deposits very slender crystals, which are to be collected on a suction-filter and dried in a vacuum. The filtered liquid when concentrated and cooled yields a second crop of crystals, and others may be obtained in like manner.

The crystals thus obtained gave by analysis 51·43 and 51·36 per cent. carbon, 3·07 and 3·35 hydrogen, agreeing nearly with the formula of naphthol picrate, $C_6H_2(NO_2)_3.OH,C_{10}H_7.OH$, which requires 51·47 C and 2·95 H.

α-Naphthol picrate crystallises from alcoholic solution on rapid cooling in slender orange-yellow needles, and by slow cooling in larger needles of an orange-red colour. It melts at 189—190° to an opaque dark-red liquid; dissolves very freely in alcohol and ether, and crystallises readily therefrom; sparingly in cold chloroform, somewhat more readily at higher temperatures, and crystallises out on cooling. It is but very slightly soluble in carbon bisulphide, and in water either cold or boiling. It is decomposed by ammonia, the liquid on distillation with steam yielding the α-naphthol in the free state.

β-Naphthol picrate crystallises in thin silky orange-yellow needles of somewhat lighter colour than the α-compound, and melts at 155° to a dark-red limpid liquid. It is very soluble in alcohol, ether, and chloroform, less soluble in carbon bisulphide, nearly insoluble in cold, sparingly soluble in hot water. Ammonia decomposes it, separating the β-naphthol, which may be obtained in the crystalline form by heating the solution and then leaving it to cool. H. W.

Derivatives of Naphthalene Hexhydride. By A. AGRESTINI (*Gazzetta*, **12**, 495—499).—With the view of preparing Graebe's naphthalene tetrahydride (*C. J.*, 1873, 1008), the author heated in a sealed tube at 235°, for 7½ hours, 10 g. naphthalene, 3 g. red phosphorus, and 98 g. hydriodic acid (b. p. 127°). On decolorising the resulting liquid with acid sodium sulphite, neutralising with sodium carbonate, and distilling with steam, then treating the distillate with ether, drying it with calcium chloride, and again distilling, an oil was obtained lighter than water; and on boiling this oil for some time with pellets of sodium, distilling, and treating the distillate with picric acid, a crystalline precipitate was formed consisting of naphthalene picrate. The oil separated from this precipitate was then distilled in a current of steam, dried with calcium chloride and with sodium, and subjected to fractional distillation, the greater part of it passing over at 195—196° under a pressure of 773·9 mm. The analysis of this distillate gave, as a mean result, 89·53 p.c. carbon and 10·57 hydrogen, agreeing closely with the formula $C_{10}H_{14}$ or $C_{10}H_8,H_6$, which requires 89·55 C and 10·45 H.

The chief product obtained by the process above described is therefore naphthalene hexhydride. It is a colourless, fragrant liquid, lighter than water, and boiling at 204—205°. It does not combine with picric acid. It is probably identical with the hydrocarbon $C_{10}H_{14}$ (b. p. 195—200°), which was obtained in like manner, together with others, by Wreden and Znatowicz (*Annalen*, **187**, 164).

Naphthalenehexhydrosulphonic Acids, $C_{10}H_{12}(SO_3H)_2$.—Two isomeric acids, having this composition, are obtained by the action of fuming sulphuric acid on naphthalene hexhydride, and may be separated by diluting the product with water, neutralising with lead carbonate, filtering it at the boiling heat, precipitating the lead with hydrogen sulphide, neutralising the filtrate exactly with potassium carbonate, evaporating to dryness, completing the desiccation of the potassium salt thus obtained in a vacuum, then pulverising and treating it with boiling alcohol. In this way two potassium salts are obtained, one soluble in alcohol, the other insoluble, but both having the composition of *potassium naphthalene hexhydrobisulphonate*, $C_{10}H_{12}(SO_3K)_2$.

The crystals of the former are anhydrous; those of the latter containing $1\frac{1}{2}$ mol. H_2O, and are soluble in water. Both these salts, when fused with potassium hydroxide, yield small quantities of a phenolic substance, shown by its melting point to consist of α-naphthol.

Action of Bromine on Naphthalene Hexhydride.—On treating this hydrocarbon with bromine in molecular proportions, added by successive quantities, a violent action takes place, accompanied by evolution of hydrogen bromide, and a nearly colourless liquid is obtained heavier than water, and decomposing when distilled. After purification with sodium carbonate, solution in ether, &c., it gave by analysis 37·41 p.c. C, 4·48 H, and 38·01 Br, agreeing nearly with the formula $C_{10}H_9Br$, which is that of *monobromonaphthalene dihydride.*

H. W.

Some Ethereal Oils. By BEILSTEIN and E. WIEGAND (*Ber.*, **15**, 2854—2855).—*Oil of Erecthidis* consists of a terpene, $C_{10}H_{16}$ (b. p. 175°, sp. gr. 0·838 at 18·5°), which absorbs a molecule of hydrochloric acid without the separation of a crystalline compound. The portion of the oil which boils above 200° also consists of a terpene.

Oil of Erigeron canadense consists of a terpene (b. p. 176°, sp. gr. 0·8464); it absorbs 2 mols. of hydrochloric acid to form a solid dihydrochloride melting at 47—48°.

Oil of Majorum.—The portion of lower boiling point consists of a terpene (b. p. 178°, sp. gr. 8·463) which absorbs 1 mol. of hydrochloric acid, without forming a compound. The portion boiling from 200—220° contains a sesquiterpene hydrate, $C_{15}H_{24},H_2O$, which from its behaviour towards sodium is shown to contain no hydroxyl-group.

V. H. V.

Ledum Camphor. By E. HJELT and U. COLLAN (*Ber.*, **15**, 2500—2501).—In the year 1831, Grassmann obtained from the wild marsh rosemary (*Ledum palustre*), a volatile oil, which solidifies on exposure to form the so-called ledum camphor. The substance has since been examined by Trapp, who assigned to it a formula, $C_{28}H_{48}O$, and by Ivanoff, who deduced the formula $C_5H_8O_2$. The author distilled the oil with water, and obtained the camphor in acicular needles melting at 101°, and from his analyses deduces the formula $C_{25}H_{44}O_2$. In its chemical relationship ledum camphor shows no resemblance to the other camphors.

V. H. V.

Note.—Wright (this Journal, 1875, 1038) assigns to ledum camphor the formula $C_{20}H_{32}O$.—V. H. V.

Glucosides. By H. SCHIFF (*Gazzetta*, **12**, 460—469).—*Arbutin.*—The variations in the amount of crystal-water and in melting point (142—145°, 162—168°, and 187°) observed in commercial arbutin are attributed by the author to the presence of methyl-arbutin (Abstr., 1881, 610). This latter compound has been prepared by Michael (Abstr., 1882, 174) by the action of acetochlorhydrose on the potassium-derivative of methyl-quinol, according to the equation:—

$$O : \underset{\text{Acetochlorhydrose.}}{CHO.(CH.O\overline{Ac})_4.CH_2Cl} + \underset{\text{Potassium-methyl-quinol.}}{KO.C_6H_4.OMe} + 4EtOH$$

$$= KCl + 4EtO\overline{Ac} + \underset{\text{Methyl-arbutin.}}{O : CH.(CH.OH)_4.CH_2O.C_6H_4.OMe}$$

When thus obtained it melts at 168—169°, *i.e.*, at about the temperature observed by Strecker and others for the melting point of arbutin, whereas the methyl-arbutin prepared by the author's method, viz., by the action of methyl iodide and potassium hydroxide on arbutin dissolved in methyl alcohol, melts at 175—176°. The two products differ also in their amount of crystal-water, the crystals obtained by Michael's process having the composition $2C_{13}H_{14}O_{17} + H_2O$, while those obtained by the author's method contain $C_{13}H_{14}O_{17} + H_2O$. The smaller amount of water found by Michael was perhaps due to partial dehydration. Methyl-arbutin may also be obtained in anhydrous crystals, *e.g.*, from concentrated solutions containing potassium iodide. Supersaturated solutions sometimes also deposit mammellated groups of anhydrous crystals. Methyl-arbutin is moderately soluble in cold, freely in boiling water, and in alcohol, sparingly in ether, more freely in a mixture of alcohol and ether; its solutions give no colour with ferric chloride.

The lower melting point (168°) observed for arbutin by Strecker and others, and by the author in certain fractions, may perhaps be attributed to the presence of methyl-arbutin, and may be regarded as an additional instance of the fact that a mixture may melt at a temperature lower than the melting point of either of its constituents.

Constitution of Helicin.—When hot saturated solutions of helicin (5 pts.) and urea (2 pts.) are mixed together, and the mixture is evaporated in an open vessel, there remains a dense colourless syrup, which, when left in the exsiccator over sulphuric acid, leaves a nearly colourless gummy mass, gradually changing to a white crystalline powder, which is but slightly soluble in absolute alcohol, and may be freed thereby from uncombined helicin and urea. This compound dissolves in a large quantity of boiling water, and separates on cooling in the form of a very white crystalline powder consisting of glucosalicyl-carbamide, $(NH_2.CONH)_2CH.C_6H_4.O.C_6H_{11}O_5$. It is distinguished from its components by being hygroscopic and very soluble in water. It deliquesces in alcohol of 99 p.c., dissolves readily in alcohol of 95 p.c., and is not precipitated by absolute alcohol even from highly concentrated aqueous solutions. The aqueous solution has a bitter taste, and is not precipitated by nitric acid, but gives a white flocculent precipitate with mercuric nitrate. The compound melts at a high temperature, giving off ammonia, becoming coloured, and apparently decomposing in a very complex manner.

Glucososalicyl-thiocarbamide,

$$(NH_2.CS.NH)_2CH.C_6H_4.O.C_6H_{11},$$

prepared by heating together the alcoholic solutions of 1 pt. thiocarbamide and 2 pts. crystallised helicin, is also a very white crystalline powder, even more hygroscopic than the carbamide.

The compounds just described afford additional proof of the aldehydic nature of helicin, which is, moreover, confirmed by its power of combining with organic bases, as with aniline and toluidine. With tolylene-diamine it forms *glucosalicylic tolylenediamine*,

$$C_6H_3Me:(N:CH.C_6H_4.O.C_6H_5O_5)_2,$$

which separates in deep orange-coloured crystalline groups when 5 pts. helicin and 2 pts. tolylenediamine are dissolved together in a small quantity of hot water. Like most derivatives of metatoluidine, this substance exhibits a strong tendency to form deep-coloured compounds. Its dilute aqueous solution exhibits a decided red-green fluorescence. The crystals contain water, which they lose in the exsiccator, being thereby converted into a vitreous mass, which may be recrystallised from warm water. It dissolves but slightly in cold water, easily and with red colour in dilute hydrochloric acid.

Helicin unites readily with hydrocyanic acid, and yields with Perkin's reagent a mixture of well-crystallised compounds, which, however, the author has not yet succeeded in separating.

Anhydrous helicin does not absorb dry ammonia-gas, but dissolves readily in concentrated alcoholic ammonia, forming a solution which has only the faintest ammoniacal odour, showing that the ammonia has really entered into combination, though the compound formed has but little stability, and gives off ammonia even at ordinary temperatures. It is probably an additive aldehydic combination,

$$C_6H_{14}O_5.O_6.C_6H_4.CH(OH).NH_2,$$

which, however, is not converted into the corresponding hydrosalicylamide under conditions similar to those which give rise to the formation of salicylaldehyde.

The paper concludes with theoretical speculations as to the constitution of helicin. H. W.

Poisonous Principle of Andromeda Japonica. By J. F. Eijkman (*Rec. Trav. Chim.*, 1, 224—226).—By exhausting with water the fresh leaves of this plant, well known in Japan for their poisonous properties, agitating the concentrated and filtered solution with chloroform, and mixing the chloroform with light petroleum, a precipitate is obtained which may be dissolved in ether containing alcohol, and extracted therefrom by agitation with water; on evaporating the aqueous solution thus obtained, the poisonous principle remains in the form of a transparent, colourless, brittle uncrystallisable substance, which the author has not been able to resolve into more definite constituents.

This substance, which the author designates as *Asebotoxin*, is free from nitrogen, leaves no ash when burnt, and gave, as the mean of four analyses, 60·48 p.c. C, 7·40 H, and 32·11 O. It softens at 100°, and melts at 120°. It is more soluble in hot than in cold water, and dissolves readily in chloroform, common alcohol, and amyl alcohol; also in acetic acid and in ammonia, and to a smaller amount in caustic potash and soda; in all cases without decomposition. It is but slightly soluble in pure ether, and nearly insoluble in benzene, light petroleum, and carbon bisulphide. The aqueous solution is neutral, and is not precipitated or changed in any way by ferric chloride, cupric sulphate, mercuric chloride, auric chloride, silver nitrate, or normal lead acetate, but gives a flocculent precipitate with the basic acetate. From an alkaline cupric solution it throws down a small quantity of cuprous hydroxide, but the precipitation is more abundant if the asebotoxin be previously heated with hydrochloric acid, and the filtered liquid added to the cuprous solution. Asebotoxin moistened with hydrochloric acid acquires a splendid blue colour, changing to red-violet at the heat of the water-bath. Strong sulphuric acid dissolves it with red colour, changing after a while to rose-pink, a bluish-grey substance separating at the same time.

Asebotoxin exhibits the characters of a glucoside, and is extremely poisonous, a fatal dose for a rabbit by subcutaneous injection being 3 mg. per kilogram of bodily weight.

The poisonous principle of *Andromeda japonica* has been examined with similar results by P. C. Plugge, who calls it *Andromedotoxin*, and claims priority over Eijkman. H. W.

Hæmatoxylin and Hæmateïn. By E. Erdmann and G. Schulz (*Annalen*, **216**, 232—240).—The authors' experiments confirm the formula of hæmatoxylin, $C_{16}H_{14}O_6$, deduced by Gerhardt from the analyses of O. L. Erdmann, Hesse, and others. Acetyl-hæmatoxylin has the composition $C_{26}H_{24}O_{11} = C_{16}H_9\overline{Ac}_5O_6$ [$\overline{Ac}$. calc. = 42 per cent.; exp. = 41·74 to 42·67].

The authors also confirm the formula $C_{16}H_{12}O_6$ assigned to hæmateïn (the product obtained by exposing an ammoniacal solution of hæmatoxylin to the air) by O. L. Erdmann, and by Hummel and Perkin (Trans., 1882, 367), of whose experiments, however, they take no notice.

By sulphurous acid, and more readily by hydrogen sodium sulphite, hæmateïn is converted into a colourless liquid, which, however, consists not of hæmatoxylin, but of an addition-product, that obtained with the free acid being partially decomposed by boiling, whereas the product obtained with the acid sodium salt is decomposed only when heated with an acid, yielding hæmateïn, which when thus prepared, cannot be reconverted, by any mode of treatment, into hæmatoxylin. A similar result is obtained by reducing hæmateïn with tin and hydrochloric acid.

Reim (*Ber.*, **4**, 331; *C. J.*, 1871, 541) by treating hæmatoxylin with strong nitric acid, obtained an oxidation-product, regarded by him as identical with Erdmann's hæmateïn, but really isomeric therewith, inasmuch as it crystallises in brown-red needles much more soluble in boiling water than hæmateïn, and differs from the latter in many other characters, especially in its behaviour to sulphurous acid, by which it is immediately reduced to hæmatoxylin, whereas Erdmann's hæmateïn is not reduced by similar treatment. Lastly, Reim's oxidation-product is converted by boiling with acetic chloride in a reflux apparatus into an acetyl-derivative, less soluble in alcohol than pentacetylhæmatoxylin, and crystallising therefrom in spherical groups of small white needles, melting with partial decomposition at 216—219°. No such acetyl-derivative can be obtained from Erdmann's hæmateïn.

Attempts to split up hæmatoxylin and hæmateïn into similar molecules have not hitherto yielded very definite results. Hæmatoxylin reduced by hydriodic acid (b. p. 127°) yields at first a red body, not obtainable in definite form, and afterwards, when heated therewith in sealed tubes, a mixture of hydrocarbons, a small portion of which volatilises with steam, while the rest forms a black mass soluble in benzene.

By heating hæmatoxylin with strong ammonia at about 180°, a nitrogenous body is obtained, which has the properties of an amidophenol, and separates on addition of acids as a light red precipitate soluble in excess of the acid.

The authors confirm the observation made by R. Meyer, that hæmatoxylin by dry distillation yields a mixture of resorcinol and pyrogallol. The two bodies may be separated by prolonged boiling with benzene, which dissolves pyrogallol more readily than resorcinol.

Hæmatoxylin yields formic acid when fused with potassium hydroxide. H. W.

Compounds of the Pyrroline Series. By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, **15**, 2759—2585).—*Tetrolurethane*, EtO.CO.N $\vdots$ C_4H_4, prepared by the action of ethyl chlorocarbonate (diluted with anhydrous ether) on potassium pyrroline, is a colourless oily liquid boiling at 180°. It is almost insoluble in water, and is resinified by contact with hydrochloric acid. By boiling with alkalis it is converted into ethyl alcohol, pyrroline, and an alkaline carbonate. On treatment with ammonia at 110°, tetrolurethane yields *tetrolcarbamide*, $NH_2.CO.N \vdots C_4H_4$. This substance crystallises in colourless plates (m. p. 167°), which can be sublimed without decomposition. Tetrolurethane is decomposed by ammonia at 130°, splitting up into alcohol, pyrrol, and urea.

Allylpyrroline, $C_4H_4 \vdots NC_3H_5$, obtained by warming potassium pyrrol with a mixture of allyl bromide and anhydrous ether, is a colourless oil, which boils at 105° under a pressure of 48 mm., but decomposes when distilled under the ordinary atmospheric pressure. On exposure to the air, it acquires a brown colour, and is partially converted into resin. It is almost insoluble in water, and gives a white precipitate with mercuric chloride.

Tetriodopyrroline, C_4I_4HN, is best prepared by cautiously pouring an ethereal solution of iodine into a flask containing 100 c.c. of anhydrous ether and 10 grams of potassium-pyrroline. The iodine is added until a permanent coloration is produced, but a large excess of iodine must be avoided. After removing the ether from the mixture by distillation, the residue is exhausted with boiling alcohol to separate the potassium iodide from the iodopyrroline; the alcoholic solution is treated with animal charcoal, and poured into water; and the precipitated product is further purified by solution in alcohol, reprecipitation by water, and recrystallisation from alcohol. Tetriodopyrroline forms long prisms soluble in ether, acetic acid, and in hot alcohol. The crystals decompose without melting between 140° and 150°. With silver nitrate, their alcoholic solution gives a white precipitate which rapidly blackens. Tetriodopyrroline is insoluble in an aqueous solution of potash, but dissolves readily in alcoholic potash. On evaporating the alcohol, a white crystalline compound remains, which is soluble in water.

W. C. W.

Substitution-derivatives of Quinoline. By P. FRIEDLÄNDER and A. WEINBERG (*Ber.*, **15**, 2679—2685).—The readiness with which the chlorine in α-chloroquinoline can be replaced by hydroxyl and other radicals has been already shown by Friedländer and Ostermaier (Abstr., 1882, 732). The authors find that in the case of β- and γ-chloroquinoline the substitution takes place with much greater difficulty, and that the replacement of hydroxyl by chlorine in hydroxy-quinolines by means of phosphorus pentachloride takes place readily only in the case of the α-compound. From these results it is inferred that the readiness of the substitution depends on the fact that the carbon-atom on which the substitution takes place is directly united with nitrogen. β-chlorocarbostyril, C_9H_6NOCl, obtained by heating dichloroquinoline with dilute hydrochloric acid at 120°, is found to be isomeric with the compound obtained by Baeyer and Bloem from orthamidophenylpropiolic acid (*Ber.*, **15**, 2147), although both melt at nearly the same temperature, viz., 242° and 246°. The β-compound differs from Baeyer's in yielding (with phosphorus pentachloride) a dichloroquinoline melting at 104°. On melting β-chlorocarbostyril with potash, β-hydroxycarbostyril melting above 300° is obtained; it is soluble in concentrated hydrochloric acid, and crystallises from it in slender colourless needles. With alkalis it forms stable salts.

By the action of bromine-vapours on the ethyl-derivative of carbostyril in the cold, an unstable addition-product is formed, which readily gives off bromine and hydrobromic acid, yielding amongst other products the ethyl-derivative of monobromocarbostyril. On heating this with hydrochloric acid, γ-bromocarbostyril is produced, identical with the body obtained by Baeyer and Bloem from orthamidophenylpropiolic acid (*Ber.*, **15**, 2149). By the action of fused potash the corresponding hydroxy-compound is produced, accompanied, however, by small quantities of indole, and by an isomeric hydroxycarbostyril. The latter is separated from γ-hydroxycarbostyril by means of hot alcohol. It forms white concentrically grouped needles melting at 189°. From the acid properties of this body, and from the readiness with which *one* hydroxyl-group can be replaced by chlorine, &c., it is assumed that one hydroxyl-group is present in the benzene-ring. In this case the body may be termed hydroxyquinophenol. The body, C_9H_6ClNO (m. p. 180°), obtained from it by the action of phosphorus pentachloride, possesses properties similar to those of hydroxyquinophenol. A. K. M.

Cyanethine and Bases derived from it. By E. v. MEYER (*J. pr. Chem.* [2], **26**, 337—366).—The author has already shown in a previous paper (Abstr., 1881, 54) that cyanethine probably contains an *amido*-group, which is easily replaced by hydroxyl on treatment with hydrochloric acid. The hydroxyl is further replaced by chlorine by the action of phosphorus pentachloride. These bodies may all be regarded as derivatives of the base *cyanconiine* which has been already prepared.

Cyanconiine, $C_9H_{14}N_2$.—In the perfectly pure state this base is a colourless oil of about 0·93 sp. gr., and boils at 204—205°. With mercuric chloride it yields a sparingly soluble double salt, which, dried over sulphuric acid, has the composition $HgCl_2,C_9H_{14}N_2+\frac{1}{2}H_2O$. Simple salts of cyanconiine have not yet been obtained. On heating it with ethyl iodide at 160°, reaction takes place, and an *ethylcyanconiine* is produced, which, however, has not been obtained in the free state. By treating the product of the reaction, after purification, with platinic chloride, a platinochloride, $(C_9H_{13}EtN_2)_2,H_2PtCl_6$, is obtained. Acetic chloride acts violently on cyanconiine, and a crystalline body is produced, which appears to be formed by the combination of equal molecules of the base and the chloride. Bromine-water added to an aqueous solution of the base causes the separation of an oil which soon becomes crystalline. This is an unstable polybromide, which, on standing in the air, gives off some of its bromine. The crystalline residue on treatment with ammonia yields *bromocyanconiine* as a sparingly soluble oil.

Chlorocyanconiine (*loc. cit.*), when treated with zinc and hydrochloric acid, yields a double salt of a base containing more hydrogen than cyanconiine. This salt has the formula

$$ZnCl_2,C_{18}H_{30}N_4,2HCl,$$

and yields cyanconiine on oxidation. The base $C_{18}H_{30}N_4$ has not been isolated.

Action of Nitrous Acid on Cyanethine.—When gaseous nitrous acid is passed into a solution of cyanethine in glacial acetic acid, the following reaction takes place: $C_9H_{13}N_2.NH_2 + NO.OH = N_2 + H_2O + C_9H_{13}N_2,OH$. The *hydroxycyanconiine* thus produced is identical with that prepared in other ways.

By the action of the iodides of the alcoholic radicles at 160° substituted cyanethines are obtained.

Methylcyanethine melts at 74°, and boils between 257—258°. It dissolves easily in water, forming a strongly alkaline solution, which absorbs carbonic anhydride from the air. It expels ammonia from its salts, and forms double salts with mercuric chloride, silver nitrate, &c. Heated with hydrochloric acid in a sealed tube at 180°, it yields *methylamine* and the *hydroxy-base* above mentioned. Hence methylcyanethine is probably represented by the formula $C_9H_{13}N_2.NHMe$. It undergoes no alteration when treated with nitrous acid as above described.

Ethylcyanethine forms hard crystals melting at 45°. It boils at 259—261°, and closely resembles the methyl-derivative.

By the action of methyl iodide, ethyl iodide, and ethylene bromide at 150° on hydroxycyanconiine, derivatives of the latter are obtained.

Methyl-hydroxycyanconiine, $C_9H_{13}MeN_2O$, forms snow-white needles melting at 76·5°. It boils at 275—276°. It dissolves in water, forming a slightly alkaline solution, which is intensely bitter and only slightly poisonous. Its platinochloride crystallises in yellow rhombic prisms. It also forms a characteristic double salt with mercuric chloride. The base is insoluble in alkalis, in this respect differing widely from the parent base.

Ethyl-hydroxycyanconiine closely resembles the methyl-derivative. It melts at 43° and boils at 267—268°. It is isomeric with the *ethoxycyanconiine* formerly described (prepared by the action of alcoholic potash on chlorocyanconiine), inasmuch as the latter splits up into ethyl chloride and the hydroxy-base when treated with hydrochloric acid, whilst the former remains unchanged.

Ethylene-hydroxcyanconiine melts at 153·5°, and is very sparingly soluble in water, wherein it differs widely from the methyl and ethyl-derivatives.

By digesting a mixture of *hydroxycyancoiine* with alcoholic potash and ethyl iodide, the chief product is the ethyl hydroxy-base, but a small quantity of ethoxy-base seems to be also formed. The author concludes from these experiments that the hydroxycyanconiine and its silver and ethyl-derivatives must be formulated respectively as $C_9H_{12}N(NH).OH$, $C_9H_{12}N(NAg).OH$, and $C_9H_{13}N(NMe).OH$.

Action of Bromine on Cyanethine.—50 grams of cyanethine is dissolved in from five to six times its weight of dilute sulphuric acid, and 90 grams of bromine added in small portions at a time, the whole being warmed and shaken in a strong closed flask. A yellow oil separates, which is extracted with ether. The acid solution contains ammonia, propionic acid, and *monobromocyanethine* as hydrobromide. Bromocyanethine, precipitated by ammonia from the solution of its hydrobromide, crystallises from alcohol, in which it is easily soluble, in crystals resembling those of cyanethine. It melts at 152—153°. Nascent hydrogen converts it into cyanethine, and nitrous acid into *monobromohydroxycyancoiine.* The latter forms delicate needles, melting at 172°. It gives an unstable silver derivative on addition of silver nitrate and a few drops of ammonia.

The oil extracted with ether is a mixture of several substances. It dissolves in potash, and the yellow solution contains (besides potassium bromide) the potassium salts of a fatty acid (probably propionic), of *isoadipic acid*, and of an acid containing nitrogen. The oil, when treated with twice its volume of concentrated ammonia and allowed to remain for a time, yields beautiful crystals of the amide of a *butylenedicarboxylic acid*, $C_4H_8(CONH_2)_2$. From 30 grams of cyanethine about 2—3 grams of the body are obtained. On saponification with moderately dilute sulphuric acid, it yields the corresponding acid. It melts at 192°, and is identical with the *β-butylenedicarboxylic acid* which Otto and Beckurts obtained from *α-dichloropropionic acid*, and is in all probability *dimethylsuccinic acid*, COOH.CHMe.CHMe.COOH.

Behaviour of Hydroxycyanconiine with Bromine and Potassium Hydroxide.—The action of bromine alone on hydroxycyanconiine is exactly similar to its action on cyanethine. The same yellow oil is produced, and the same products are found in the acid solution. But when potash is used in addition, the result is different, a colourless solution being obtained, and this, when distilled by itself, yields, besides ammonia, a body which, on oxidation with chromic mixture, yields aldehyde and propionic and acetic acids.

Fused potash decomposes hydroxycyanconiine completely, giving off ammonia, whilst the "melt" contains the salts of propionic and acetic acids and potassium cyanide.

The author concludes the paper with some remarks on the constitution of cyanethine. The experiments described seem to warrant the conclusion that the body contains both an *amido-* and an *imido*-group, and the formation of *dimethylsuccinic acid* points to the presence of the group $<\begin{smallmatrix}\text{CHMe.C—}\\ \text{CHMe.C—}\end{smallmatrix}$. Hence the author formulates cyanethine as follows :—$C_9H_{15}N_3 = C_6H_3NMe_3(NH)(NH_2)$. E. H. R.

Specific Rotatory Power of Salts of Nicotine. By P. Schwebel (*Ber.*, **15**, 2850—2853).—The author has made a series of observations on the specific rotatory power of dilute solutions of salts of nicotine. The values for the rotatory power $[\alpha]_D$ of the hydrochloride $C_{10}H_{14}N_2,HCl$ in aqueous solution, varied from + 14·44 to 20·02 (L = 100·15) according to the concentration, and agree with those calculated from the formula $[\alpha]_D = 51·5 - 7931q + 0·004238q^2$. The values for the acetate varied from + 1·667 to + 4·083, in accordance with the formula $[\alpha]_D = 49·68 - 0·68199q + 0·002542q^2$, for the neutral sulphate from + 1·483 to + 14·717, according to the formula $[\alpha]_D = 19·97 - 0·05911q$. The molecular specific rotatory powers of nicotine and the above salts, are given in the table below :—

	$\frac{A.P}{100} = M.$
Nicotine	−261·71
,, hydrochloride........	+102·23
,, acetate..............	+110·29
,, sulphate	+ 83·43

It is to be observed that whereas the free base is lævorotatory, its salts are dextrorotatory, and these values for the molecular rotatory power bear no relation to one another. V. H. V.

Caffeine, Theobromine, Xanthine, and Guanine. By E. Fischer (*Annalen*, **215**, 253—320).—*Derivatives of Caffeine. Chlorocaffeine*, $C_8H_9N_4O_2Cl$, first obtained by Rochleder (*Jahrb.*, 1850, 435), is best prepared by the action of dry chlorine on powdered caffeine, the reaction being assisted towards its close by heating to 75—80° ; it can also be prepared by the action of phosphoric pentachloride on caffeine. It forms white crystals melting at 188°, sparingly soluble in cold water and ether, more readily in boiling water and hot alcohol. It is reconverted into caffeine by the action of nascent hydrogen.

Bromocaffeine (Abstr., 1881, 614), when heated with alcoholic ammonia for 6 to 8 hours at 130°, is converted into *amidocaffeine*, $C_8H_9N_4O_2.NH_2$; this crystallises in slender needles, melts at above 360°, and can be sublimed. It is sparingly soluble in water and alcohol, more readily in hot acetic acid. Notwithstanding the entry of the amido-group, it has less basic power than caffeine. It is also formed in small quantity by the action of potassium cyanide in dilute alcoholic solution on bromocaffeine. Bromocaffeine, when boiled with aqueous potash, does not yield hydroxycaffeine; with alcoholic potash it yields *ethoxycaffeine*, $C_8H_9N_4O_2.OEt$, crystallising in colourless needles, which melt at 140° and distil at a higher temperature with but little decomposition. It has feeble basic properties. If heated with hydrochloric acid it is resolved into ethyl chloride and *hydroxycaffeine* (*loc. cit.*); this melts at above 345°, and sublimes in considerable quantity at the same temperature; it yields unstable salts with bases. The *sodium salt*, $C_8H_9N_4O_3Na + 3H_2O$, crystallises in slender interlaced needles. The *barium salt*, $(C_8H_9N_4O_3)_2Ba + 3H_2O$, forms groups of very fine prisms; both salts are very soluble in water. The *silver salt* is obtained in slender needles by mixing ammoniacal solutions of hydroxycaffeine and a silver salt, and boiling to expel ammonia; it is insoluble in water; by heating it with ethyl iodide it is converted into ethoxycaffeine. Hydroxycaffeine, when heated with phosphorus pentachloride and oxychloride, is converted into chlorocaffeine. Oxidising agents react readily with hydroxycaffeine; concentrated nitric acid destroys it even in the cold; chlorine or bromine, according to circumstances, gives either dimethylalloxan with small quantities of apocaffeine, or in concentrated hydrochloric solution in the cold, yields no alloxan, but a mixture of apo- and hypo-caffeine; in both cases an additive-compound of the halogen and hydroxycaffeine seems to be first formed, and then decomposed by the water present. A compound of this kind is obtained by the action of bromine on dry caffeine, but it is too unstable to purify; as, however, it yields diethoxyhydroxycaffeine when treated with alcohol, it would appear to be a dibromide, $C_8H_9N_4O_2(OH)Br_2$.

Diethoxyhydroxycaffeine, $C_8H_9N_4O_2(OH)(OEt)_2$, is best prepared by the action of bromine on an alcoholic solution of hydroxycaffeine, cooled by a freezing mixture of ice and salt: the yield is nearly quantitative. It crystallises in triclinic prisms, showing combinations of $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $0P$ $\infty P'$, and $'\breve{P}\infty$, mostly developed in tables parallel to $\infty\breve{P}\infty$; the properties of this substance and of the corresponding methoxy-compound, have been already described (*loc. cit.*).

Allocaffeine, $C_8H_9N_3O_5$, is obtained as a bye-product in the preparation of diethoxyhydroxycaffeine; it forms a sandy powder, melts at 198°, is nearly insoluble in water, and sparingly soluble even in boiling alcohol; it is slowly dissolved by boiling with concentrated hydrochloric acid, and on evaporation is decomposed into readily soluble products.

Apocaffeine, $C_7H_7N_3O_5$, is formed together with hypocaffeine (Abstr., 1881, 614; 1882, 217) by the action of hot hydrochloric acid on diethoxycaffeine. It crystallises in monoclinic prisms, having the axial relations $a : b : c = 0{\cdot}8025 : 1 : 0{\cdot}6976$; melts at 147—148°, and is decomposed on further heating; it is readily soluble in hot water, alcohol, and chloroform, sparingly soluble in cold water, benzene, and carbon bisulphide.

Caffuric acid, $C_6H_9N_3O_4$, is obtained together with carbonic anhydride by boiling apocaffeine with water; the statement that hypocaffeine is formed at the same time (Abstr., 1882, 217) is found to be erroneous, and was due to the presence of hypocaffeine in the apocaffeine employed (cf. Maly and Hinteregger, *ibid.*, 632). By the action of hydriodic acid, caffuric acid is converted into *hydrocaffuric acid*, $C_6H_9N_3O_3$, crystallising in colourless prisms, melting between 240° and 248°, and resolidifying at 235°; it is readily soluble in hot water. On boiling it with baryta-water, methylamine is formed, together with the barium salt of an acid (methylhydantoincarboxylic acid ?), stable in alkaline solution, but yielding methylhydantoin when the barium is precipitated by carbonic anhydride.

Hypocaffeine, $C_6H_7N_3O_3$ (m. p. 182°), is not derived from the decomposition of apocaffeine as previously stated (Abstr., 1881, 614), but is formed at the same time and apparently independently of the latter in the decomposition of diethoxyhydroxycaffeine by hydrochloric acid. It can be distilled in great part unchanged, and is readily soluble in hot water and alcohol, sparingly in cold water. The barium salt, $(C_6H_6N_3O_3)_2Ba$, crystallises in slender white needles, the silver salt, $C_6H_3N_3O_3Ag$ or $C_{18}H_{19}N_9O_9Ag_2$, in aggregates of plates. On boiling it with baryta-water, hypocaffeine is converted into caffoline (Abstr., 1882, 217, 628).

When caffoline is boiled with acetic anhydride, carbonic anhydride and *acetylacecaffeine*, $C_6H_{10}N_3O_2\overline{Ac}$, are formed; this crystallises in monoclinic forms, showing the combinations $\infty Ꝑ \infty$, $0P$, ∞P, $Ꝑ\infty$, $\frac{2}{5}P\infty$. It melts at 106—107°, is readily soluble in water, alcohol, chloroform, and benzene, sparingly in ether. On treatment with hydrochloric acid, acecaffeine hydrochloride is obtained as a crystalline mass, readily soluble in water, and yielding the free base on treatment with silver oxide.

Acecaffeine, $C_6H_{11}N_3O_2$, crystallises in prismatic or tabular forms of the rhombic system, having the axial relations $a : b : c = 0·6707 : 1 : 1·2245$, and showing the combination ∞P, $0P$, $\check{P}\infty$, and, less frequently, $\infty\check{P}\infty$. It melts at 110—112°, distils without decomposition, and is readily soluble in water and alcohol. On oxidation with chromic acid, it yields a substance closely resembling cholestrophane. By the action of chlorine a chloro-derivative is obtained, crystallising in colourless needles. When heated with baryta-water, ammonia, methylamine, and dimethylcarbamide are formed.

THEOBROMINE.—By the action of chlorine on theobromine, monomethylalloxan and methylcarbamide are obtained. *Bromotheobromine*, $C_7H_7N_4O_2Br$, is prepared in a manner similar to bromocaffeine, and forms a white crystalline powder, sparingly soluble in hot water, nearly insoluble in the cold; like theobromine, it possesses acid properties, and dissolves readily in aqueous solutions of alkalis, but only sparingly in ammonia. The potassium salt is nearly insoluble in alcohol, and does not yield an ethoxy-compound on long boiling with alcoholic potash. The silver salt is obtained as a crystalline precipitate by mixing ammoniacal solutions of bromotheobromine and silver nitrate. On heating this silver salt with ethyl iodide, *bromethyltheobromine* is obtained; it closely resembles bromocaffeine. By the action of alcoholic potash, it yields *ethoxyethyltheobromine*, crystallising in needles (m. p. 155°). *Hydroxyethyltheobromine*, $C_7H_6EtN_2O_4.OH$, is obtained on boiling the ethoxy-compound with hydrochloric acid; it closely resembles hydroxycaffeine in appearance; treated with bromine and alcohol it is converted into *diethoxyhydroxyethyltheobromine* (m. p. 152°), which is much more readily soluble in alcohol than the corresponding caffeine-compound, and is decomposed by evaporation with hydrochloric acid into methylamine and *apoethyltheobromine*. This last, on being boiled with water, gives a substance which, by its behaviour with basic lead acetate, is undoubtedly a homologue of caffuric acid.

Hypoethyltheobromine, $C_7H_9N_3O_3$, is obtained, together with the apo-compound, by the action of chlorine on a solution of hydroxyethyltheobromine cooled to −10°. It forms colourless crystals melting at 142°, and closely resembles hypocaffeine; it is sparingly soluble in cold, readily in hot water, and can be distilled unchanged. The author considers that these results show that the same methylamine-group is split off in the formation of apo- and hypo-compounds, from both caffeine and theobromine.

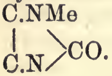
XANTHINE.—From the resemblance which xanthine bears to caffeine and theobromine, Strecker (*Annalen*, **118**, 72) considered that the three bases formed a homologous series, but was unsuccessful in his attempts to methylate xanthine.

Xanthine is best prepared from guanine as follows:—10 grams of guanine is dissolved in a mixture of 20 grams concentrated sulphuric acid and 150 grams water, heated to boiling, and after cooling to 70—80°, a solution of 8 grams of sodium nitrite is added, the mixture being well stirred. The yield is nearly quantitative, the xanthine is only of a pale orange colour, and is free from Strecker's nitro-body.

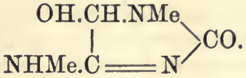
By the action of hydrochloric acid and potassic chlorate xanthine is converted into alloxan and urea.

On heating the lead salt of xanthine with $1\frac{1}{4}$ times its weight of methyl iodide in closed tubes for 12 hours at 100°, a yellow mass is obtained, from which, by boiling with water, treatment with hydrogen sulphide, and evaporation with ammonia, a crystalline powder is obtained, possessing all the properties of *theobromine*. To remove all doubt as to its identity with natural theobromine, it was converted into caffeine by Strecker's method; the melting point of the sample so prepared agreed perfectly with that of natural caffeine.

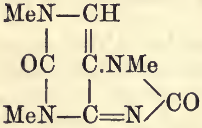
Constitution of Caffeine and its Derivatives.—The following are the principal facts to be considered in assigning a formula to caffeine:—1. Its decomposition by chlorine into dimethylalloxan and monomethylcarbamide. 2. The presence of a single hydrogen-atom other than those contained in the three methyl-groups, and capable of replacement by chlorine, bromine, or the amido- or hydroxyl-groups. 3. The direct union with a molecule of bromine, showing a double carbon linking. 4. The conversion of caffeine by addition of oxygen and successive elimination of methylamine and carbonic anhydride, into caffuric acid, a substance easily resolved into mesoxalic acid, methylamine, and methylcarbamide. 5. The ready formation of methylhydantoin from hydrocaffuric acid, showing the presence in the latter of the group



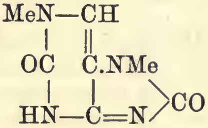
(6.) It has already been shown (Abstr., 1882, 628) that caffoline has the constitution



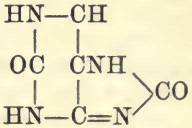
From these considerations caffeine and its homologues are best represented by the formulæ—



Caffeine.

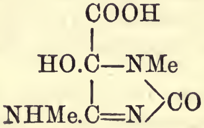


Theobromine.

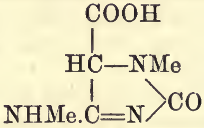


Xanthine.

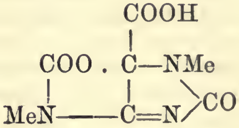
The following formulæ are assigned by the author to the more important caffeine-derivatives.



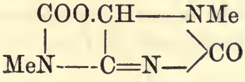
Caffuric acid.



Hydrocaffuric acid.



Apocaffeine.



Hypocaffeine.

A. J. G.

Some Derivatives of Morphine. By E. Grimaux (*Ann. Chim. Phys.* [5], **27**, 273—288).—The substance of Part I of this paper has already been abstracted (Abstr., 1881, 829) from the *Comptes rendus*.

Part II.—By acting on the sodium compound of morphine with ethyl iodide, *ethylmorphine*, $C_{17}H_{18}NO_3Et$, is obtained. This body is homologous with codeïne, itself an ether of morphine, and the author therefore proposes the generic name *codeïnes* for this class of bodies. Codeïne proper would then be *codomethyline*, the body under discussion, *codethyline*, &c. Codethyline crystallises with 1 mol. H_2O in plates, soluble in boiling water, alcohol, and ether. At 83° it fuses to a clear liquid, which solidifies on cooling to a transparent vitreous mass. Heated for some time at 100°, it turns brown, and after cooling fuses at 55—60°. Its hydrochloride crystallises in groups of needles. Sulphuric acid does not colour it. Heated to 20° with sulphuric acid and ferric chloride, it gives a blue colour, a reaction apparently common to all ethers of this class, and not, as Hesse suggested, confined to codeïne proper. Dried in the air at the ordinary temperature, codethyline has the formula $C_{19}H_{23}NO_3,H_2O$, but loses $\frac{1}{2}$ mol. of H_2O in a vacuum. This seems to support Wright and Matthiessen's double formula. Heated with methyl iodide, it forms the addition-product

$$C_{19}H_{23}NO_3,MeI,$$

which, if treated with silver oxide, yields a tertiary base fusing at 132°, and giving with sulphuric acid the same reaction as methocodeïne. Other halogen compounds, such as the alcoholic iodides, epichlorhydrin, allyl bromide, benzyl chloride, chloromethyl acetate, ethylene bromide, &c., give similar compounds with the sodium salt of morphine.

Ethylene-dimorphine, or *Dicodethine*, $(C_{17}H_{18}NO_3)_2C_2H_4$, crystallises in small colourless needles, insoluble in ether, soluble in alcohol. On heating, it decomposes below 200°, without fusion. Heated to 20° with sulphuric acid and ferric chloride, it gives a blue coloration. Its hydrochloride crystallises in small colourless prisms, easily soluble in water. With chloromethyl acetate, *oxacetylcodeïne*, or *morphine-glycollic acid*, $C_{17}H_{18}NO_3.CH_2.\overline{Ac}O$ is produced. This body, obtained as a deliquescent gummy substance, drying up in a vacuum to an amorphous mass, is very unstable, and decomposes on being boiled with water.

When codeïne methiodide is treated with silver oxide, it yields a compound which seems to be an ammonium base. On evaporating the product in a vacuum on a brine-bath, an oil is deposited, partially crystallising on complete evaporation. From this residue ether extracts a substance of the formula $C_{19}H_{23}NO_3$, crystallising in bright plates, and having all the properties of a tertiary base; it appears to be formed by the dehydration of methylcodeïne hydroxide, and to be analogous to some bodies obtained by Claus from the cinchona alkaloïds. *Methocodeïne* fuses at 118·5°, and soon turns brown if kept at this temperature. Codethyline methiodide, if treated with silver oxide, yields a base analogous to methocodeïne, but melting at 132°.

With aldehydes, morphine yields compounds similar to those obtained by Baeyer with the phenols. If morphine is treated with methylal or chloromethyl acetate, it forms a compound apparently of the formula $CH_2(C_{17}H_{18}NO_3)_2$. The ethers of morphine form similar compounds. Benzaldehyde appears to act in like manner.

L. T. T.

Specific Rotatory Power of Apocinchonine and Hydrochlorapocinchonine under the Influence of Acids. By A. C. Oudemans, Jun. (*Rec. Trav. Chim.*, **1**, 173—185).—This paper gives the results of a large number of observations leading to the conclusion that, in regard to variation in specific rotatory power under the influence of acids, the two bases above mentioned conform to the laws already demonstrated with regard to the four biacid cinchona-bases (p. 81). The statement of Hesse that the specific rotatory power of hydrochlorapocinchonine is the same in its basic as in its neutral salts, is regarded by the author as destitute of foundation. H. W.

Behaviour of Conglutin from Lupines towards Saline Solutions. By H. RITTHAUSEN (*J. pr. Chem.*, **26**, 422—440).—In a preliminary communication (Abstr., 1881, 1160) it was stated that crude as well as purified conglutin from lupine seeds was almost entirely soluble in a 5 per cent. solution of sodium chloride, and a portion remaining undissolved proved the presence of two sorts of proteïds present. It was also shown that on adding water to the saline solution, a portion of this proteïd was precipitated, whilst from the mother-liquor copper sulphate separated another portion; the proportions in which these substances were present were also different, the more nitrogenous being present in larger proportion in the soluble part, the less nitrogenous in the insoluble. The present communication deals more fully with observations made. The results are, that lupines contain large quantities of albuminoïd matter relatively poor in carbon, but rich in nitrogen, the composition being, C 50·16, H 7·03, N 18·67, S 1·07, O 23·07, corresponding with the formula $(C_{44}H_{74}N_{14}O_{15})_3S$. This albuminoïd matter is soluble at the ordinary temperature in a 5 per cent. sodium chloride solution, and by the addition of 4—5 times the volume of water, is reprecipitated to the extent of 80—90 per cent. It is likewise soluble in water containing a little potassium hydroxide without decomposition, and is precipitated by acetic or hydrochloric acids. In the sodium chloride mother-liquor, a substance remains dissolved, which is precipitated by salts of copper, and is soluble in solutions of lime or potash. The body heretofore named conglutin is divided by sodium chloride solutions into a soluble and an insoluble substance, the latter being however dissolved by potash-solution, and consisting of legumin originally present, and not of a product of decomposition; otherwise the formation of ammonia, &c., in presence of potash would have been noticed. The composition of the substances, one precipitated by addition of water to the salt solution, the other separated from the mother-liquors by potash or copper salts, appears to be identical, and the properties possessed are those of glutin, and for this substance the author retains the name conglutin. Conglutin is present in larger quantities than legumin, from which it may be easily separated by treatment with potassium hydroxide, addition of hydrochloric acid, purification by alcohol, treatment of the dried precipitate with salt solution, which dissolves the conglutin. The above is true for the seeds of the blue or yellow lupines, although the albuminoïd in the blue contains rather less sulphur. E. W. P.

Albuminoïds in Peach Kernels and Sesame Cake. By H. RITTHAUSEN (*J. pr. Chem.*, **26**, 440—444).—Peach kernels, when treated with a 5 per cent. solution of sodium chloride, yield up nearly all their albuminoïd matter, but this substance is reprecipitated only by the addition of acids; in composition it resembles conglutin and the albuminoïd in hazel-nuts and almonds, but is most probably combined with potash, seeing that it is precipitated only by acids, and not by the addition of small quantities of water to its solution. Treatment of these kernels with sodium chloride causes the production of a larger amount of hydrocyanic acid than water alone.

In a specimen of sesame cake the author found that the albuminoïd contained 2·36 per cent. S (see *Pflüger's Archiv.*, **21**, 92—96); a later examination proves that this excess of sulphur is due not to the albuminoïd, but to calcium sulphate occurring in the ash of the preparation. E. W. P.

Physiological Chemistry.

Oxidations and Syntheses in the Animal Organism. By O. Schmiedeberg (*Chem. Centr.* [3], **13**, 598).—The method employed by the author is the same as in previous experiments, benzyl alcohol, salicylaldehyde, toluene, and benzene being the substances operated on; they undergo but slight changes when oxidised. In the experiments with the kidneys, a canula is tied in the ureter, and the secretion always again mixed with the blood. The lungs were also made use of through the pulmonary artery.

Benzyl alcohol is only very slightly oxidised by continued shaking with blood; the oxidation is much more energetic if the blood mixed with benzyl alcohol is passed through the kidneys, contact with the cells of the organs apparently assisting oxidation.

Salicylaldehyde is not oxidised by blood alone, but when it is passed through the kidneys along with blood, plenty of salicylic acid is formed; on the other hand only a small quantity is formed by passing through the lungs.

Toluene is not oxidised by passing through organs; and even in the living animal only slightly. Two grams toluene were injected in various places into a dog, and only 2½ milligrams of benzoic acid were found in from 500—600 c.c. of its blood.

Benzene is converted into phenol in the organism; appearing in the urine as phenolsulphuric acid. *Phenol* is converted into catechol and quinol, which are likewise found in the urine, combined with sulphuric acid. The author gave a dog a large quantity of benzene, along with meat; the oxidation products were phenol and catechol, combined with sulphuric acid. Another dog that had been fed for three days on pure fat and starch, received on the fourth day, within 48 hours, 24 grams of benzene, mixed with the same sort of food; the urine was at first yellow, but very soon became dark in the air. It contained 1·6907 gram of phenol, of which 1·005 gram was combined with sulphuric acid, the remainder being in the form of phenylglyconic acid. The author regards these changes as synthetical, water being eliminated, and the requisite oxygen being supplied from the blood.

D. A. L.

Decomposition and Synthesis in the Animal Organism. By O. Schimiedeberg (*Chem. Centr.* [3], **13**, 599—600).—*Benzylamine* is readily decomposed in the organism, yielding benzoic and hippuric acids and urea. Other experiments show that it is not decomposed by passing through dogs' kidneys; on the other hand it is readily attacked on passing through pig's kidneys, which also can produce hippuric from benzoic acid. The organs, and frequently the blood of dogs and pigs, also decompose hippuric acid; blood with hippuric acid passed through pig's or dog's kidney, when the kidney artery is tied, gave rise to benzoic acid; this change is due to a soluble ferment, "histozym," and is not the work of bacteria. The ferment can be extracted by means of glycerol, and is precipitated by alcohol as a white chalk-like mass. Thus the two processes of decomposition and synthesis go on side by side, even in living animals, success depending on the most prominent agency. The quantity of histozym in the blood or organs is very variable, the dog's liver and pig's kidneys being the richest. Dog's kidneys may be rendered active both for decomposition and oxidation of benzylamine, by the introduction of histozym from pig's kidneys.

Benzyl alcohol is produced when finely powdered pig's kidney or blood is digested with benzylamine. With regard to the difference between dogs and rabbits in their power of producing hippuric acid, the author attributes it to the action of the histozym giving way to the synthetical process; with dogs, in the kidneys only; with rabbits, on the other hand, in other organs as well; therefore in the dog the kidneys alone produce hippuric acid, whilst in the rabbit other organs also produce it. When histozym is injected into the blood of dogs, they suffer from fever, symptoms of general sickness, and diarrhœa.

D. A. L.

Experiments on the Poisonous Action of Potato Brandy. By Brockhaus (*Chem. Centr.* [3], **13**, 669).—The following substances were taken into consideration, aldehyde, paraldehyde, acetal, and propyl, isobutyl, and amyl alcohols. The author tried the experiments on himself, and took the substance either (1) in the morning fasting, with water; or (2) in the afternoon or evening, with wine or good old brandy.

The aldehyde in the first case acted violently on the mucous membrane; in the second on the nervous system. The effect is soon over. The author attributes the greater intoxicating effect of new wine in part to this substance. The action of paraldehyde and acetal is of a similar character to that of aldehyde, but more lasting, the effects remaining to a slight degree until the next day. The alcohols above mentioned give rise to burning in the mouth, heat in the head, pain in the forehead, nausea, sensation of suffocation, intoxication varying in intensity directly with the increase in the formula of the alcohol. Amyl alcohol is an extremely violent poison. It is at any rate evident that the impurities in potato-spirit are very much more injurious to mankind than ethyl alcohol. The better the material is dissolved, the stronger the action. The author concludes that the greater part of the visible drunkenness is due to the consumption of bad spirits. He further points out that even solutions of pure ethyl alcohol, such as good wine, and spirits and beer, taken in excess, are likewise harmful to human health, and the more concentrated the alcohol the quicker and more violent is the injurious effect. He therefore recommends the prohibition of the sale of bad spirits, and objects to the drinking of spirits in any form as a pleasure.

D. A. L.

Chemistry of Vegetable Physiology and Agriculture.

Schizomycetic Fermentation. By G. MARPMANN (*Arch. Pharm.* [3], **20**, 664—673).—In this paper the author has collected all the facts known concerning the various kinds of fermentation. Specific bacteria fermentation is that in which, by reason of the growth of bacteria, reduction products are formed, whilst oxidation processes by means of the same agents, such as nitrification, are not fermentation. Nencki explains the reducing action of bacteria by their power of decomposing water, one hydrogen-atom of which reduces, whilst the hydroxyl-group is assimilated by the bacteria.

Glycerol.—Fitz describes three glycerol fermentations: (*a*) in the ethyl alcohol fermentation produced by a slender bacillus, probably identical with *B. subtilis*, in which neither butyric nor succinic acid, nor butyl alcohol is formed; neither can this bacillus decompose calcium lactate; (*b*) butyl alcohol alone is produced by a bacillus 0·005—6 mm. long by 0·002 mm. broad; (*c*) succinic acid is never formed by bacilli from glycerol, but Fitz found in blue pus a small micrococcus, which did act in this way. Schulze has found other bacteria, which besides forming ethyl and butyl alcohols, butyric and caproic acids, also produce a phorone of the composition $C_9H_{14}O$.

Tartaric Acid.—According to Gautier, Mediterranean wines under certain conditions rapidly become thick when exposed to the air; the red colour changes to a blue-violet, and a brown deposit is formed, as also acetic and lactic acids; the cause of this is a bacillus of varying length, but 0·0012 mm. broad. König found succinic acid amongst the products of the fermentation of tartaric acid: hydrogen ammonium tartrate yields butyric acid and ethyl butyrate, under the influence of *Ascococcus Billrothii.*

Sugar.—The mass resembling frog spawn, into which beet-sugar juice is frequently converted, is due, according to Cienkowski and v. Tieghem, to *Ascococcus mesenteroïdes* (0·0018—0·002 mm. thick), whereby sugar is converted into cellulose. The lactic ferment of sugar consists of a thin scum, built up of cells 0·001—3 mm. broad, and nearly double as long. These cells are active only as long as oxygen is present: consequently the conversion is indirect. This ferment described by Boutroux does not produce succinic acid, but the acid is formed from grape-sugar by *Bacillus amylobacter*, fully described by v. Tieghem. *B. amylobacter* exists in the cells of all milky-juiced plants; a butyric fermentation of albumin is caused by *B. subtilis.*

Nitrogenous Matter.—Normal urine is decomposed by *Micrococcus ureæ* (0·00125—0·002 mm. broad) with formation of ammonium carbonate; pathological urine is affected by other bacteria. The most important fermentation of albuminous matter is occasioned by *Bacterium Termo* (0·0015—0·002 mm. long), and it is this bacterium which induces the decay of all organic matter, and to which, as preserving the balance between animal and vegetable, our thanks are due.

All the other schizomycetes are in some way or another harmful to us. Ptomaïnes are produced by bacteria as yet undescribed, and the same bacteria also produce phenol, which is remarkable, as phenol is detrimental to their existence; also in salting matter phenylpropionic and phenylacetic acids, indole, cresol, and scatole, &c., have been found. Reference is made to various fermentations, and to *Dispora caucasica*, which forms "kephir." E. W. P.

Progress in the Knowledge of Bacteria. By G. MARPMANN (*Arch. Pharm.*, **3**, 20, 905—924).—In this communication the author reviews the work that has been done in the subject of disinfection. He points out the great difference between antisepsis and disinfection, which difference is not generally taken sufficiently into account in considering the action of carbolic acid, which at times acts as an antiseptic when in 2 per cent. solutions, but at other times a 5 per cent. solution is required. To shield a fermentable substance from the attacks of schizomycetes is vastly different to destroying a ferment, and arresting its action when in contact with fermentable matter. In the first case, a relatively small quantity is necessary as compared with that requisite in the second case. Again a large quantity of phenol is necessary to render the air of a room antiseptic, whilst on the other hand a small quantity distributed through the air is sufficient to preserve healthy substances from the attacks of pathogenous bacteria.

Kosegarten has shown that potassium chloride is unable by itself to hinder the formation of bacteria in a mixture of cheese, water, and urine, but the addition of borax brings about the desired result. The formation of mildew is more easily prevented by borax than by salicylic acid. Wernich (*Virch. Arch.*, **8**) has examined the action of thymol, hydrocinnamic, and phenolacetic acids, indole, scatole, cresol, and phenol on schizomycetes, and finds that the action of the first is far superior in all respects to that of the last-mentioned substance. Most investigators consider that the present methods of disinfection are insufficient to destroy bacteria, and exert only a temporary influence on their development. There are only two methods of testing the vitality of those bacteria which cease to move when dead. The first method, introduced by Engelmann, consists in supplying oxygen by means of chlorophyll to the bacteria, when, if they are still alive, motion may be detected. This method is uncertain, however; for the elimination of oxygen by the chlorophyll cells is caused to cease by the antiseptics employed to destroy the bacteria. A second and more certain method is that of Loew-Bokorny (*Pflüger's Archiv.*, **25**). In this the reducing action of bacteria on salts of platinum, gold, and silver in alkaline solutions is taken advantage of. The author then describes several experiments which he has made, using this reaction as indicative of life remaining in the bacteria. In a dilute solution of extract of meat, a 2 per cent. solution of hydrochloric acid does not destroy bacteria, a 5 per cent. only partly, but death occurs with a 10 per cent. solution; the same may be said of sodium chloride. Goulard water is not fatal to bacteria; it acts only by retarding or preventing development, and keeps wounds clean. Lead water

(Ph. Germ. ?) has but little influence; but if three times the usual strength be employed, then death ensues: hence this preparation is to be preferred to Goulard water. An aqueous emulsion of *Ung. hydrarg. cinereum* (Ph. Germ.) slowly kills *B. termo* and *crythosporus*. A retarding action on *B. termo* is noticed when 2—5 per cent. solutions of iodine tincture are employed: whilst the concentrated tincture is probably fatal; this then accounts for the observed actions of iodine (and mercury) on ulcers, &c. Appended is a valuable list of the literature on the subject which has appeared during 1880 and 1881.

E. W. P.

Direct Fermentation of Starch. By V. MARCANO (*Compt. rend.*, **95**, 856—859; compare Abstr., 1882, 1311).—The Indians of South America make an alcoholic liquor called *chicha*, by the fermentation of Indian corn. The corn is first allowed to soak for from four to six hours to soften it, and afterwards fermented. The fermentation is not due in the first instance to the action of a diastase present in the grain; because if powdered maize be boiled with water for a quarter of an hour and then left at rest, fermentation soon sets in. The effect is produced by a minute organism, which can be detected by the microscope.

The first action of this organism, however, is to form a diastase, which thus either produces or aids fermentation. This is shown by the fact that a mixture of maize-starch with water saturated with chloroform, remains almost unaltered: chloroform prevents the action of those organisms which cause fermentation, but does not interfere with the action of diastase, whereas a similar solution without chloroform is soon found to contain (after being freed from organisms by filtration through porous porcelain under pressure) matter capable of producing fermentation. Alcohol precipitates the diastase from the solution.

The same organism causes lactose, mannite, and dulcite to ferment, and it may be used to produce *koumiss* by adding it to milk containing lactose in proportion to the strength required.

The organism which causes maize-starch and starchy grain in general to ferment, and which is found in the stalks of the Indian corn, is identical with that which produces the fermentation of the juice of the sugar-cane in sugar manufactories. The germs are found in the cells of the stalks of the plant.

E. H. R.

The First Product of Plant Assimilation. By A. MORI (*Chem. Centr.* [3], **13**, 565; compare Abstr., 1882, 243).—The author detected a substance of aldehyde nature both by nitrate of silver and rosaniline sulphite in plants containing chlorophyll, which had been exposed to the sun. If, however, the same plants were left 24 or 48 hours in the dark, so that the first products of assimilation had time to alter, little or no separation of silver took place. This supports Baeyer's view, that the assimilation of carbonic acid under the influence of light gives rise to formaldehyde, thus: $CO_2 + H_2O = CH_2O + O_2$.

D. A. L.

Function of Resins in Plants. By H. DE VRIES (*Chem. Centr.* [3], **13**, 565).—The author is of opinion that the primary function of the resins of *Coniferæ*, and analogous juices of other plants, is to render service in cases of injury, by covering the wound with a protecting coating, and by favouring the healing of the wound. D. A. L.

Chemistry of the Maize Plant. By H. Leplay (*Compt. rend.*, **95**, 1033—1036, and 1133—1136).—The maize was analysed at three different stages of vegetation, viz.:—(1.) July 1st, when the organs of reproduction have not yet appeared or just begin to appear. (2.) August 1st, when fertilisation has been effected and the ear and grains have formed, but when the grains are easily crushed between the fingers, and yield a milky juice containing but little starch. (3.) September 1st, when the grain is ripe and hard, and no longer contains a milky juice, but is full of starch.

Between the first and second stage the stalks, leaves, and roots of the maize increase in weight, and at the second stage the weight of the leaves is greater than that of the stalks. Between the second and third stages, the weight of the leaves and stalks diminishes, until at the third stage the stalks have lost nearly half their weight, and the leaves more than half. At this stage the weight of the ear is nearly the same as that of the leaves, and is but little inferior to that of the stalks. Between the second and third stages, the weight of the root remains practically the same.

The total amount of sugar, without regard to its chemical nature, increases considerably during the formation of the ear, but diminishes considerably during the formation of the starch in the grain. When the organs of reproduction begin to form, the sugar is uniformly diffused throughout the stalks and leaves, but between the first and second stages it increases from 2·27 up to 10·54 per cent. in that portion of the stalk below the ear, and up to 11·63 per cent. in the stalk above the ear. It also increases by 4 per cent. in the sheathing leaves, and by 2·54 per cent. in that part of the leaves which hangs freely. At the same time sugar is found in the ear and in the support of the ear, to the extent of 8·72 per cent., and in the milky grains in smaller amount, about 5·81 per cent. During the ripening of the grain and the formation of starch, sugar disappears entirely from the leaves, diminishes in the stalk from 10·54 to 2·36 per cent., in the support of the ear from 8·72 to 5·81 per cent., and in the grain itself from 5·81 to 2·36 per cent.

In the first stage of vegetation, the stalks and the part of the leaves forming the sheath contain no reducing sugar; the free portions of the leaves contain crystallisable sugar to the extent of about one-fourth the total amount of the sugar. Between the first and second stages, the saccharose increases in the leaves by 55 per cent. of the original amount, and in the stalks by 10 times; whilst between the second and third stages both crystallisable and non-crystallisable sugars disappear entirely from the leaves; the non-crystallisable sugar disappears entirely from the stalk, and the crystallisable sugar diminishes by more than 80 per cent. It appears, therefore, that the sugar is formed in the leaves and accumulates in the stalk until the starch begins to form in the grain, when the sugar travels towards the ear into the support of the grains, and lastly into the grains themselves, where it is transformed into starch. This process goes on until the leaves are entirely, and the stalks and supports almost entirely exhausted. The function of the sugar is evidently to furnish to the grain the elements necessary for the formation of starch. Since the sugar remaining in the stalk is entirely crystallisable, it would appear that the reducing sugars are the most readily converted into starch. The transformation is explained by the elimination of 3 mols. H_2O from the reducing sugars, and 2 mols. H_2O from the crystallisable sugars, thus:—

Reducing sugars .... $C_{12}H_{24}O_{12} = C_{12}H_{18}O_9 + 3H_2O$
Crystallisable sugars ...... $C_{12}H_{22}O_{11} = C_{12}H_{18}O_9 + 2H_2O$.

In the first stage of vegetation, potassium and calcium exist in combination with vegetable acids in the soluble state in the juices, and in the insoluble state in the tissues in all parts of the plant. After the first stage, no more potassium is absorbed from the soil. Between the first and second stages, the quantity of potassium in the stalk diminishes very considerably, it being transferred to the ear which is in process of formation, and in which the amount of potassium continually increases until the grain is ripe. Between the first and second stages, the amount of potassium in the leaves remains constant; but between the second and third stages it diminishes by more than 16 per cent., whilst the amount in the stalk increases by 25 per cent. During the development of the grains and whilst they are soft, the amount of potassium which they contain is five times as great as that in their support; but after the grains are ripe, the amounts in the grains and in the support are about equal.

The distribution of the calcium differs considerably from that of the potassium. Unlike the potassium, the total amount of calcium increases by 143 per cent. between the first and third stages. Whilst the potassium diminishes in the stalks between the first and second stages, the calcium increases by 141 per cent. Between the second and third stages, the calcium diminishes in the leaves, and still more in the stalks, but increases in the ear and especially in the grains, in which, from the time of their formation to maturity, it increases to the extent of 188 per cent. The leaves and stalks apparently constitute a reservoir which furnishes calcium and potassium to the grain, with, however, this difference, that the total amount of potassium in the whole plant remains constant after the first stage, whilst calcium is continually absorbed from the soil.

Between the first and second stages, the total potassium existing in an insoluble form in the juices and tissues diminishes by 75 per cent., whilst the total calcium present in an insoluble form increases by 59 per cent. In the stalks, the potassium in an insoluble form disappears entirely, whilst the calcium increases by 41 per cent. In the leaves, the potassium diminishes by 72 per cent., whilst the calcium increases by 62·6 per cent.

The potassium and calcium exist in the maize, as in the beetroot, in combination with vegetable organic acids. The acids are formed from the carbonic acid absorbed by the roots partly in the form of potassium and calcium bicarbonates and partly in solution in water. The equations which represent the conversion of the carbonic acid into different organic acids are the same as in the case of the beetroot.

C. H. B.

Chemistry of the White Silesian Beetroot. By H. LEPLAY (*Compt. rend.*, **95**, 893—895 and 963—966).—The author concludes that the organic acids which exist in the beetroot in the form of calcium and potassium salts are the result of the transformation of the calcium and potassium bicarbonates absorbed from the soil along with water saturated with carbonic anhydride, by the roots of the plant. The transformation may be represented by the following equations:—Conversion of potassium bicarbonate into potassium oxalate, $K_2CO_3,CO_2 = K_2C_2O_4 + O$; conversion of the bicarbonate, carbonic anhydride, and water, into potassium acetate, $K_2CO_3,CO_2 + 2CO_2 + 3H_2O = 2KC_2H_3O_2 + O_8$; conversion of the bicarbonate, carbonic anhydride, and water into potassium malate, $K_2CO_3,CO_2 + 2CO_2 + 2H_2O = K_2C_4H_4O_5 + O_6$; conversion of the bicarbonate, carbonic anhydride, and water into potassium tartrate, $K_2CO_3,CO_2 + 2CO_2 + 2H_2O = K_2C_4H_4O_6 + O_5$; conversion of the bicarbonate, carbonic anhydride, and water into potassium citrate, $K_2CO_3,CO_2 + 4CO_2 + 3H_2O = K_2C_6H_6O_7 + O_9$.

The tissues always contain a certain quantity of calcium in the form of an insoluble organic compound, apparently formed from calcium bicarbonate, carbonic anhydride, and water, thus: $CaCO_3.CO_2 + 10CO_2 + 10H_2O = C_{12}H_{20}O_{10},CaO + O_{24}$. The changes which take part in the transformation of the substances absorbed from the soil are (1) reduction of the carbonic anhydride with elimination of oxygen; (2) condensation or assimilation of carbon; (3) assimilation of the elements of water in the same proportion as in water. The author gives a table showing the relative importance of each of these three changes in the formation of the various acids. The changes differ essentially among themselves, and do not follow the same order. The oxygen which is not used up in the formation of organic acids and tissues, apparently plays an important part in the formation of complex nitrogenous compounds.

The nitrogen compounds, such as albumin, nitric acid in the form of potassium nitrate, &c., existing in different parts of the beetroot, appear to be produced by the organic transformation of the ammonium bicarbonate absorbed from the soil by the roots of the plant. Since the juice of the beetroot is never acid, it is evident that the nitric acid exists only in the form of potassium nitrate, the potassium having been absorbed by the roots in the form of bicarbonate. It is probable therefore that the albumin, &c., are formed by the simultaneous alteration of the ammonium and potassium bicarbonates. The forces which take part in the formation of vegetable acids and tissues differ essentially from those concerned in the production of the nitrogen compounds. The changes which take place in the formation of the acids and tissues are reduction of carbonic acid, condensation or assimilation of carbon, assimilation of the elements of water in the same proportions as in water, and elimination of oxygen. In the formation of the nitrogen compounds, on the other hand, there is no reduction of carbonic acid, no condensation of carbon, no assimilation of water, no evolution of oxygen, but water is eliminated and oxygen is assimilated. The two series of changes are complementary. The conversion of the potassium bicarbonate into vegetable acids and tissues furnishes the oxygen and potassium necessary for the conversion of the ammonium bicarbonate into albumin, potassium nitrate, &c., and the production of these compounds liberates in the nascent state the water required for the formation of the acids and tissues. Equations are given showing the formation of tissues, albumin, &c., from the bicarbonates. All the elements contained in the potassium, calcium, and sodium bicarbonates absorbed by the roots, are found in the beetroot in the form of tissues, salts of vegetable acids, albumin, potassium nitrate and nitrite, water, carbonic acid, and nitrogen.

Under conditions unfavourable to the complete conversion of the bicarbonates into these compounds, secondary organic substances, such as asparagine, are formed, but these must be regarded as abnormal products, although formed in a similar manner. C. H. B.

Chemistry of the Nymphæa. By W. GRÜNING (*Arch. Pharm.* [3], **20**, 582—605, and 736—761).—Amongst popular remedies in Germany, *Nymphœa alba* and *Nuphar luteum* have long occupied a prominent place, but were omitted from the officinal list of medicinal plants in the beginning of the present century; they have since attracted the attention of chemists on account of their tannin, as a probable substitute for other tanning materials.

Morin in 1821 published an examination of the rhizome of *N. alba*, and Dragendorff in 1879 described an alkaloïd obtained from it; he promised further researches, but did not carry them out; the author undertook their examination at his request, and made both qualitative and quantitative estimations of the constituents of different portions of the two species, *N. alba* and *Nuphar luteum.*

Moisture and Ash.—Seeds and stalks dried at 110°, and the residue ignited; *N. luteum* showed a richness in alkali which, calculated from sulphates, equals Na_2O, 4·63 per cent., and K_2O, 32·15 per cent.

Fat and Resin.—The former, obtained by treating the pulverised substance with light petroleum, was greenish in colour and thick, easily saponified with soda. The seeds of *N. luteum* yielded a fat, congealing at the ordinary temperature, melting on the hand, and transparent when cold; the resin is the residue of the fat operation treated with ether; in the case of nuphar an intermediate washing with water is given to remove the tannin.

Matter soluble in ether should theoretically equal the sum of those soluble in light petroleum and in ether, but in fact there is a difference.

Soluble in Alcohol.—After extraction with absolute alcohol, evaporation, drying, and weighing, the residue was treated with water, a part of the solution again evaporated, the remainder of the aqueous solution was employed for estimation of tannin by Sackur's process—precipitation by copper acetate.

Soluble in Water.—20 grams macerated for one or two days at ordinary temperatures in 400 c.c. water, a part evaporated, dried and weighed, and a part precipitated with alcohol, the precipitate dried and ignited—the nitrogen in both estimated by soda-lime; part treated with lead acetate for tannin, and freed from lead with sulphuretted hydrogen; the remainder was employed to estimate glucose and saccharose. An examination for vegetable acids other than tannin showed the presence of citric, oxalic, and malic acids. Tests for salicylic, tartaric, benzoic, succinic, and fumaric acids yielded negative results.

Soluble in Soda Solution.—Part of the residue from the previous operations was treated with an aqueous solution of 1 per 1,000 of soda, filtered, the filtrate neutralised with acetic acid and decomposed with alcohol; the precipitate after deduction of ash was called metarabic acid.

Starch.—The residue from the soda treatment, boiled with water, a small quantity of diastase added, left to digest four hours at a temperature of 40°, filtered, 4 per cent. hydrochloric acid added and boiled in connection with an upright condenser for three hours: the resulting sugar, estimated by Fehling's solution, was calculated to starch.

Pararabin.—The residue, after removal of starch, was digested for a day with 1 per cent. solution of hydrochloric acid, quickly boiled and filtered, the filtrate treated with alcohol, and the precipitate (ash deducted) reckoned as pararabin.

Wood gum of Thomon was sought, but not found.

Cellulose.—After the various processes described, the portions of the plants were treated with freshly prepared chlorine-water, and successively with clean water, dilute soda solution, and again fresh water; the loss of dry matter between two weighings, less albuminous matter, was reckoned as lignin and similar substance.

The following table (p. 371) shows the results of the analysis.

Alkaloids.—The author succeeded in separating an alkaloïd from *N. luteum*, and also from *N. alba.* Dragendorff had already isolated it in the case of the latter; the chemical and physical properties appear to be identical as well as their behaviour towards group reagents, but in their colour reactions there is a decided difference; *nupharine*, as the alkaloïd of *N. luteum* is named by the author, is a whitish, brittle mass, which on being rubbed sticks to the fingers. It solidifies at 40—45°; at 65° it is of a syrupy consistence; it is easily soluble in alcohol, chloroform, ether, amyl alcohol, acetone, and in dilute acids, but almost insoluble in light petroleum; the acid solution has a peculiar and characteristic smell, and is acted on by most of the group reagents for alkaloïds, potassium chromate, picric acid, iodide of potassium, &c. With trouble the author discovered colour reactions which distinguish it from all other alkaloïds. A small quantity when dissolved in dilute sulphuric acid and warmed on a steam-bath, assumes a brown colour, which gradually passes into a dark black-green; the addition of a very few drops of water causes the colour to disappear, with precipitation of a voluminous yellow-brown substance. The acid solution when placed over sulphuric acid and lime, after 10 or 12 days, becomes a magnificent green, increasing in intensity for about another 10 days, until it becomes a dark blue-green; a few drops of water causes the colour to disappear immediately with separa-

	Nuphar.		Nymphæa.		
	Rhizoma.	Seeds.	Rhizoma.	Roots.	Seeds.
Moisture	10·30	11·31	10·56	6·71	9·06
Ash	5·19	0·89	5·47	10·07	2·12
Fat	0·77	0·51	0·49	0·59	1·06
Resin soluble in ether	0·60	2·11	1·55	1·38	0·21
Resin insoluble and phlobaphene	1·54	1·97	2·52	0·30	0·42
Mucous matter with traces of albumin	1·31	0·26	3·62	6·94	1·47
Tannin	2·27	6·72	10·04	8·73	1·10
Matter not precipitated by copper acetate	0·54	—	0·03	1·00	0·86
Glucose	5·93	—	6·25	5·62	0·94
Saccharose	1·21	—	—	—	—
Substances soluble in water indirectly estimated	4·40	1·38	1·92	3·60	1·18
Metarabin, &c.	2·50	0·86	3·26	6·11	0 46
Soluble in dilute soda solution not precipitated by alcohol	8·36	0·59	5·80	3·60	1·51
Starch	18·70	44·00	20·18	4·09	47·09
Pararabin	3·81	—	1·80	1·20	—
Albumin	3·99	7·08	4·06	7·21	9·79
Lignin, &c.	14·82	6·45	14·26	8·99	4·78
Intercellular substance	—	3·22	—	2·47	0·98
Cellulose	14·11	13·21	9·36	17·42	11·66

tion of a yellow crystalline precipitate, which when removed from the filtrate, liquefies in air, or over sulphuric acid, with return of the green colour. This experiment can be repeated frequently with the same sample.

The alkaloïd is tasteless, but its acid solution is intensely bitter; it has not yet been obtained crystalline.

The formula given to the alkaloïd is $N_2C_{18}H_{24}O_2$. The formula requires an equivalent of 300; by experiment it was found 285·5; the differences are attributed to impurities in the sample.

The same formula has been given by Pelletier and Couerbe to menispermine and paramenispermine; the three alkaloïds are probably isomeric. With Wild's polariscope nupharine is optically inactive. Its physiological effects were tried on cats, with no toxic effect.

The alkaloïd of *Nymphœa alba* does not give the green reaction with dilute sulphuric acid, but on the contrary, it gives the following, which are not given by nupharine. Concentrated sulphuric acid and potassium chromate colour its solution first red-brown, after some hours clear green. Concentrated sulphuric acid alone produces a red-brown, which passes into grey. Frohde's reagent colours first red, then dirty green. The alkaloïds are not present in the seeds of *N. luteum* nor in the blossoms or seeds of *N. alba*.

In the second paper the author continues the examination of the two plants of the family, *N. alba* and *Nuphar lutea*. As far as examination of two members of it allows him to come to a conclusion, he thinks that the tannin contained in them is their most important constituent from a chemical point of view; after that the alkaloïds and then the starch. The tannins of the two species differ slightly in their properties, but are closely related in their reactions. They both differ from tannin derived from other sources in yielding characteristic secondary products. The insoluble tannin found in them is very characteristic, but a somewhat similar substance was found by Löwe in oak-bark, and as methods of examination are now in use which were not then employed, it is probable that the substance has often escaped detection, and will be more frequently found in future.

The insoluble tannin of oak-bark is the anhydride of the soluble acid; the insoluble acid of Nymphæa appears to be a hydrate of its phlobaphene, and the author thinks it more than probable that the phlobaphene is an intermediate product between the soluble and insoluble tannin.

The tannins of Nymphæa are also notable for yielding many secondary products, which have individually been found in other tannins, but their presence together has not been hitherto noted. Ellagic and gallic acids are easily obtained; another substance, which rapidly absorbs oxygen from the air and passes into a body of the nature of phlobaphene, and a second substance, which by similar absorption of oxygen passes into two bodies, or assumes two phases with properties similar to chlorophyll. Sugar was looked for in consequence of Strecker and others having asserted it to be one of the derived products of tannin from gall-nuts and oak-bark, but it was not found.

The author's experiments lead him to believe that the molecule of the tannin obtained from Nymphæa is of a very complex nature.

J. F.

Analyses of Tobacco Ash. By R. Romanis (*Chem. News*, **46**, 248).

	Menjone tobacco on granite soil of Mandalay.	Grown on alluvial soil at Karrawaddy.		Indian.	
		Midrib.	Leaf.	Midrib.	Leaf.
K_2O	17·88	31·49	22·65	32·19	19·02
KCl	—	2·55	—	0·63	0·40
Na_2O	4·12	—	4·45	—	—
NaCl	0·74	1·84	1·09	—	—
CaO	27·27	28·93	20·78	37·40	36·51
$CaOP_2O_5$ ...	—	—	—	—	8·84
MgO	7·58	6·64	8·90	6·12	7·31
$MgOP_2O_5$ ..	—	—	—	11·95	—
$Fe_2O_3P_2O_5$ ..	6·94	12·58	10·27	—	7·76
SO_3	10·92	4·40	7·35	4·62	6·50
SiO_2	24·53	11·56	24·56	6·19	13·76
	99·98	99·99	100·05	99·10	100·10

E. W. P.

Composition of Different Varieties of Fodder-Cabbage. By M. Dugast (*Annales Agronomiques*, 1882, 226—239).—The plants were grown on two sorts of soil, one rather stony, and belonging to the miocene period, the other moor, which had been cleared for some years. The samples taken represented as nearly as possible the general characteristics of the crops, and were gathered early in November and January of the following year. They were then dried in an oven and ground before being subjected to analysis. The percentage of water varied from 90 in the leaves to 70 in the roots, and was greater in January than November. The following analysis of the "chou moellier" will give a general idea of their composition:—

—	Dry substance.		—	Ash.		
	Leaves.	Stalks.		Leaves.	Stalks.	Roots.
Proteïn	19·46	13·29	Phosphoric acid	6·29	6·25	5·05
Glucose	14·26	14·60	Lime	36·11	20·35	10·14
Saccharose	0·32	4·01	Magnesia	7·25	6·48	8·87
Starch	13·19	24·98	Ferric oxide	2·17	2·58	2·72
Cellulose	14·07	14·17	Sulphuric acid	13·79	16·03	13·23
Pectose	5·35	10·05	Chlorine	11·52	15·58	6·54
Fat	2·94	0·95	Manganese sesquioxide	0·04	0·06	0·05
Ash	8·14	7·85				
Not determined	22·27	10·07	Potash	15·57	24·41	20·37
			Soda	5·58	6·21	5·08
			Silica	1·99	1·62	—

The percentage of ash in the roots was 5·93.

Generally speaking, the amount of proteïn was greater in the leaves than in the stalks: in the former it varied from 11·9 to 21·2 per cent., and in the latter from 7·34 to 13·29 per cent. The samples taken in 1881 were richer in proteïn than those of the following year. The percentage of fat was also much greater in the leaves than in the stalks. The ash was found to vary considerably as regards some of its constituents. Phosphoric acid ranged from 4·6 to 11·1, and lime from 46·05 to 21·2 per cent., the latter being found principally in the leaves, whilst the stalks were richer in potash.

The rule generally followed in practice that it takes 5 or 6 kilos. of cabbage to replace one of hay, is confirmed when we compare the relative amount of nitrogenous bodies they contain, as shown by the above analyses.

J. K. C.

Loss and Gain of Nitrogen in Arable Land under the Influence of Different Systems of Cultivation. By P. P. Déhérain (*Annales Agronomiques*, 1882, 321—356).—It is evident that in a perfect system of culture, the land which has received manures and yielded crops should in the end be as rich as before in reproductive qualities, or even richer; taking the nitrogen present for example, the sum of that originally contained in the soil, together with the quantity furnished by manures, should be equal to the nitrogen left in the soil together with that abstracted by crops. In practice, however, this is not the case, and a loss of nitrogen, represented by the difference of the above quantities, always takes place; to ascertain this loss under varying circumstances, and how to reduce it to a minimum, was the object of this investigation.

Three series of four plots of land each received from 1875–77 large quantities of manures, viz., stable dung, sodium nitrate, and ammonium sulphate; from 1878 to 1881 different crops were raised without the addition of fresh manures, samples of soil and crops being taken and analysed at various stages. One series was left without manure the whole time.

Four plots were planted exclusively with maize: in 1875 the soil was found to contain 2·04 grams nitrogen per kilogram; the quantity of nitrogen was again determined in 1878 and 1881, and found to be as follows:—

	Stable dung.	Sodium nitrate.	Ammonium sulphate.	Unmanured.
1878......	2·01	1·79	1·88	1·67
1881......	1·68	1·45	1·62	1·45

It appears, therefore, that from 1875—1878 the soil was losing nitrogen the whole time, although large quantities were being furnished by the manure, while it underwent still greater absolute loss in the four following years, that plot indeed which had been manured with sodium nitrate becoming as poor as the unmanured soil. A calculation was made to ascertain the actual loss of nitrogen incurred between 1875—1878, taking into consideration that furnished by the manure, and extracted by the crops; and the result showed that the plot manured with stable dung was the best, the losses in the other cases being greater than the quantities supplied by the manure. By subtracting the nitrogen contained in the crops of the unmanured plot from that of the crops of each of the three other plots, the amount of nitrogen supplied by the manure was roughly obtained. The percentage utilised in the case of the stable dung was 13·5, whilst in sodium nitrate 7·7, and in ammonium sulphate only 0·5 per cent. of the nitrogen had been utilised.

From 1878—1881 the losses of nitrogen, although still great, were not nearly so large as in the three preceding years, the annual loss being only about half; in some cases, however, it was still greater than the amount of nitrogen in the crops, especially in the case of sodium nitrate.

Another series of four plots was sown from 1875—1879 with potatoes, and in 1880 and 1881 with corn, the same conditions with respect to manure being observed as before; the quantities of nitrogen per kilogram of soil are shown below:—

	Stable dung.	Sodium nitrate.	Ammonium sulphate.	Unmanured.
1878......	2·08	1·78	1·74	1·74
1881......	1·69	1·67	1·54	1·69

Whilst the soil manured with stable dung contained in 1878 more nitrogen than at the commencement of the experiments, all the others had become impoverished, especially in the case of the soil treated with ammonium sulphate. The absolute loss of nitrogen calculated as before, from 1875—1877, proves also to be greatest in this case, and is more than double the quantity furnished by the manure. In all cases the crops contained less than one-third of the nitrogen afforded by the manures, and the percentage of utilised nitrogen was found to be in stable dung 7·5, sodium nitrate 6·3, and ammonium sulphate 1·5 per cent. only. The worst crops were also obtained with the last, and the best with the first of these manures, both before and after 1877. The annual loss of nitrogen was greater in the case of the soil manured with stable dung, after the manuring had ceased, than before, but the reverse happened with the other three plots. The amount of nitrogen extracted by the potatoes was much less than by the maize crops.

The next series of plots was grown with beetroot from 1875—1877, with maize in 1878, and with hay in the two following years. Loss of nitrogen was observed as in the previous cases in the first four years, the soil being impoverished to a far greater degree than was the case either with potatoes or maize, the final percentage of nitrogen in the soil in 1879 being much less than before, and varying very little in the manured plots. In the next three years, crops of hay were raised containing considerable quantities of nitrogen, but at the end of the time all the soils were found to have gained appreciable amounts of it, instead of undergoing loss as in all the former instances. That this gain was not confined to the upper strata of the soil was shown by several analyses of samples taken from below at varying depths.

Further experiments showed that a loss of nitrogen in a soil was accompanied by a corresponding, although much greater, loss of carbon; whereas, when the quantity of nitrogen increased, no decrease in the carbon took place.

The ameliorating effect of allowing land to grow crops of hay occasionally has long been known to agriculturists, and meadow lands often contain very large quantities of combined nitrogen. The cause of the loss of the latter in cultivated soils is probably due to the greater surface exposure produced through ploughing and breaking up the soil, and consequent oxidation of the organic compounds, the nitrogen being probably converted into nitrate and washed away with the drainage-water. J. K. C.

Analysis of a new Guano from Australia. By A. B. Griffiths (*Chem. News*, **46**, 260).

Nitrogenous matter and ammonia salts.	Phosph. acid.	Lime.	Salts of alkalis.	Sand.	Water.
46·721	15·021	15·999	1·421	2·714	15·918

E. W. P.

Utilisation in Agriculture of the Slag from the Basic Dephosphorising Process. (*Chem. Centr.* [3], **13**, 668—669; comp. this vol., 133).—A slag of the following composition—

	SiO_2.	CO_2.	S.	P_2O_6.	Fe_2O_3.	Mn_2O_3.	CaO.	Al_2O_3 and sand.
Percentage..	6·20	1·72	0·56	19·33	9·74	9·50	47·60	2·68

had 10·94 per cent. of its phosphoric, that is 56·6 per cent. of the total phosphoric acid, soluble in ammonium citrate, and therefore in a form easily assimilated by plants.

After treatment with sulphuric acid—(1.) 1000 grams slag with 700 grams 66 per cent. sulphuric acid; the dried mass contained 12·13 per cent. phosphoric acid, of which 1·15 per cent. was soluble in water, 9·35 in ammonium citrate, and 1·63 in hydrochloric acid. (2.) 1000 grams slag with 1000 grams 66 per cent. sulphuric acid; superphosphate contained 8·07 per cent. phosphoric acid, of which 4·61 per cent. was soluble in water, 2·75 in ammonium citrate, and 0·71 in hydrochloric acid; after the lapse of three months matters had altered, evidently on account of the iron present, and the quantity soluble in water was now only 0·63 per cent., against 6·56 per cent. in ammonium citrate and 0·88 per cent. in hydrochloric acid. It will thus be seen that conversion with sulphuric acid is not profitable, but as more than half of the phosphoric acid is soluble in the soil-fluids containing carbonic anhydride, and hence is rendered available to plant-roots; the slag can be used directly as manure. There is an objection to this application, however, namely, the deleterious effect on plants of the lower oxides of iron and manganese, and of the hydrogen sulphide resulting from reduction of the sulphur-compounds; this gives rise to the suggestion that the slag should be applied early in the autumn only to those fields which are not going to be tilled until the spring, so that the objectionable substances may become harmless by oxidation during the winter. Moreover, it is advisable to strew the slag on the straw in the stable, or to place it in layers between the manure on removing it from the stable; in this way the oxidation of the noxious compounds goes on spontaneously, and at the same time the carbonic anhydride formed by the decomposition of the manure renders some more of the phosphoric acid available. D. A. L.

Analytical Chemistry.

Microchemical Reaction Methods. By A. TSCHIRCH (*Arch. Pharm.* [3], **20**, 801—812).—The author describes the great advantages of the microscope in technical chemistry, especially in the examination of foods, and expresses regret that many chemists consider their laboratories complete without such an instrument: he enumerates many examples of its usefulness such as starches, textile materials, &c.; even in the domain of pure chemistry, its application is necessary in the hæmatin reaction for the detection of blood-stains, the composition of urinary deposits, the search for strychnine, atropine, &c.

These advantages led to its more extensive employment in pure chemistry, and the name of microchemistry was given to it by Döbereiner. The author thinks that microchemistry must always be distinguished by a series of colour reactions, that in the same manner as the changes of colour, &c., in experiments on the large scale are examined in the test tube, so must they be similarly observed on the slide of the microscope. The actual process is simple. The objects to be examined must be either in thin sections, fine powder, or as fibres; a drop of the reagent is placed on a slide and allowed to flow slowly towards the object, the operator observing through the instrument: many physical as well as chemical changes may be thus detected; expansion or contraction, refractive changes, commencement of coloration, evolution of gas bubbles, solution, &c. The iodine starch reaction of Stromeyer was the first to be employed with the microscope; from it is learned the topography and division of starch in plants, the way it is stored up, and the process of its conversion; this reaction has also taught the difference between pure cellulose and woody fibre and the nature of intercellular substance. The reactions with zinc chloride and iodine, and with sulphuric acid and iodine, are also striking instances of the value of microchemistry, affording an easy method of distinguishing vegetable from animal fibres, the first colouring pure cellulose violet, and the second dissolving it with an intensely blue colour, the lignin encrusting the fibres having been previously removed by maceration in nitric acid, alkalis, or Schultze's maceration fluid. Thus sulphuric acid and iodine stain cork dark-yellow, thereby affording a trustworthy test for all membranes or sections containing suberin. The solubility of pure cellulose in "cuoxam" discovered by Schweitzer is also credited to microchemistry: the reagent may be prepared by digesting copper turnings in concentrated ammonia, or by decomposing a concentrated solution of copper sulphate with ammonia until the precipitated hydroxide is redissolved.

The maceration process of Schultze is a valuable aid to operations in microchemistry; the substance is treated with nitric acid and potassium chlorate either in the cold, or in cases of obstinate samples, is boiled for a short time, when the cells are isolated by the solution of the intermediate lamellæ. Amongst the instances given of its utility in food analysis is the separation of those peculiar cells of radiating branchial form which exist in the tea leaf, and are not found in other leaves used for its adulteration (they are, however, found in some of the camellia family).

This treatment has also the advantage of dissolving the coloured incrustations of cinnamon, roasted coffee, &c., and leaving the substances ready for further examination. Potash plays an important part in microchemistry, as it renders many objects transparent which are not made so by other reagents; it was by successive treatment with potash solution, acetic acid, and iodine that Böhm was able to perceive in chlorophyll the small particles of starch which had hitherto escaped observation. The most striking success in the science is that of Sachs with Trommer's sugar-test which, with slight modifications, enables the microscopist to identify, and even estimate quantitatively, cane- and grape-sugar, dextrin, gums, and albuminous substances in single cells.

The author alludes to the tinctorial methods which are employed in the examination of microbes, but which do not come under the strict domain of chemistry; he urges more extensive use of the microscope, together with the micropolariscope and spectroscope, and the study of botany and physics among chemists. J. F.

An Instrument for Correcting Gaseous Volume. By A. VERNON HARCOURT (*Proc. Roy. Soc.*, **34**, 166—167).—The author has devised an instrument to facilitate the correction of the observed volume of a gas, measured at any common temperature and pressure, to the volume the gas would occupy under standard conditions, and thus to dispense with corrections for readings of thermometer, barometer, and tension of aqueous vapour. The instrument consists of two small glass tubes side by side; the one is open above and drawn out, the other terminates in a bulb whose capacity is about four and a half times that of the tube. These tubes are fixed to an upright on which a scale is drawn; they are connected below with a small cylinder containing mercury, closed above by a leather cap, which can be pressed down by a button attached to a screw. The bulb and a portion of the stem are charged with a drop of water, and then with a quantity of moist air, which occupies $3\frac{1}{3}$ c.c. under standard conditions; the stem below this level, which is taken as 1000, being filled with mercury. To use the instrument, the pressure of the screw on the mercury is increased or relaxed until the level of the mercury is the same in both tubes; the reading of this level on the scale represents the volume occupied at the actual atmospheric pressure and temperature by a mass of moist air, which, under standard conditions occupies a volume 1000. Any volume of gas under the same conditions may be corrected to its true volume under standard conditions by multiplying by 1000, and dividing by the number read on the scale of the instrument. The author proposes to name the instrument an *aerorthometer*. V. H. V.

Improvements of Gas Analysis Apparatus. By J. GEPPERT (*Ber.*, **15**, 2403—2410).—The author at the outset draws attention to the length of time required, and the numerous readings of barometer and thermometer and corrections for tension of aqueous vapour necessary for a gas analysis by Bunsen's apparatus. To avoid these difficulties and to reduce the number of readings to two, the author has devised a form of apparatus consisting essentially of a suspended eudiometer and barometer tube, enclosed in a water jacket. The vacuum of the barometer is moistened with a drop of water, by which the correction for tension of aqueous vapour is dispensed with; the barometer is not provided with a scale, for alterations of external pressure affect the mercury level of the barometer and eudiometer equally, and it is thus only necessary to read, by some external scale, the difference of these levels. A minute description of the apparatus, which does not present any further novelties, cannot be rendered intelligible without the accompanying diagrams. V. H. V.

Estimation of Organic Nitrogen as recommended by Ruffle and Tamm-Guyard. By C. ARNOLD (*Arch. Pharm.* [3], **20**, 924

—927).—The author finds neither of these two methods (of which the first is to be found in the *Chem. Soc. J.*, Trans., 1881, 87, and the other in Abstr., 1882, 773) to be satisfactory; he quotes analyses showing the great differences which may exist between the true percentages of nitrogen, and that as found by either of these methods. The best results he has ever obtained were when employing both methods combined, burning the substance with a mixture of equal parts of anhydrous sodium acetate, sodium thiosulphate, and soda-lime. For details, see *Repert. Anal. Chem.*, 1882, 21. E. W. P.

Estimation of the Halogens in Carbon-compounds. By E. MULDER and H. J. HAMBURGER (*Rec. Trav. Chim.*, **1**, 156).—The authors recommend the method of ignition with pure lime, prepared by igniting precipitated calcium carbonate in a current of pure hydrogen. They observe however that in some cases this method does not yield exact results; thus an analysis of benzene hexchloride made by it yielded in four experiments 57·4, 58·2, 58·5, and 58·4 per cent. chlorine, whereas the calculated quantity is 73·2; but by using a mixture of lime and potassium nitrate, the percentage of chlorine obtained was 73·0. H. W.

Analysis of Silicates. By W. KNOP (*Chem. Centr.* [3], **13**, 637—639).—The method is as follows:—2 grams of the finely powdered mineral are fused with 10 grams of sodium carbonate; when cold the mass is dissolved in water at the ordinary temperature, which operation lasts 48 hours; a sufficient quantity of pure ammonium chloride solution is now added to decompose the dissolved mass, and the whole is evaporated to dryness. It is now gently boiled with water, which dissolves manganous chloride and phosphate, lime, and manganese, whilst the silica and undecomposed silicates of the sesquioxides remain undissolved, and are filtered off. The filtrate is made alkaline with ammonia, oxidised with chlorine-water, and after digesting 4 to 6 hours at 50—60° on a water-bath, the precipitated manganic oxide and phosphate are collected on a filter. The filtrate is made up to 200 c.c., and the calcium and manganese are determined in it in the usual way. The silica and sesquioxide silicates are treated with hydrochloric acid, evaporated to dryness, taken up with strong hydrochloric acid, and the silica is collected on the same filter as the manganese precipitate; this dissolves the manganese, and the filtrate is again treated with ammonia, chlorine-water, &c., to obtain the manganese, iron, and alumina. The iron is estimated in a separate portion by titration with permanganate. The advantages claimed for this process are: 1, that the evaporation with ammonium chloride at a temperature 80—90°, can be conducted without the least loss by spirting; 2, that the calcium and magnesium are removed before the precipitation of the iron, manganese, and aluminium, thus preventing these precipitates being contaminated by those substances. As yet only silicates containing small quantities of calcium and magnesium have been examined.

To recognise and even estimate the fluorine present, the author recommends the following method. The finely powdered mineral is warmed at 50—60° C. with concentrated sulphuric acid, the gas evolved being driven over, by means of dry air, into a glass cylinder partially filled with a colourless solution of aniline in equal parts of alcohol and ether. If fluorine is present, aniline silicofluoride is precipitated. This can be decomposed with soda, and the soda silicofluoride tested. The quantity of fluorine present can be calculated from the ash of the aniline salt. D. A. L.

Estimation of Phosphoric Acid and of Manganese. By K. BROOCKMANN (*Zeits. Anal. Chem.*, **21**, 551—552).—Instead of igniting the ammonium magnesium phosphate precipitate with the filter, the author dissolves it in dilute nitric acid, evaporates the solution, and ignites the residue. O. H.

Volumetric Estimation of Phosphoric Acid. By KRATSCHMER and SZTANKOVÁNSKY (*Zeits. Anal. Chem.*, **21**, 523—530).—Silver nitrate precipitates the whole of the phosphoric acid from neutral or slightly acetic acid solutions of the alkaline phosphates. If silver nitrate is added to nitric acid solutions of the earthy phosphates, and the solution then exactly neutralised with ammonia, the whole of the phosphoric acid is precipitated as silver salt. The authors found their method on this reaction, proceeding as follows:—In a measuring-flask excess of standard silver solution is added to the acid phosphate solution to be examined; ammonia is then added to neutralisation; the fluid is heated to boiling; the precipitate allowed to settle; and the excess of silver in the clear filtrate is estimated preferably by Volhard's thiocyanate method. O. H.

Behaviour of Alkaline Phosphates to Various Indicators. By G. TOBIAS (*Ber.*, **15**, 2452—2456).—Berthelot and Louguinine, using litmus as the indicator, have shown that the ratio $1\cdot5NaOH : H_3PO_4$ corresponds to the point of neutralisation; this result is confirmed by the isolation of sodium and thallium salts, containing this proportion of alkali to acid which are neutral to litmus. Shlickum, using cochineal, and Joly, using "helianthin," estimated that one equivalent of alkali requires one equivalent of acid. The author has further examined these results with the use of litmus, phenolphthaleïn, and cochineal as indicators. In the case of litmus and phenolphthaleïn, the ratio $2KOH$ (or $2NaOH$ or $2NH_3$) : H_3PO_4 corresponds with the point of neutralisation, but in the case of cochineal the ratio, $NaOH$ (or NH_3) : H_3PO_4 obtains. It is well known that disodium hydrogen phosphate, in concentrated solution, takes up a further proportion of alkali, and thus functions as an acid salt, but this fact cannot be recognised by a suitable indicator. If a red alkaline solution of phenolphthaleïn be added to disodium hydrogen phosphate melted in its water of crystallisation, the red colour disappears, but immediately reappears when the salt is solidified, which shows that the recrystallisation effects a dissociation into the hydrogen salt and free alkali. The author draws attention to the uncertainty accompanying the use of these several indicators. V. H. V.

Testing of Silver Nitrate. (*Chem. Centr.* [3], **13**, 666.)—The silver salt is dissolved in the smallest possible quantity of water and filtered, hydrofluosilicic acid is then added drop by drop; a precipitate indicates the presence of alkalis; if the solution remains clear it is mixed with an equal volume of alcohol; a precipitate shows than an alkali is present in small quantity. To test for nitrous acid or nitrites, the liquid is evaporated down and treated with a solution of 1 part magnesia (?) in 100 parts acetic acid; a change of colour from violet to yellow shows the presence of these substances. Free mineral acids bring about a similar change, but in this case the colour returns on diluting with water. D. A. L.

Estimation of Titanic Acid in Presence of Iron. By E. Wiegand (*Zeits. Anal. Chem.*, **21**, 510—516).—Pisani has proposed (*Compt. rend.*, **59**, 289) a method for the volumetric estimation of titanic acid, founded on its reduction in acid solution by means of zinc, and the oxidation of the titanic oxide formed with, potassium permanganate. As the titanium is oxidised before any ferrous salts present are affected, the end point of the reaction can be ascertained by means of a thiocyanate. The author has carefully examined Pisani's method, and concludes that it is not capable of giving trustworthy results.

O. H.

Detection and Estimation of Titanium. By A. Weller (*Ber.*, **15**, 2592—2599).—Titanium may be detected by the coloration which is produced by a neutral solution of hydrogen peroxide. 1 mgram. of titanic acid dissolved in 1 c.c. strong sulphuric acid gives an orange colour, and 0·1 mg. gives a bright yellow colour with a few drops of hydrogen peroxide. This test cannot be applied in presence of vanadic, molybdic, or chromic acid. Titanic acid can be accurately estimated by means of a colorimetric process based on this reaction. A normal titanium solution is prepared by dissolving pure potassium titanofluoride in sulphuric acid, and diluting with water. The colorimetric determination is carried on in two similar four-sided bottles of 125 c.c. capacity. Two sides of the vessel are cut parallel, the other two sides are blackened. Light from a narrow slit is allowed to pass through each of the flasks and fall on a sheet of paper.

W. C. W.

Detection of Arsenic Microscopically. By H. Hager (*Chem. Centr.* [3], **13**, 690—691).—This method is founded on the fact that arsenic and arsenious acids are reduced by oxalic acid or ammonium oxalate. Sulphuric acid can be tested by simply boiling with pure oxalic acid; the pure acid remains colourless; if it contains arsenic it turns brown. Dilute acetic acid or vinegar is tested by adding a few drops of glycerol to 3 or 4 c.c. vinegar or 2 c.c. dilute acetic acid, and about 1·5 c.c. ammonia, and shaking well; to this mixture 8 drops of concentrated solution of oxalic acid or 12 drops of ammonium oxalate solution, are added. Concentrated acetic or hydrochloric acid is tested by mixing 1·5 c.c. of the acid, 3 drops glycerol, 0·25 gram oxalic acid, and a few drops of ammonia (to excess in case of acetic acid). The test mixture for phosphoric acid is 2 c.c. of the acid, 3 drops glycerol, 0·25 gram oxalic acid, 6 drops strong potash, ammonia, and then an equal bulk of water. To test sulphur for arsenic, an ammonia extract is made, and 2 c.c. of this are mixed with an equal quantity of acetic acid, 4 or 5 drops glycerol, 25 drops of strong ammonium oxalate solution, or 20 drops saturated oxalic acid. A drop or so of any of these solutions is put on an object-glass, heated over a spirit-lamp, until visible vapour ceases to come off, or until the glycerol has disappeared, and is then examined with a power of about 100 diameters. Brown or black or grey amorphous or crystalline specks or rings are evidences of arsenic. Should there be doubt, it is advisable to reheat the glass and examine again. By this means 0·00001 of arsenic can be detected. D. A. L.

Examination of Bismuth Subnitrate. By W. Lenz (*Arch. Pharm.* [3], **20**, 577—578).—The tests for this compound, provided in the German Pharmacopeia, are boiling with acetic acid, precipitation of the solution with sulphuretted hydrogen water, and dilution of the filtrate with water; any residue that may be left is regarded as lime or magnesia. The author, in an examination of the commercial salt, found the residue to consist of potash, and it was quite free from either lime or magnesia. He was unable to make a quantitative estimation, owing to the smallness of the sample; but as the other properties of the substance fulfilled the requirements of the Pharmacopeia, he does not think there was intentional adulteration. He thinks that in the original preparation of the salt, potash was substituted for ammonia for reasons of convenience; he recommends pharmacists to bear the substitution in mind. J. F.

New Form of Apparatus for Estimating Ammonia in Potable Waters. By C. R. Tichborne (*Chem. News*, **46**, 247—248).—To prevent the weak solution of ammonia which distils over during the estimation of this gas in potable waters, becoming stronger by reason of ammonia in the air of the laboratory, the receiver should be connected with two bulb-tubes, similar to Liebig's potash bulbs, but with two pear-shaped bulbs on each side to prevent regurgitation of the fluid, and three absorption bulbs at the bottom; the centre bulb of these three is provided with a glass tap, for filling and emptying the apparatus. The bulb farthest from the receiver prevents the admission of any laboratory air to the second set of bulbs, which in its turn retains any ammonia which might escape from the receiver.

E. W. P.

Determination of Sulphur in Coal-gas. By O. Knublauch (*Ber.*, **15**, 2397—2403).—The principle of the author's method consists in passing a mixture of 4—5 parts of air with 1 part of coal-gas over heated platinised asbestos, and absorbing the sulphuric and sulphurous acid in a dilute solution of potassium carbonate (10 grams in 1 litre). The liquid in the absorption tubes is oxidised by dilute potassium permanganate, and the excess removed by the addition of oxalic acid; the whole is then precipitated by barium chloride. About 20 litres of gas, the burning of which lasts from 50—60 minutes, are used for a determination. To show the accuracy of the process, the details of several analyses are given in the paper. V. H. V.

Sulphur in Coal. By T. M. Drown (*Dingl. polyt. J.*, **246**, 154). —With a view of investigating the sulphur compounds contained in coal, the author used hydrochloric acid mixed with bromine, in order to determine the amount of sulphur present as metallic sulphide; the sulphur volatilised on burning this residue in a current of oxygen was absorbed in a solution of potassium permanganate, and estimated; finally the sulphur remaining in the ash was determined. Among others the following coal analyses were made :—

	A.	B.
Water	0·75	3·48
Volatile constituents	15·35	25·25
Coke free from ash..............	66·10	66·63
Ash	17·80	4·64

The ash contained—

	SiO_2.	$Al_2O_3Fe_2O_3$.	CaO.	MgO.	SO_3.
A........	47·74	34·17	7·61	0·98	5·30
B........	28·89	65·92	2·49	0·57	2·02

The sulphur determinations in the samples of coal and the coke obtained gave the following results :—

		With bromine.	By burning the residue in oxygen.	In the ash.	Total.	By burning the coal direct in oxygen.	In the ash.	Total.	By fusing with soda and potassium nitrate.
A.	Coal	1·660	0·640	0·040	2·340	1·983	0·203	2·186	1·940
	Coke	1·073	0·747	0·065	1·885	1·287	0·477	1·764	—
B.	Coal	0·041	0·450	0·031	0·522	0·431	0·058	0·489	0·474
	Coke	0·034	0·406	0·060	0·500	0·429	0·087	0·516	0·495

A large portion of the sulphur is therefore present in organic combination.
D. B.

Flashing Point of Petroleum. By J. T. Stoddard (*Ber.*, **15**, 2555—2557).—The author suggests the use of the following simplified modification of Liebermann's apparatus (Abstr., 1882, 1326) for determining the flashing point of petroleum. A glass cylinder 10 cm. high and 2—3 cm. wide, is fitted at the lower end with a perforated cork, through which is passed a glass tube drawn out to a point. The cylinder, filled to about one-third of its height with the oil to be tested, is placed in a suitable water or oil-bath, care being taken that the oil in the apparatus and the liquid in the bath shall be nearly at the same level. A current of air is forced through the drawn out tube with sufficient rapidity to produce a foam half a centimeter deep. The temperature of the bath when the mixture of petroleum vapour and air ignites is noted.
W. C. W.

Detection of Sulphurous Acid in Wine. By L. LIEBERMANN (*Ber.*, **15**, 2553—2555).—The author points out that the distillate from a wine may contain ammonia and other volatile bases, in which case the carbonic, formic, and acetic acids in the distillate would be precipitated on the addition of silver nitrate. Hence Wartha's method (*Ber.*, **15**, 1395) for detecting sulphurous acid in wines is untrustworthy. W. C. W.

Estimation of Fixed Organic Acids in Wine. By C. SCHMITT and C. HIEPE (*Zeits. Anal. Chem.*, **21**, 534—541).—The authors operate as follows:—To 200 c.c. of wine, evaporated to about one-half, basic lead acetate is added until the reaction is alkaline. The precipitate is washed with cold water, decomposed with sulphuretted hydrogen, and the solution of the acids thus obtained is concentrated until about 50 c.c. are left; this is exactly neutralised with potassium hydroxide, and further concentrated. An excess of a saturated calcium acetate solution is then added, and after 4—6 hours the precipitate is separated, washed until the fluid amounts to 100 c.c., ignited, and the alkalinity titrated with standard hydrochloric acid. From the volume of normal acid used, the amount of tartaric acid is calculated, and 0·0286 gram is added as a correction for the solubility of the calcium tartrate.

The filtrate from the calcium precipitate is again concentrated to 20—30 c.c., and 60—90 c.c. of 96 per cent. alcohol is added. The precipitate of calcium malate, succinate (tartrate), and sulphate is collected, dried at 100°, and weighed. It is then dissolved in the minimum quantity of hot dilute hydrochloric acid, the solution rendered slightly alkaline with potassium carbonate, and the precipitated calcium carbonate separated by filtration. After neutralisation with acetic acid, the filtrate is concentrated to a very small bulk, and precipitated hot with barium chloride, the precipitate consisting of barium sulphate and succinate. From it the barium succinate is extracted with dilute hydrochloric acid, the barium estimated as sulphate, and from the weight of the latter the amount of succinic acid is calculated, 233 $BaSO_4$, corresponding to 118 of $C_4H_6O_4$. The weights of the sulphuric, succinic, and tartaric acids (0·0286 gram tartaric acid), calculated into the corresponding calcium salts, are subtracted from the total weight of the lime precipitate, the difference being calcium malate, 172 parts of which correspond to 134 of malic acid.

O. H.

Detection of Rosaniline Hydrochloride in Wine by Means of Stearin. By C. H. WOLFF (*Chem. Centr.*, [3], **13**, 670).—The wine to be tested is warmed, and then shaken with a piece of stearin, which becomes dyed the characteristic colour, if rosaniline hydrochloride be present; natural wine colour only discolours the stearin. Sodium rosanilinesulphonate, which is more frequently used than the rosaniline hydrochloride for colouring wines, both because the colour is more stable and more like wine colour, only dyes stearin blue-violet; in neutral solutions this reaction is not very sensitive. The presence of the rosaniline hydrochloride on the stearin may be rendered evident by treating it with amyl alcohol, which on warming becomes coloured red, and by spectroscopic examination shows the rosaniline absorption spectrum, even when only a very small trace of the dye-matter is present. D. A. L.

Glycerol in Beer. By C. AMTHOR (*Zeits. Anal. Chem.*, **21**, 541—545).—The amount of glycerol present in pure Strassburg ales was found to vary from 0·05—0·3 per cent. O. H.

Test for Organic Acids in Phenol. By W. BACHMEYER (*Zeits. Anal. Chem.*, **21**, 548).—Whilst most organic acids destroy the colour of aqueous Brazilwood solution, phenol is without action upon it. The author utilises this difference for the detection of organic acids in phenol. O. H.

Rapidity of Separation of Cuprous Oxide by the Action of Invert-sugar on Fehling's Solution. By F. URECH (*Ber.*, **15**, 2687—2690).—In his first experiments, the author obtained very irregular results, which he found were due to the varying diameters of the vessels in which the precipitation took place. The narrower the beaker the more rapidly does the reduction proceed, other conditions being the same, but if exactly similar glasses are employed satisfactory results can be obtained. The solution of invert-sugar employed contained five times the quantity required for the reduction of the copper solution; the temperature at which the reaction took place was 13°. The results show that under such conditions the rate of separation of the cuprous oxide is directly proportional to the time. When, however, equivalent quantities of invert-sugar and copper solution are employed, the reduction takes place more slowly as the operation proceeds. A. K. M.

Detection of Benzoic and Boric Acids in Milk. By E. MEISSL (*Zeits. Anal. Chem.*, **21**, 531—533).—For benzoic acid, the author renders 250—500 c.c. of the milk alkaline with lime or baryta-solution, evaporates to about one quarter of the original bulk, adds gypsum, and dries completely on the water-bath. The dry mass is finely powdered, moistened with dilute sulphuric acid, and extracted with 50 per cent. alcohol, in which the benzoic acid is readily soluble, whilst only traces of the fat are taken up. The alcoholic solution is neutralised with baryta, concentrated, and after acidulation, shaken up with small quantities of ether; from this the benzoic acid crystallises almost pure.

For boric acid, 100 c.c. of the milk are incinerated, after having been rendered alkaline with baryta. The ash is dissolved in the smallest possible quantity of strong hydrochloric acid, the solution evaporated to dryness; turmeric solution is then added, and a drop or two of dilute hydrochloric acid. On evaporation on the water-bath as little as 0·001 per cent. of boric acid in the milk gives a distinct vermilion coloration. O. H.

Test for Sodium Carbonate in Milk. By W. BACHMEYER *Zeits. Anal. Chem.*, **21**, 548—551).—The milk to be tested is skimmed, and three separate quantities of 15 c.c. each are mixed in flat basins with 3, 5 and 10 c.c. respectively of a moderately strong solution of tannin, the mixture being allowed to stand in a cool place for 8—12 hours. Pure milk remains either unaltered, or shows a pale grey colour, whilst in the presence of as little as 0·03 per cent. of anhydrous sodium carbonate, a deep bluish-green colour is developed, which on the addition of a few drops of dilute acetic acid becomes red. The depth of coloration depends greatly on the proportion of tannin to soda, hence the use of three separate samples with different quantities of tannin. O. H.

Sulphocarbometer. By A. and T. GELIS (*Compt. rend.*, **95**, 967—969).—This apparatus was devised for the valuation of thiocarbonates. It consists of two parts; a flask of about 80 c.c. capacity provided with a metal collar with a screw thread, and a bulb surmounted by a tube graduated in tenths of a cubic centimeter. This bulb-tube is fitted with a metal collar and stopcock, which screws into the metal collar of the flask. The flask is filled with a solution of sodium or potassium hydrogen sulphite of 35° B.; 50 grams of the thiocarbonate are placed in the bulb-tube, the stopcock of the latter is then closed, and the two parts of the apparatus are screwed together. The stopcock is then opened, and the reaction between the bisulphite and the sulphocarbonate is retarded or accelerated by placing the flask in cold or hot water, as the case may require. The liberated carbon bisulphide rises into the upper tube, and its volume is read off. The number of cubic centimeters multiplied by 1·27 (the sp. gr. of the bisulphide) and by 2 gives the percentage amount of carbon bisulphide in the thiocarbonate. C. H. B.

New Colour Reactions of the Alkaloïds. By B. ARNOLD (*Arch. Pharm.* [3], **20**, 561—566).—The author describes the behaviour of various alkaloïds with certain reagents; the most distinctive are the following:—

Conine.—One drop, when mixed with a few drops of syrupy phosphoric acid, and the mixture evaporated in a white porcelain capsule over a small flame, becomes a fine green to blue-green.

Nicotine similarly treated gives a deep yellow to orange, the residue is soluble in water; the same colour. The reaction is more surely obtained when the mixture is heated for 5 to 10 minutes on the water-bath. Conine when so heated shows a clearer green.

Aconitine.—The well-known violet colour given by this alkaloïd when evaporated with phosphoric acid, is obtained easily and surely by agitating a few particles with syrupy phosphoric acid and warming 10 to 15 minutes on the water-bath.

The syrupy acid used as the reagent is obtained by dissolving the anhydride of the glacial acid in the officinal phosphoric acid of the German Pharmacopeia.

The author suggests that the ptomaconine of Selmi should be tested by this reagent.

Portions of other alkaloïds yielded characteristic reactions when rubbed with a few drops of concentrated sulphuric acid and gently warmed; (30 to 40 per cent.) alcoholic or aqueous potash solution is then dropped in by means of a capillary tube with constant stirring until in excess. Narcotine, morphine, and codeïne give the most striking reactions.

Narcotine in course of heating with the acid takes a yellow, or if warmed longer a violet colour. On the addition of alcoholic potash, it becomes a fine orange-red, which on adding water passes to yellow; treated with *aqueous* potash solution, the final reaction shows a gamboge-yellow, soluble, unchanged in water.

Morphine on the addition of the alcoholic solution becomes yellowish to dirty red, then turns to steel-blue and sky-blue. The continued addition of the potash solution causes after a short time a transition to a fine cherry-red. Water partially dissolves the residue to a red-violet colour: the residue is a fine blue to blue-green, and dissolves with that colour on adding water. Treated with *aqueous* potash solution it passes from red to a fine moss-green, and on further addition of the potash solution to a dirty yellow-brown. The more strongly the morphine is heated with the acid, the more intense is the blue produced on the addition of alcoholic potash.

Codeïne gives no reaction with alcoholic potash: with the aqueous solution it passes from reddish to pure green, and then to a dirty white; if it is heated with sulphuric acid until it begins to brown, it gives all the reactions of morphine, and seems to change into that body.

Solanine with the alcoholic solution passes from yellow to blue or red-violet, particularly after standing some time; with more potash it becomes whitish-grey. Sulphuric acid dropped into the mixture to excess causes a cherry-red, which disappears on adding water. Solanine treated with the aqueous potash solution passes from yellow to violet, then to green, and finally dirty yellow-brown. Sulphuric acid added as above causes the same reactions, but the process must be carefully conducted. The cherry-red and its disappearance are very strongly characteristic of this alkaloïd. The reaction is most successful when the substance is dissolved in *cold* sulphuric acid and warmed, but not until the solanine becomes brown, as in that case the colour reactions do not take place.

Another method of examination adopted by the author is to rub small portions of certain alkaloïds with concentrated sulphuric acid on a white porcelain slab; to the mixture he then adds a few crystals of sodium nitrite. Certain changes of colour occur, which again alter when alcoholic or aqueous potash solution employed in the previous experiments is added in drops, with constant stirring, until in excess; previous warming with the sulphuric acid is not desirable, unless when specially directed.

Atropine with sodium nitrite shows a deep yellow to orange. Alcoholic potash produces a splendid red-violet, quickly passing into pale rose: the more nitrite used, the deeper the colour. Aqueous potash does not produce a colour reaction.

Narceine with sodium nitrite, first gives a dirty brown-green, then clear blue margin, the mixture gradually passes to a fine violet, red-violet, and a blood-red. Alcoholic potash changes this to a yellow, but aqueous potash causes the violet to pass through yellow to a dirty brown. When the blue margin appears as above, if the mixture is very gently warmed, it becomes a magnificent blue-violet.

Narcotine with sodium nitrite passes gradually through red, brown, and green into a cherry-red. Alcoholic potash added changes this to a dirty orange; *aqueous* potash when dropped into the mixture after the sodium nitrite, shows a green spot after each drop. When it has been added in excess, all becomes a dirty green; when narcotine is warmed with sulphuric acid until yellow, or till the characteristic violet appears, and sodium nitrite is then added, a fine cherry-red immediately makes its appearance.

Strychnine with sodium nitrite gives a dirty yellow. Alcoholic potash changes it to a fine orange-red, the aqueous solution causes it to turn brownish-green, and finally dirty red-brown.

Digitaline with sodium nitrite gives a brown to dirty cherry-red colour, changed by alcoholic potash to a dirty yellow-grey, by aqueous potash to brown: the reaction with the sulphuric acid and sodium nitrite is peculiar to this alkaloïd.

Two or three samples of each alkaloïd were obtained from different sources. The processes followed in the experiments require considerable amount of practice, and it is sometimes difficult to exactly specify the shade of colour, for example, whether one should be called brownish-green or greenish-brown; yet with practice the characteristic reactions can be very accurately produced. J. F.

Quantitative Estimation of Cinchona Alkaloïds. By H. Meyer (*Arch. Pharm.* [3], **20**, 721—736, and 812—824).—The author criticises the methods employed by different chemists in the estimation of the total alkaloïds present in cinchona barks, and having examined several, proposes certain alterations which he believes to be improvements. Having carried out most carefully the processes recommended by Prollius, Hager, Moens, and De Vrij, repeatedly and on the same sample of bark, he found differences of no unimportant character in the results, both between experiments made by the same method and between different processes with each other. In the method proposed by Prollius, the fatty wax, always more or less present in bark, is estimated as alkaloïd. De Vrij does not extract the whole of the alkaloïd by his method, but calculates as if the undissolved alkaloïd in each sample examined always bears the same ratio to the dissolved portion: this the author believes not to be the case.

The system of Moens presents difficulties in the way of filtration and removal of the separated alkaloïd. Johnson (*Pharm. Zeit. Russ.*, 1880) found in three analyses of Bolivian bark by this method 2·93 per cent., 2·67 per cent., and 3·08 per cent., whilst in the residual gypsum, acid fat, &c., he found 7·42 per cent., 7·89 per cent. and 7·4 per cent., more than double the quantities first obtained. To avoid troublesome washing and facilitate the process generally, the author devised the following method. Into a tared flask he brings 10 grams of finely powdered bark and 12 grams of freshly prepared calcium hydroxide with 180 c.c. of 90 per cent. alcohol, and boils on the water-bath for one hour. When perfectly cool, the contents of the flask are made up to 190 c.c. with 90 per cent. alcohol; it is then carefully shaken, allowed to settle, and 100 c.c. filtered off. The sp. gr. of the filtrate will average 0·84; the quantity taken represents the alkaloïds contained in 5 grams of the original bark. It is placed in a dish previously rinsed with alcohol; 20 c.c. of 1 per cent. diluted sulphuric acid is added; it is then warmed on a water-bath; and the alcohol is evaporated with constant stirring. The quinovine and quinovic acid with the waxy fat remain suspended in the fluid, which now amounts to about 10 c.c.; after cooling, 10 c.c. distilled water is added, and the whole filtered into a separating funnel of about 150 c.c. capacity. Dish and filter are repeatedly washed with distilled water until the filtrate gives no precipitate with picric acid: 50 c.c. of chloroform are now added, and caustic soda solution to strong alkaline reaction. The liquid is well shaken up, and after the mixture clears, the chloroform is allowed to run off into a tared flask, and is removed by distillation; and the flask after being heated in an air-bath for an hour at 100°, is cooled in an exsiccator and weighed. This shaking up with chloroform is repeated as long as any weighable residue is found. Three operations are generally sufficient. The sample of the same bark which treated by Moens' method gave 4·9 per cent. alkaloïd yielded in this way 5·4 per cent.

The author then proceeds to examine the methods of Hielbig and Eykman; the chief feature of both is maceration of the bark for 24 hours previous to the treatment with lime and alcohol. Five experiments were made, and their results show that maceration in acid does not exert any influence on the yield of alkaloïd, but only tends to lengthen the process. The method of Prollius consists in treating the finely divided bark with a mixture of alcohol, chloroform, and ammonia; the infusion obtained is of a wine-red colour, the colouring matter is precipitated by calcium hydroxide, the filtrate is of a wine-yellow tint; an aliquot part is taken and evaporated to dryness, and the dry matter reckoned as alkaloïd. This method is defective in that the fat and some other alkaloïds remain in the residue. The author introduced modifications with a view to improve the process, but finally condemns it as untrustworthy.

De Vrij's process is fully described by him in "*Haaxmans tydscrift*," and criticised by Eykmann in the same journal. Its distinctive feature is percolation of the infusion until the percolate gives no precipitate with caustic soda solution. The author employs picric acid, and the difference is important, because the solubility of the alkaloïds in water and soda-solution is far greater than in picric acid; and in an experiment made it was found that a percolate which yielded no precipitate with the soda-solution, was rendered strongly opalescent on addition of picric acid. Two experiments made by this method on bark of the same kind as that previously used, and yielding 5·4 per cent. of alkaloïd, gave only 4·6 per cent. and 4·35 per cent. by this method. The loss is caused apparently by the tannates of the cinchona bark being precipitated in the course of the process. De Vrij's method is pronounced defective because it does not extract the whole of the alkaloïds; the author treated residues from the process, and found in them appreciable quantities of alkaloïds; the quantity so left is variable, not bearing a fixed proportion to the quantity extracted, the process is also tedious, taking five days to carry out. Eykman's own method is the following: A maceration fluid is prepared by mixing 15 c.c. chloroform and 4 c.c. glacial acetic acid; the finely powdered bark is carefully mixed with it in a test tube, the lower end of which is drawn out to a fine point and sealed; in this lower end is placed a plug of lint or shredded linen; the mixture is left for at least 24 hours, and then the fine point is broken off; the liquid is allowed to flow off, and then displaced with 98 per cent. alcohol; and the extract is quickly evaporated on the water-bath with a steady heat until it becomes thick. It is then, whilst warm, rubbed up with 5 c.c. hydrochloric acid of 10 per cent.; after cooling an equal quantity of water is added; the liquid filtered in a separating funnel, and the residue is washed. The method, owing to the small quantity of alcohol used, and its comparative rapidity, caused special attention to be given to it; but the author condemns it as not being more trustworthy than De Vrij's; he found the quantity of alcohol far too small for perfect deplacement, and the time occupied in that part of the process to be eight hours instead of five, as stated by Eykman, besides which the total alkaloïds are not extracted; the comparative results will be found in the accompanying table. The process of v. Hager was next examined, and is quickly dismissed as yielding results much too low. That of Gunning was the last method taken into consideration. 10 grams of powdered bark is mixed with a potash solution (6 grams in 12 of water) and kneaded to a homogeneous mass, which is left at rest for three hours, then mixed with 10 grams of gypsum, and dried. The dry mass is next extracted with amyl alcohol until no more alkaloïd is taken up, and evaporated; the dry residue gives the alkaloïd contents. This method is the only one which employs strong potash-solution, with a view not only of extracting the alkaloïd from its combinations, but also, by partially destroying the bark itself, to obtain perfect extraction; the author, however, prefers his own process, and believes that treatment with lime and alcohol is sufficient to extract all the alkaloïd present in the bark. The following are some of the general conclusions drawn by him from his investigations:—(1.) All the alkaloïd passes into solution on boiling the finely pulverised bark with calcium hydroxide and 90 per cent. alcohol for one hour. (2.) Previous maceration with acid or acidified alcohol is without beneficial influence. (3.) The separation of the alkaloïd is effected more readily by agitation than by precipitation. (4.) The separation of quinovic acid, quinovine, and the waxy fats can be done without loss by treating the alcoholic infusion previous to evaporation with dilute sulphuric acid in excess, and then cautiously evaporating with stirring. (5.) That repeated boilings and displacement of the lime is necessary to obtain the total alkaloïds. (6.) That the author's method allows the total alkaloïds to be obtained in 12 hours if necessary, or taking into account other laboratory work, in parts of two days. (7.) All other methods are incorrect, in that they do not extract the whole of the alkaloïds, (8.) except those of Gunning and Prollius, which yield high results in consequence of extracting matters which are not alkaloïds.

The following table shows the comparative results of different methods; the figures are the mean of several experiments, and were made on samples of absolutely dry bark.

Method.	Cort. cinch. succirub. Javanens.		Cort. cinch. Calisayæ.	Cort. cinch. offic.
	Pure alkaloïd per cent.			
Hager	—	3·75	2·76	—
Prollius, unmodified	6·33	—	—	—
Prollius, modified, *without* previous acid maceration	—	4·14	3·7	5·12
Prollius, modified, *with* previous acid maceration	—	4·77	4·17	5·54
De Vrij	—	4·60	3·86	5·85
Eykman, chloroform, &c.	—	4·72	3·9	5·81
Gunning, unmodified	8·12	—	—	—
Gunning, modified	—	5·16	—	—
Meyer	—	5·4	4·6	6·57
Meyer, maceration, with 2 *per cent. sulphuric acid*	—	5·42	4·59	6·67
Meyer, maceration with H_2SO_4 containing 90 per cent. alcohol	—	5·38	4·61	6·65
Meyer, maceration with 50 per cent. alcohol	—	5·4	4·57	—

J. F.

Estimation of Tannin. By A. GAWALOVSKI (*Zeits. Anal. Chem.*, **21**, 552—553).—Instead of igniting the precipitated copper tannate (Fleck-Hager's method), and multiplying the resulting cupric oxide by 1·034, the author dries the cupric tannate precipitate, weighs, ignites, and subtracts the resulting oxide from the total weight, the difference being the weight of the tannin. O. H.

Estimation of Tannin. By F. SIMAND (*Dingl. polyt. J.*, **246**, 133—140).—The author has abandoned the use of Löwenthal's improved method (*ibid.*, **228**, 53) of estimating tannin, as he found that the percentage of tannin in the same material was subject to certain variations. A series of experiments was therefore made, the object being to replace the gelatin used by Löwenthal by a substance capable of absorbing tannin. The method was founded on oxidation with potassium permanganate or calcium hypochlorite, with indigo solution as indicator in presence of sulphuric acid. The first substance experimented with was powdered skin, which Hammer and Löwenthal had used some time ago for extracting tannin from solutions. Although more satisfactory results were obtained than with gelatin, the absorption of the tannin was a slow operation, requiring often 24 hours' agitation or more, and even then tannic acid was present in the filtrate; moreover, the difficulty experienced in preparing the skin rendered this method impracticable. The author then tried the gelatinous tissue of bones. Tubular bones were treated with dilute hydrochloric acid, and after removing the lime salts the residue was washed and used for extracting tannic acid from infusions. The results were as satisfactory as those obtained with powdered skin, whilst the absorption of the tannin was effected more readily. Later on, when Müntz showed that tannin is absorbed by nitrogenous vegetable substances, the author, assuming that all nitrogenous animal substances softening in water are capable of absorbing tannin, used horn shavings after removing the lime salts, with equally good results. In the original paper, the method pursued by the author in his laboratory for preparing the skin powder, extracted bones, and horn shavings is described in detail, and numerous tannin estimations with these substances are given. D. B.

Detection of Adulterations of Flour with Rye-meal. By WITTMACK (*Bied. Centr.*, 1882, 790).—The method depends on the difference of the microscopical appearances presented by the husk, gluten cells, and starch grains.

	Wheat. mcm.	Rye. mcm.
Thickness of husk	43—50	31—40
Length of epidermis cells of husk	116—160	136—400
Breadth of ditto	20—28	26—32
Thickness of the cell walls ..	5·8—6·0	4·3—5·8
Glandular markings on the cell	very close and well defined.	not so close.
Length of the cells underlying the epidermis of the husk..	114—192	72—90
Breadth of ditto	14—17	11—14
Thickness of cell walls	5·8—8·7	3·3—5·0
Glandular markings on the cell	very close and well defined.	not so close, often undefined.
Long diameter of gluten cells.	56—72	40—64
Shorter, ditto	32—40	24—40
Diameter of isodiametrical gluten cells	40—48	32—36
Diameter of starch grains....	28—35	42—52

These differences, however, are sometimes of little use, as careful milling removes all traces of husk, and as the difference between the starch grains and gluten cells of the two flours is so slight, no great reliance can be placed on their indications. However, there are always remains of the hairs which grow from the end of the seeds, to be found in flour, and by their means the presence of rye in wheat meal can be detected. Measurements are as follows:—

	Wheat. mcm.	Rye. mcm.
Thickness of wall of the hairs	7	3—4
Breadth of lumen	1·4—2·0	7
Seldom to	5·0	

To aid detection of the hairs when mixed with flour on the microscopic slide, the starch should be brought into solution by soda or potash. E. W. P.

Creasote from Beechwood Tar. By A. GRÄTZEL (*Arch. Pharm.* [3], **20**, 605—610).—This substance, discovered by Reichenbach, and highly esteemed for its medicinal properties, is not a simple body, but a mixture of numerous homologous phenols—guaiacol (b. p. 200°), creosol (b. p. 219°), and small proportions of products boiling at about 232°, and resembling the others in their reactions; the proportions in which they exist are variable, and in great measure dependent on the quality of the tar employed, which in turn varies according to the treatment given to the timber in the wood-vinegar factories where it is produced. The rough creasote, in addition to pyrogallic dimethyl ether and methylpyrogallic dimethyl ether examined and described by Hofmann, contains another substance, recently isolated by the author and named by him *cœrulignol.*

This possesses so strong and dangerously astringent properties that a single drop on the tongue causes bleeding; creasote must therefore be absolutely freed from it; its absence can be very accurately known by the barium hydroxide test.

Beechwood tar creasote boiling between 195° and 235° is of a wine-yellow colour; in flasks of large diameter it is of a deep-yellow, similar in appearance to a solution of potassium dichromate, and if pure should possess the following properties:—

1. The addition of an equal measure of saturated solution of soda should leave the mixture quite clear, or at most with the yellow colour described, and the addition of 10 to 20 times the bulk of distilled water should not cause any opacity; if there is opacity, it is caused by the presence of lime in the water, or the presence of cœrulignol, or some neutral oil.

2. Its aqueous solution, when treated with aqueous solution of ferric chloride, should give a blue colour, rapidly passing into brown.

3. From aqueous solutions, zinc chloride should throw down a white precipitate, soluble in excess of the reagent.

4. Mixed with an equal quantity of glycerol of 1·250 sp. gr., it should not dissolve, but after warming the mixture should take up 50 per cent. of the glycerol, the remainder separating clear.

5. With an equal, or less than equal, bulk of collodion solution, it should not form any gelatinous compound.

6. With strong ammonia, after 24 hours, it ought to show an olive-green colour, not blue.

7. Baryta-water with alcoholic solution of creasote, should not show any colour whatever, either blue or passing to red.

8. 1 part of creasote is soluble in 30 parts of boiling water; on cooling so much of it should separate that but 1 part should remain dissolved to 80 parts of water. Water containing carbonic acid dissolves creasote less readily; therefore in an aqueous solution left exposed to the air separation takes place and the solution is troubled.

The remainder of the paper contains information on cases in which creasote may be usefully employed in medicine and surgery, its effects and modes of application, and is not of chemical interest. J. F.

Properties of Chlorinated Organic Gases and Vapours. By Berthelot (*Ann. Chim. Phys.* [5], **27**, 227—229).—In testing for the presence of volatile chlorinated compounds dissolved in the blood or other animal fluid, by passing their vapour, mixed with air and steam, through red-hot tubes, and leading the resultant gases into a solution of silver nitrate, the possible generation of acetylene and hydrocyanic acid forms two serious sources of error. The author proposes to eliminate these by leading the gases issuing from the heated tube into water, and boiling this for some time. Hydrocyanic acid and acetylene are thus driven off, whilst the hydrochloric acid remains dissolved, and may be tested for as usual by acidifying and adding silver nitrate. L. T. T.

Estimation of Hæmoglobin in Blood by Optical Means. By E. Branley (*Ann. Chim. Phys.* [5], **27**, 238—273).—In the first part of this paper the author discusses the relative accuracy of the results obtained with various instruments for the above purpose. He has obtained the best results by the combined use of the spectroscope and polariscope. In the instrument which he recommends—a modification of those used by Trannin and Violle—the cell containing the substance under examination is divided horizontally, and between this and the spectroscope a Wollaston double refractor, and a polariscope are introduced; the double refractor, giving two images of each half cell, is so arranged that the ordinary image of one half and the extraordinary of the other are thrown on to the prism of the spectroscope, so as to give spectra in juxtaposition. The part of the spectrum observed is that between the bands D and E. The substance under examination is introduced into one half cell, the standard of comparison into the other, a lime (or magnesia) light being used as the source of light. By turning the Nicols prism, the two spectra are brought to the same brightness, and the absorption of light reckoned from the angle of rotation. In this apparatus it is only necessary to compare a standard solution of hæmoglobin once for all with water, all estimations afterwards being made against water. With this apparatus, the author has made a large number of careful determinations. He has experimentally verified the law of absorption for a coloured liquid, $I_1 = Ia^e$, where I is the intensity of the light incident on the slit, a is the coefficient of expansion, and e the thickness of the layer of liquid; and also the law of the proportion between the absorption and the quantity of colouring matter dissolved in a given volume. The author has examined human blood in various pathological states, and also the blood of the ox, dog, horse, cock, and carp, and hæmoglobin prepared from the blood of the dog and horse, and finds that the hæmoglobin in all of them is identical. The colouring matter of blood changes very rapidly. At temperatures near the freezing point, no change takes place for three or four days, but at 15° decomposition sets in within about 24 hours, and at higher temperatures within a much less time; when frozen, it does not change. Hæmoglobin, treated with carbonic oxide, shows no appreciable variation in absorptive power. The author also gives a number of determinations of the hæmoglobin in blood taken from persons and animals in various stages of disease, &c., and points out the pathological value of such determinations. L. T. T.

Technical Chemistry.

Cleansing of Glass Laboratory Vessels. By A. Müller (*Arch. Pharm.* [3], **20**, 841—844).—The use of sea or river sand is injurious, as the sharp fragments of quartz scratch the surface of the glass. Lead shot, which is an excellent mechanical cleanser, is condemned, because it leaves part of its substance on the glass, which has to be removed by dilute nitric acid. Its use is strongly condemned for cleansing beer and wine bottles. Clean wood-ash is recommended for domestic use, as it acts both mechanically, and chemically by its potash. Powdered rock-salt is also used. For glass vessels used in the laboratory, the author recommends a piece of india-rubber cut into the form of a tongue or other convenient shape, and fastened to a flexible wire as a handle. When great cleanliness is required, he rinses the vessels and dishes with potassium dichromate and sulphuric acid. The acid from the desiccators mixed with the dichromate from estimation of nitric acid answers the purpose. J. F.

Preparation of Silver Bromide Gelatin-emulsion. By J. B. Obernetter (*Chem. Centr.* [3], **13**, 687).—The author dissolves gelatin and silver nitrate together in water, filters, and leaves the liquid to solidify. The jelly is cut into convenient pieces, washed (thus far operations may be conducted in daylight), and then, in the dark, immersed in a solution of a bromide. After an hour or so, the pieces are well washed. Thus prepared, the emulsion is very efficient for photographic purposes. It can be applied by melting and pouring on the plate; or may be preserved any length of time after being treated with alcohol. D. A. L.

Antiseptic Properties of Carbonic Anhydride. By H. Kolbe (*J. pr. Chem.* [2], **26**, 249—250).—The fact that putrefying meat has an alkaline reaction led to experiments on the effect of exposing meat, in suitable vessels, to the action of the vapour from the spontaneous evaporation of hydrochloric, nitric, and aqueous sulphurous acids respectively, the result being that meat was well preserved, but at the same time lost its original flavour, acquiring a taste similar to meat kept in vinegar. The author was thus led to try experiments with carbonic anhydride. The apparatus employed consists of a tinned-iron cylinder, at the top of which and outside is a channel partially filled with glycerol, into which the rim of the cover dips; in the side of the cylinder near the bottom and in the top of the cover tubes are soldered, which can be closed. The tube in the cylinder serves for the admission of carbonic anhydride, whilst the one in the cover is for the escape of the air. The meat is suspended on a tinned-iron hook, and a porcelain plate is put below the meat to catch whatever falls from it;

the cylinder is then filled with carbonic anhydride, and the tubes closed. A lump of beef, with fat alone weighing from 2 to 5 kilos., was experimented on at varying temperatures. After eight days, the meat had the same colour and odour as fresh meat; it had a slightly but decidedly acid reaction; the broth made from it had the same odour and taste as that made from fresh meat, and the cooked flesh was tender and soft. After 14 days, the outside had become grey; the interior, however, was red and juicy, and the meat was good. After three weeks, the meat was as good as after 14 days, but was softer and required less time for cooking and making broth. After five weeks, the meat was not quite free from putrid flavour. Carbonic anhydride therefore prevents putrefaction in beef to some extent, but this is not the case with mutton, veal, fish, lobster, oysters, and vegetables, which undergo change in carbonic anhydride after a short time; thus mutton, after eight days in the gas, began to be tainted.

A mixture of carbonic anhydride and carbonic oxide, such as that given off when oxalic acid is decomposed by sulphuric acid, acts also as an efficient antiseptic for beef; in fact, in this case the meat does not even become grey, but retains its red colour throughout. Small white spots of mould, however, are formed; but the meat underneath them is of the same red colour as the parts unaffected. D. A. L.

Sinidor. (*Chem. Centr.* [3], **13**, 576.)—This is prepared by heating magnesium acetate with magnesia until the mass becomes slimy, or it can be made less pure by adding caustic alkali to a solution of neutral magnesium acetate. It is a basic magnesium acetate, and it is proposed to use it for destroying bad odours and for disinfecting and preserving organic substances. D. A. L.

Carlsbad Salts. By E. Harnack (*Chem. Centr.* [3], **13**, 670—671).—The preparation of the so-called "Sprudelsalz" has been conducted very imperfectly, the usual preparation being, in fact, principally crystalline Glauber salts. This state of things is now being improved, and the process employed is this:—The spring water is boiled, and the precipitate (iron, manganese, calcium, magnesium, and silica) filtered off, the filtrate is evaporated and saturated with carbonic anhydride from the spring to reconvert the carbonate into bicarbonates. The salts then have the following constitution, nearly approaching the natural proportions:—

Sodium bicarbonate	35·95	36·34	per cent.
Lithium bicarbonate	0·39		
Sodium sulphate	42·03	45·28	”
Potassium sulphate	3·25		
Sodium chloride		18·16	”
Sodium fluoride		0·09	”
Sodium borate		0·07	”
Silica	0·03	0·04	”
Ferric oxide	0·01		

A litre of the water yields 5½ grams of salts; they form a pure white very fine powder, containing very little moisture and no water of crystallisation. It is very soluble in water; a heaped-up tablespoon (about 5½ grams) dissolved in a wine bottle (litre) of water, gives approximately the concentration of Carlsbad-spring water.

The author recommends the following proportions for the artificial preparation of the salt, the other ingredients having no therapeutic value in his opinion.

Sodium bisulphate 100 parts, sodium bicarbonate 80 parts, sodium chloride 40 parts. The German Pharmacopœia gives 44, 36, and 18 parts respectively of these ingredients, besides 2 parts potassium sulphate. 6 grams of this mixture should be dissolved in 1 litre of water. D. A. L.

Bauxite. By A. IVAN (*Chem. Centr.* [3], **13**, 575—576).—The author does not consider French bauxite superior to the Austrian. The former in the crude form contains 43 to 64·5 alumina, 1·5 to 40 ferric oxide, 0·0 to 0·45 chalk (calc. carb.), 4 to 38 silica and titanic acid, and 11 to 16 water.

The practical value of bauxite depends on the high amount of alumina in proportion to the silica; it is this which, after ignition, makes it hard and fire-resisting. Ignited bauxite constitutes artificial emery, which differs from the natural only in its containing less iron, which constituent can be extracted by acids from the former, but not from the latter. Natural bauxite should be exposed for 3 or 6 months to weathering influences, and should then be treated with hydrochloric acid to remove iron. As a powder, it does not bind readily, and also contracts considerably when heated to redness; to overcome the former defect it is mixed with some sort of cement, whilst the latter is remedied by mixing it with burnt bauxite powder (artificial emery). For the preparation of fire-resisting material it is mixed with fire-clay; for grindstones or millstones with clay; mixed with dolomite or magnesite, it forms an extremely solid and hard fire-resisting material. It may also be mixed with silicates, borax, lime, metallic chlorides, gypsum, &c. Besides the uses already mentioned, it may be used for plastering, for roofs, for all kinds of crushing, grinding, or polishing stones, &c., for tiles, fire-bricks, retorts, crucibles, and such like, and in several chemical industries. D. A. L.

Calcination of Alunite. By P. GUYOT (*Compt. rend.*, **95**, 1001—1003; compare this vol., p. 250).—When powdered alunite is roasted, the free alumina first loses its water and thus becomes soluble in acids. The alum and basic aluminium sulphates require more prolonged heating to render them soluble in water. The best results are obtained with about three hours' roasting at a temperature of 800°. Under these conditions there is a minimum loss of alumina rendered insoluble in acids by the action of heat. C. H. B.

Glass, Enamels, Porcelain, Stoneware, and Refractory Clays. By G. WAGENER (*Dingl. polyt. J.*, **246**, 30—37, and 84—90).—*Composition of Porcelain Enamels.*—In former communications (Abstr., 1882, 563 and 1245), the author mentioned that enamels which fuse at the temperature of the porcelain or Bohemian glass furnace, are of a neutral character, and consist of the silicates $K_2(Na_2)O,6SiO_2$, $Ca(Ba)O,2SiO_2$, $Mg(Fe,Mn,\&c.,)O,SiO_2$, $Al_2O_3,3SiO_2$, $K_2(Na_2)O,5SiO_2$, and CaO,SiO_2. This opinion has been confirmed by the analysis of many enamels which contain practically the theoretical amount of SiO_2 for the formation of these compounds. The relative amounts of these silicates are capable of much variation, the quantity of alkaline silicate, however, must be sufficient to completely fuse the mixture into a shining transparent mass without traces of devitrification. Porcelain may be considered as a difficultly fusible glass, being rendered opaque by the presence of crystalline or non-crystalline substances, such as $Al_2O_3,2SiO_2$, $Al_2O_3,3SiO_2$, and Al_2O_3,SiO_2. The first refers to the Meissen, Sèvres, and Parian wares, containing 23—35 per cent. Al_2O_3 and 64—77 per cent. $Al_2O_3,2SiO_2$; they require a high temperature, and only yield glass with the greatest difficulty. The author calls these alumina-porcelain. The second series, comprising Berlin and similar porcelains, consists of glass free from alumina 25 per cent.; $Al_2O_3,3SiO_2$ 73 per cent.; and free silica 2 per cent. It is more easily fusible than the former, and owing to the difficulty of separating the enamel and mass, Berlin porcelain vessels will resist sudden and extreme variations of temperature without cracking on the surface. This type the author proposes to call glass or silicate-porcelain. Bohemian and Japanese, as well as most of the porcelains of commerce, belong to the third group; they contain an excess of SiO_2, can be burnt at lower temperatures, and may be called silica-porcelain. The composition of stoneware closely resembles that of silica-porcelain, but the coloured varieties are different.

In conclusion, the author tries to establish a method for determining the degree of refractoriness to heat shown by various earths from their chemical composition. As the compounds $Al_2O_3,3SiO_2$, $Al_2O_3,2SiO_2$, and Al_2O_3,SiO_2, are only fused with difficulty, the proportion of these to that of the other silicates present, gives some indication as to the refractoriness. D. B.

Weather-proof Cement Work. By C. PUSCHER (*Chem. Centr.* [3], **13**, 573—574).—An object is soaked for 24 hours in solution of ferrous sulphate (1 part in 3 of water), and then dried in the air. The ferric oxide produced is chemically combined in the cement, and makes it denser, harder, heavier, and weather-proof, filling up most of the pores, and giving it an ochre colour. Ornamental cement work is brushed over with the solution four times, and allowed to dry. The cement work can be rendered extremely resisting by warming and then coating with a hot mixture of equal parts of paraffin and paraffin oil. By treating twice with a 5 per cent. soap solution, drying and polishing, the surface is made efficient for oil painting. Chalk objects and room walls treated in this manner will stand any amount of washing. Light ochre colour can be obtained by adding alum to the ferrous sulphate; and various shades of green by painting with chrom-alum. D. A. L.

Application of Electricity in Metallurgy. By F. FISCHER (*Dingl. polyt. J.*, **246**, 27—30).—The successful application of thermo-

electricity for the determination of metals suggested its use for metallurgical purposes. Thus, Bunsen (*Annalen*, **82**, 137 and 128, 154) prepared magnesium electrolytically from magnesium chloride, by the aid of his zinc-carbon elements, whilst for the preparation of magnesium by means of sodium, Sonstadt (*ibid.*, **170**, 115; **174**, 439) recommends the use of the double salt $KMgCl_3$, the metal being subsequently purified by distillation in a current of hydrogen. For a similar purpose, Reichardt (*ibid.*, **176**, 141, and **188**, 74) uses the mineral carnallite, and other investigators tachydrite, the former being specially suitable for the electrolytic preparation of magnesium. The production of aluminium, according to Bunsen (*ibid.*, **133**, 273), by electrolising the double chloride of sodium and aluminium, melting at 200°, is of great importance. The practical difficulty of separating the deposited aluminium from the saline mixture is said to be surmounted by properly regulating the temperature; it is moreover essential to use vessels made of lime or magnesium, where possible, as aluminium absorbs silicon from clay vessels, and is rendered brittle.
D. B.

Toughened Glass. By T. Lubisch (*Chem. Centr.* [3], **13**, 687).—In this process the red hot object is dipped into a warm bath, consisting of water and starch, or gum, kept at 100°, and is taken out again when the red glow has almost gone; it is then allowed to cool in an oven, kept at a slightly lower temperature than the object. Any glass object can be treated by this method; and the glass can be cut by a diamond or ground, &c., with sand, and is quite as tough as glass prepared by the "oil-process." D. A. L.

Bromine Amalgamation Process. By H. Arnold (*Dingl. polyt. J.*, **246**, 154).—The silver in combination with sulphur, antimony, and arsenic is converted into silver bromide by means of bromine. The pounded ore is heated with steam in closed pans, and after the addition of bromine, the action is continued for a few hours. The mixture is then subjected to amalgamation by the usual pan or vat process. Experiments made at Leadville gave a yield of 82 per cent. silver, whilst by the ordinary amalgamation process only 46 per cent. is obtained. This process is said to be specially suitable for ores containing both silver and gold. D. B.

Roasting of Zinc-blende and Neutralisation of the Evolved Gases with Calcium Sulphide Solution. By Kosmann (*Chem. Centr.* [3], **13**, 668).—In certain blends which contain as much as 20 per cent. of sulphur, it is not advisable to absorb the sulphurous anhydride evolved in roasting by Schnabel's process with zinc oxide, for then 25 parts of ore would require 12½ parts of zinc oxide, rendering the process too costly. A better method is to send a spray of calcium sulphide solution into the gases from the furnace by means of steam under 5 atmospheres pressure; in this way from 50 to 58 per cent. of the sulphurous anhydride is absorbed. With improved appliances better results may be obtained. It is recommended first to absorb the sulphurous acid by Freytag's method by sulphuric acid, and then to treat with calcium sulphide. D. A. L.

Roessler's Method for the Separation of Gold, Silver, Lead, and Copper from Sulphides by Air-blast. (*Chem. Centr.*, [3], **13**, 543.) The sulphides are melted in a graphite crucible in a blast furnace; by means of a suitable arrangement of tubes air is blown on to the surface of the molten mass; the sulphur burns off as sulphurous anhydride (which is converted into sulphuric acid), and a mixture of gold and silver is precipitated and removed in the first place; by further treatment an alloy of copper and silver, or lead and silver. These simple alloys are treated in the usual manner for the separation of the metals. Complicated alloys are mixed with an excess of sulphur, and treated as sulphides. This process may be used for the extraction of lead or copper from sulphurous ores, and in fact for many purposes. A blast furnace is not positively necessary, any suitable arrangement will do. Any volatile metals or products can be collected in a cooling chamber. D. A. L.

Separation of Copper from Lead by Refining in Freiberg. (*Chem. Centr.* [3], **13**, 570—571.)—The first separation is by the Pattinson process, a lead of the composition "*a*" yielding 5·1 per cent. of dross of the composition "*b*."

	Ag.	Pb.	Cu.	Bi.	As.	Sb.	Sn.
a ..	0·544	—	0·940	0·066	0·449	0·82	0·21
b ..	0·17	62·40	17·97	—	2·32	0·98	0·04

	Ni and Co.	Fe.	Zn.	S.	O.	Slag, &c.
a	0·055	0·027	0·022	0·2	—	—
b	1·09	0·43	0·07	4·0	1·87	8·66

The dross is fused with borax, by which means a regulus consisting of three layers is obtained, containing respectively per cent.—

	Ag.	Cu.	Pb.	Ni.	As.	S.
c	0·34	1·79	96·50	0·08	0·75	—
d	—	37·60	25·68	8·60	27·0	—
e	—	47·70	32·80	0·25	1·15	17·72

The author is of opinion that the separation of the copper depends on the amount of sulphur and arsenic with which it combines, and not on the formation of a lead-copper alloy. D. A. L.

Modification of the Hunt-Douglas Process for the Extraction of Copper. (*Chem. Centr.*, **13**, 684—686.)—By the Hunt-Douglas process about two-thirds of the copper is extracted as cuprous chloride, thereby greatly diminishing the amount of iron required for its precipitation, whilst the remaining third is in the state of cupric chloride: theoretically therefore the amount of iron required to precipitate a given weight of copper is only two-thirds that used in other processes, but in practice it is much less, from the absence of ferric salts; moreover, a still further saving of iron is effected by reducing the cupric chloride in solution to cuprous chloride by the action of copper sulphide, and the silver can then be precipitated by metallic copper. The process has its drawbacks however, inasmuch as in treating the ore with the ferric chloride solution, ferric hydroxide is precipitated, which chokes the filter; moreover, before the silver can be precipitated, the whole of the cupric chloride in solution must be reduced to cuprous chloride, which occasions much loss of time; and if the ore is rich in copper, the quantity of liquor in this case is necessarily very large, on account of the sparing solubility of cuprous chloride: Claudet's method of precipitating the silver with an iodide is not applicable, as insoluble cuprous iodide is formed.

In order to overcome these difficulties, Sterry Hunt has modified his process in the following manner:—The copper sulphate solution obtained by extracting roasted pyrites or by the treatment of copper ore with dilute sulphuric acid is mixed with sodium chloride in the proportions of somewhat less than 1 mol. NaCl to 1 mol. $CuSO_4$, sulphurous acid is now passed into the solution, when almost the whole of the copper is precipitated as cuprous chloride, the reaction taking place in two stages, thus:—

$$2CuSO_4 + 2NaCl = CuSO_4 + CuCl_2 + Na_2SO_4;$$
$$CuSO_4 + CuCl_2 + SO_2 + 2H_2O = Cu_2Cl_2 + 2H_2SO_4.$$

The excess of sulphurous acid is removed by some of the prepared copper solution, and after the cuprous chloride has been separated, the dilute sulphuric acid is used for extracting copper from suitable ores or from copper slags. If the ore contains zinc, nickel, or cobalt, these gradually accumulate in the sulphuric acid liquor, and may be recovered when this is rich enough. The cuprous chloride is washed and reduced by iron, or where economical reasons prohibit the use of iron, the cuprous chloride may be converted into the oxide by boiling with milk of lime and then smelted. The ferrous or calcium chloride formed can be used instead of sodium chloride in the treatment of a fresh quantity of copper sulphate solution. The sulphurous acid is obtained by the roasting of pyrites ores.

If the ore contains no silver, it is of no moment whether the sodium chloride is in such proportions as to decompose one-half of the copper sulphate present or more; in the latter case excess of cupric chloride is formed, and on treatment with sulphurous acid, hydrochloric acid goes into solution as well as sulphuric acid. If silver is present, however, this is partly dissolved by the excess of cupric chloride, and is again precipitated with the cuprous chloride, causing the amount of silver extracted from the residue of the ore to be less than it should be.

The advantages of this modification of the process are that the silver is not dissolved along with the copper, no ferric hydroxide is formed, the copper is purer, and the amount of iron used is considerably diminished, less than 50 pounds of iron being required for each 100 pounds of copper produced. The one drawback is the large quantity of sulphurous anhydride required, which is costly when not derived from the ore itself. C. E. G.

Improvements in the Manufacture of Iron. (*Dingl. polyt. J.*, **246**, 99.)—This paper gives an outline of the improvements made in the production of iron during the past 20 years. D. B.

Iron Industry. (*Dingl. polyt. J.*, **246**, 95—99, and 148—152.)—Referring to the preparation of puddled iron of second quality, Tiemann mentions that roasted spathic iron ore is not used, black band, mill furnace-slag, and bog-iron ore being worked very largely, whilst calcareous iron-stone from the oolites of Lorraine is but little used. The Ilseder-Hütte produces pig-iron from the oolitic iron-ores occurring in great abundance in the neighbourhood of the foundry; it is chiefly worked into puddled iron and steel. The following is the composition of the most important of these ores:—

	Fe.	Mn.	SiO_2.	Al_2O_3.	CaO.	MgO.	P_2O_5.
I.	40·78	5·27	10·70	4·76	5·09	0·44	1·2—1·82
II.	43·91	3·68	4·87	1·00	8·96	—	—
III.	30·80	3·40	3·90	1·00	21·61	—	—

The iron industry of Lorraine and Luxemburg has been developed during the last 15 years owing to the abundant occurrence of oolitic calcareous iron-stones belonging to the jurassic formation. These ores contain 26—50 per cent. iron, 0·15—0·6 manganese, 3—22 silicic acid, 2—40 lime, and 0·3—0·8 phosphorus.

Lürmann's form of slag worked in a furnace with closed front (*ibid.*, **194**, 106, 475; **217**, 460), and the introduction of Whitwell and Cowper's apparatus (*ibid.*, **197**, 315; **205**, 98; **229**, 246) may be regarded as novelties in the production of puddled iron.

According to Schilling, the manufacture of spiegeleisen on a large scale was not commenced until the introduction of the Bessemer and Siemens-Martin processes. After discussing the production of spiegeleisen and the progress made in working it, Schilling mentions that for the preparation of spiegeleisen containing a large percentage of manganese (19—21 per cent.) the same process as that for ordinary spiegeleisen is used. The progress made in the German manufacture of specular iron and ferromanganese is due to the improvements in the working appliances, whereby a product of uniform composition is obtained. Hilgenstock discusses the preparation of Bessemer pig-iron for the last 17 years. The following table gives the composition of German Bessemer iron from various localities and at different times:—

	Si.	Mn.	S.	P.	C.	Cu.
January, 1867..........	4·216	6·195	0·029	0·097	—	—
April, 1867............	1·842	3·450	—	0·124	—	—
September, 1868	4·383	6·115	0·045	0·088	2·850 0·550	0·220
October, 1868	3·689	5·970	0·060	0·085	3·217 0·760	0·181
March, 1871	3·800	7·130	—	0·078	—	—
April, 1871............	2·000	10·580	—	0·110	3·500 0·780	0·080

	Si.	Mn.	S.	P.	C.	Cu.
May, 1871	3·218	6·336	0·029	0·065	4·069	—
February, 1872	1·500	2·870	—	0·240	—	—
November, 1873	4·050	5·650	—	0·076	—	—
October, 1874	2·360	3·384	—	0·083	—	—
October, 1874	1·390	4·920	—	0·102	—	—
September, 1875	2·700	7·100	trace	0·090	—	—
November, 1875	2·520	5·810	0·010	0·055	—	0·176
November, 1875	1·990	4·010	0·030	—	—	0·220
September, 1877	1·920	3·890	—	0·085	—	—
January, 1878	2·220	3·370	0·040	0·093	—	0·180

Referring to the preparation of pig-iron according to the Thomas-Gilchrist process, Hilgenstock mentions that not only is the furnace room required less per ton of iron, but the cost of production is much below that of Bessemer pig-iron.

In conclusion, it is stated that, with due regard to the great progress in the iron industry during the last 15 or 20 years, the question under what conditions the largest yield of white iron is obtained from the blast furnace still remains unsolved. D. B.

Influence of Charcoal on the Amount of Phosphorus in Pig-iron. (*Dingl. polyt. J.*, **246**, 101.)—It is well known that iron prepared with charcoal from ores containing small quantities of phosphorus shows a larger percentage of phosphorus than corresponds with the amount in the ore employed. By the use of charcoal, Tamm found that the percentage of phosphorus was increased by 0·01, whilst Särnström recently analysed two samples of wood charcoal containing 0·016 and 0·005 per cent. phosphorus respectively. D. B.

Steel from Pig-iron containing Phosphorus, at Creusot. By Delafond (*Chem. Centr.* [3], **13**, 667—668).—Steel can be readily made from iron containing phosphorus, either in the Bessemer pot or in a reverberatory furnace, by using a lining of lime mixed with magnesia. By this means the phosphorus is got rid of as much as possible; the silica is almost entirely eliminated, and large quantities of the sulphur are driven off. The process is most successful in a reverberatory furnace. This "basic" steel is purer and more homogeneous than "acid" steel, and its tenacity is more uniform than that of the latter. Samples from both show them to be statically and dynamically alike. There are, therefore, two processes for the manufacture of steel—one with acid the other with basic lining. The latter is the best when a reverberatory furnace can be used; in the converter, however, it gives way to the former, for the alkaline coating cannot deal with large quantities of silica. Some of the analytical results are given below:—

Constituents.	Per cent. in crude iron.	Per cent. in "acid" steel.	Per cent. in "basic" steel.
Carbon	3·0	0·40	0·43
Silicon	1·30	0·30	trace
Manganese	1·5 to 2	0·66	0·76
Phosphorus	2·5 to 3	0·075	0·060
Sulphur	0·2	0·040	0·029

	In slag from decarbonising.	In slag from dephosphorising.	Basic lining.
Silica	22·0	12·0	7·7
Lime	47·0	54·0	53·0
Magnesia			35·8
Manganese and iron oxides	11·0	11·0	—
Phosphoric acid	12·0	16·0	—
Sulphuric acid	5·0	5·0	—

D. A. L.

Influence of Sulphur and Copper on the Working of Steel. By Wasum (*Chem. Centr.* [3], **13**, 666).—The author finds that steel is not made red-short, even when it contains as much as 0·862 per cent. copper, besides 0·233 carbon, 0·091 silicon, 0·050 phosphorus, 0·709 manganese, and 0·060 sulphur. Neither do copper and sulphur together make it red-short, unless the amount of the latter is sufficient by itself to do so; 0·1 per cent. sulphur may be regarded as harmless. D. A. L.

Galvanising and Nickeling of Iron in Cleveland, Ohio. (*Chem. Centr.* [3], **13**, 541—542.)—The sheets of iron are washed in dilute sulphuric acid, and then with water; any inequalities are thus removed, and the plates are immersed in ordinary hydrochloric acid, after which they are dried in a hot oven. The zinc is melted in a large iron pan, along the middle of which an iron screen is fixed, so that it just dips into the bath and extends about 3 inches above the rim; the surface of the zinc is thus divided into two sides—in the one is placed ammonium chloride, in the other wet sand. The iron plates hot from the oven are dipped one at a time perpendicularly into the ammonium-chloride side, and are pushed under the iron screen into the other side, whence they are drawn out by tongs and pulleys. Drops of zinc are removed by touching with an iron rod. When they are completely removed from the bath, the sand is wiped off and the plate is finished. The nickeling is conducted in wooden tanks lined with asphalt; the solution used consists of $\frac{3}{4}$ lb. nickel-ammonium sulphate dissolved in 1 gallon of water. The object to be nickeled, after it has been made *perfectly* clean by washing respectively with potash and dilute hydrochloric or sulphuric acid and scouring with pumice-stone, is suspended in the bath by means of thin iron wire from a copper bar which is connected with the negative conductor of a dynamo-electric machine, whilst from another copper bar, connected with the positive conductor, a nickel plate is suspended in the bath, care being taken that the nickel plate does not touch the object. After 10—15 minutes under the influence of the current, the object becomes sufficiently nickeled, and is withdrawn, washed first with cold and then with warm water, and subsequently well dried. Care must be taken to regulate the current, as if it is too strong the deposited nickel will be dull, whilst if it be too feeble the deposit will be granular. The polisher is a disc of wood covered on the surface with a piece of leather which has been immersed in thin lime-water, rolled in emery powder, and dried. D. A. L.

Argentine. By C. Pascher (*Chem. Centr.* [3], **13**, 540).—Argentine is reduced tin used for stamping fabrics and paper. A very dilute—60 litres of water to 120 grams of the salt—and strongly acid solution of a tin salt is reduced by metallic zinc, and the spongy tin is collected, without pressing, on a sieve, well washed with water, and dried at a gentle heat. It is then rubbed fine in a pestle, put through a hair sieve under water, and mixed with the necessary quantity of starch-paste, when it is ready for use. The same water may be used several times for the solution and precipitation, and the zinc chloride solution when sufficiently concentrated may be used for soldering, or to clean iron ware before tinning. Finely divided antimony can be prepared in a similar manner. To tin metals, except lead, the precipitated tin, without starch, is stirred into a hot concentrated solution of ammonium chloride to a magma, and this is spread on the metal, which is then heated until the tin melts; in about a minute the tinning is complete, and the article is washed with water and polished with chalk. By using a mixture containing from 5 to 10 per cent. of the precipitated antimony, and 5 per cent. of ammonium chloride, along with the argentine made into a magma with water, a white covering of Britannia metal can be obtained. Zinc goods may be tinned by painting with concentrated solutions of tin-salts containing 5 per cent. ammonium chloride, then drying and heating until the reduced tin fuses, and so on until the tinning is complete, which is rendered evident by a grey instead of a bright deposit forming. A mixture of zinc-dust, tin, and ammonium chloride may be used for tinning iron. D. A. L.

Application of Aluminium Palmitate. By K. Lieber (*Dingl. polyt. J.*, **246**, 155).—Basic aluminium palmitate has the property of thickening ethereal or fatty oils, and has therefore been recently used for chemical cleaning and for the preparation of lubricators. As a cleaning agent it facilitates the application of benzene, prevents its rapid volatilisation, and decreases the risk of fire. It forms an excellent material for converting easily melted lubricating oils into solid lubricators at a small cost, and that without affecting the lubricating property of the oil. D. B.

Preparation of Thiocarbonates for the Destruction of Phylloxera. By F. Sestini (*Gazzetta*, **12**, 476—482).—The use of potassium thiocarbonate as a remedy against phylloxera is preferable to that of free carbon bisulphide, inasmuch as the latter is very injurious to the vine itself, but the high price of the potassium salt has hitherto stood in the way of its extensive application. Various cheaper substitutes have, however, been proposed, and the author of the present paper recommends a mixture of the thiocarbonates of potassium and calcium, prepared by agitating together in a reflux apparatus at the temperature of 60° C., 200 g. CS_2, 200 K_2CO_3, 1000 water, and 200 quick-lime previously slaked with 100 g. water. After agitation for 10 hours the liquid is left to cool, and is then found to contain 1050 g. K_2CS_3, holding in combination 80 g. CS_2 and 650 g. CS_2 containing 150·55 g. combined CS_2. The product is pasty and may be kept in earthen jars and transported in wooden casks, like those used for the carriage of petroleum. The cost of preparing 100 kilos. solution of K_2CS_3 containing 8 per cent. CS_2 and 65 kilos. $CaCS_3$ containing 10·7 per cent. CS_2, is 25 lire (= 16*s*. 8*d*.). H. W.

New Dyes. (*Dingl. polyt. J.*, **246**, 200—201.)—By the action of diazo-compounds on resorcinol and its homologues, compounds of the general formula $R.N_2.C_6H_3(OH)_2$ are obtained, from which by the further introduction of a diazo-group, compounds of the formula $R.N_2.C_6H_2(OH)_2.N_2.R$ can be produced. They form anhydrous yellow and brown dyes.

For the preparation of azo-dyes from methylnaphthalene, the latter is converted into amidomethylnaphthalenesulphonic acid, and then into the corresponding diazo-compound. By the action of β-naphthol and its sulphonic acids on this, dyes are obtained. Yellowish-red dyes can also be obtained from methylnaphthalene by converting it into methylnaphthol, and acting on this with diazosulphanilic acid, diazonaphthalenesulphonic acid, or with amidoazobenzenedisulphonic acid. Methylnaphtholsulphonic acid gives red dyes with the diazo-compounds of the hydrocarbons.

A blue dye is obtained by heating methyl orange with an excess of hydrogen ammonium sulphide at 105—110°, and subsequent oxidation of the product with ferric chloride. A. K. M.

Meat Extract from South America. By NIEDERSTADT (*Arch. Pharm.* [3], **20**, 580—582).—Extract of meat prepared under Liebig's directions has been followed by various similar preparations; the sample examined by the author is from St. Elena, in the Argentine Republic, an establishment under the direction of Dr. Kemmerich. The extract has a fine meaty smell, and the taste of freshly roasted meat; it dissolves in water to a clear brown liquid, and is free from fatty and gelatinous matters, which the author believes assists its keeping properties. The nitrogenous and proteïn matters consist of creatine, syntonine, sarcosine, fibrin, &c., and, in the author's opinion, directly available for the formation of blood, muscle, and nerve substance. Analyses by three chemists are given.

	Fresenius.	Bischoff.	Niederstadt.
Organic matter	61·13	62·42	66·07
Inorganic (ash)	20·99	20·69	20·08
Moisture	17·88	16·89	13·85
Nitrogen	9·55	8·30	8·02
Fat and gelatin	absent	absent	absent
Soluble in alcohol	68·43	72·98	69 60
Insoluble in alcohol	—	—	16·55

Composition of Ash.

Ferrous oxide	trace	0·22	0·32
Lime	0·43	0·52	1·76
Magnesia	2·86	3·89	2·03
Soda	11·63	11·51	11·32
Potash	44·26	41·79	44·04
Chlorine	8·34	9·46	8·36
Sulphuric acid	1·77	1·54	1·62
Phosphoric acid	32·35	32·55	32·12
Silicic acid	0·24	0·82	0·31
	101·88	102·30	101·88
Deduct oxygen for chlorine	1·88		1·88
	100·00		100·00

J. F.

American Storax. By F. A. Flückiger and W. v. Miller (*Arch. Pharm.* [3], **20**, 646—648, and 648—651).—Flückiger considers that the storax from Asia Minor is identical with that from the Mexican *Liquidambar styraciflua*, but when growing in the United States the tree does not give so good a yield. The gum then appears in the market as "sweet gum," is mixed with benzoic acid, and is harder than the ordinary *Styrax liquidus.* Miller has made analyses of American storax, and found it to contain a styrolene, whose bromine compound melted at 73°; besides the styrolene, oxygenated compounds were present, viz., styracin and phenylpropyl cinnamate. E. W. P.

Alteration of Syrup of Tolu. By Malenfant (*J. Pharm.* [5], **6**, 466—473).—Syrup of tolu, when prepared by heating the balsam with water for four hours in the water-bath, is perfectly odourless at first, but after a time acquires a benzene-like odour. The author shows by experiments that this is due to the decomposition of the ethereal cinnamates present, these yielding first cinnamic acid, which is then further decomposed into cinnamene and carbonic anhydride. Cinnamic acid when boiled either with distilled or with ordinary water for several hours, shows no sign of decomposition, but if left at rest for a month or six weeks, it acquires the persistent odour above referred to. If, however, the acid is simply left in contact with *cold* water for the same time, without previous boiling, no alteration takes place. E. H. R.

Adulteration of Cochineal. By J. Löwe (*Dingl. polyt. J.*, **246**, 90—92).—According to the mode of killing the insect, cochineal is found in commerce either in the form of white dusty or of brownish-black shining granules. Both qualities are often adulterated to a considerable extent, the former, however, being more generally adulterated. The addition of mineral matter is detected by an ash determination, real cochineal containing not more than 0·5 per cent. In order to retain their natural appearance, samples of cochineal when adulterated are exposed to the action of moist air, whereupon they swell up and become sticky. The adulterant is then dusted over the granules in quantities of 10—12 per cent. After re-drying, the original appearance returns, and without chemical investigation it is impossible to distinguish these samples from the natural colouring matter. D. B.

Prevention of Boiler Incrustation. By Baudet (*Chem. Centr.* [3], **13**, 576).—A mixture of 15 pts. sodium thiosulphate, 10 pts. rain-water, and 10 pts. glycerol, is added to the water.

D. A. L.

Liquid Carbonic Anhydride as a Fire Extinguisher. By W. Raydt (*Chem. Centr.* [3], **13**, 671—672).—The author's apparatus consists of an iron cylinder filled with liquid carbonic anhydride, and a large water vessel which is connected with the carbonic anhydride reservoir in such a way that the gas when set free must pass through and force out the water, and thus a solution of carbonic anhydride can be directed on the fire. It has been found efficient. Liquid carbonic anhydride occupies 450 times less space than the gas, therefore a 100-litre cylinder would hold 45,000 litres of carbonic acid gas.

D. A. L.

Analysis of Petroleum-coke. By A. Lidoff (*Jour. Russ. Chem. Soc.*, 1882, 323—324).—In the manufacture of gas for lighting purposes by distillation of crude petroleum, a peculiar kind of hard, very difficultly combustible glistening coke of a steel-grey colour is found in the retorts. Its sp. gr. is 1·829. This coke has the following percentage composition:—Water (hygroscopic) = 0·24 per cent., hydrogen = 0·65, carbon = 94·27, ash = 4·52. The ash contains in 100 parts:—

Fe_2O_3.	CaO.	SiO_2 (sand).
76·71	5·48	15·07

besides a little soda and carbonic acid. From these data it will be seen that this coke is purer, denser, and less combustible than ordinary coke from coal, and the author recommends it for the manufacture of carbon electrodes, especially for electric lighting purposes. The presence of ferric oxide is due to the corrosive action of petroleum vapour at high temperatures on the cast-iron retorts. B. B.

General and Physical Chemistry.

Electromotive Force of a Daniell's Element. By E. KITTLER (*Ann. Phys. Chem.* [2], **17**, 865—897).—In the introduction, the author remarks on the uncertainty arising from the use of a Daniell's element as the unit of electromotive force (E.M.F.), on account of the various components, as dilute sulphuric acid, zinc sulphate, or the chlorides, used for its construction. The researches of Fromme and Svanberg tend to establish that the E.M.F. of the combination $Zn|ZnSO_4|CuSO_4|Cu$ increases with dilution of the zinc sulphate, but decreases with concentration of copper sulphate; but, on the other hand, those of Baumgartner appear to show that the E.M.F. decreases with the proportion of copper sulphate. Again, Poggendorff, Svanberg, and Baumgartner have shown that in the combination $Zn|H_2SO_4|CuSO_4|Cu$, the E.M.F. is increased in proportion to the strength of the acid, while J. Thomsen finds precisely the reverse. The E.M.F. of a Daniell's element is a function of the difference of potential of the liquids at the point of contact, which varies according to the concentration of one or the other liquid. As then in the combination $Zn|ZnSO_4|CuSO_4|Cu$ solutions of two salts come in contact, which would follow Volta's law as regards the difference of potential, yet in the combination $Zn|H_2SO_4|CuSO_4|Cu$ the difference of potential is dependent on the chemical and heat changes involved.

For the measurement of the E.M.F., the author used an Edelmann's cylinder quadrant electrometer, the aluminium needle of which was charged by a Zamboni's dry pile. Instead of the ordinary clay cells, the author used a glass syphon, bent at right angles, and terminating in a capillary tube, so that only small surfaces of the different liquids came in contact. The copper and zinc used were chemically pure, and the strength of the acid and salt solutions were determined by their specific gravities and by analysis.

The normal element used consisted of zinc in sulphuric acid of sp. gr. = 1·075 at 18°, and copper in concentrated copper sulphate solution of sp. gr. 1·19, the E.M.F. of which was shown to be constant during 6—8 hours, and decreased only 0·6 per cent. after 20 hours. Further, no change was observed with a variation of 6·5 degrees. The E.M.F.'s of the Latimer Clark cell (the English unit), the normal cell, and the cell $Zn|ZnSO_4|CuSO_4|Cu$, stand in the relation 886 : 1000 : 1217; but the normal cell has the advantage over the Latimer Clark in being more independent of the temperature.

The author made a long series of experiments to ascertain the dependence of the E.M.F. of the Daniell's cell on the degree of concentration of the acid. Solutions were used varying from sp. gr. 1·357, to that containing one drop of sulphuric acid of sp. gr. 1·075 in a litre of water.

The tabulated results show that the E.M.F. of a Daniell's element, in which the copper is surrounded by a concentrated copper sulphate solution, increases with the proportion of the sulphuric acid, up to a certain limit; the maximum value corresponded to a sp. gr. 1·186—1·222 (25—30 per cent. H_2SO_4), above which the E.M.F. decreases. The author explains the sudden decrease of E.M.F. in the case of the more concentrated acid by the increased dissolution of the zinc, and the formation of zinc sulphate. Experiments, in which the concentration of the acid was varied as before, and also the strength of the copper sulphate solution, established that the E.M.F. increases with the degree of dilution of the copper sulphate solution, and is at its maximum when the copper is surrounded with pure water. (Thus the E.M.F. of a cell of $Zn|H_2SO_4$ sp. gr. = $1·076|H_2O|Cu$ is to the E.M.F. of the normal cell in the ratio 1076 : 1000.) This, however, holds good only for concentrated acid; with dilute acid, the E.M.F. decreases with the degree of dilution of the copper sulphate solution. Hence there exists a degree of concentration of the acid for which the E.M.F. of the Daniell's cell is the same, whatever be the strength of the copper sulphate solution; this acid is of sp. gr. = 1·0011 at 16°, and consists of 750 c.c. H_2O and 100 c.c. H_2SO_4 of sp. gr. = 1·007. The author made observations of change of E.M.F. of various elements with the time of contact, which proved that with the same time of contact the E.M.F. decreases the more rapidly the more dilute the copper sulphate solution, and the stronger the acid. The E.M.F. of the ordinary Daniell's cell is somewhat less (1000 : 940) than that of the author's normal cell, and this difference is traced by experiment to the use of the clay cylinder; the E.M.F. also decreases much more rapidly, for even after 20 minutes' contact, a difference of 1·0 per cent. was observed. The substitution of a copper cylinder for the copper plate had no effect, but an amalgamated zinc cylinder, instead of chemically pure zinc, caused a great decrease of E.M.F.

The E.M.F. of the normal cell is equal to 1·195 volts, or in absolute units = $1·195 \times 10^8 M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}$; the E.M.F. of the cell $Zn|ZnSO_4|CuSO_4|Cu$ = 1·089 volts; the E.M.F. of the Latimer Clark = 1·437 volts; and the E.M.F. of the ordinary Daniell's cell = 1·14 volts. In a note the author adds some results obtained with the combination of amalgamated zinc, sulphuric acid, and copper. These show that the E.M.F. of this cell increases at first rapidly with concentration of the acid; then slowly until it reaches a maximum, which corresponds to the same degree of concentration of acid as that used in the normal Daniell element. The E.M.F. of the former then stands to that of the latter in the ratio 929 : 1000, but this varies according to the quality of the copper. V. H. V.

Galvanic Polarisation. By F. STREINTZ (*Ann. Phys. Chem.* [2], **17**, 841—858).—In the course of some experiments on the decomposition of water by the Leyden jar discharge, the author was led to a study of galvanic polarisation. As a result, it is proved that the difference of potential between a platinum electrode covered with hydrogen and an electrode free from gas undergoes a reversal after a short time. This phenomenon can be observed in the case of other metals as palladium, platinum, gold, silver, and aluminium. In the course of his memoir, the author observes that two strips of platinum, although cut from the same piece of foil, are not electrically indifferent when placed in acidulated water; this difference of potential is practically unaltered by heating the strips in a flame, or in boiling acid. Again, if one strip is heated in the flame or acids, or in an electric circuit, it becomes electro-negative to a strip which has not been so treated. The same observations hold good in the case of platinum and palladium. From the tabulated results, the following conclusions are arrived at:—

(1.) The E.M.F. of hydrogen polarisation is dependent on the nature of the electrode; it is largest for gold, and smallest for aluminium (Fromme).

(2.) The values for the E.M.F. are characteristic for each metal, and vary with its nature. In all cases there is a great decrease of E.M.F. immediately following the breaking of the circuit. But if opportunity is afforded to the hydrogen-occluding metals of taking up a larger quantity of gas, the decrease of E.M.F. is only about 15 per cent. of the initial value; the percentage loss for gold and silver is far greater, and aluminium loses all its E.M.F. In the next place, the value for the E.M.F. for palladium remains the same, but decreases in the case of other metals. Aluminium plates show a reversal of electric condition on breaking the circuit, after it has been closed for a long or short time; but this phenomenon occurs with platinum or palladium only after a short close of the circuit.

Experiments are described in which a current from four Daniell cells was passed through a voltameter with palladium electrodes. Immediately after the closing of the circuit, a rapid evolution of oxygen took place from the anode, while not the smallest trace of hydrogen was evolved from the kathode. After some time bubbles appeared, and subsequently increased. On breaking the circuit, the evolution of oxygen ceased at once, but that of the hydrogen decreased gradually, and had not entirely ceased after the lapse of half an hour. These observations offer an independent confirmation of Graham's experiments. If the palladium kathode is made the anode, the evolution of gas ceases and no difference of potential can be observed. On increasing the electric current, gas bubbles are formed at the anode, and the increase of oxygen polarisation increases, while that of the hydrogen decreases. On breaking the circuit, the oxygen polarisation rapidly disappears, and gives way to the hydrogen polarisation. The author explains these phenomena by supposing that the oxygen evolved from the surface of the pole is burnt with the hydrogen, also at the surface of the plate. Subsequently the hydrogen inclosed in the inner layers of the metal reaches the surface and is there burnt. If the process is interrupted, the remaining hydrogen molecules cause the decrease of the oxygen polarisation, and consequently the increase of the hydrogen polarisation.

In some further experiments, the author shows that the smaller the resistance offered by the circuit, the greater, the difference of potential between the electrodes. As the oxygen polarisation increases with decrease of resistance, it appears that the electrolysing circuit gives up some of its energy to the voltameter. This would necessarily follow from the separation of water into oxygen and hydrogen, in accordance with Joule's law. V. H. V.

Amalgamation Currents. By H. HAGA (*Ann. Phys. Chem.* [2], **17**, 897—901).—The researches of Moser on the electric currents produced by the amalgamation of zinc led Obach to examine whether such currents were not thermo-electric currents due to a change of temperature accompanying the amalgamation. Exner has, however, remarked that Obach's experiments were not decisive; for either the sum or the difference of the thermic and the amalgamation current might have been observed. The author has re-examined the question with a form of apparatus which permitted the measurement at once, of a change of temperature by a thermo-electric needle, and of a comparison of the current produced with a possible amalgamation current. If the observations by these methods agreed, then there is no amalgamation current proper, but only a thermo-electric current due to the change of temperature involved. This was found to be the case, thus offering a confirmation of Obach's original suggestion.

V. H. V.

Electricity of Flame. By J. ELSTER and H. GEITEL (*Ann. Phys. Chem.*, **16**, 711).—Referring to a former communication (*ib.*, **16**, 193), the authors state that Hankel's views on the electricity of flames, published in 1859, but only recently come to their knowledge, have been confirmed by their experiments, which show that galvanic elements may be formed of heated gases and metals, without the use of flame.

R. R.

Actinoelectric and Piezoelectric Properties of Quartz, and their Relation to the Pyroelectric. By W. G. HANKEL (*Ann. Phys. Chem.* [2], **17**, 163—175).—The author has previously observed the direct transformation of light into electricity in quartz, a phenomenon which he calls *actinoelectricity* (cf. Abstr., 1880, 838), as distinguished from *pyroelectricity* or the transformation of heat into electricity. J. and P. Currie have observed that in the case of hemimorphous crystals, increase or decrease of pressure in the direction of the hemimorphous axes causes a difference of potential at the ends of the axes. This phenomenon the author proposes to call *piezoelectricity*. In the present communication, the author discusses these several phenomena in relation to the crystallographic habitus of quartz.

Pyroelectricity.—The author has made a series of observations on the difference of potential caused by heating an edge or surface of a quartz crystal in a miniature oven to 120°; he shows that the crystals have generally three polar electric axes, viz., the three secondary axes of the crystals. Those ends of the axes which terminate in rhombi or trapezia are the positive poles, whilst the opposite ends are negative, if the temperature of the crystal is falling, but with rise of temperature the electro-polarity is reversed. In perfectly normal crystals, both ends of the primary axes are positively electrified.

Actinoelectricity.—If the rays from the sun, or electric light, or a flame be made to traverse a quartz crystal, then all the six edges are electric poles, alternately positive and negative according to the direction of the light rays. Thus, one end of every secondary axis is positively, the other negatively electrified; and in this respect the phenomenon of actinoelectricity resembles pyroelectricity.

At the commencement of the radiation, the increase of potential difference is greatest, but it diminishes in the course of time, as shown by the following experiments:—

Time after commencement.	Potential difference.
5′	+ 18·7
10	+ 28·5
15	+ 34·5
20	+ 37·5
25	+ 39·5
30	+ 41·0

On removal of the source of radiation, the actinoelectricity disappears again at first quickly, then slowly. The radiation from the electric light causes a difference of electric potential seven times greater than that caused by a fish-tail burner at the same distance; the effect of the sun in May is equal to that of a flame at 244 mm. distance from the crystal.

Piezoelectricity.—If pressure be exerted in the direction of the secondary axes, their ends which terminate in rhombi or trapezia show negative electricity on increase of pressure, but positive with decrease of pressure. By these facts the connection between the phenomena of pyro-, actino-, and piezo-electricity is brought out, and also their relation to the crystallographic axes. V. H. V.

Electrical Energy and Chemical Action. By F. Braun (*Ann. Phys. Chim.* [2], **16**, 561—593).—The paper describes an investigation instituted to test the truth of W. Thompson's theory, according to which the chemical energy, or heat of combination, due to the action in a galvanic battery, is wholly converted into electrical energy. The author's conclusion is that a part only of the heat of combination is transformed into current energy, the rest remaining in the cell, and forming part of what has been regarded as heat due to secondary actions. He asserts also that certain galvanic elements, from which polarisation is absent, supply more electricity than the equivalent of the heat due to their chemical actions. He likewise refers to cases in which endothermic chemical actions may produce galvanic currents, and thus constitute another difficulty for Thompson's theory. The values of the fractions representing the maximum electromotive effect of certain combinations are stated in the paper; thus, for example, only 83 per cent. of the heat of the combination $ZnSO_4$, and 68 per cent. of that of $CuSO_4$, can possibly be transformed into electrical energy. R. R.

Specific Conductivity of Sulphuric and Pyrosulphuric Acids, and the Specific Gravity of Concentrated Sulphuric Acid. By W. Kohlrausch (*Ann. Phys. Chem* [2], **17**, 69—85).—The author draws attention to the interest attached to determinations of the specific conductivity of mixtures of water and sulphuric acid, as offering starting points for conclusions on the dependence of electric conductivity on temperature coefficients, viscosity, chemical constitution, temperature of solidification, &c.

Experiments in elucidation of these points have previously been made by F. Kohlrausch and Grotian; the former of whom came to the conclusion that the hydrates, $2H_2O,SO_3$ and H_2O,SO_3, correspond with the minima of specific conductivity. In order to decide the question, the author has examined the specific conductivity of sulphuric acid of various degrees of concentration, as a function of its percentage composition and the temperature of its solution.

The method adopted by the author consists in measuring the resistance of a Wheatstone bridge, with alternating currents, the electromotive force being supplied by a battery of four Leclanché's cells; observations were made by a telescope, mirror, and scale on Kohlrausch's electro-dynamometer. The necessary corrections were made for the self-induction of the resistance bridge. The sulphuric acid was contained in glass cells fitted with platinum electrodes, the capillary ends of which were connected with a drying apparatus filled with phosphoric anhydride and calcium chloride; these cells were heated in an oil-bath, the temperature of which was accurately ascertained. Determinations were made of the specific resistance of these glass cells. The percentage composition of the sulphuric acid was ascertained by mixing it with a known weight of water, and determining the composition of the mixture by its sp. gr. or by precipitation with barium chloride. If $k_{18} \times 10^8$ be the specific conductivity of the acid at 18°, deduced from that of quicksilver at 0°, multiplied by 10^8, α the temperature coefficient of the first order, β the coefficient of the second order, then the specific conductivity at the temperature t is represented by the formula $k_t = k_{18}[1 + \alpha(t - 18) + \beta\ (t - 18)^2]$. From the tabulated results, the author concludes that the specific conductivity of sulphuric acid at 18° decreases from 78·37 per cent. SO_3 to 81·43 per cent. SO_3; then increases until it reaches a maximum at 83·3 per cent. SO_3, and from this point again decreases. It does not, however, reach a minimum at that concentration, which corresponds with the constitution of pyrosulphuric acid, but at that of pure sulphuric acid, SO_3,H_2O. *A slight addition either of water* (0·17 *per cent.*). *or of sulphuric anhydride* (0·25 *per cent.*) *to the hydrate* SO_3,H_2O, *increases its conductivity*. F. Kohlrausch has observed that the minimum of conductivity does not strictly coincide with the hydrate H_2O,SO_3; this the author attributes to a partial dissociation of the acid into sulphuric anhydride and water; but the lower the temperature of observation, the less is the error due to the dissociation. The crystallised acid is a very bad conductor, and more perfect crystallisation corresponds with more imperfect conductivity.

F. Kohlrausch's experiments have previously established that the temperature coefficient is dependent rather on the specific conductivity than on the percentage composition of the acid; for the smaller the specific conductivity, the greater the temperature coefficient. The author in the main confirms these results, but remarks that for higher percentage composition the values for α increase when the specific conductivity remains constant.

Most remarkable is the fact that with change of concentration of the acid from 98·75 to 99·75 per cent. H_2SO_4, the value for α increases from 0·028 to 0·04, that of β from 0·0002 to 0·0004, whilst the specific conductivity decreases by about a sixth of its amount. Taking into consideration the fact that the solid acid is practically a non-conductor, that those hydrates which have the highest melting point have the lowest specific conductivity, the conclusion drawn by Wiedemann and Kohlrausch is inevitable, that there is an intimate relation between the viscosity or internal friction and electric resistance.

The author made several determinations of the sp. gr. of sulphuric acid of various degrees of concentration; from his results it follows that the sp. gr. of sulphuric acid reaches a maximum with a concentration of 97 per cent. (sp. gr. = 1·8385), then slowly decreases to a minimum with concentration of 99·5, and from this point again increases.

In a note the author adds some results of the specific conductivity of rain-water collected in the Tyrol, and kept in glass vessels for about four months; the values for $k10^{10}$ varied from 3·3 to 4·1, which differ considerably from that ($k10^{10} = 0·7$) obtained by F. Kohlrausch with water distilled with careful exclusion of glass. The contact with the glass increases its conductivity. V. H. V.

Particles of Matter in the Electric Spark. By F. Wächter (*Ann. Phys. Chem.* [2], **17**, 903—927).—In the spark discharge from statical electric apparatus the author, in conjunction with Keitlinjen, has observed that the surface dissipation takes place from the positive electrode, while on the other hand, the researches of Plücker, Gassiot, and others have shown that under certain conditions the dissipation takes place from the negative electrode. (It is to be observed that no such discrepancy of statement exists with regard to the spark from the current or dynamic apparatus, for all observers are agreed that the stream of particles flows from the positive to the negative electrode.) The object of the present paper is to explain the above-mentioned discrepancy by observations of the conditions on which depend the passage of particles through a gaseous medium from the positive or negative pole, and also of the difference of properties exhibited between these two different electric streams. The author arrives at the following results:—

(1.) The passage of particles from the anode takes place in atmospheric air under pressures of 4500 to 10 mm.; but from the kathode only under pressure of 63 to 0·005 mm.

(2.) The quantity of particles dissipated from the anode in the same time and under the same conditions decreases, but that from the kathode increases with decrease of pressure.

(3.) The particles from the anode are driven off through a wider space than those from the kathode.

(4.) The particles from the anode start from a relatively small surface, independently of the atmospheric pressure; those from the kathode start from a large surface, which increases with decrease of pressure.

(5.) The particles from the anode are separated from that part of the anode which lies nearest to the kathode; those from the kathode are separated from the whole of its surface.

(6.) The separation of particles from the anode is favoured by a constriction or by a pointed shape of the electrode; that from the kathode by a chemically pure or unoxidised surface.

(7.) The direction of the particles from the anode is in the direction of the line of least electric resistance; the direction of those from the kathode is always normal to its surface, and is independent of the position of anode and the direction of the electric current.

(8.) The particles from the anode follow all manner of paths, while those from the kathode move only in a straight line.

(9.) The particles from the anode are diverted by a magnet as diamagnetic substances; those from the kathode resemble paramagnetic substances.

(10.) The particles from the anode are dissipated, not only in the luminous, but also in the non-luminous discharge; those from the kathode only in the non-luminous discharge.

(11.) The quantity of matter dissipated from the anode is measureable, and seems to depend on some mechanical impulse; those from the kathode seem to arise from a process of evaporation.

(12.) Heating the kathode influences most markedly the passage of particles; but the same phenomenon could not be observed in the case of the anode.

(13.) The particles from the kathode bring about the passage of the current from the electrode by the molecules of the gas; but this is not the case with those from the anode.

(14.) The passage of particles from the anode requires a greater difference of potential, and they follow one another after longer intervals than those from the kathode.

All these facts confirm the author's view that the difference between positive and negative electricity is a difference not of quantity, but of quality. V. H. V.

Electric Shadows. By P. RIESS (*Ann. Phys. Chem.* [2], **17**, 901—903).—The author remarks at the outset that no satisfactory explanation has hitherto been given of the electric shadows; he adduces descriptions of some phenomena on which their explanation may be based.

An electrified surface is illuminated in an ordinary atmosphere at those points where there is an opposing electrified air-current; if the interposing body be a conductor, this surface is not illuminated, but there appear upon it shadows, the forms of which are dependent on that of the interposing body and the discharged air-current. If this current be not discharged, but only diverted by a non-conducting air-current, there appear no shadows, on account of the repulsion exerted by a part of the current being sent back in its former direction. When the interposing body is merely an imperfect conductor, the shadows appear or disappear according to the power of the machine. The fact that a conducting strip causes almost the same shadows, whether its surfaces or edges are opposed to the air-current, shows that in either case the amount of discharge is the same, and proves that the quantity of the discharge of an electrified air-current is greater the smaller the angle with which it falls upon the surface of the interposing body. In a rarefied atmosphere a positively electrified surface remains dark before a negatively electrified air-current, and only a negatively electrified surface is illuminated when in contact with a positively electrified air-current. V. H. V.

Specific Heat of Gaseous Compounds of Chlorine, Bromine, and Iodine with one another and with Hydrogen. By K. Strecker (*Ann. Phys. Chem.* [2], **17**, 85—103).—The author has made a series of observations on the specific heat of these compounds in the apparatus and by the method of experiment described in his former paper (Abstr., 1881, 784). In order to arrive at more exact results, the haloïd acids were prepared by various methods, and their purity was carefully ascertained; specimens of iodine mono-chloride and bromide were prepared and purified by fractional distillation. As Löwig found the vapour-density of hydrobromic acid to be 2·71—a number which differs from the theoretical value, 2·8—the author determined its vapour-density at various pressures, the results of which show that at ordinary atmospheric pressures the vapour-density approaches the theoretical value, but that for other pressures it differs in a most marked way from Mariotte's law.

Pressure.	Vapour-density.	Pressure.	Vapour-density.
690 mm.	2·788	216	2·698
622 ,,	2·789	211	2·706
512 ,,	2·795	204	2·708

In the original paper there are tabulated for the above compounds a series of determinations of—

$$K = \frac{\text{specific heat of the gas at constant pressure,}}{\text{specific heat of the gas at constant volume,}}$$

and of the kinetic energy of their molecules; the values obtained are identical, whatever the method adopted for the preparation of the substance.

The author draws the following conclusions:—Gases whose molecules consist of 2 atoms are separable into two groups, the one containing oxygen, nitrogen, carbonic oxide, nitrous oxide, hydrochloric, hydrobromic, and hydriodic acids, the other containing chlorine, bromine, iodine, chlorine and bromine iodides, and probably bromine chloride. The atoms of the molecules of the first group differ from these of the second group in their reciprocal action (cf. *supra*).

V. H. V.

Relation between Pressure and Temperature in the Saturated Vapours of Water and Carbonic Anhydride. By A. Jarolimek (*Monatsh. Chem.*, **3**, 835—837).—Zeuner gives for the relation between the pressure and value of saturated water-vapour the expression $p^{0·93932} \frac{1·650}{v}$ or $pv^{1·0646}$ 1·764). Substituting this expression in Zeuner's equation of condition for aqueous vapour:

$$pv = 0·0049287T - 0·187815p^{\frac{1}{4}}.$$

the equation for the relation between the pressure and temperature of saturated water-vapour becomes—

$$T = 334{\cdot}774p^{0{\cdot}06068} + 38{\cdot}106p^{0{\cdot}25} \quad \ldots . (1),$$

which gives exact results only for pressures between 1 and 8 atmospheres. Compared with the results of Regnault's well-known experiments, the values of T, given by equation (1) for pressures between $p = 2$ and $p = 7$, are too large, while for $p = 0{\cdot}0004$ to 1 and $p = 9$ to 28, they are too small.

The author now proposes a formula which gives very exact results for all values of p, viz., from 0·0004 to 28 atmospheres (and, therefore, between the temperatures −32° and + 230°). This formula is—

$$T = 326{\cdot}7p^{0{\cdot}04233} + 46{\cdot}3p^{0{\cdot}3039} \quad \ldots . (2).$$

He also proposes another formula which gives exact results only for the higher pressures, viz., from 9 to 28 atmospheres, but, on the other hand, has the advantage of great simplicity. Putting $t - 100 = T - 373 = x$; $95 - p = y$ and $94 = r$, this second formula is $x^2 + y^2 = r^2$, which is the equation of a circle, and may also be written in the form—

$$t = 100 + 2\sqrt{94^2 - (95 - p)^2} \quad \ldots . (3).$$

A table is given showing the values of t corresponding with the various pressures as deduced from the formulæ (1), (2), and (3), also those calculated from Zeuner's formula, and those determined by the experiments of Regnault.

If the relation between pressure and temperature be represented graphically, it will be found that the curve for saturated water-vapour likewise holds good for the vapour of carbonic anhydride, provided that, while the degrees of temperature in the axis of abscissæ have the same values as for water-vapour, they be reckoned, no longer from the boiling point of water ($t = 100°$), but from that of carbonic anhydride (−78·2°), and that the ordinates representing the pressures have 4·3 times the values of those for water-vapour. Hence it appears that, at any given distance from the boiling point, the excess of pressure of the vapour of carbonic anhydride above that at the boiling point is $\frac{4}{3}$ times as great as in the case of water-vapour. H. W.

Absorption of Gases by Liquids under High Pressure. By S. v. WROBLEWSKI (*Ann. Phys. Chem.* [2], **17**, 103—128).—The author's researches have shown that gases in their diffusion through caoutchouc membranes follow Graham's law. Stefan's experiments (Abstr., 1879, 347) would seem to show that the rate of diffusion of gases, as carbonic anhydride, through liquids is in accordance with this law; but the author criticises the results and their interpretation. The author has made a number of experiments on the absorption of gases by liquids under high pressures, and the present paper contains a description of the apparatus used, and the methods of experiment for a study of the behaviour of carbonic anhydride with water. It has for a long time been assumed that carbonic anhydride forms with water a definite hydrate, the properties, composition, and curve of critical pressure of which the author has minutely examined. Experimental results are given to prove the correctness of Clausius's formula, $C = VPk$, for determining at 0° C. the relation between pressure and volume of a gas which does not follow Marriotte's law (C is a constant, P = pressure, V = volume, k a coefficient, which is a function of temperature and pressure, and dependent on the nature of the gas); for any temperature t, the formula becomes $C = \frac{V}{1 + dt}Pk$. Observations were made at temperatures 0° and 11·3°, and the results are in accordance with these formulæ within the limits of experimental error.

If water is introduced into a eudiometer tube filled with carbonic anhydride, cooled to 0°, and the pressure increased, the carbonic anhydride begins to liquefy at a pressure of 35 atmospheres; the liquid carbonic anhydride, however, does not mix with the water, and, on gradually diminishing the pressure, it is found that the only difference due to the compression consists in the water containing a larger quantity of carbonic anhydride in solution. If, on the contrary, the pressure be released suddenly, but not allowed to sink below 12·3 atmospheres, there appears on the inner surface of the eudiometer tube and on the surface of the water a thin opaque rime. The author proves this to be not frozen water, but the hydrate of carbonic anhydride, and its formation is dependent on the following conditions:—

1. At 0° and at higher temperatures the hydrate can be obtained only at the critical pressure for the liquefaction of carbonic anhydride.
2. After a preliminary compression, an expansion is necessary which causes a momentary sinking of temperature.
3. At pressures greater than the critical, the hydrate remains solid, but it disappears below this pressure to reappear again when the pressure is increased.
4. The hydrate is decomposed at pressures far below the critical.

The following results were obtained for the critical pressure of the hydrate at various temperatures:—

Temperature.	Pressure in atmospheres.	Temperature.	Pressure in atmospheres.
0·48	12·7	6·1	23 3
2·7	16·7	6·8	26·1
5·3	21·8		

These numbers, however, must be regarded merely as approximate, and the author proposes to repeat the experiment in a more refined apparatus. The composition of the hydrate was determined by taking such a volume of carbonic anhydride that at 0° it exerted a pressure of 16 atmospheres; after the pressure was exactly ascertained, the whole of the water was converted into the hydrate, and the remaining gas brought to the same volume and its pressure reascertained. The quantity of carbonic anhydride entering into combination can be expressed by the formula $Q = V(Pk - P'k')$ in which k and k' are the coefficients corresponding with the pressures P and P'. The mean results of the analyses show that about 8 molecules of water are required for 1 molecule of carbonic anhydride. The composition of the hydrate, therefore, is not CO_2,H_2O as formerly assumed.

V. H. V.

Osmose of Salts. By J. E. ENKLAAR (*Rec. Trav. Chim.*, 1, 252—270).—The apparatus employed consists of a bottle of about 150 c.c. capacity, the neck of which is fitted with a cork through which passes a capillary tube. The bottom of the bottle is removed, and over the carefully ground edges is stretched a membrane of hare's or rabbit's bladder. This bottle is suspended in a beaker containing distilled water, and the beaker is placed in a large glass cylinder provided with a well-fitting glass stopper, and resting on legs in the middle of an iron vessel containing water, which should be kept at a constant temperature by means of a Bunsen burner furnished with an automatic regulator. The water must completely surround the cylinder containing the diffusiometer. Special precautions are taken to keep the liquid inside the bottle at the same level as the liquid in the beaker, both when introducing the bottle into the beaker and when withdrawing it at the end of the experiment. The experiments detailed in this paper are confined to solutions of the chlorides of the alkalis and alkaline earths. 50 c.c. of a solution of the particular chloride of known strength was placed in the bottle, and the latter was suspended in 100 c.c. of distilled water contained in the beaker. After six hours, the duration of each of the experiments, the amount of chlorine which had passed through the membrane into the water was determined by standard silver solution. In most of the experiments the temperature was 30·5°.

The hare's or rabbit's bladder forms a very thin transparent membrane which, if carefully purified by prolonged treatment with water, alcohol, and ether, is far superior to parchment paper. The membrane acquires its maximum transmissive power only after it has been used several times, and this maximum is apparently reached with different degrees of rapidity for different salts. Drying the membrane exerts considerable influence on the results: a hare's bladder which had been dried for a long time at the ordinary temperature was used in three successive experiments, in each of which the solution in the bottle contained 1·4615 gram NaCl; the amounts of chlorine which passed through in the three experiments were respectively 0·4716, 0·4858, and 0·5071; after the third experiment the rate of osmosis became constant. If the experiments are to be comparable, it is necessary to employ animal membranes of the same kind and of the same age, to take care that the membrane is at a constant distance from the bottom of the beaker in which it is suspended, and to pay special attention to the tension of the membrane.

Experiments with potassium, sodium, ammonium, calcium, and magnesium chlorides prove that the law that "the rate of diffusion of molecules of salts in water is proportional to the density of the saline solutions," or, in other words that, other conditions being the same, the quantity of a salt which passes through the membrane is proportional to the amount of salt dissolved, is strictly accurate, and not merely an approximation, as Beilstein supposed.

A series of experiments with different mixtures of any two out of the five chlorides previously mentioned showed that in the case of mixed solutions of sodium, potassium, and ammonium chlorides each of the salts retains its own rate of diffusion. The results obtained with mixtures of calcium chloride with alkaline chlorides are not so conclusive, but the differences between the observed and calculated values are not greater than the errors of experiment. Mixtures of magnesium chloride with potassium or ammonium chloride in molecular proportion obey the general law, but mixtures of potassium chloride and magnesium chloride in the proportion of 2 mols. of the former to 1 mol. of the latter, show differences between the observed and calculated values which are considerably greater than errors of experiment. It is well known that magnesium chloride forms well-defined double salts with the alkaline chlorides, and the author concludes that in the above mixtures the different salts unite in the proportions in which they are mixed, forming double salts, the rates of diffusion of which are inversely proportional to their molecular weights. This supposition is supported by the experimental results. In the case of mixtures of either calcium or magnesium chloride with alkaline chlorides, it is possible that double salts are formed which, however, allow just as much chlorine to pass through the membrane as would have passed through if the salts had remained uncombined and each had retained its own rate of diffusion.

Numerous experiments were made with a view to ascertain the accuracy or inaccuracy of the statement, that the rates of diffusion of salts from their solutions into pure water are in the inverse ratio of their molecular weights. The experimental results are fairly in accordance with this law, especially if the salts are grouped according to the number of chlorine-atoms in the molecule; but it would appear that although the molecular weight is the main factor which determines the rate of diffusion of a salt, other causes, such as influence of heat, the form of the molecules, and the nature of the membrane, exert an appreciable influence. Experiments were also made with a view to test the value of the rate of diffusion as a means of investigating the constitution of mixtures of various salts in solution. The solutions actually employed were mixtures of potassium nitrate with chlorides of the alkalis and alkaline earths. The results obtained showed that complete decomposition took place, with formation of potassium chloride and a corresponding quantity of nitrate of the other metal. In the case of magnesium chloride, however, the results indicated that complete decomposition of the magnesium chloride does not take place unless the potassium nitrate is in considerable excess. This is probably due to the formation of the relatively highly stable double chloride of magnesium and potassium.

When a mixed solution of sodium chloride and hydrochloric acid passes through a membrane, the rates of diffusion of the two compounds are lower than when each passes alone through the membrane; it follows, therefore, that in the mixed solution they do not pass through independently of each other. This retarding influence is exerted by a very small quantity of the free acid, and is but slightly affected by the actual quantity of acid present. The quantity of hydrochloric acid which passes through the membrane into pure water from a solution of sodium chloride of known strength is proportional to the amount of hydrochloric acid originally contained in the solution.

Tables giving details of the experimental results are given in the original paper. C. H. B.

Constitution of Liquid Compounds. By H. SCHRÖDER (*Ann. Phys. Chem.* [2], **16**, 660—693).—This paper, a continuation of former ones (*ibid.*, **11**, 997—1016, and **14**, 653—670), relates to the molecular volumes of liquid compounds taken at their boiling point. To each class of compounds is assigned a "structural formula," which has always an extremely simple relation to the ordinary atomic formula.

The present paper discusses the *steres* of several classes of compounds, and concludes with a table of 120 compounds, showing that the sum of the *steres* in the "structural formula" has a nearly constant ratio (1 : 7) to the molecular volume at the boiling point. R. R.

Rupert's Drops. By I. TAYLOR (*Chem. News*, **46**, 253).—Rupert's drops may be successfully prepared by dropping the molten glass into a cold saturated solution of ammonium chloride in a cylinder about 18 inches long. D. A. L.

Explosion of a Tube containing Liquid Carbonic Anhydride. By L. PFAUNDLER (*Ann. Phys. Chim.* [2], **17**, 175—176).—In the course of the solidification of liquid carbonic anhydride in a sealed glass tube, a violent explosion took place. The tube in question had often been heated to 31° without injury. The author attributes the explosion either to a disintegration of the glass at the low temperature, so that it was no longer able to withstand the tension of the liquid carbonic anhydride, or more probably to the sudden expansion of the carbonic anhydride in its solidification. V. H. V.

Inorganic Chemistry.

Action of Platinum and Palladium on Carbonic Oxide and Hydrogen. By M. TRAUBE (*Ber.*, **15**, 2854 (compare this vol., p. 150). —Palladium, whether hydrogenised or not, and platinum, in presence of water and oxygen, oxidise carbonic oxide to carbonic anhydride with intermediate formation of hydrogen peroxide. Platinum foil or wire when shaken up in water in an atmosphere of hydrogen and air, causes the formation of hydrogen peroxide in large quantities. The author proposes to carry on further researches on the problematical catalytic action of platinum and palladium. V. H. V.

Researches on the Hyponitrites. By BERTHELOT and OGIER (*Compt. rend.*, **96**, 30—35, 84—88).—The authors have prepared silver hyponitrite by Divers' method, and state that in order to obtain it pure, it is necessary to dissolve the crude product in dilute nitric acid, and reprecipitate by neutralising exactly with ammonia. They ascribe to the salt thus obtained the formula $Ag_4N_4O_5$, and not AgNO. The latter formula was founded on analyses of the salt dried at too high a temperature. The percentage of silver found increases with the temperature at which the salt has been dried: hence the authors dried their product in a vacuum at the ordinary temperature, and in a dark place. Under these conditions it retains a small quantity of water, but no reduced silver. The analyses agree better with the formula $Ag_4N_4O_5$, than with the old formula AgNO. By the action of heat under different conditions, of dilute acids, of oxidising agents, more especially bromine and potassium permanganate, and estimation of the products of the reactions or of the quantities of oxidising agent used, the authors bring further evidence in support of the new formula.

From the results obtained by oxidation with bromine, the heat of formation of silver hyponitrite is calculated to be $-9{\cdot}3$, and that of hyponitrous acid $-38{\cdot}6$ calories. The instability of the acid is in accordance with this result.

The authors further deduce the heat given out in the oxidation of this body by bromine and permanganate, and the heat of neutralisation of hyponitrous acid by the alkalis. E. H. R.

Nitrogen Selenide. By Verneuil (*Bull. Soc. Chim.* [2], **38**, 548—550).—Wöhler's method of obtaining this body by the action of gaseous ammonia on strongly cooled selenium tetrachloride gives very variable results. The author has, however, obtained a body of constant composition, NSe, by passing gaseous ammonia into bisulphide of carbon in which selenium tetrachloride is suspended. A mixture of ammonium chloride and nitrogen selenide is thus obtained. The former is removed by washing with water, and the residue purified by boiling with carbon bisulphide. Thus prepared it is an amorphous orange-coloured substance, insoluble in water, ether, and alcohol, very sparingly soluble in bisulphide of carbon, benzene, and glacial acetic acid. When dry, it explodes as easily as silver fulminate if struck or heated to 230°. Potash decomposes it with evolution of ammonia and formation of selenide and selenite of potassium. Hydrochloric acid acts in a similar manner, ammonium selenite and chloride being formed. Cold water has no action, but at 100° it causes very slow decomposition. E. H. R.

Pyrosulphuric Chloride. By J. Ogier (*Compt. rend.*, **96**, 66—68).—This paper is a reply to Konowaloff (*Compt. rend.*, **95**, 1284), who found the vapour-density of the above compound to be that required by Avogadro's law for the formula $S_2O_5Cl_2$, whilst the author found it to be one-half less. From repeated experiments, the author concludes that his previous determinations were correct, that the substance used by him was not contaminated with impurity to an appreciable extent, and that the body does not undergo dissociation.

E. H. R.

Mechanical Properties of Aluminium. By W. H. BARLOW (*Chem. Centr.*, 1882, 777).—From observations made on a bar 3 feet long and ¼ inch square, the specific gravity of aluminium is found to be 2·688; its tenacity about 12 tons for ¼ inch; its elasticity coefficient, 10,000. The ductility of a piece 2 inches long was only 2·5 per cent.; the metal can, however, be improved in this direction. When its strength is compared with its *weight*, it gives a mechanical value almost equal to steel. D. A. L.

Potash Alum from Felspar. By H. PEMBERTON, Jun. (*Chem. News*, 1883, 5).—The author is of opinion that Spiller's suggestion for the manufacture of potash alum from felspar by treatment with sulphuric acid and a fluoride will not answer in America; firstly, because of the large quantity of sulphuric acid required; and secondly, if fluorspar be the fluoride employed, because of the large amount of calcium sulphate formed, whilst if cryolite is used, it will be necessary to purchase and introduce the potash, and then enormous quantities of sodium sulphate will be formed. With regard to the utilisation of the evolved silicon fluoride as silica and hydrofluosilicic acid, there is no market for such quantities as would be produced. D. A. L.

Double Chloride of Potassium and Thallium. By C. RAMMELSBERG (*Ann. Phys. Chem.* [2], **16**, 709).—The paper gives the analysis and crystalline properties of a new double chloride of potassium and thallium, $2KCl,TlCl_3 + 3H_2O$. R. R.

Thallium and Lithium Phosphates. By C. RAMMELSBERG (*Ann. Phys. Chem.* [2], **16**, 694—709).—The paper contains analyses of the following salts, with some details relating to their preparation and chemical and physical properties:—Trithallium phosphate, Tl_3PO_4; monothallium phosphate, H_2TlPO_4; a compound of mono- and di-thallium phosphates, $HTl_2PO_4 + 2H_2TlPO_4$; isomorphous mixtures of thallium and ammonium phosphates, corresponding with H_2RPO_4, in which Tl : Am = 1 : 2, and with HR_2PO_4, Tl : Am = 1 : 36; phosphates of higher oxides of thallium, $Tl_2P_2O_8,Tl_2H_6O_6$, and $3Tl_2P_2O_8,Tl_2H_6O_6$; trilithium phosphate, Li_3PO_4; monolithium phosphate, $H_2Li_2PO_4$; an acid phosphate of lithium, $H_5LiP_2O_8$. All attempts to obtain HLi_2PO_4 failed. R. R.

Compounds of Tin with Bromine. By K. REIS and B. RAYMANN (*Chem. Centr.*, 1882, 773).—*Tin tetrabromide.*—The product from the action of ordinary Stasfurt bromine on tin is subjected to fractional distillation. The fraction boiling at 181—190° consists of $SnClBr_3$. The fraction 202—203° is pure $SnBr_4$. Tin tetrabromide forms a white iridescent mass at the ordinary temperature; it crystallises from its solution in $SnClBr_3$ in clear colourless crystals which deliquesce in the air. It melts at 33°, and boils at 203·0° (corr.); its sp. gr. at 35° is 3·349; it dissolves in water without perceptible decomposition, but on heating the solution, tin hydroxide is precipitated. Fused tin tetrabromide dissolves iodine and sulphur readily. The vapour of tin tetrabromide does not decompose readily when passed through a red-hot tube even when mixed with air, oxygen, or carbonic oxide. *Ammoniostannic bromide.*—When tin tetrabromide is warmed in an atmosphere of ammonia it readily absorbs the gas, forming a white mass of no constant composition. When this product is heated, ammonia is given off, the mass becomes yellow, and a yellow sublimate of the constitution $SnBr_4,2NH_3$ is deposited. *Bromostannic acid*, $H_2SnBr_6,8H_2O$, can be prepared by the action of tin tetrabromide and bromine on amyl alcohol, or by the direct action of hydrobromic acid on tin tetrabromide. It forms small colourless crystals. The sodium, calcium, strontium, manganese, and iron salts have 6 mols. H_2O, the nickel salt 8 mols., the magnesium and cobalt salts 10 mols. *A hydrate of tin tetrabromide* is produced when tin tetrabromide is exposed to moist air, or when it is dissolved in a small quantity of water, and then allowed to evaporate over sulphuric acid; it forms colourless, transparent, brilliant crystals which fume in the air; their constitution is thus represented: $SnBr_4,4H_2O$. *Tin oxybromide* was obtained by accident whilst preparing barium bromostannate; the mixed solutions of $SnBr_4$ and $BaBr_2$ became coloured by free bromine, and in order to overcome this inconvenience metallic tin was added. On evaporating the solution, barium bromide crystallised out first, but was succeeded by crystals of the formula $Sn_3Br_6O,12H_2O$; these are decomposed by water even in the cold; this decomposition is explained by the equation $Sn_3Br_6O + 2H_2O = H_2SnO_3 + 2SnBr_2 + 2HBr$. From the mother-liquor of these crystals another oxybromide, $SnBr_8O_2,10H_2O$, is deposited. D. A. L.

Preparation of Stannic Oxide from Sodium Stannate. By P. T. AUSTIN (*Chem. News*, **46**, 286).—Stannic oxide, SnO_2, is precipitated when a solution of sodium stannate is boiled with sodium hydrogen carbonate, or when a current of carbonic anhydride is passed through a strong solution of sodium stannate containing an excess of soda. D. A. L.

Uranyl Potassium Chromate. By WIESNER (*Chem. Centr.*, 1882, 777).—According to Berzelius, the body $UO_2.CrO_4$ is precipitated from uranium nitrate by potassium chromate. The author did not succeed in obtaining it in this manner, but found instead the following series of double salts:—

$$UO_2.CrO_4,K_2CrO_4 + H_2O;\ 3(UO_2.CrO_4),2K_2CrO_4 + 7H_2O;$$
$$4(UO_2.CrO_4),3K_2CrO_4 + 7H_2O;\ 3(UO_2.CrO_4),K_2Cr_2O_7 + 14H_2O.$$

The last of these forms silky golden-yellow crystals. They are all decomposed by water. The author regards them as the products of the decomposition by water of some body formed during the precipitation. D. A. L.

Natural Formation of Manganese Dioxide, and some Reactions of Peroxides. By BERTHELOT (*Compt. rend.*, **96**, 88—90).—Manganese dioxide seems to be formed naturally from the carbonate by the oxidising action of the air, either free or dissolved in water.

The carbonate, at the moment of its separation from waters surcharged with carbonic anhydride, becomes oxidised to dioxide. The author shows, from a consideration of the heats evolved in the reactions $MnO + CO_2$ (dissolved) $= MnCO_3$ and $MnO + O = MnO_2$, that the results are in accordance with thermochemical theory, and that the same is true of the formation of ferric oxide from ferrous carbonate, which is supposed to take place in nature in a manner exactly similar to that described above.

The inverse reaction should and does take place between barium dioxide and carbonic anhydride, and further, thermochemical data indicate, what is true as a matter of fact, that hydrogen dioxide cannot be formed by the action of acids on manganese dioxide or ferric oxide, whilst it can easily be produced by the action of acids on barium dioxide. In the former case an *absorption* of heat would take place, whereas in the latter case heat is *developed.* E. H. R.

Mineralogical Chemistry.

Silver Amalgam from the Sala Mines. By T. NORDSTRÖM (*Jahrb. f. Min.*, 1882, **2**, Ref., 361—362).—The silver amalgam found at Sala, in dolomite with quartz and blende, has the following composition:—

Ag.	Hg.	Fe.	Zn. Pb.	$CaCO_3$.	Insol. gangue.	Total.
46·30	51·12	0·81	trace	0·21	1·01	99·45

With this exception, silver amalgam has never been found in Sweden.
B. H. B.

A Remarkable Platinum Nugget. By P. COLLIER (*Jahrb. f. Min.*, 1883, **1**, Ref., 27).—This was found near Plattsburg, New York. It was 4 cm. long, 3 wide, and 2 high, and weighed 104·4 grm.; it consisted of a mixture of 46 per cent. Pt with 54 per cent. chrome-iron. The former had a sp. gr. 17·35, whilst that of the mixture was only 10·446. The analysis of the chrome-iron gave the following result:—

Cr_2O_3.	FeO.	Al_2O_3.	SiO_2.	CaO.	MgO.	Total.
54·944	31·567	5·690	3·731	3·405	0·941	100·278

The platinum had the following composition:—

Pt.	Fe.	Pd.	Ir.	Rh.	Cu.	Al_2O_3.	CaO.	Mg.
82·814	11·040	3·105	0·627	0·286	0·397	1·953	0·062	0·030

Total = 100·314.

Osmium was present, but the amount could not be estimated. The nugget was somewhat magnetic. B. H. B.

Substance Resembling Dopplerite from a Peat Bog near Scranton, Pa. By H. C. LEWIS (*Jahrb. f. Min.*, 1883, **1**, Ref., 31—32).—This substance occurs in irregular veins. When exposed to the air, it becomes more elastic. It is black, and burns slowly without flame. It is soluble only in caustic potash, and gives a dark brown solution. From this solution it is thrown down by acids as a reddish-brown precipitate. When completely dried, the substance is brittle and almost as hard as coal (H. = 2·5); it also acquires the lustre and conchoïdal fracture of genuine coal. It burns with a yellow flame. Sp. gr. = 1·032. Streak dark-brown. The dried substance has the following composition:—

C.	H.	O + N.	Total.
30·971	5·526	63·503	100

corresponding with the formula $C_{10}H_{22}O_{16}$. It resembles dopplerite in its physical characters, but differs from the latter by the small percentage of carbon and the large amount of oxygen it contains. The author is of opinion that it is an intermediate product between peat and coal, and proposes the general name *Phytocollite* for all similar substances of variable composition. B. H. B.

Idrialite. By R. SCHARIZER (*Jahrb. f. Min.*, 1883, **1**, Ref., 31).—In the quicksilver mines of Idria a green resin has been found; this consists of idrialite in a tolerably pure state. It is a massive, pistachio-green mineral containing idrialin, $C_{80}H_{56}O_2$. Its sp. gr. is greater than 1, but less than 1·85. It has a hardness of 1—2, and an uneven fracture. When dissolved in hot concentrated sulphuric acid, it gives a deep indigo-blue solution, and on distillation gives a straw-yellow product which is pure idrialine. The dark-coloured mineral formerly described as idrialite contains only a very small amount of idrialin.

B. H. B.

Artificial Production of Mellite. By C. FRIEDEL and M. BALSOHN (*Jahrb. f. Min.*, 1882, **2**, Ref., 30—31).—By allowing solutions of mellitate of sodium and of an aluminium salt to mix very slowly for about a fortnight, crystals may be obtained of sufficient size to examine crystallographically; they had all the properties of the natural crystals. H. B.

Cryolite, Pachnolite, and Thomsenolite. By C. KLEIN (*Jahrb. f. Min.*, 1882, **2**, 89—90).—Brandl, in a recent paper before the Bavarian Academy, described the analyses of specimens of the above minerals, which had been crystallographically determined by Groth. Their formulæ are $AlF_3,3NaF$; AlF_3,CaF_2,NaF, and AlF_3,CaF_2,NaF,H_2O respectively. The author, whilst admitting the service done by Brandl in determining the true composition of pachnolite, points out that the composition of cryolite and of thomsenolite was already determined with certainty, as in 1877 he showed that the crystals examined by Wöhler were in reality cryolite, that the crystals of thomsenolite also examined by Wöhler—who then called it pachnolite—had all the properties ascribed to it by Kreuner, and re-analysed gave the formula adopted by Wöhler, which is the same as that given by Brandl. H. B.

Minerals Found near Massa in the Apuanian Alps. By A. D'ARCHIARDI (*Jahrb. f. Min.*, 1882, 2, Ref., 353—354).—In the Frigido valley, near Massa, not far from the celebrated Carrara marble quarries, a lode comes to the surface. It consists of iron spar with quartz and copper pyrites, together with magnetic pyrites and a dark-grey metallic mineral, which the author believes to be coppite. Blende is also occasionally found, and a grey fibrous mineral not yet investigated. The copper pyrites contains 26—30 per cent. Cu, and has a sp. gr. of 4·1. The magnetic pyrites consists of

S.	Fe.	Ni.
39·65	58·18	2·17 per cent.,

thus indicating the formula $(FeNi)_7S_8$.

To the grey mineral, the author gives the name of *Frigidite.* It rarely occurs crystallised, being usually in granular masses. Sp. gr. = 4·8. H. = 4. Before the blowpipe, it acts like tetrahedrite, which it very much resembles in appearance. The analysis gave the numbers under I: the results obtained, after subtracting the impurities and reducing to 100, are shown under II—

	S.	Sb.	Cu.	Fe.	Ni.	Ag.	Zn.	SiO_2.	Total.
I.	29·60	25·59	19·32	12·67	7·55	0·83	trace	2·20	96·96
II.	31·23	27·00	20·39	13·37	7·97	0·04	trace	—	100·00
III.	27·01	29·61	30·10	13·08	—	—	—	—	99·80

It is, therefore, not Becchi's coppite, the composition of which is given under III.

The above composition may be interpreted in various ways, and all the interpretations agree equally well with the analysis.

The mineral may be regarded as a mixture of nickel tetrahedrite with copper pyrites, as a somewhat different tetrahedrite with ullmannite and iron pyrites, or lastly as a mixture of tetrahedrite with antimony-nickel. There is, however, no doubt that frigidite is an impure tetrahedrite. B. H. B.

Galena with Octohedral Cleavage. By A. BRUN (*Jahrb. f. Min.*, 1883, 1, Ref., 9—10).—In the Glacier de Lochant (Chaîne du Mt. Blanc) the author found a fine twin crystal of galena; the twin face was O, and the crystal was formed by the faces of the octohedron and the cube. The octohedral cleavage was very distinct. Sp. gr. = 7·67. It contained some bismuth and a little iron. This is the third known example of galena with an octohedral cleavage; the other two are from the Habach valley and from Pennsylvania respectively.

B. H. B.

Analysis of Miargyrite from Pribram. By J. RUMPF (*Jahrb. f. Min.*, 1882, 2, Ref., 17).—The analysis gives 21·68 S, 41·15 Sb, 36·71 Ag, agreeing well with the accepted formula, $Ag_2S.Sb_2S_3$.

H. B.

Alaskaite, a New Bismuth Mineral. By G. A. König (*Jahrb. f. Min.*, 1883, **1**, Ref., 25—26).—Alaskaite occurs with tetrahedrite and copper pyrites in Colorado. The colour is lead-grey to white; the lustre metallic. The mineral is soft and has a sp. gr. of 6·878. It decrepitates on being heated, and melts without the formation of a sublimate. It is decomposed by hot hydrochloric acid, leaving a residue of silver chloride with copper pyrites and heavy spar. The analysis gave the following results:—

	Sb.	Bi.	Pb.	Ag.	Cu.	Zn.	S.
I.	—	51·49	12·02	8·08	3·00	0·26	15·72
II.	0·51	46·87	9·70	7·10	2·85	0·64	15·07
III.	—	51·35	17·51	3·00	3·74	0·20	16·21

The ratio of R : Bi : S is here 1 : 2 : 4; the formula is then RBi_2S_4, or $(PbZnAg_2Cu_2)S + Bi_2S_3$. B. H. B.

Compact Magnetic Iron Ore from Cogne, Valley of Aosta. By M. Zecchini (*Jahrb. f. Min.*, 1882, **2**, Ref., 386).—With this ore, a small quantity (about 6 per cent.) of an apparently rhombic mineral is found. Analysis I gave the composition of the magnetic iron ore; Analysis II that of the accompanying mineral:—

	H_2O.	Insoluble silicates and free SiO_2.	Fe_2O_3.	FeO.	MgO.	CaO.
I.	0·60	5·54	18·09	73·47	1·65	0·55
II.	11·19	SiO_2 43·15	4·10	—	40·31	trace

	CoO.	Nickel and chromium oxides.	Total.
I.	0·21	trace	100·11
II.	—	—	98·75

B. H. B.

Occurrence of Iron Ores at Taberg in Smaaland (Sweden). By A. E. Törnebohm (*Jahrb. f. Min.*, 1882, **2**, Ref., 66—67).—The ore is associated with a variety of hyperite, rich in olivine and magnetite, and the whole forms together an immense lense-shaped mass. Its period of formation is more remote than that of most other Swedish ores. A somewhat similar mass occurs at Launghult (Kronoberg). Analyses of the ores from these localities are given, and also that of a similar ore from Rhode Island. H. B.

A Manganese Mineral from Upsala. By G. de Geer (*Jahrb. f. Min.*, 1882, **2**, Ref., 361).—This mineral has the following composition:—

Gangue.	CuO.	Mn_2O_3.	H_2O.	Total.
7·24	1·17	73·19	16·27	97·87

The formula is then $Mn_3O_4,4H_2O$, and the author suggests for it the name *manganese-ochre*. B. H. B.

Pseudomorphic Senarmontite Crystals. By C. HINTZE (*Jahrb. f. Min.* 1883, **1**, Ref., 32).—Several senarmontite crystals from South Ham, in Canada, have a dark rough surface. On closer investigation, it was found that only the kernel of the crystals consisted of senarmontite, whilst the outer layer was antimonite; so that the crystal is a pseudomorph of antimonite after senarmontite. The kernel has, however, not been converted directly into antimonite, but first into an aggregate of valentinite fibres, which were afterwards converted into antimonite. B. H. B.

Artificial and Natural Gay-Lussite. By A. ARZRUNI (*Jahrb. f. Min.*, 1882, **2**, Ref., 17, 18); and **Reproduction of Gay-Lussite.** By A. FAVRE and C. SORET (*ibid.*, 18, 19).—From the clarified soda liquors there are deposited crystals of gay-lussite at a temperature of 40° on the bottom of the vessel, and also in the carbonising tower, where the gases from burning coke are passed through the solution; these crystals were examined and compared with natural crystals. They contain from 32—36 per cent. Na_2CO_3, while the formula $Na_2CO_3 + CaCO_3 + 5H_2O$ requires 35·8 per cent. The predominating faces are ∞P and Ꝑ∞, ½P and 0P being more subsidiary. All faces in the zone ∞P, Ꝑ∞, ½P are striated parallel to the zonal axis. A table embracing all published and also new measurements is given; those of the artificial crystals agree very well with those of the natural crystals. Their optical behaviour agrees with Des Cloizeaux's observations.

A snail and a piece of wood, after being immersed in a solution of sodium silicate for 27 years, were examined. The shell was eaten away and the wood covered with a crust containing silica, soda, water, and alumina, and with a thin skin of organic matter; between the two were small crystals of gay-lussite. They had the chemical and physical properties of this mineral. Measurement showed the following forms to possess almost the interfacial angles of the native mineral:—∞P . ½P . Ꝑ∞; ∞Ꝑ∞ is probably also present. H. B.

Composition of Dawsonite. By C. FRIEDEL, M. CHAPER, and J. HARRINGTON (*Jahrb. f. Min.*, 1883, **1**, Ref., 15—16).—This Canadian mineral was discovered by J. Harrington in 1874, and a mineral of similar chemical composition has now been observed by Chaper in Tuscany. It occurs there in small, white, finely fibrous bundles in crevices in a dolomitic marl. When the substance is heated strongly in a closed tube, it gives up water; it is infusible before the blowpipe, and is coloured blue by cobalt solution. Friedel's analyses gave the following results (I):—

	CO_2.	Al_2O_3.	Na_2O.	H_2O.	CaO.	MgO.	Total.
I.	29·09	35·89	19·13	12·00	0·42	1·39	97·92

thus indicating the composition $Al_2O_3,Na_2O,2CO_2,2H_2O$. Friedel regards the compound as an aluminium hydroxide, in which one atom of hydroxyl is replaced by the monad radicle $NaCO_3$, thus leading to the formula $Al(OH)_2(NaCO_3)$.

II and III are Harrington's original analyses. He has also analysed the mineral which he recently found, together with calcspar, dolomite, iron pyrites, galena, and a small quantity of a manganese mineral, in the Montreal Reservoir (IV).

	CO_3.	Al_2O_3.	Na_2O.	H_2O.	CaO.	MgO.
II.	29·88	32·84	20·20	11·91	5·95	trace
III.	30·72	32·68	20·17	(10·33)	5·65	0·45
IV.	32·23	24·71	15·64	9·06	16·85	trace

	K_2O.	MnO_2.	SiO_2.	Total.
II.	0·38	—	0·40	101·56
III.	—	—	—	100·00
IV.	—	0·23	0·84	99·56

On subtracting the accidental impurities, the analyses correspond very well with the composition demanded by the formula:

	I.	II.	III.	IV.	Calculated.
CO_2	29·27	27·96	29·06	27·78	30·49
Al_2O_3	37·88	36·42	36·70	36·12	35·55
Na_2O	20·19	22·41	22·65	22·86	21·48
H_2O........	12·66	13·21	11·59	13·24	12·47

Harrington determined the specific gravity to be 2·40. The Tuscan dawsonite is accompanied by dolomite, cinnabar, calcspar, iron pyrites, fluorspar, and bitumen. B. H. B.

Strontianite in Westphalia. By E. VENATOR (*Jahrb. f. Min.*, 1883, **1**, Ref., 28).—Numerous veins of strontianite occur in the Senonian marl between Hamm and Münster; and in order to obtain the mineral, more than 1200 miners are employed. The minerals filling the veins consist of strontianite, calcspar, marls, and sometimes iron pyrites. The thickness of the veins is very variable, the maximum being three metres. Faults are exceedingly rare. B. H. B.

Turquoise of New Mexico. By B. SILLIMAN (*Jahrb. f. Min.*, 1883, 1, Ref., 27).—The paper gives an account of the occurrence of turquoise in the augite trachyte of the Cerillo Mts. The rock is quite altered by hot springs, and in the yellowish-white product of this action small concretions of bluish-green kalaite are found which occasionally pass into the azure-blue variety valued as a precious stone.
B. H. B.

Artificial Production of Phosgenite. By C. FRIEDEL and E. SARASIN (*Jahrb. f. Min.*, 1882, **2**, Ref., 31).—By heating a mixture of lead carbonate and chloride in a closed flask at 180° in presence of water, small quadratic crystals were obtained; they always contained much of the ingredients and were not suitable for analysis, but the author believes that the optical behaviour demonstrates it to be phosgenite. H. B.

Natural Barium Nitrate. By P. GROTH (*Jahrb. f. Min.*, 1883, **1**, Ref., 14).—This new mineral was found in an old collection of

Chilian minerals. The crystals are 4 mm. in size; they are colourless and consist of octohedra. Twin crystals similar to those of spinelle also occur.
B. H. B.

Examination of the Ores from Amberger and of the accompanying Phosphates. By J. B. SCHOBER (*Jahrb. f. Min.*, 1882, **2**, Ref., 20—21).—The bulk of this paper is of technical interest. The sparingly occurring phosphates, wavellite, vivianite, and cacoxene are described in an appendix; analyses of the last two are given; the last one has been much changed, and has lost most of the phosphoric acid.
H. B.

Existence of Apatite in the Pegmatite of Lyons. By F. GONNARD (*Jahrb. f. Min.*, 1882, **2**, Ref., 352).—Apatite occurs in the eruptive rocks in the neighbourhood of Lyons, partly in microscopic, partly in macroscopic crystals. It occurs in gneiss at Beauman with dumortierite, a mineral recently discovered there, also with garnet, near Greillon, and in pegmatite in the Roche Cardon and Sainte Foy.
B. H. B.

Mineralogical Notes. By A. WEISBACH (*Jahrb f. Min.*, 1882, **2**, Mem., 249—259).—1. *Apatite.*—In the collection of the School of Mines in Freiberg is a short columnar crystal of apatite from the tin lodes of Ehrenfriedersdorf. It appears to be a combination of the pyramid, $\frac{1}{2}P$, with the hexagonal prism and the basal plane. It has, however, been found that the latter is not a true basal plane, but an extremely flat pyramid having the symbol $\frac{1}{70}P\frac{4}{3}$. The middle edges form an angle of 1° 23′, the polar edges 179° 18′. It is the flattest pyramid which has yet been observed in any mineral species.

2. *Lautite.*—Under this name a mineral from Lauta, near Marienberg in Saxony, has recently been introduced. It is composed of Cu, As, and sulphur, and its chemical formula was asserted to be $CuAsS$. The author is of opinion that it is not a true mineral species, but a mixture of native arsenic and a copper sulpho-salt. The latter he determines to be Cu_3AsS_3. The so-called lautite is a mixture of 71 per cent. of this sulpho-salt and 29 per cent. arsenic.

3. *Bronzite.*—The crystals of this mineral, which was found in the meteorite of Rillersgrün, had the following form:—∞P, $0P$, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $\infty\bar{P}3$, $\infty\bar{P}2$, $\infty\breve{P}2$, $\frac{1}{4}\breve{P}\infty$, $\bar{P}\frac{4}{3}$, $\bar{P}2$, $\bar{P}4$, $\frac{1}{2}\bar{P}2$, $\frac{1}{2}P$, $\frac{3}{4}\breve{P}\frac{3}{2}$.

4. *Keramohalite.*—By many dealers a mineral from Schwarzenberg in Saxony, is frequently sold under the name of tectizite. This is, however, not an iron but an aluminium sulphate, as the analysis proves—

Al_2O_3.	FeO.	CaO.	H_2SO_4.	H_2O.	Total.
12·69	5·46	0·14	34·26	46·70	99·25

The formula is thus $Al_6S_8O_{33},48H_2O$, which differs but very slightly from that of keramohalite.

5. *Bismuth carbonate*, from Guanajuato in Mexico, contained 91·68 per cent. bismuth oxide and 8·29 per cent. CO_2. Total 99·97. This corresponds exactly with the composition of the Schneeberg variety.

6. *Domeykite,* from Zurickau, gave on analysis the following results:—

Cu.	Fe.	Ni.	As.	O.	Residue.	Total.
65·08	0·64	0·44	26·45	2·49	3·84	98·94

The presence of oxygen is owing to a copper arsenate, a product of the decomposition of the domeykite. The "residue" consists of porphyry.

7. *Eulytine.*—Among the colours assigned in the text-books on mineralogy to this mineral (bismuth silicate), black is not mentioned. A series of examples possessing this characteristic exist, however, in the Werner Museum at Freiberg.

8. *Winklerite.*—Analysis of this mineral from Almeria in south Spain gave the following results:—

H_2O.	O.	SiO_2.	BiO.	CuO.	As_2O_3.	FeO.
12·12	4·11	0·29	1·70	15·01	20·50	0·71

Co_2O_3.	Ni_2O_3.	CaO.	Total.
23·80	12·98	9·27	100·49

The mineral analysed was associated with olivenite in such a way that it was impossible to separate them perfectly. On subtracting the constituents which may be regarded as impurities in the above analyses, we obtain—

	H_2O.	O.	Co_2O_3.	Ni_2O_3.	Total.
	10·6	4·1	23·8	13·0	51·5
or	20·6	8·0	46·2	25·2	100·0

a composition which may be represented by the general formula—

$$R_2O_3,2H_2O, \text{ or } Co_4Ni_2O_9,2H_2O.$$

9. *Uranium Ochre.*—This was found at Johanngeorgenstadt. It gave on analysis the following result (sp. gr. = 3·953):—

CaO.	UO.	H_2SO_4.	H_2O.	Residue.	Total.
2·08	77·17	3·18	16·59	0·39	99·41

This leads to the formula $CaU_{16}S_2O_{31} + 25H_2O$. B. H. B.

Relation between the Chemical Composition and Optical Characters in the Group of Pyromorphites and Mimetesites. By C. Jannettaz and L. Michel (*Jahrb. f. Min.*, 1882, **2**, Ref., 347—348).—Pure pyromorphite is uniaxal, pure mimetesite biaxal. Crystals occur in which the centre is pyromorphite and the exterior is mimetesite, and chemical analysis now shows that crystals occur with uniaxal centre and biaxal exterior, which contain no As_2O_3. For such cases the authors suggest that the apparently biaxal interference figure is caused by non-parallel aggregation of uniaxal individuals.

B. H. B.

Dietrichite. By A. Arzruni (*Jahrb. f. Min.*, 1882, **2**, Ref., 19).—The author considers the formula to be $ZnO,Al_2O_3,4SO_3 + 22H_2O$, instead of $+23H_2O$, as given by Dietrich. The analysis by Dietrich gives $RO : H_2O = 1 : 20·3$, $R_2O_3 : H_2O = 1 : 23·0$, $SO_3 : H_2O = 4 : 21·9$, and hence the point cannot be considered as definitely settled. This mineral is doubly refractive, the depolarising direction being parallel to the length of the fibres. H. B.

Thenardite from Aguas Blancas. By C. Baerwald (*Jahrb. f. Min.*, 1882, **2**, Ref., 19—20).—The crystals are clear and transparent, but in the air soon become covered with a white crust. Measurements gave the axial relations $a : b : c = 0·4771 : 1 : 0·7984$. Plane of the optical axis is $\infty P\breve{\infty}$, the axis a is acute bisectrix; double refraction +; dispersion weak $\rho > v$; $2V = 89° 59'$ for Li, 90° for Na, and $90° 0\frac{1}{2}'$ for Tl light. Analysis gave—

Na_2O.	SO_3.	CaO.	H_2O.
41·91	53·34	2·66	0·93 = 99·84

The author supposes the calcium to be present in some unknown form, and not as glauberite. H. B.

Arsenates from Laangban. By W. Lindgren (*Jahrb. f. Min.*, 1882, **2**, Ref., 362—363).—1. *Berzeliite.*—Honey-yellow colour, waxy lustre, translucent, fracture imperfectly conchoïdal, brittle, H. = 5, sp. gr. = 4·09—4·07. It melts before the blowpipe to a brown globule. Soluble in hydrochloric and in nitric acids. It occurs as small granules in limestone.

2. *Doubly-refracting Berzeliite.*—No distinct cleavage, doubly refracting, crystalline system unknown, yellowish colour, H. = 5, sp. gr. = 3·89—4·04. The analysis gave—

As_2O_3.	CaO.	MgO.	Mn_2O_3.	PbO. FeO.	Insol. residue.	Total.
62·00	20·00	12·81	4·18	trace	0·68	99·67

The formula is therefore $3(Ca,Mg,Mn)O,As_2O_5$.

3. *Karyinite.*—Doubly refracting, not pleochroic. The analyses are not trustworthy, as it is never free from berzeliite.

4. A calcite occurring with the karyinite gave on analysis the following results:—

$CaCO_3$.	$MgCO_3$.	$MnCO_3$.	$ZnCO_3$.	Total.
92·64	4·18	2·80	1·09	100·71

B. H. B.

Analysis of Columbite. By E. D. Hallock (*Jahrb. f. Min.*, 1883, **1**, Ref., 26).—Columbite from Middletown, Conn., with the sp. gr. 6·13, gave on analysis—

Acids.	FeO.	MnO.	CaO.
82·64	11·77	4·95	4·93 = 104·29
82·56	12·08	0·50	0·45 = 95·59

The high sp. gr. of the fused precipitate of the mixed acids indicates a large percentage of TiO_2. B. H. B.

Crystalline Form of Sipylite. By J. W. MALLET (*Jahrb. f. Min.*, 1883, **1**, 28).—This mineral has already been described by the author (*Amer. J. Sci.*, 1877, **15**, 397). He now determines the crystalline form to be a tetragonal pyramid, the polar edges of which form an angle of 100° 45′, and the middle edge 127°. Cleavage is parallel to the pyramid faces. Sp. gr. = 4·883 at 18°. B. H. B.

Wulfenite. By S. KOCH (*Jahrb. f. Min.*, 1883, **1**, Ref., 11—13).—The author examined a large series of crystals of wulfenite from Juma County, Arizona: from Utah, Mexico, Phenixville, Bleiberg, and Rucksberg in Banat. From the angular measurements he calculated for wulfenite a general ratio of the axes, $a : c = 1 : 1·57767$. Twenty-nine crystal forms altogether occur in wulfenite, of which seven were first observed by the author ($\frac{1}{7}P$, $\frac{1}{8}P$, $\frac{1}{264}P\infty$, $\frac{1}{16}P\infty$, $\frac{2}{5}P\infty$, $\infty P\frac{7}{4}$, $\frac{1}{2}P\frac{9}{8}$). Pyramids of the second order, and prisms form the majority of the faces. Hemimorphism was never observed.

B. H. B.

Anatase and Xenotime from Burke Co., N. Carolina. By W. E. HIDDEN (*Jahrb. f. Min.*, 1883, **1**, Ref., 14).—Anatase occurs in the form of greenish-yellow crystals, in the gold sands near Brindletown, together with monazite, xenotime, fergusonite, samarskite, zircon, and brookite. The crystals have the combination $0P . P$.

The xenotime is yellowish-grey, and is combined with zircon in such a way that the two minerals have the same principal axis.

B. H. B.

Pseudobrookite. By A. SCHMIDT (*Jahrb. f. Min.*, 1882, **2**, Ref., 24—25).—To the already known forms the author adds $\infty P\breve{2}$, accepting the first proposals of Groth (*Zeitsch. f. Kryst.*, **3**, 306). New measurements gave the angles $\infty P\bar{\infty} : \infty P\bar{2}$ = 153° 23′—153° 51′, and $\infty P\bar{\infty} : P\bar{\infty}$ = 138° 30′—138° 57′, from which

$$a : b : c = 0·992 : 1 : 1·130.$$

A discussion follows on Groth's proposal to interchange the a and b axes, whereby the form approaches much more nearly to that of brookite. This alteration the author does not accept. No fresh analysis is, however, given. H. B.

Tin Ores, Aventurine Glass, and Green Aventurine Quartz, from Asia, and Krokydolite Quartz, from Greenland. By H. FISCHER (*Jahrb. f. Min.*, 1882, **2**, 90—98).—The author discusses the interest attaching to a correct knowledge of the localities whence the ancients obtained their minerals, whether ornamental stones, as the turquoise and lapis lazuli, or as metallic ores. Besides the localities mentioned in mineralogical lists, a number have been collected together, and appeared in Gurlt's *Bergbau-und Hüttenkunde*, 1877, 9; the knowledge of these localities of the East is of great historic interest, and the author by drawing attention to them wishes to make them better known. The aventurine glass offered for sale in Allahabad and North India generally, is not of Venetian origin: the articles are brought in by the Afghans (Cabulis), who are practised in the production of artificial stones; it is, however possible that they are only middlemen, for Badakschan is the only known locality where this glass is made. In Delhi the Venetian product is used. The author suggests that Marco Polo, who visited Central Asia in the 13th century, learnt the art of making this glass from some native tribes, and brought it to Venice; in these districts chalcedony and agates are still cut, polished, and bored, and it is possible that this is the source of the Assyrian and Babylonian cylinders and talismans, and of the agate and other beads, &c., found in ancient Roman and German tombs. Sections of the cut aventurine quartz ornaments showed the presence of a number of thin plates, with their long axes for the most part parallel; they are beautifully dichroic, varying from emerald-green to blue-green; they are chromium mica. In a collection of stone axe-heads from Athens, some were found made of a remarkable rock; its section showed a ground-mass of red quartz, in which groups of fine needles of a pure blue were thickly imbedded; they are probably glaucophane. Other specimens appeared to have come from the emery districts of Asia Minor, but no satisfactory sections could be obtained. H. B.

Composition of Minerals of the Chondrodite Group. By H. SJÖGREN (*Jahrb. f. Min.*, 1883, **1**, Ref., 23—24).—The author accepts the opinion of Rammelsberg and Groth, that water is present in the three members of the chondrodite group, and being of the opinion that the differences in the analyses prove them not to have the same composition, he adopts the following formulæ:—

$$\text{Clinohumite} = Mg_5\left[Mg\binom{HO}{F}\right]_2(SiO_4)_3.$$

$$\text{Humite} = Mg_3\left[Mg\binom{HO}{F}\right]_2(SiO_4)_2.$$

$$\text{Chondrodite} = Mg_4\left[Mg\binom{HO}{F}\right]_4(SiO_4)_3.$$

B. H. B.

Iron Glance and Augite, from Ascension. By G. v. RATH (*Jahrb. f. Min.*, 1883, **1**, Ref., 16—17).—On a plate of iron glance, 90 mm. in diameter, with the faces $0R$, $+R$, $-\frac{1}{2}R$, $\frac{4}{3}P_2$, $\infty P2$, and $-\frac{1}{4}R$, small reddish-yellow crystals of augite, 1 mm. long, were developed. The augite had the following faces:— $+P$, $+5\grave{P}5$, $-P$, ∞P, $-\infty\bar{P}3$, $+P\bar{\infty}$, $\infty\bar{P}\infty$, $\infty\grave{P}\infty$. From this it is proved that the augite was formed by sublimation. B. H. B.

Nephrite or Jade of Siberia. By E. JANNETTAZ and L. MICHEL (*Jahrb. f. Min.*, 1883, **1**, Ref., 29—30).—In the bed of a stream in the Bagoutal Mountains, near the Chinese frontier, Alibert found loose blocks of a jade-like substance. They were greenish-white to emerald-green, had a greasy lustre, and were more or less translucent, according to the colour. Fracture splintery. Hardness, 6·5. Sp. gr. 3·08—3·2. Before the blowpipe, it melted easily to a light-green globule. The chemical analysis gave—

	SiO_2.	MgO.	CaO.	Fe_2O_3.	Al_2O_3.	H_2O.	Total.
I.	56·60	23·04	13·45	2·38	1·37	3·03	99·87
II.	55·13	19·67	14·13	8·5		3·1	100·53

I. Analysis of the light-coloured variety. II. The green variety.

B. H. B.

Jadeite Axe from Rabber, Hanover. By A. ARZRUNI (*Jahrb. f. Min.*, 1883, **1**, Ref., 30).—The axe in question is 12 cm. long, has a cutting edge 5 cm. broad, and on the opposite side has a somewhat flattened conical point, 2 cm. in diameter. Under the microscope a thin section showed the confused fibres, characteristic both of nephrite and of jadeite, but in places rhomb-shaped crystal sections could be seen, with cleavage planes cutting each other at angles of 87—89°, and 93—91°. As this angle agrees with the results obtained by Descloizeaux with jadeite from Thibet, the author concluded that the axe was made of the same mineral, and that this belonged to the pyroxene group: consequently jadeite must belong to the monoclinic system.

B. H. B.

Danburite, from the Scopi, in Graubündten. By E. LUDWIG (*Monatsh. Chem.*, **3**, 819—821).—This mineral occurring, surrounded by earthy chlorite, in a rock-cleft on the Scopi, agrees in composition, chemical characters, primary form, and optical properties, with danburite, from Russel, in New York (*Chem. J.*, Abstr., 150—151), but differs from the latter in the mode of development of its crystals. Sp. gr., 9·85. Analysis gave—

SiO_2.	B_2O_3.	CaO.	MgO.	Al_2O_3,Fe_2O_3,Mn_2O_3.
48·52	28·77	23·03	0·30	traces

The mineral may be regarded as the calcium salt of a borosilicic acid, $Si_2B_2H_2O_8$.

H. W.

Helvite, from Virginia. By R. HAINES (*Chem. News*, 1883, 6).—The mineral is found mixed with orthoclase, with pale-red topazolite, and a variety of garnet. The helvite crystals were shown to be isometric by the polariscope, but were not sufficiently perfect for angular measurements. H. is about 6; colour sulphur-yellow; lustre somewhat resinous, partially translucent; fusibility about 4, to a brown glass. The mineral gives no water in closed tubes; with fluxes, it gives the reactions for manganese; is soluble in hydrochloric acid, with evolution of hydrogen sulphide, and separation of gelatinous silica. Sp. gr. 3·29. Analysis yields the following results:—

Silica insoluble in acid and in sodium carbonate, 9·22.

Total SiO_2.	BeO.	Al_2O_3.	MnO.	FeO.	CaO.	K_2O.	Na_2O.	S.	Moisture.
32·32	11·47	2·68	45·38	1·85	0·64	0·39	0·92	4·50	0·30
Second deter. 32·49	—	—	—	—	—	—	—	—	—

2·25 is to be deducted for oxygen replaced by the sulphur.

D. A. L.

Melanite from Lantigné (Rhône). By A. Lacroix (*Jahrb. f. Min.*, 1882, 2, Ref., 352—353).—In a bed of magnetic iron ore near Lantigné the author found specimens of two different varieties of garnet. Both occur in crystals and in compact aggregates. In both cases the forms 2O2 and ∞O occur. Sp. gr. 3·66 for the first, and 3·62 for the second variety. The garnet gives up water when heated in a closed tube, and melts before the blowpipe to a magnetic globule. The second variety gives the manganese reaction when melted with borax, and when treated with soda and nitre on platinum foil. From the analysis, the formula $3CaO,Fe_2O_3,3SiO_2$ is deduced. Marcasite, quartz, galena, cerussite, malachite, and iron glance also occur in the same locality. B. H. B.

Change of Colour in Felspar under the Influence of Light. By E. Erdmann (*Jahrb. f. Min.*, 1882, 2, Ref., 363).—Green felspar (Amazon stone) from pegmatite veins at Ammeberg, when first taken from the mine, is of a greenish-grey colour, but after exposure to the air for some time, it assumes a bright emerald-green colour. By placing fragments in variously coloured glass tubes, and submitting them to the action of light for 11 months, the author came to the conclusion that light alone effects the change, air and moisture having no influence. When the dark-green felspar is heated, it again loses its colour. B. H. B.

Bechi's so-called Picranalcime from the Monte Catini Mine, Monte Caporciano. By E. Bamberger (*Jahrb. f. Min.*, 1882, 2, Ref., 22).—Crystals of this picranalcime were examined crystallographically, optically, and chemically. In all these properties it agrees with analcime; it is nothing but analcime, and "picranalcime" must be removed from mineralogical lists. Magnesia is not contained in it.

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	H_2O.
57·08	21·51	13·63	0·32	8·32 = 100·86

H. B.

Spodumene and the Products of its Alteration. By G. J. Brush and E. S. Dana (*Jahrb. f. Min.*, 1882, 2, Ref., 355—358).—This paper gives the results obtained in a study of the spodumene from Branchville, Connecticut, and of the various minerals derived from its alteration.

The unaltered spodumene occurs in crystalline masses, with albite, a little quartz and mica, apatite, lithiophilite, columbite, garnet, uraninite, &c. In addition to this massive variety, spodumene also occurs, unaltered, as nuclei of distinct pseudomorphous crystals. The fresh spodumene is perfectly transparent, sometimes colourless, sometimes pink. It shows the prismatic cleavage with unusual perfection. The analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Li_2O.	Na_2O.	K_2O.	Loss.	Total.
64·25	27·20	0·20	7·62	0·39	trace	0·24	99·90

Sp. gr. 3·193. The formula is then $Li_2Al_2Si_4O_{12}$.

Alteration of the Spodumene.—As the results of the alteration, β-spodumene and cymatolite were found. The following independent minerals were also found: albite, microcline, muscovite, and killinite.

The β-spodumene is compact, apparently homogeneous, having a rather indistinct fibrous structure. H. = 5·5—6. Sp. gr. = 2·644—2·649. Colour, white to greenish-white. The results of the analysis were as follows:—

SiO_2.	Al_2O_3.	Li_2O.	Na_2O.	K_2O.	Loss.	Total.
61·51	26·56	3·50	8·14	0·15	0·29	100·15

The ratio obtained, $R_2O : R_2O_2 : SiO_2 = 1 : 1 : 4$, is the same as that of spodumene, in which, however, half of the lithium has been removed and its place taken by sodium. The formula is then $(LiNa)_2Al_3Si_4O_{12}$.

It is not entirely decomposed by treatment with hydrochloric acid, 67·56 per cent. remaining insoluble. The analysis gave the following results, I being the soluble, II the insoluble part:—

	SiO_2.	Al_2O_3.	Li_2O.	Na_2O.	K_2O.	Total.
I.	48·13	40·50	10·90	—	0·47	100·00
II.	68·18	20·07	—	11·74	—	100·00

The insoluble part closely resembles albite, $Na_2Al_2Si_6O_{16}$, while the soluble part has the composition $Li_2Al_2Si_2O_8$. This the author calls *Eucryptite.*

The β-spodumene is therefore a mechanical mixture of eucryptite and albite. The microscopical examination of thin sections confirms this view.

Eucryptite crystallises in the hexagonal system with basal cleavage. Sp. gr. = 2·647. In form and composition, it resembles nepheline.

Cymatolite has a fibrous structure. Sp. gr. = 2·692—2·699. Colour white to pink. Chemical analysis gave—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
59·38	26·67	0·62	7·68	3·51	2·01	99·87

The ratio obtained is $R_2O : Al_2O_3 : SiO_2 = 1 : 1 : 4$. The formula is therefore $(Na,K,H)_2Al_2Si_4O_{12}$. It is derived from the β-spodumene, and is also a mechanical mixture.

Albite occurs pseudomorphous after spodumene. An analysis gave—

SiO_2.	Al_2O_3.	MgO.	Na_2O.	K_2O.	Loss.	Total.
67·60	20·09	0·15	11·69	0·11	0·14	90·78

thus corresponding to the formula $Na_2Al_2Si_6O_{16}$.

Microcline arises from the alteration of the spodumene. The composition is shown by the following analysis:—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	Loss.	Total.
64·55	19·70	0·58	15·62	0·12	100·57

Killinite probably consists of very finely divided mica, impregnated with more or less amorphous silica. The want of homogeneity renders the analysis very variable.

The cymatolite is often further changed into an impure kaolin, and associated with this is a pink clay-like mineral resembling montmorillonite. The analysis of which gave—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Li_2O.	Na_2O.	K_2O.
51·20	22·14	trace	0·18	3·53	3·72	trace	0·18	0·38

Loss.	P_2O_5.	Total.
17·08	1·42	99·83

The authors suggest that this is the result of the further alteration of the cymatolite. B. H. B.

Hiddenite, an Emerald-green Variety of Spodumene. By J. L. Smith, E. S. Dana, and L. Smith (*Jahrb. f. Min.*, 1882, **2**, Ref., 345—346).—This mineral occurs, together with quartz, mica, rutile, beryl, and orthoclase in the gneiss and mica slates of Alexander Co., N. Carolina. The following 18 crystalline forms occur: $\infty P\bar{\infty}$, $0P$, $\infty P\frac{\bar{3}}{2}$, ∞P, $\infty P\grave{2}$, $\infty P\grave{3}$, $2P$, P, $\infty P\grave{\infty}$, $4P$, $\frac{3}{2}P$, $-6P\grave{3}$, $-8P\frac{\grave{4}}{3}$, $-4P\grave{2}$, $\frac{4}{3}P\grave{2}$, $4P\grave{2}$, $3P\frac{\grave{3}}{2}$, $6P\frac{\grave{6}}{5}$. Among these, the last 10 are new for the species. Twin crystals are more frequent than simple ones. The cleavage is parallel to ∞P. Sp. gr. = 3·152—3·189. The analysis gave the following result:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Li_2O.	Na_2O.	Loss.	Total.
64·35	28·10	0·25	7·05	0·50	0·15	100·40

B. H. B.

Analysis of Petalite from Utö. By K. Sondén (*Jahrb. f. Min.*, 1882, **2**, Ref., 363—364).—The following analytical results were obtained:—

SiO_2.	Al_2O_3.	Li_2O.	Na_2O.	CaO.	P_2O_5.	Loss.	Total.
76·91	16·85	4·15	0·73	0·27	0·31	0·84	100·06

From this the formula $Li_2O,Al_2O_3,8SiO_2$ was calculated.

B. H. B.

Analysis of Scapolite. By L. Sipöcz (*Jahrb. f. Min.*, 1822, **2**, Ref., 22).—1, from Malsjö; 2, from Arendal; 3, Gouverneur.

	SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
I.	52·48	25·56	0·39	—	12·44	6·52	0·79
II.	52·57	24·24	0·26	—	11·57	7·19	0·42
III.	52·65	25·32	0·11	0·23	11·30	6·64	1·58

	H_2O.	CO_2.	SO_3.	Cl.
I.	0·61	0·14	0·58	0·27 = 99·78
II.	0·69	0·39	0·90	0·23 = 98·46
III.	0·42	—	0·14	0·33 = 98·72

Scapolite from Rossie gave 0·10 per cent. SO_3, and that from Vesuvius 0·22 per cent. H. B.

New Face on Stilbite (Desmin). By M. F. HEDDLE (*Jahrb. f. Min.*, 1882, **2**, Ref., 25).—The face is $3P\breve{3}$ (rhombic) or $\infty\not{P}3$ (monosymmetrical), as shown by approximative measurement and zonal relationships. The localities are Loch Humphrey and Long Cray in Dumbartonshire, and also Farrugaric-Wuardi in Australia.

H. B.

Crystalline Form of Idocrase (Vesuvian). By G. DÖLTER (*Jahrb. f. Min.*, 1883, **1**, Ref., 8).—The author examined a series of idocrase crystals from Ala, Vesuvius, the Banat, Maine, and Pfitsch, in order to determine whether the mineral really belonged to the tetragonal system. The results he obtained agreed very satisfactorily with those obtained by Zepharovich:

$$0P : P = 142° \ 45' \ 29''$$
$$P : P = 129° \ 19' \ 39''$$

Several of the best measurements agree also with the values obtained by v. Kokscharoff:

$$142° \ 46\tfrac{1}{2}' \text{ and } 129° \ 21'.$$

Crystals occur, however, in which the results differ by several minutes from the above normal values, but the author arrives at the conclusion that the deviation is not of such a character as to support the theory that idocrase does not belong to the tetragonal system.

B. H. B.

Minerals from Fritz Island, Pennsylvania. By B. SADTLER, Jounr. (*Amer. Chem. J.*, **4**, 356—357).—These minerals were found associated with thomsenite and calcite, and more rarely with a zeolite which has been analysed by Genth (*Mineralogy of Pennsylvania*, p. 110). (1.) *Chabazite* forming well-developed rhombohedral crystals, colourless, having a vitreous lustre. Sp. gr. = 2·3 and hardness = 4. (2.) *Mesolite*, in globular concretions or tufts of fine white fibres. Hardness = 2·5 and sp. gr. 2·4. The analytical numbers show the composition of the mineral after deduction of about 0·2 per cent. of calcite, which could not be completely removed. (3.) *Apophyllite* occurring in tetragonal tablets, modified by octohedral planes. The crystals are colourless with pearly lustre. The analytical results are as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	
(1.)	50·28	17·83	trace	6·96	0·22	2·40	2·43	20·21	—	= 100·33
(2.)	43·29	24·02	trace	12·15	—	—	3·40	16·01	—	= 99·87
(3.)	51·02	—	1·49	24·40	—	5·87	—	16·75	0·40	= 99·93

H. W.

Prehnite from Tuscany, &c. By A. CORSI and E. BECHI (*Jahrb. f. Min.*, 1882, **2**, Ref., 26—29).—*Prehnite from Impruneta.*—The form and behaviour of the specimen was normal; the analysis of Corsi (I) and of Bechi (II) gave—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O,K_2O.	H_2O.	
I.	42·35	24·67	0·92	25·77	0·45	—	4·81	= 98·97
II.	43·80	23·90	0·70	24·60.	1·70	3·8	0·30	= 98·80

Corsi's analysis leads to the generally accepted formula

$$H_2Ca_2Al_2Si_3O_{12},$$

and he believes that Bechi's analysis is for some reason incorrect.

Specimens from Impruneta are pseudomorphs of prehnite after analcite.

An analysis of specimens from Figline (Prato) is given under III. Bechi has described and analysed a mineral resembling prehnite from Monte Catini, but the analysis (IV) of Corsi shows it to be nothing but prehnite. No. V is the analysis of a sample from Monte Perrone, Elba.

Bechi, in replying, gives three analyses of prehnite from Monte Catini, which agree with those of other observers; they are Nos. VI, VII, VIII; his analysis No. II is therefore incorrect.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Mn_3O_4.	N.	
III.	42·36	24·14	1·10	26·87	0·30	4·85	—	—	= 99·62
IV.	42·86	24·20	0·99	27·03	—	4·96	—	—	= 100·04
V.	44·03	23·20	2·05	26·24	—	4·90	—	—	= 100·42
VI.	43·41	23·64	1·03	24·54	—	5·09	1·87	0·22	= 99·80
VII.	44·00	24·79	1·53	23·98	—	5·06	1·03	0·20	= 100·59
VIII.	43·63	23·39	2·40	26·08	—	4·30	—	—	= 99·80

H. B.

Prehnite and Laumontite from Monte Catini. By E. BECHI (*Jahrb. f. Min.*, 1882, **2**, Ref., 29—30).—The following analysis is given of small globules of a zeolite supposed to be laumontite:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	
53·78	19·28	3·13	8·34	0·52	15·00	= 100·05

H. B.

Epistilbite. By C. O. TRECHMANN (*Jahrb. f. Min.*, 1882, **2**, Mem., 260—268). — This mineral was found in basalt near Hartlepool among the fragments of "whinstone," used as road metal. As there is no rock in the neighbourhood resembling this basalt, it seems probable that it was originally brought there by ship as ballast, and afterwards utilised for road-making. The analysis gave the following results:—

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
I.	56·54	19·17	8·75	1·25	15·68	101·39
II.	56·76	18·20	8·61	1·69	15·52	100·78

Sp. gr. = 2·247; hardness, 4 to 4·5. The following forms occur in the crystals:—∞P, $0P$, $\infty\breve{P}\infty$, $\breve{P}\infty$, $+\frac{1}{2}P$. B. H. B.

Epistilbite and Heulandite. By P. JANNASCH (*Jahrb f. Min.*, 1882, **2**, Mem., 269—280).—This paper gives the results of analyses of heulandite and epistilbite from Iceland:—

Analysis of Heulandite (Berufjord).

SiO_2.	Al_2O_3.	CaO.	SrO.	Li_2O.	K_2O.	Na_2O.	H_2O.	Total.
57·72	16·47	7·00	0·49	trace	0·44	1·63	16·91	100·66

Sp. gr. = 2·216.

Analysis of Epistilbite (Berufjord).

SiO_2.	Al_2O_3.	CaO.	Li_2O.	K_2O.	Na_2O.	H_2O.	Total.
57·57	17·49	7·98	trace	trace	1·69	15·29	100·02

Sp. gr. = 2·255. B. H. B.

Zinc Aluminite, a New Mineral Species. By E. Bertrand and Damour (*Jahrb. f. Min.*, 1882, **2**, Ref., 351—352).—This mineral occurs, with other zinc minerals, at Laurium, in the form of greenish-white hexagonal tablets. The angle does not always measure 120°, 123° and 124° having been observed. The sp. gr. is 2·26; the hardness is less than 3. Heated in a closed tube, it gives up water. It is soluble in nitric acid, leaving 5 to 7 per cent. of clay as residue. The analysis gave

SiO_2.	Al_2O_3.	ZnO.	CuO.	H_2O.	Total.
12·94	25·48	34·69	1·85	25·04	100·00

from which the formula $6ZnO,3Al_2O_3,2SO_3 + 18H_2O$ is deduced.

B. H. B.

Chlorophyllite from Loquidy, near Nantes. By Baret (*Jahrb. f. Min.*, 1882, **2**, Ref., 30).—Notice of and mode of occurrence at the above locality. H. B.

Chemical Composition of Epidote. By E. Ludwig (*Jahrb. f. Min.*, 1882, **2**, Ref., 22—23); **Chemical Composition of Epidote from Quenast.** By A. Renard (*ibid.*, 23).—Ludwig, in criticising the work of Laspeyres, upholds the correctness of previous analyses of epidote, and refers more especially to one of his previous analyses of Sulzbach epidote (*Jahrb. f. Min.*, 1873, 89), showing that it is perfectly free from quartz and giving fresh analyses of it. The mean of two analyses agrees well with the formula $Si(Al,Fe)_6Ca_4H_2O_{26}$, calculating for 70 per cent. Al-epidote and 30 per cent. Fe-epidote. He further holds that most other analyses agree with this formula, and considers it unnecessary to have resource to Laspeyres's hypothesis, that the iron existed originally as ferrous oxide, and became converted in course of time into the ferric condition.

Renard gives the following analysis made on microscopically tested material:—

SiO_2.	Al_2O_3.	Fe_3O_3.	FeO.	CaO.	H_2O.
38·26	24·75	11·07	0·56	23·63	2·26 = 100·53

Considering the ferrous oxide as isomorphous with the lime, the formula given by Tschermak and Ludwig is deduced. The mineral is easily decomposed by heating it in a sealed tube with hydrochloric acid at 125—130°. H. B.

Hornblende and Anthophyllite after Olivine. By BECKE (*Jahrb. f. Min.*, 1883, **1**, Ref., 32—33).—Near Rosswein, in Saxony, the author found blocks of a rock containing green patches, with a radial structure. These patches contain a hard black kernel of olivine, which is surrounded by a radiated layer, 5—6 mm. thick. This cover consisted of two zones; an inner one, which is of a brown colour, consisting of anthophyllite with grains of magnetic iron ore, and an outer one, which is leek-green, formed by hornblende together with granules of a spinel-like mineral. Clinochlore occurs as a secondary constituent in the hornblende zone, and serpentine in the olivine kernel.

The author is of the opinion that the formations described above result from a reciprocal action of the silicate of the felspar and the olivine. B. H. B.

Gedrite in the Gneiss of Beaunan, near Lyons. By F. GONNARD (*Jahrb. f. Min.*, 1883, **1**, Ref., 27).—This mineral occurs in gneiss in almond-shaped masses, which have a lamellar or fibrous structure. The colour is straw-yellow to brown; the other distinctive characters coincide with those of an anthophyllite containing alumina. B. H. B.

Bole from Steinkirchen, near Budweis, in Bohemia. By G. STARKL (*Jahrb. f. Min.*, 1882, **2**, Ref., 21).—After drying at 100°, it contained—

H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	MnO.	
10·53	46·734	26·166	12·345	1·641	1·315	0·978	0·280	= 99·989

It fills clefts in granite. H. B.

Polyhydrite from St. Christoph Mine, Breitenbrunn, in Saxony. By G. STARKL (*Jahrb. f. Min.*, 1882, **2**, Ref., 21—22).—Colour chestnut-brown, streak ochreous yellow; brittle when fresh; lustre glassy. H. = 2—3, G. = 2·1272—2·2012. Soluble in hydrochloric acid. The amount of water contained varies with the moisture of the air; but when fresh, it is 34·604 per cent. After drying at 100°, it gave:—

H_2O.	SiO_2.	CaO.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	
16·749	34·131	4·236	8·867	32·656	3·308	0·422	= 100·369

whence the formula $Ca_2MnSi_3O_9 + Fe_8Al_4Si_9O_{36} + 18H_2O$. Further examination is necessary, and it is especially necessary to show that the mineral is homogeneous. H. B.

Chromic Tourmalin and the Deposits of Chrome-iron in the Urals. By A. COSSA and A. ARZRUNI (*Gazzetta*, **12**, 520—535).—The chrome-iron ore of the Ural mountains occurs most frequently in minute granules disseminated through serpentine, but occasionally also in kidney-shaped masses, and in beds of various thickness.

The wide diffusion of chromic oxide, Cr_2O_3, as a constituent in small quantity of various silicates, and especially of *fuchsite*, talc, emerald, and diallage, in which its presence is revealed by the characteristic green colour, renders it highly probable that this oxide is the original, or at least the most ancient form in which chromium occurs. Its combination with ferrous and ferric oxide in the chromites is an occurrence of later date, probably due to the substitution of Cr_2O_3 for an equivalent quantity of Fe_2O_3 in magnetite—a view which is supported by the presence of nests of magnetite in chloritic and talcose schists and in serpentine, at distances of a few meters from beds of chromite. Moreover, it is impossible to overlook the simultaneous action of chromium and other modifying agents, *e.g.*, water and carbonic acid, on the rocks which enclose the deposits of chrome-iron ore. Simultaneously with the partial transformation of talc and serpentine into mesitine, brucite, and texasite, with traces of nickel derived from the so-called noble serpentine, the action of chromium manifests itself in the formation, by epigenesis, of many chromiferous silicates at the expense of serpentine, talc, and chlorite.

These chromiferous minerals are *uwarowite;* an adamantine garnet containing calcium and iron with traces of chromium (*demantoïd*); chromiferous clinochlore or *kocubejite;* chromiferous pennine, or *kämmererite* and *rhodochromite;* and two minerals hitherto unexamined, viz., a chromiferous mica of fine emerald-green colour, and a dark-green chromiferous tourmalin. These two minerals were found in a mine of chrome-iron ore situated four kilometers to the north-east of the village of Syssert on the left bank of the Kimenka, which is a small affluent of the River Syssert.

The tourmalin, which occurs also in a few other localities, forms prismatic crystals belonging to the rhombohedral system and having the axes $a:c = 1:0{\cdot}45149$, this value of c being greater than has hitherto been observed in tourmalins. The chromic tourmalin differs also from other tourmalins by its optical properties. It has a strong dichroïsm. When viewed by daylight, the rays which vibrate parallel to the optic axis exhibit a yellowish-brown colour, while those which vibrate at right angles to that axis are bluish-green.

When heated before the blowpipe in thin fragments, this mineral fuses readily to an opaque greyish-white non-scariaceous globule. With borax, it gives a deep emerald-green, and with phosphorus salt a green glass, enclosing a skeleton of silica. Quantitative analysis gave the following results:—

Fluorine	0·65	FeO, with trace of MnO	2·91
SiO_2	36·79	MgO	4·47
B_2O_3	9·51	CaO	0·72
Al_2O_3	30·56	Na_2O, with trace of K_2O	1·36
Cr_2O_3	10·86	Water	2·25
			100·08

Assuming that the chromic oxide replaces part of the alumina, the chromic tourmalin of the Urals may be placed in Rammelsberg's third group (*Handbuch der Mineralchemie*, 2te Auflage, p. 544).

The chromates of the Urals occur in talcose and chloritic schists, amongst which may be specially mentioned a variety of talcose schist (called by the miners *litwyanite*), distinguished by the green colour of its talc, and including spathic fragments of mesitine, together with iron pyrites and magnetite. The most abundant chromate of the Urals is crocoite, or chromate of lead. H. W.

Dioptase from the Corderillas of Chili. By M. Bauer (*Jahrb. f. Min.*, 1882, **2**, Ref., 24).—The crystals obtained were small and transparent, and were recognised by their characteristic form,

$$\infty P2.—2R.$$

Sp. gr. 3·325; H. = 5. Qualitative analysis showed only copper, silica, and water. The statement of Dana, "reported as found in the Duchy of Nassau, between Oberlahnstein and Braubach," is due to a confusion between "smaragdochalcite" and dioptase. H. B.

Chemical and Microscopical Researches on Italian Rocks and Minerals. By A. Cossa (*Jahrb. f. Min.*, 1882, **2**, Ref., 47—49).—This publication is a collection of the author's papers, arranged chronologically. The description of the lherzolite, from Piedmont, is very complete; many analyses of the rocks and of the contained minerals are given. The examination of rocks from many localities is fully detailed. H. B.

The Granite Hills of Königshain, in Oberlausitz, with especial regard to the Minerals found therein. By G. Woitschach (*Jahrb. f. Min*, 1882, **2**, Ref., 12—17).—The granite makes its appearance at many points, but is otherwise covered with diluvial deposits or clay schists. The texture of the granite varies from porphyritic to coarsely granular, and to granite of normal appearance. Potash mica is absent. The upper layers contain cavities, in which are the crystals of various minerals, either attached or broken, and imbedded in a clay-like material. These various minerals amount to 31 in number.

Microcline, crystals composed of albite and microcline laminæ, after the manner of perthite. Crystals of pure microcline were also identified optically. The crystals are either simple or twins, according to one or more of the well known laws. *Albite*, crystals or shapeless masses. *Quartz*, mostly darkly coloured. *Mica*, meroxene and zinnwaldite of Tschermak. *Chlorite*, small plates. *Aphrosiderite*.

The analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	P_2O_5.	H_2O.
27·06	19·56	11·71	28·91	1·18	0·38	trace	9·73 = 98·73

whence $(Fe,Ca.Mg)_5(Fe)_2Si_5O_{18} + 2Al_2H_6O_6$. *Diaspore*, probable. *Cassiterite* occurs in the felspar. *Hæmatite*, in small amount. *Anastase*, one crystal. *Pyrite*, *wolfranite*, at Mengelsdorf, in large quantity, as veins. *Molybdenite*, in small quantity. *Magnetite*, in usual forms, and also pseudomorphous after mica. *Fergusonite*, *æschynite*, *zircon*, and *melacon* occur in various conditions; analysis of partially decomposed crystals is given; water 5·024 per cent. *Thorite*, *xenotime*, *fluorite*, *beryl*, *epidote*, all in small quantities only. *Tourmalin*, *hyalite*, *psilomelane*, frequent. *Calcite*, rare. H. B.

The Rapakiwi Granite, from Finland. By T. v. UNGERN-STERNBERG (*Jahrb. f. Min.*, **2**, Ref., 382—383).—This rock is an amphibole-biotite-granite, with accessory zircon, magnetite, ilmenite, apatite, and triphyline. The analysis gave the following results:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	70·329	1·030	11·828	3·730	2·376	trace	2·547	0·200
II.	71·008	—	11·861	3·921	2·312	—	1·235	0·257

	K_2O.	Na_2O.	H_2O.	CO_2.	P_2O_5.	Ca.	F.	Total.
I.	3·085	2·410	1·377	0·135	0·515	0·144	0·136	99·842
II.	3·020	2·585	0·929	0·092	0·848	0·882	0·928	99·878

B. H. B.

Phyllite from Rimogens, in the Ardennes. By E. GENITZ (*Jahrb. f. Min.*, 1882, **2**, Ref., 67—68).—This rock is a crystalline mixture of quartz, green mica, tourmalin, and yellowish-brown microliths. These microliths were regarded as zircon, but the author shows that this is erroneous, the form being that of rutile, and further, of the isolated particles, 76·3 per cent. is made soluble by fusion with hydrogen potassium sulphate, and then yields 59·64 per cent. titanic acid.

Small lense-shaped collections of biotite (?) around a magnetite or pyrites crystal occur in the phyllite; they are not a secondary product. H. B.

Micaceous Porphyrite of Morvan. By A. MICHEL-LÉVY (*Jahrb. f. Min.*, 1883, **1**, Ref., 37—41).—The chemical analysis of a rock from Goie, in Morvan, which the author describes as "micaceous andesite porphyrite," in which the augite has become converted into chalcedony, gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	P_2O_5.		Total.
67·55	15·00	5·00	3·00	1·10	1·40	6·10	0·60	trace	=	99·75

This analysis would indicate an orthophyr rather than a porphyrite. B. H. B.

The Melaphyres of the Little Carpathians. By G. E. STEIN (*Jahrb. f. Min.*, 1882, **2**, Ref., 59).—The rock occurs in isolated or connected bosses, in the red sandstone. The predominating constituents are plagioclase, augite, and augite microliths, and decomposed olivine. There are also present magnetite, picolite, apatite, and occasionally bronzite and orthoclase in the varieties rich in augite. Secondary products are delessite, quartz, calcite, iron oxides, and silica. The magma is partially or completely devitrified. The structure varies from irregular to fluidal porphyritic or mandelstein. A variety from Peterklin contains globules 3—30 mm., formed by the decomposition of the rock. H. B.

The so-called Andesites of South and Central America. By C. W. Gümbel (*Jahrb. f. Min.*, 1882, **2**, Ref., 59—63).—These eruptive rocks, generally classified according to the amounts of augite, or hornblende and quartz they contain, are to be divided into two groups; those of the first are lighter coloured trachytic rocks, containing much silica (over 57 per cent.), those of the second group being darker, more resembling basalt, and contain less silica—under 57 per cent. when quartz particles are absent; the rocks of the second group are also the older. If this division is supported by an examination of the rocks *in situ*, the author would propose to retain the name andesite for the lighter more acid rocks, while he would class the others as olivine-free felspar basalts. Detailed descriptions are given, together with the analyses of specimens collected by Wagner, in 1870. H. B.

Examination of Ophites from the Pyrenees. By J. Kühn (*Jahrb. f. Min.*, 1882, **2**, Ref., 63—64).—The examination of specimens from over 100 localities has resulted in the harmonising of various results obtained by other authors, whose examinations have not been so extended. The essential constituents of an ophite are ordinary augite, "diallage-like-augite," diallage, uralite, viridite, felspar, epidote, titanic iron; as accessories are magnetite, pyrites, hæmatite, apatite, hornblende, quartz, calcite, and biotite. By the expression "diallage-like augite" is to be understood ordinary augite, which has become fibrous by decomposition. H. B.

The Clay Ironstone of Rheinhesse. By Tecklenburg (*Jahrb. f. Min.*, 1882, **2**, Ref., 50).—These deposits lie directly on tertiary limestone; they are accompanied by various clays and marls. The author supposes them to have been formed from, and by the disintegration of, a superincumbent bed of limestone containing 1—2 per cent. magnesium carbonate, and 0·3—2·5 per cent. iron and manganese carbonates and hydrates. By the percolation of water, this upper layer was acted upon, and the solution penetrating further, gave rise to the formation of numerous cavities. Those cavities lying above the general water level became filled with air, and when again the solution found its way into them, the iron and manganese were deposited as hydrates, and the liberated carbonic acid, acting on the walls of the cavities, enlarged them, thus allowing of the further growth of the contained nodules by the periodic recurrence of these processes. H. B.

The Lake Deposits of Kolsnaren, Viren, and Högsjön, Södermanland, Sweden. By A. W. Cronquist (*Jahrb. f. Min.*, 1882, **2**, Ref., 51).—The result of the author's examination is that these deposits are of no technical value. The deposit lies 2—3 meters or more below the lowest water level, and either forms a band 3—300 meters wide following the shore, or else is more generally deposited; the thickness does not exceed a few millimeters. The mean percentage of ferric oxide is 52·4—54; sulphur, 0·07—0·06; and phosphorus, 0·012—0·93. H. B.

Artificial Formation of Various Rocks. By F. Fouqué and A. Michel-Lévy (*Jahrb. f. Min.*, 1882, **2**, Ref., 64—65).—The authors in continuing their researches have succeeded in preparing samples having all the characteristics of basalt and diabase. A mixture of 2 parts olivine, 1 augite, and 2 of labradorite, fused for 48 hours at a white heat, deposited well-defined olivine and magnetite crystals; after another 48 hours at a bright red heat, there were formed lense-shaped labradorite crystals, augite microliths, a second generation of magnetite, and picotite octahedra; but little of the glassy magma remained, the whole exactly resembling many natural basalts. Employing a mixture of anorthite and augite, lense-shaped plagioclase was obtained at a white heat, and after several days at a bright red heat, irregular augite crystals cementing the felspars together had formed, the characteristic structural appearance of the ophites. On replacing the anorthite by labradorite, the augite separated in microliths, owing to the small difference in fusibility of the ingredients; the sections resembled those of a trachyte. H. B.

Meteorite of Louans (Indre-et-Loire). By A. DAUBRÉE (*Jahrb. f. Min.*, 1882, **2**, Ref., 30).—The stone fell 25th January, 1843, and buried itself half a meter in the soil. It weighed 3 kilos.

H. B.

Analysis of a Spring Water from Rindö, near Stockholm. By A. W. CRONQUIST (*Jahrb. f. Min.*, 1882, **2**, Ref. 51).—The water contains in 100,000 parts:—

CO_2.	FeO.	CaO.	MgO.	SO_3.	Cl.
26·5	19·5	2·4	2·2	6·5	1·7

H. B.

Organic Chemistry.

Isomeric Monochlorallyl Iodides. By P. v. ROMBURGH (*Rec. Trav. Chim.*, **1**, 233—238).—Dilute solutions of aluminium iodide and allylidene chloride in carbon bisulphide react very violently at 0°, with liberation of iodine and production of a carbonaceous mass, but no allylidene iodide is formed. Aluminium chloride alone reacts violently with allylidene chloride, with evolution of torrents of hydrochloric acid.

Allylidene chloride was heated with excess of dry potassium iodide at 100° for 24 hours, the product treated with water, and the dense liquid thus obtained was dried over calcium chloride and distilled. The purified product has the composition C_3H_4ClI, and boils at 162° with partial decomposition. It is a colourless liquid, with a penetrating odour and very acid taste; its sp. gr. at 15° is 1·977. The same product is obtained when allylidene chloride is heated with calcium iodide at 100°, but the reaction proceeds more quickly, and the yield is greater. Calcium iodide is, however, without action on the analogous compound, ethylidene chloride, and hence it appeared probable that the product C_3H_4ClI is not $CH_2 \vdots CH.CH \vdots ClI$, but that the allylidene chloride has been converted by intermolecular displacement into CHCl ⁚ CH.CH_2I, just as concentrated hydrochloric acid converts allylidene chloride into β-chlorallyl chloride. This chlorallyl iodide combines readily with mercury, forming a compound very soluble in boiling alcohol, from which it separates in small white plates, which rapidly become yellow when exposed to air and light: this behaviour also would indicate that the iodine compound is a chloro-derivative of allyl iodide. Moreover it appears to be identical with the following compound.

β-chlorallyl iodide, C_3H_4ClI, is obtained by heating dry calcium iodide with β-chlorallyl chloride at 100°, treating the product with water, decolorising the dense liquid thus obtained with spongy copper, drying over calcium chloride, and distilling. It boils at 162° with partial decomposition, and is a colourless liquid with an irritating odour and a sharp taste; its sp. gr. at 18° is 1·97. It rapidly decomposes and becomes coloured. β-chlorallyl iodide combines readily with mercury, forming white plates, which are very soluble in alcohol, and rapidly become coloured when exposed to air and light. It reacts readily with silver nitrate and with potassium cyanide. When treated with potassium hydroxide, it yields β-chlorallyl alcohol, which the author has previously described (*Bull. Soc. Chim.*, **36**, 557).

α-Chlorallyl iodide, C_3H_4ClI, is obtained by heating α-chlorallyl chloride with calcium iodide at 100°. It boils with decomposition at about 150° under ordinary pressure, or at 95° under a pressure of 40 mm.; sp. gr. at 15° = 1·913. This iodide also combines with mercury. When heated with dilute potash or with silver oxide, it yields *α-chlorallyl alcohol*, a colourless liquid, with a slightly aromatic odour; it boils between 136° and 140°, and does not act violently on the skin like the β-derivative. α-chlorallyl iodide reacts readily with silver nitrate forming α-chlorallyl nitrate, a heavy, almost colourless liquid insoluble in water; it boils at about 140°. When heated with potassium cyanide, the iodide forms a yellowish liquid, with an odour resembling that of the nitrils; when boiled with potash solution, it evolves ammonia.

C. H. B.

Trimethylene Glycol and Trimethylene Bases. By G. Niederist (*Monatsh. Chem.*, **3**, 838—849).—Trimethylene bromide (m. p. 161—163°) is decomposed by heating with water much more quickly than ordinary propylene bromide, yielding trimethylene glycol, $OHCH_2.CH_2.CH_2.OH$, identical with that which Reboul and Geromont obtained by saponification of trimethylene diacetate (*C. J.*, 1871, 697, and 1874, 1153). This glycol becomes viscid at − 30°, and when exposed to the temperature of a mixture of solid carbon dioxide and ether, becomes very viscid, and soon deposits warty groups of needle-shaped crystals, finally solidifying to a silky crystalline mass. The crystals quickly deliquesce when taken out of the freezing mixture.

Action of Ammonia on Trimethylene Bromide.—When this bromide and alcoholic ammonia are left to act on one another in sealed tubes at ordinary temperatures, a saline mass is formed, containing, together with a large quantity of ammonium bromide, an amorphous body insoluble in water, together with the hydrobromides of certain non-volatile bases very slightly soluble in alcohol, easily in water. One of these hydrobromides (*a*) forms a sparingly soluble double salt with cadmium bromide, the other (*b*) with auric bromide. The same hydrobromides treated with strong potash-lye, yield the free bases.

The alcoholic solution filtered from the saline mass above mentioned yields on evaporation large quantities of a body identical with the amorphous insoluble substance which separates in the tubes. If the tubes are heated, the formation of this insoluble body is limited to the quantity which separates in them, and the resulting ammonium bromide is found to be drenched with a thick liquid, very sparingly soluble in alcohol, and containing a large quantity of the hydrobromides precipitable respectively by cadmium bromide and auric bromide.

The insoluble substance which collects in the tubes, and is obtained in the distillation of the alcoholic solution, forms, after washing with hot water, a very bulky jelly, insoluble in all the ordinary solvents, and not altered by boiling with strong acids. By boiling with strong potash-lye, it is converted into a non-brominated body which likewise resists the action of all ordinary solvents, and shrinks up when dried in a vacuum over sulphuric acid.

The *brominated body* in the dry state is a white to yellowish, horny, strongly hygroscopic mass, which quickly softens when exposed to the air, and swells up in water to the original volume, perhaps 20 times as great as that of the dried substance. The *non-brominated* compound in the dry state is white and friable; heated in a vacuum, it melts and decomposes at about 260°, giving off ammonia and methylamine, and yielding as distillate a mixture of very hygroscopic bases, which have an odour of pyridine, fume in the air, and form crystallisable platinochlorides.

The above-mentioned *cadmium salt* of the hydrobromide (*a*) separates in the first instance as an oily mass, which may be purified by repeated solution in hot water, reprecipitation by hydrobromic acid, and final washing with alcohol. Under absolute alcohol, it hardens after some time to a white porcelain-like mass easily pulverised under alcohol. The white powder thus obtained is highly hygroscopic, and dissolves readily in hot water, but if heated for some time in a vacuum at 100°, it becomes insoluble in water, and swells up to a transparent jelly. On adding soda-lye to its very dilute solution, the cadmium is precipitated, and the concentrated filtrate treated with stronger soda-lye yields the free base in white flocks, gelatinising when heated, and not volatilising with aqueous vapour. Its solution in hydrochloric or hydrobromic acid is precipitated by the chlorides of zinc, mercury, gold, and platinum, also by tannin and by iodised potassium iodide. All the double salts thus obtained are amorphous.

The analysis of the cadmium salt leads to the empirical formula $C_{16}H_{42}N_4Br_6Cd$, but on the supposition that the trimethylene group in the base remains intact, this formula must at least be trebled to give the molecular formula.

The *aurobromide*, obtained on adding auric bromide to the solution of the hydrobromide (*b*), after separation of the oily cadmium salt, separates in brick-red flocks, and forms, after drying in the exsiccator, an amorphous, transparent, brittle, pomegranate-red mass, which dissolves readily in hot water, but is decomposed by prolonged heating, with separation of metallic gold. Its analysis leads to the formula $(C_3H_6)_4N_3H_7,4HBr,4AuBr_3$. By decomposing this salt with hydrogen sulphide, the *hydrobromide* $C_{12}H_{35}N_3Br_4$ is obtained, as a white amorphous deliquescent mass, sparingly soluble in alcohol, and precipitated thereby from its concentrated aqueous solution in white flocks; and this hydrobromide treated with potash-lye yields the *free base* in white flocks, easily soluble in water, and not volatilising with aqueous vapour. H. W.

Action of Anhydrides on Aldehydes, Ketones, and Oxides. By A. P. N. FRANCHIMONT (*Rec. Trav. Chim.*, **1**, 243—251).—Ordinary aldehyde when heated with benzoic chloride on a sand-bath for six hours, yields a pitchy mass which contains crystals of benzoic acid, but from which no other substance could be isolated. Paraldehyde gives a precisely similar result. Valeraldehyde when treated in the same way yields hydrochloric acid and benzoic acid, together with liquid products which boil at a high temperature with partial decomposition. Acetone yields large quantities of hydrochloric acid, together with benzoic acid and the ordinary condensation-products of acetone. The same result is obtained when the acetone and benzoic chloride are left in contact for a long time at the ordinary temperature. When benzoic bromide is left in contact with acetone for a long time at the ordinary temperature, it behaves in a precisely similar manner, and does not, as Claisen has stated, form a crystalline addition-product. Acetone when heated with acetic chloride, or when left in contact with this compound for several months at the ordinary temperature, yields hydrochloric acid and the ordinary products of condensation, notably mesityl oxide. This observation has been confirmed by Beilstein and Wigand (*Bull. Soc. Chim.*, **38**, 167). When acetone is heated with acetic bromide at 125° in sealed tubes, the tubes are invariably shattered, but if the two liquids are left in contact at the ordinary temperature for several months, a thick dark-coloured liquid is formed, which evolves large quantities of hydrobromic acid. When this liquid is distilled, about half passes over below 120°, but it decomposes if heated to a higher temperature. Acetone, as Geuther has stated, does not combine with acetic anhydride.

Ethylidene acetochloride, the addition-product formed by the combination of aldehyde with acetic chloride, can be obtained in a state of purity by heating aldehyde or paraldehyde with an equivalent quantity of acetic chloride on the sand-bath for about six hours, and fractionating the product. Whether obtained from aldehyde or from paraldehyde, it is an optically inactive liquid which boils at 121·5° under a pressure of 746 mm.; sp. gr. at $15° = 1·114$. When distilled, it decomposes very slightly into aldehyde and acetic chloride, and consequently no satisfactory determinations of the vapour-density could be obtained. It is rapidly decomposed by water, and the chlorine was determined by heating the liquid in a sealed tube with water and silver nitrate. The method of Carius is not applicable, since the action of the strong nitric acid produces chloropicrin, which is only oxidised with difficulty.

By fractionation of that portion of the original product which boils above 125°, ethylidene diacetate was obtained (b. p. 167° at 744 mm.; sp. gr. at 15° = 1·073). 25 grams of this compound were obtained from 176 grams of aldehyde. The diacetate is formed only in very small quantity, when paraldehyde is heated with acetic anhydride in sealed tubes at 160—170° for six hours, although a large proportion of the paraldehyde is depolymerised. It can, however, be obtained by heating either aldehyde or paraldehyde with acetic anhydride for 12 hours at 183° in stout tubes which contain only a small quantity of the mixture; the ordinary aldehyde apparently gives the best yield. The diacetate has a feeble not unpleasant odour resembling that of the other diacetins; it has not the onion-like smell described by Geuther, and, contrary to the statement of the same chemist, it does not decompose when distilled. Determinations of the vapour-density by V. Meyer's method gave 5·08 and 5·13 (calculated, 5·069).

That portion of the crude product obtained by heating the aldehyde with acetic chloride which boils below 120° is very small. It consists mainly of aldehyde and acetic chloride, but apparently contains no ethylidene chloride.

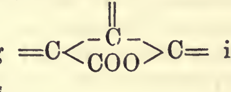
Compounds of the same class as ethylidene acetochloride, which are formed by the union of two anhydrides, show a greater or less tendency to split up under the influence of heat into more stable compounds, frequently into the original substances. This tendency apparently reaches a maximum in the case of the ketones. The same tendency is exhibited in different degrees by the compounds of the acid halides with the aldehydes, and reaches a maximum in the case of carbon oxychloride, which apparently will not combine with aldehyde under ordinary conditions. Mixed anhydrides, such as butylbenzoic anhydride, behave in a similar manner. C. H. B.

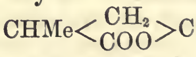
Paraldehyde. By A. P. N. Franchimont (*Rec. Trav. Chim.*, **1**, 239—242).—The generally accepted view of the constitution of paraldehyde would indicate that it is related to the ethers, since it contains oxygen united with two carbon-atoms which are not themselves in direct union with one another. It is, however, well known that phosphorus pentachloride acts on paraldehyde in a very different manner from its action on ethers.

Perfectly pure and dry paraldehyde may be boiled for several hours with metallic sodium, out of contact with air, without the metal being attacked. It can indeed be purified by distillation with sodium. It is also known that paraldehyde forms no aldehyde resin when boiled with even very strong solutions of potassium hydroxide; it does not reduce an ammoniacal solution of silver nitrate even when boiling, and does not combine with ammonia or with alkaline bisulphites at the ordinary temperature. When heated, it dissolves mercuric chloride, which is deposited on cooling; it also dissolves mercuric iodide, although to a less extent. Mercuric bromide is but very slightly soluble in paraldehyde at the ordinary temperature, and the two compounds may remain in contact at 16° for two days without any trace of ordinary aldehyde being formed, but when heated to about 90° the paraldehyde is evidently depolymerised, the liquid boils rapidly, and pure and dry aldehyde distils over.

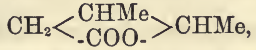
When paraldehyde is mixed with dry acetic chloride in equivalent proportions, there is at first a considerable reduction of temperature (in one case from 20° to 10° in three quarters of an hour, the temperature of the room being 16°), but after some hours the liquid acquires the temperature of the room and is now found to contain ordinary aldehyde. This is the first experimental proof that the depolymerisation is attended by absorption of heat. When paraldehyde and acetic bromide are mixed in equivalent proportions with similar precautions, the temperature is at first reduced even more rapidly, in one case from 20° to 5° in three minutes, but it afterwards rises with very great rapidity, and in a few minutes reaches 92°, when the mixture begins to boil and evolves large quantities of ordinary aldehyde. If heated to 100° or higher, it forms in both cases the same products as ordinary aldehyde. When acetic anhydride is mixed with paraldehyde, there is no reduction of temperature, and the two liquids may remain in contact for two days without any ordinary aldehyde being formed. Even at 100°, no depolymerisation takes place, but at 132° aldehyde is given off.

The reduction of temperature is also observed with benzoic chloride, hydrochloric acid (with the dry gas the temperature rises), and sulphuric acid. This fact may be shown as a lecture experiment by putting into one test-tube some aldehyde, and into another some paraldehyde, placing a thermometer in each tube, and then adding some strong sulphuric acid. With the aldehyde there is evolution of heat, but with the paraldehyde there is absorption of heat, and these changes can be rendered evident by throwing the images of the thermometers on to the screen. C. H. B.

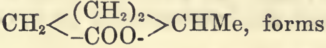
Non-saturated Acids (Part VI). By R. Fittig (*Annalen*, **216**, 26—29).—The results of the researches of Gottstein, Young, Jayne, Penfield, Hjelt, and Beer, afford evidence in favour of the author's view that the ring  $=\mathrm{C}<{}^{\overset{\|}{-\mathrm{C}-}}_{\mathrm{COO}}>\mathrm{C}=$ is characteristic of all lactones and lactonic acids. W. C. W.

Two New Caprolactones. By L. Gottstein (*Annalen*, **216**, 29—38).—*α-Methylvalerolactone*,  $\mathrm{CHMe}<{}^{\mathrm{CH_2}}_{\mathrm{COO}}>\mathrm{CHMe}$, is obtained by the action of sodium amalgam on crude β-acetisobutyric acid prepared from ethyl α-bromopropionate and ethyl acetoacetate by the process described by Conrad and Limpach (*Annalen*, **192**, 153). The alkaline solution is acidified with sulphuric acid and boiled for a few minutes. When cold, it is neutralised with potassium carbonate and extracted with ether. On evaporating the ether, the lactone remains as a colourless liquid which boils at 206° and does not solidify at −17°. It is soluble in 20—25 times its volume of water; when the cold saturated solution is warmed, a portion of the lactone separates out, but is redissolved when the temperature reaches 80°.

The formation of the lactone takes place in two stages: β-acetoisobutyric acid unites with a molecule of hydrogen, yielding the unstable α-methyl-γ-hydroxyvaleric acid, which loses a molecule of water and forms symmetrical caprolactone. The barium salt of α-methyl-γ-hydroxyvaleric acid, $C_6H_{11}O_3$, is obtained by boiling the lactone with baryta-water.

β-Methylvalerolactone,  $CH_2<\begin{matrix}CHMe\\ \text{-COO-}\end{matrix}>CHMe$, has not been obtained in a state of purity. It is formed by the action of sodium amalgam on an aqueous solution of β-acetobutyric acid prepared from ethyl acetosuccinate (*Annalen*, **192**, 153). The crude lactone boils between 205° and 212°. W. C. W.

δ-Lactone of Normal Caproic Acid. By L. WOLFF (*Annalen*, **216**, 127—138).—*γ-Acetobutyric acid*, $COMe.(CH_2)_3.COOH$, is formed when ethyl acetoglutarate is boiled for several hours with hydrochloric acid diluted with twice its bulk of water. It is a thick liquid boiling at 275°, miscible with water, alcohol, and ether. It solidifies in a freezing mixture to a crystalline mass melting at 13°, which absorbs moisture from the air, forming the hydrate $C_6H_{10}O_3 + H_2O$. This compound crystallises in monoclinic prisms ($a : b : c = 0{\cdot}7691 : 1 : 0{\cdot}8845$, $\beta = 75° 20'$) which melt at 36°. The acetobutyrates of calcium, zinc, and potassium are crystalline salts freely soluble in water. Calcium acetobutyrate crystallises with 1 mol. H_2O. The needle-shaped crystals of the silver salt, $AgC_6H_9O_3$, are soluble in hot water.

δ-Acetobutyric acid is converted into the δ-lactone of normal caproic acid by the action of sodium amalgam on its aqueous solution at 30°. The lactone,  $CH_2<\begin{matrix}(CH_2)_2\\ \text{-COO-}\end{matrix}>CHMe$, forms thin colourless crystals melting at 18°, boiling at 230°, soluble in alcohol, ether, and water. The aqueous solution of the lactone changes into δ-hydroxycaproic acid, and conversely a solution of δ-hydroxycaproic acid undergoes partial decomposition into the lactone and water. When the δ-lactone is dissolved in boiling baryta-water, the barium salt of δ-hydroxycaproic acid, $Ba(C_6H_{11}O_3)_2$, is obtained as an amorphous mass. On adding silver nitrate to a solution of the barium salt, a gelatinous precipitate is thrown down, which dissolves in hot water, but separates out again on cooling. If the jelly is separated from the mother-liquor, it slowly changes into a crystalline mass. W. C. W.

Hepto- and Octo-lactones. By S. YOUNG (*Annalen*, **216**, 38—45).—*α-Ethyl-valerolactone*,  $CHEt<\begin{matrix}CH_2\\ COO\end{matrix}>CHMe$, obtained by the action of sodium amalgam on an aqueous solution of the α-ethyl-β-acetopropionic acid, described by Thorne (this Journal, Trans., 1881, 336), is a colourless liquid which does not solidify at 18°, and boils at 219·5°. Its sp. gr. at 16° is 0·992.

Barium hydroxyheptylate, $Ba(C_7H_{13}O_3)_2$, is obtained as a gummy amorphous mass when ethyl-valerolactone is dissolved in boiling baryta-water. The *silver salt*, $C_7H_{13}O_3Ag$, is deposited in crystals from a warm saturated solution on cooling. Hydroxyheptylic acid cannot exist in the free state.

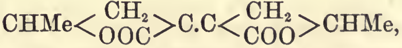
The ethyl salt of methylethylacetosuccinic acid is produced by the action of an excess of sodium ethylate and methyl iodide on ethyl β-ethylacetosuccinate. On treating the free acid (prepared by saponifying this compound with hydrochloric acid) with water and sodium amalgam, *α-ethyl-β-methylvalerolactone*,  $\mathrm{CHEt}<\substack{\mathrm{CHMe}\\ \text{-COO-}}>\mathrm{CHMe}$, is obtained. This lactone boils at 226·5°; in other respects it closely resembles ethyl valerolactone. It dissolves in hot baryta-water, yielding barium hydroxyoctylate. Silver hydroxyoctylate is crystalline.

W. C. W.

Lactones from Allylmalonic, Diallylmalonic, and Diallylacetic Acids. By E. Hjelt (*Annalen*, **216**, 52—77).—An account of most of the compounds described by the author has already appeared in this Journal (Abstr., 1882, 946—948).

Carbovalerolactonic acid,  $\mathrm{COOH.CH}<\substack{\mathrm{CH_2}\\ \mathrm{COO}}>\mathrm{CHMe}$, prepared by boiling a solution of allylmalonic acid in fuming hydrobromic acid with water, is a thick syrupy liquid sparingly soluble in ether, but freely miscible with water. The free acid is decomposed by heat at 200°, splitting up into carbonic anhydride and valerolactone.

Barium carbovalerolactonate, $(C_6H_7O_2)_2Ba$, crystallises in anhydrous scales. When carbovalerolactonic acid is treated with hot solutions of alkalis, *hydroxypropylmalonates* are produced. *Barium hydroxypropylmalonate*, $C_6H_8O_5Ba$, forms needle-shaped crystals which are less soluble in alcohol and in water than barium carbovalerolactonate. The crystals are also less soluble in hot than in cold water. *Silver hydroxypropylmalonate* and the *calcium salt* have been previously described (*loc. cit.*).

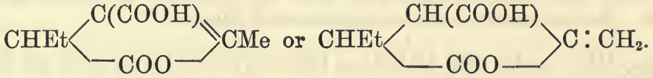
Nonodilactone,  $\mathrm{CHMe}<\substack{\mathrm{CH_2}\\ \mathrm{OOC}}>\mathrm{C.C}<\substack{\mathrm{CH_2}\\ \mathrm{COO}}>\mathrm{CHMe}$, prepared by the action of water on a solution of diallylmalonic acid in hydrobromic acid, crystallises in needles or thin plates (m. p. 105°) belonging to the rhombic system. It is soluble in warm alcohol and hot water. The lactone boils above 360° with slight decomposition. It dissolves in warm baryta-water, forming a barium salt, $BaC_9H_{14}O_6$, which decomposes on warming its solution, yielding barium carbonate, a hygroscopic salt, $Ba(C_8H_{15}O_4)_2$, and a lactone, $C_8H_{14}O_3$. The hydroxylactone is a thick liquid which does not solidify at −13°. It is freely soluble in water, and sparingly soluble in ether.

When *dibromononodilactone* is treated with baryta-water, a barium salt of the acid $C_9H_{16}O_8$ is first formed, which is decomposed by boiling with water, yielding barium carbonate and a trihydroxylactone, $C_8H_{14}O_5$.

W. C. W.

Peculiar Decomposition of the Ethereal Salts of Substituted Acetoacetic Acids. By S. Young (*Annalen*, **216**, 45—52).—On being distilled, ethyl β-ethylacetosuccinate undergoes partial decomposition, splitting up into alcohol and ethyl ketolactonate, $C_{12}H_{20}O_5 = C_{10}H_{14}O_4 + C_2H_6O$. When the fraction boiling above 265° is saponified by boiling with dilute hydrochloric acid, *ketolactonic* acid (m. p. 181°) crystallises out. This acid is sparingly soluble in cold water. It forms crystalline silver and barium salts having the composition $C_8H_9AgO_4$ and $Ba(C_8H_9O_4)_2 + 2H_2O$. It also forms a second series of salts, *e.g.*, $C_8H_{10}Ag_2O_5$. The barium salt of this series is obtained in an impure state by adding baryta-water to the acid and precipitating the excess of barium by carbonic acid. The sparingly soluble silver salt may be obtained by double decomposition with silver nitrate. Both these salts decompose at 60°. When ketolactonic acid is boiled with baryta-water, an amorphous salt, having the composition $Ba(C_7H_{11}O_3)_2$, is produced.

The constitution of ketolactonic acid may be represented by the formula—



$$\mathrm{CHEt}\left\langle\begin{matrix}\mathrm{C(COOH)}\\ \mathrm{COO}\end{matrix}\right\rangle\mathrm{CMe} \text{ or } \mathrm{CHEt}\left\langle\begin{matrix}\mathrm{CH(COOH)}\\ \mathrm{COO}\end{matrix}\right\rangle\mathrm{C\!:\!CH_2}.$$

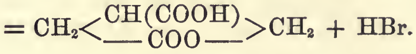
W. C. W.

Decomposition of Formic Acid by the Silent Discharge. By Maquenne (*Compt. rend.*, **96**, 63—66).—Monohydrated formic acid submitted to the action of the silent discharge in Berthelot's apparatus, is decomposed, with formation of carbonic anhydride, carbonic oxide, and hydrogen. The greater the pressure, the less is the volume of carbonic oxide produced, its place being taken by carbonic anhydride and hydrogen in nearly equal volumes. The variation in the manner of decomposition is not due to difference of pressure only. The first reaction is expressed by the equation $CH_2O_2 = CO + H_2O$, and the formation of carbonic anhydride and hydrogen is due to a secondary reaction between the first-formed products, viz., carbonic oxide and water. The author has proved this to be the case by direct experiments on moist carbonic oxide. E. H. R.

Synthesis of Optically Active Carbon Compounds. By E. Mulder (*Rec. Trav. Chim.*, **1**, 231—232).—Several years ago, before Pasteur and Jungfleisch had discovered that optically inactive tartaric acid can be converted into the optically active varieties by the action of heat, the author advanced the idea that optically active compounds might be obtained by the action of ferments, and, later, by the action of heat and light on compounds prepared synthetically. He considers that in the experiments of Lebel and Lewkowitsch (who have recently shown that optically active compounds are produced by the action of *Penicillium glaucum* and other moulds on inactive amyl alcohol, and on amygdalic acid obtained by synthesis), the optically active bodies are formed by the splitting up of the original substances, with destruction of the lævorotatory portion. In order to decide this point, it will be necessary to ascertain whether inactive tartaric acid yields dextrotartaric acid under the influence of *Penicillium glaucum*, or, better, to make a chemical separation of the amyl alcohol or amygdalic acid, as Pasteur has done in the case of uvic acid. C. H. B.

Itamalic, Paraconic, and Aconic Acid. By A. Beer (*Annalen*, **216**, 77—97).—*Itamalic acid*, $C_5H_8O_5$, cannot exist in the free state, but calcium itamalate, $C_5H_6O_5 + H_2O$, is obtained by boiling an aqueous solution of itamonobromopyroracemic acid for six hours in a flask fitted with a reflux condenser; the acid liquid is extracted with ether, and the liquid which remains on distilling off the ether is boiled with chalk. The bulky precipitate which is thrown down on the addition of alcohol to this solution of the crude calcium salt, is digested with alcohol, and afterwards treated with small quantities of hot water, in order to remove calcium bromide. The pure salt forms a white chalky powder, sparingly soluble in water. *Silver itamalate*, $C_5H_6O_5Ag_2$, decomposes at 50°. *Paraconic acid* is produced whenever an itamalate is decomposed by an acid. This acid can best be prepared by boiling itamonobromopyroracemic acid with water, and removing the hydrobromic acid from the product by means of silver oxide. Its formation may be represented thus:—

$$\underset{\text{Itabromopyroracemic acid.}}{CH_2Br.CH(COOH).CH_2.COOH} = \underset{\text{Itaconic acid.}}{CH_2{:}C(COOH).CH_2.COOH} + HBr$$



$$= CH_2<\begin{matrix}CH(COOH)\\ \text{—}COO\text{—}\end{matrix}>CH_2 + HBr.$$

Paraconic acid.

Paraconic acid, $C_5H_6O_4$, melts at 57°, and is exceedingly deliquescent. Calcium paraconate, $Ca(C_5H_5O_4)_2 + 3H_2O$, crystallises in small white needles. It is converted into calcium itamalate by boiling with calcium carbonate. These results do not agree with those obtained by Swarts (*Bull. Acad. Belg.* [2], **18**, 21; **24**, 25). When itadibromopyroracemic acid, prepared by Kekulé's method (*Annalen*, Suppl. **1**, 339), is boiled with water for two hours, *aconic acid*, $C_5H_4O_4$ (m. p. 163°) is obtained; by prolonged treatment with water, this acid is decomposed, yielding oily products. Sodium aconate is obtained in beautiful triclinic tables [$a : b : c = 0{\cdot}538 : 1 : 0{\cdot}6985$], when excess of itadibromopyroracemic acid is boiled with a solution of sodium carbonate.

Aconic acid does not yield a bromine addition-compound. The product of the action of nascent hydrogen on aconic acid has not yet been identified. W. C. W.

Ferrous Citrate and its Double and Secondary Salts. By R. Rother (*Pharm. J. Trans.* [3], **13**, 629—630).—*Ferrous citrate*, $FeH\overline{Ci}$, is best prepared by heating until action ceases (about three hours) excess (60 pts.) of fine iron filings with 210 pts. of citric acid, and 1500 parts of water; thus prepared, it is a dingy white sparingly soluble salt. When prepared by the action of citric acid on ferrous hydrate or carbonate, it dissolves rapidly in the ferric citrate formed by atmospheric oxidation, hence ferrous citrate has been considered deliquescent. *Sodioferrous citrate*, $FeNa\overline{Ci}$, obtained by the action of one equivalent of sodium hydrogen carbonate on one equivalent of ferrous citrate, forms very soluble apple-green scales. When ferrous citrate is acted on by two equivalents of the carbonate, *sodioferrous hydroxycitrate*, $Na_2\overline{Ci}Fe.OH$, is formed, a very soluble grass-green amorphous substance. Ferrous citrate is not entirely dissolved by sodium phosphate, a green solution, however, is obtained, which, with citric acid, gives a green gelatinous precipitate, requiring large quantities of sodium citrate for solution. Sodium phosphate precipitates ferrous phosphate from ferrous sodium citrate and ferrous sodium hydroxycitrate; the precipitate is redissolved by the addition of citric acid, or if that acid is present beforehand, precipitation is altogether prevented. The emerald-green solution thus produced contains two amorphous salts, one a double citrate of sodium and iron, $FeNa_2H_2\overline{Ci}_2$; the other a citrophosphate of these metals, $FeNa_2H_2\overline{Ci}PO_4$. Phosphoric acid, when added to any of these salts in sufficient quantity, discharges their colour; the solution is apparently permanent, but with small quantities of acid, ferrous phosphate is formed. Sodioferrous citrate behaves rather peculiarly with insufficient phosphoric acid, for if the addition of acid is stopped so as to leave the solution pale green, an abundant precipitate of triferrous phosphate, $Fe_3(PO_4)_2,8H_2O$, is produced, which requires for its solution much more phosphoric acid. Ferrous citrate may be converted into ferric citrate by carefully evaporating to dryness with 45 parts of nitric acid. D. A. L.

A Metacymene and a New Isomeride of Thymol. By P. Spica (*Gazzetta*, **12**, 543—554).—In a former paper (p. 321 this vol.), the author stated that the monohydrated barium salt of the sulphonic acid obtained from camphor-cymene is a derivative of *meta*-cymene. In the present communication he describes several other derivatives of this hydrocarbon, and examines its constitution more fully.

The hydrocarbon $C_{10}H_{14}$, obtained by converting the barium salt just mentioned into a sodium salt, heating the latter with hydrochloric acid, and distilling the product with steam, is converted by gentle oxidation with dilute nitric acid into *metatoluic acid*, and by further oxidation with chromic acid mixture into *isophthalic* or *metaphthalic acid*, a result which shows it to be a metacymene, $\overset{1}{C}H_3.C_6H_4.\overset{3}{C_3}H_7$; but whether it contains normal propyl or isopropyl, or in other words whether it is a normal cymene or an isocymene, is a question to be decided by further experiment. With this view the sulphonic acid obtained from the hydrocarbon in question was compared with those prepared by Claus and Stüsser from normal cymene (Abstr., 1880, 632), and by Kelbe from isocymene (*ibid.*, 878, and 1882, 299). This acid, separated from its lead salt by hydrogen sulphide, forms a syrupy liquid, which crystallises by evaporation under reduced pressure, in groups of prisms, deliquescent, and moderately soluble in alcohol, ether, chloroform, and benzene. Its *sodium salt*, $C_{10}H_{13}.SO_3Na,H_2O$, crystallises in large transparent nacreous scales; the *potassium salt*, $C_{10}H_{13}SO_3K$, in stellate groups.

The *sulphochloride*, $C_{10}H_{13}.SO_2Cl$, obtained by treating the sodium salt with phosphorus pentachloride, is a heavy uncrystallisable oil, having an ethereal odour, decomposing when heated, and thickening but not solidifying in a mixture of ice and salt. Heated with alcoholic ammonia, it yields the *sulphonamide* $C_{10}H_{13}.SO_2NH_2$, which on addition of water separates as an oil, but afterwards solidifies to a crystalline mass, and is deposited from its solution in dilute alcohol in transparent plates, melting after purification at 75—75·5°. Now the α-sulphonic acid obtained by Kelbe from *meta*-isocymene yields a sulphonamide which melts at nearly the same temperature, viz., at 73°, and an uncrystallisable sulphochloride; whereas the corresponding acid obtained by Klaus and Stüsser from normal *meta*cymene, yields a crystalline sulphochloride melting at 175°, and a sulphonamide which has not yet been crystallised, whence it appears most probable that the cymene obtained by Spica is identical with that of Kelbe, viz., *meta*-isocymene; but on the other hand the sulphonic acid obtained from Spica's *meta*cymene agrees in the solubility of its barium salt and the characters of its copper and potassium salts, more nearly with that of Claus than with that of Kelbe. The constitution of the cymene obtained by Spica must therefore be regarded as requiring further investigation.

The potassium salt of the sulphonic acid obtained from this hydrocarbon is converted by fusion with potassium hydroxide into the corresponding phenol, $C_{10}H_{13}.OH = C_6H_3MePr.OH$, which is a new isomeride of thymol, forming a colourless liquid, slightly soluble in water, miscible with alcohol and ether, thickening but not solidifying in a mixture of ice and salt. It has a sp. gr. of 1·00122 at 0°, and 0·91971 at 100°; boils at 227·5—229·5°. Its aqueous solution does not colour ferric chloride. Its *ethyl salt*, $C_{10}H_{13}.OEt$, is a colourless liquid, smelling somewhat like orange oil, insoluble in water, volatilising with steam. Sp. gr. 0·93866 at 0°, 0·85758 at 100°; b. p. 227·2—229·2°. H. W.

Four Metameric Benzanisethyl-hydroxylamines. By R. Pieper (*Annalen*, **217**, 1—23).—According to present theoretical views, the replacement of hydrogen in hydroxylamine, NH_3O, or $NH_2.OH$, by benzoyl ($C_7H_5O = \overline{Bz}$), anisyl ($C_8H_7O_2 = \overline{An}$), and ethyl, may give rise to three metameric compounds, viz.:—

$$N\overline{Bz}\overline{An}(OEt),\ N\overline{An}Et(O\overline{Bz}),\ N\overline{Bz}Et(O\overline{An}).$$

Eiseler, moreover, obtained two ethylic ethers of this class, distinguished by the names ethylic anisbenzhydroxamate and ethylic benzanishydroxamate (this Journal, 1875, 766); and the author of the present paper has prepared two other bodies having the same percentage composition, but differing in their chemical behaviour both from each other and from Eiseler's compounds.* Moreover it appears that Eiseler's ethylic benzanishydroxamate can exist in two different modifi-

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* To account for the isomerism of these and other derivatives of hydroxylamine, it is supposed that the three H-atoms in that base possess different functions, and the several isomerides are distinguished by formulæ in which the substituted radicles are numbered and arranged according to the order in which they have been introduced into the molecule, thus—

		1.	2.	3.	
Benzanisbenzhydroxylamine	N	$\overline{Bz}$	$\overline{An}$	$\overline{Bz}$	O
Dibenzanishydroxylamine	N	$\overline{Bz}$	$\overline{Bz}$	$\overline{An}$	O
Anisdibenzhydroxylamine	N	$\overline{An}$	$\overline{Bz}$	$\overline{Bz}$	O.—H. W.

cations (α and β), analogous to the two ethylic dibenzhydroxamates described by Gürcke (*Annalen*, **205**, 279), that is to say, chemically alike, but differing greatly in their physical characters.

I. EISELER'S COMPOUNDS.—*α-Ethylic Benzanishydroxamate*,

$$N\overline{Bz}\overline{An}OEt.$$

The α-modification of this ether, prepared by the action of ethylic iodide on the silver salt of benzanishydroxamic acid, melts according to Eiseler at 69°. Pieper, however, finds that it melts at 74° (uncorr. like all the following), and supposes that Eiseler obtained a different modification, just as two modifications of ethylic dibenzhydroxamate are known to be obtained by the action of ethylic iodide on silver dibenzhydroxamate. The modification melting at 74° forms monoclinic crystals, having the axes $\grave{a} : \bar{b} : \acute{c} = 1 : 51813 : 0{\cdot}66584$, and exhibiting the forms $\infty P\bar{\infty}$, ∞P, $-P$, $+ P$, $+ P\bar{\infty}$. Plane of optic axes perpendicular to the clinodiagonal principal section. This ether, heated with potash-lye, yields anisic and α-ethylbenzhydroxamic acids (m. p. 54°), according to the equation $N\overline{Bz}AnEtO + H_2O = C_8H_8O_3 + N\overline{Bz}H.EtO$. By hydrochloric acid it is resolved into ethyl benzoate, anisic acid, and hydroxylamine: $N\overline{Bz}\overline{An}OEt + 2H_2O = \overline{Bz}OEt + AnOH + NH_3O$.

β-Ethylic Benzanishydroxamate is formed by the action of anisyl chloride on ethylbenzhydroxamic acid dissolved in aqueous potash: $N\overline{Bz}HEtO + \overline{An}Cl = HCl + N\overline{Bz}\overline{An}EtO$. The insoluble portion of the product was triturated with aqueous sodium carbonate, then washed and recrystallised from ether. This ether differs from the α-modification both in melting point (89°) and in crystalline form. The crystals are monoclinic. Axes $a : b : c = 0{\cdot}748118 : 1 : 0{\cdot}802848$, $\beta = 75° 21' 15''$. Forms P, ∞P, $\infty P\bar{\infty}$, $\infty P\breve{\infty}$. Plane of optic axes parallel to the clinodiagonal principal section.

The analogy of this β-modification to ethylic β-dibenzhydroxamate is shown by the fact that, like the latter, it is decomposed by potash, with formation of β-ethylbenzylhydroxamic acid, melting at 67—68°.

Decomposition of Ethylic Benzanishydroxamate by Heat.—This ether, when heated above its melting point, decomposes suddenly, with evolution of aldehyde, leaving a residue from which aqueous sodium carbonate extracts nothing but anisic acid, while benzonitril remains undissolved. The decomposition is represented by the equation $N(CO.C_6H_5)(C_8H_7O_2)(C_2H_5O)O = NC.C_6H_5 + C_8H_7O_2.OH + C_2H_4O$. In this case, therefore, as in the distillation of the dibenzhydroxamic acids, the acid radicle which first enters the molecule suffers decomposition.

Ethylic Anisbenzhydroxamate, $N\overline{An}\overline{Bz}EtO$, prepared by Eiseler (*loc. cit.*), forms triclinic crystals which have not yet been examined.

II. *Benzethylbenzhydroxylamine*, *Benzethylanishydroxylamine*, and *Anisethylbenzhydroxylamine.*—The first of these compounds,

$$N\overline{Bz}.Et\overline{Bz}O,$$

which Lossen obtained by the action of benzoic chloride on the silver compound of ethylic benzhydroxamate (this Journal, 1877 [ii], 328), may be prepared more simply by acting on the same ether in alkaline solution with benzoyl chloride. When purified by washing with aqueous sodium carbonate, and recrystallisation from ether and light petroleum, it forms transparent colourless rhombic crystals, melting at 48—49°, easily soluble in alcohol and ether, insoluble in water. Axes, $a : b : c = 0\cdot6242293 : 1 : 2\cdot5873036$. Forms $0P$, P, $\frac{1}{2}P\bar{\infty}$. Plane of optic axes parallel to $\infty P\bar{\infty}$.

Benzethylanishydroxylamine, $\mathrm{N\overline{Bz}Et\overline{An}O}$, obtained by the action of anisic chloride on ethylic benzhydroxamate, crystallises in triclinic prisms, having the axes $a : b : c = 0\ 7727191 : 1 : 1\cdot08549157$. Forms $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, $0P$, ${}_{\prime}P$, $P_{\prime}$, $\infty{}^{\prime}_{\prime}P$, ${}^{\prime}P_{\prime}\breve{\infty}$. The crystals are moderately soluble in ether and alcohol, insoluble in water and in light petroleum, and melt at 64°.

This compound is but partially decomposed, even by prolonged heating over an open fire with strong potash-lye (1 : 1), the product consisting of ethylic benzyhydroxamate (m. p. 67°), which separates on passing carbonic anhydride into the filtered solution, and anisic acid, which may be precipitated from the liquid, after a second filtration, by hydrochloric acid. The decomposition by potash may therefore be represented by the equation $\mathrm{N\overline{Bz}Et\overline{An}O + H_2O = N\overline{Bz}EtHO + C_8H_8O_3}$.

Benzethylanishydroxylamine (2 g.) heated for two hours in a sealed tube at 100°, with hydrochloric acid of sp. gr. 1·12 (9 c.c.), is resolved into ethylhydroxylamine, benzoic acid, and anisic acid: $\mathrm{N\overline{Bz}Et\overline{An}O + 2H_2O = NHEtHO + C_7H_6O_2 + C_8H_8O_3}$. By very gentle action of very dilute hydrochloric acid, however, the first products obtained are ethylic benzhydroxamate and anisic acid, the same as with potash-lye: $\mathrm{N\overline{Bz}Et\overline{An}O + H_2O = N\overline{Bz}EtHO + C_8H_8O_3}$.

By dry distillation, benzethylanishydroxylamine is completely resolved, after fusion, into phenyl cyanate and ethyl anisate:

$$\mathrm{N(COPh)Et(C_8H_7O_2)O = N(CO)Ph + C_8H_7O.OEt},$$

whereas the metameric body, ethyl benzanishydroxamate, similarly treated, yields phenyl isocyanide, anisic acid, and aldehyde:

$$\mathrm{N(COPh)AnEtO = NCPh + C_8H_8O_3 + C_2H_4O}.$$

Ethylic Anishydroxamate, $\mathrm{N\overline{An}EtHO}$, prepared by the action of anisyl chloride on a solution of ethylhydroxylamine hydrochloride in excess of sodium carbonate, crystallises in well-formed tabular crystals, melting at 84°, insoluble in water, slightly soluble in ether, readily in alcohol. By heating with strong hydrochloric acid, it is converted into anisic acid and ethylhydroxylamine. Like ethylic benzhydroxamate, it exhibits the characters of a weak acid, being converted by potash-lye into a potassium salt.

Anisethylbenzhydroxylamine, $\mathrm{C_{17}H_{18}O_4 = N\overline{An}Et\overline{Bz}O}$, best prepared by adding benzoic chloride to a solution of ethylic anishydroxamate in an equivalent quantity of potash-lye, forms transparent crystals, less soluble in ether and alcohol than benzethylanishydroxylamine, insoluble in water and in light petroleum; resolved by heating with excess of potash, chiefly into benzoic acid and ethylic anishydroxamate, a small quantity of anisic acid being, however, produced at the same time, probably by further decomposition of ethylic anishydroxamate formed in the first instance. By heating with hydrochloric acid, anisethylbenzhydroxylamine is converted, first into benzoic acid and ethylic anishydroxamate, which latter is then further resolved into ethylhydroxylamine hydrochloride and anisic acid.—The decomposition of anisethylbenzhydroxylamine by hydrochloric acid takes place much less readily than that of benzethylanishydroxylamine, a fact which is analogous to that observed by Lossen with regard to trisubstitution products of hydroxylamine containing three different acid radicles, viz., that those in which the third hydrogen-atom is replaced by benzoyl are less easily decomposed by hydrochloric acid than those in which the same hydrogen-atom is replaced by anisyl.

The decomposition of anisethylbenzhydroxylamine by heat is less simple than that of benzethylanishydroxylamine, and cannot be represented by a definite equation. Considerable quantities of gas are evolved, smelling like aldehyde, but not containing either combustible gases or carbonic anhydride. The distillate smells of phenyl cyanate, deposits on standing a body melting at 224°, and yields, after removal of these two, a liquid smelling like anisic ether, and convertible by saponification into anisic acid. H. W.

Three new Phenols: Isopropyl-, Di-isopropyl-, and Dipropylmetacresol. By G. Mazzara (*Gazzetta*, **12**, 505—511).—The author has already shown (Abstr., 1882, 838, 1198), that when a mixture of metacresol and propyl- or isopropyl-alcohol in molecular proportion is heated in sealed tubes with anhydrous magnesium chloride, propyl- and isopropyl-metacresol are formed, together with their propylic ethers; and by further experiments he finds that the same reaction also gives rise to tetrasubstituted derivatives, viz., dipropyl- and di-isopropyl-*m*-cresols. The two phenols last mentioned are insoluble in dilute aqueous potash, but dissolve in the concentrated lye, and separate therefrom unaltered on addition of water, a property which, the author thinks, may have some relation to the nature and number of their lateral chains.

Isopropyl-m-*cresol*, $C_{10}H_{14}O = C_6H_3Me.Pr^{\beta}.OH$, is a colourless or faintly yellowish liquid which boils at 237·7°, and does not solidify in a mixture of ice and salt. It has a faint phenolic odour, dissolves sparingly in water, freely in alcohol and ether, giving no characteristic reaction with ferric salts. Its *nitroso-derivative*,

$$C_6H_2(NO)MePr^{\beta}.OH,$$

crystallises in yellowish needles, melting with decomposition at 155—167°, very soluble in alcohol, sparingly in benzene, but more freely than nitrosopropylmetacresol. It is very unstable. The *methylic ether*, $C_6H_3MePr^{\beta}.OMe$, is a colourless liquid, lighter than water, boiling at 215—220°.

Di-isopropyl-metacresol, $C_{13}H_{20}O = C_6H_2Me(Pr^{\beta})_2.OH$, is a faintly yellowish syrupy liquid, having a slight phenolic odour and boiling at 251°. It dissolves in alcohol and ether, and is very soluble in water; it does not solidify in a mixture of snow and salt. Its *acetyl-derivative*, $C_{15}H_{23}O_2 = C_6H_2Me(Pr^{\beta})_2.O\overline{Ac}$, obtained by the action of acetic chloride, is a very limpid liquid, having an acetic odour, soluble in alcohol and ether, not solidifying in snow and salt, boiling at 255—260°. The *methylic ether*, $C_6H_2Me(Pr^{\beta})_2.OMe$, is a colourless, very mobile liquid, lighter than water, having a somewhat unpleasant odour, boiling at 242—245°.

Dipropyl-metacresol, $C_6H_2MePr_2{}^{\alpha}.OH$, yields an acetyl-derivative in the form of a mobile liquid, having an acetic odour and boiling at 255—260°. H. W.

Action of Nitrous Acid on Guaiacol. By J. Herzig (*Monatsh. Chem.*, **3**, 825—834).—When nitrous gas is passed into an ethereal solution of guaiacol (10 g. to 100—130 c.c.), the liquid turns brown, and deposits a considerable quantity of a crystalline body; and on decanting the ethereal solution, agitating it with well cooled water, and neutralising the resulting aqueous solution with an ice-cold solution of sodium carbonate, it soon deposits a yellow crystalline powder consisting of the sodium salt of carboxytartronic acid,

$$COH(COOH)_3$$

(*Ber.*, 1879, 504; Abstr., 1879, 643).

The body already mentioned as separating in crystals when the ethereal solution is shaken with water, partly remains dissolved in the ether, and may be separated therefrom by repeatedly agitating the ether with water till it is all dissolved. This body is dinitroguaiacol, $C_6H_2(OMe)(OH)(NO_2)_2$. It may be purified by repeated crystallisation from dilute alcohol, in which it is moderately soluble when warm, and is deposited therefrom on cooling in splendid flattened needles having a golden lustre very much like that of picric acid, and nearly the same melting point as the latter, viz., 122—123°.

By the action of tin and hydrochloric acid, dinitroguaiacol is converted into the tin salt of diamidoguaiacol,

$$C_6H_2(OH)(OMe)(NH_2)_2,2HCl,SnCl_2,$$

which retains 1 mol. H_2O at 100°; and on separating the tin with hydrogen sulphide, and treating the resulting diamidoguaiacol hydrochloride with a solution of ferric chloride, the liquid acquires a splendid violet-red colour, and deposits brown-red metallically lustrous leaflets which dissolve in water with a fine red colour. The crystals thus obtained are so extremely soluble in water and in alcohol that they cannot be purified by washing. They appear, however, to consist of di-imidoguaiacol, the reaction being analogous to that by which triamidophenol is converted into the corresponding imido-compound.

Weidel and Gruber (*Ber.*, **10**, 1137), by treating triamidophenol with bromine and water, obtained bromodichromazine, and as final product, hexbromacetone, C_3Br_6O. A similar action takes place on treating a dilute solution of diamidoguaiacol hydrochloride with bromine and water, the liquid acquiring first a red, then a brown, and on addition of excess of bromine, a light yellow colour, and yielding a crystalline precipitate, which dissolves in chloroform and separates therefrom in crystals having the form and melting point (108—109°) of hexbromacetone. At the same time, there is formed a body having nearly the composition and properties of bromodichromazine, but the quantity of it obtained was not sufficient to admit of satisfactory purification.

The analogy between the action of bromine and water on diamidoguaiacol and triamidophenol renders it probable that only the two amido-groups and the HO-group of the former are concerned in the reaction above described, this analogy being probably due to the similarity of the position of the two NH_2-groups and the HO-group of the former to the three NH_2-groups in the latter. Diamidoguaiacol will, therefore, be represented by the formula $C_6H_2(OH)(OMe)(NH_2)_2$, in which $[OH : OMe : NH_2 : NH_2 = 1 : 2 : 4 : 6]$. H. W.

Quinones and Quinols. By R. NIETZKI (*Annalen*, **215**, 125—172; see also p. 146).—The preparation of quinone has already been described (Abstr., 1878, 794). In order to prepare quinol, sulphurous anhydride in excess is passed through the crude mixture containing the quinone, and the quinol is extracted from the filtered liquid by ether. For further purification of the quinol, Eckstrand recommends boiling with animal charcoal in presence of sulphurous anhydride.

The Combinations of Quinone with Phenols.—The formulæ of quinhydrone and of the combinations of quinone with phenol and resorcinol have already appeared in this Journal (Abstr., 1878, 146; 1879, 464; and 1880, 247).

Nitro-derivatives of Quinone and Quinol.—In the cold, quinone is dissolved unchanged by the strongest nitric acid, but on warming, complete decomposition takes place, oxalic acid and hydrocyanic acid being formed. Quinol, on the other hand, decomposes in the cold solution: the nitration of the latter proceeds readily if the hydroxyl hydrogen has previously been replaced by an alcohol or acid radical.

Nitro-anilic Acid.—A notice of this compound has appeared in the *Berichte* (see Abstr., 1878, 425). The *potassium salt*, $C_6N_2O_8K_2$, is best obtained by neutralising the acid with potassium hydroxide solution; it crystallises in yellow needles resembling iodoform. The *barium salt*, $C_6N_2O_8Ba$, is prepared by adding a solution of barium chloride to any solution of the acid, even in the presence of nitric acid or hydrochloric acid; the crystals resemble those of lead iodide. The *ammonium salt*, $C_6N_2O_8(NH_4)_2$, is obtained by neutralising a solution of the acid with ammonia. The sodium salt forms greenish scales, and is slightly more soluble than the potassium salt. The calcium, silver, and lead salts are also yellow crystalline precipitates. The author finds that the best way of preparing nitro-anilic acid is to treat 1 part of dinitro-quinol with a well cooled mixture of 3 parts of strong nitric acid and 6 parts of glacial acetic acid. A violent evolution of red fumes takes place. After a few minutes, the mixture is diluted with water, and an excess of potassium hydroxide solution added. On cooling, the potassium derivative separates out, about 50 per cent. of the dinitro-quinol employed being obtained.

On heating with sulphurous anhydride at 100° in a sealed tube, the acid yields a colourless body, not yet obtained in a crystalline form. By incomplete reduction with tin and hydrochloric acid, violet-coloured needles are obtained, which by further reduction yield a colourless solution. With ferric chloride this solution gives a very insoluble green crystalline precipitate resembling quinhydrone. It appears as if a diamido-tetroxybenzene were formed, which on oxidation gives dioxydiimidoquinone.

Dinitro-quinol, $C_6H_2(NO_2)_2(OH)_2$, is prepared from diacetyl-quinol by the action of fuming nitric acid and decomposition of the resulting dinitro-diacetyl-quinol with potash (Abstr., 1878, 499). It dissolves sparingly in cold, but readily in hot water, also in ether and alcohol. It forms two series of salts, of which the primary yields dark yellow, and the secondary violet solutions.

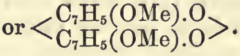
Nitro-derivatives of Diethylquinol.—(Comp. Abstr., 1878, 866, and 1879, 464).—*Mononitro-diethylquinol* is best prepared by dissolving 1 part of diethylquinol in 4—5 parts glacial acetic acid, allowing the mixture to cool, and then treating the crystalline mass with its own volume of nitric acid of sp. gr. 1·3. The nitro-body generally separates as an oil, but becomes crystalline in a short time. It crystallises from 60 per cent. alcohol in yellow needles 1 inch long (m. p. 49°). Reduced with tin and hydrochloric acid, it yields the corresponding amido-body, which forms well crystallised salts.

Dinitro-diethylquinol, $C_6H_2(NO_2)_2(OEt)_2$, is formed by suspending diethylquinol in 5 times its weight of glacial acetic acid, and pouring it into an equal volume of fuming nitric acid 1·48 sp. gr. The product contains two isomeric bodies which can be separated by repeated crystallisation. The α-compound melts at 130°, and the β-, which is less soluble, at 176°. Both form sulphur-yellow needles, which are soluble in alcohol, ether, benzene, and acetic acid. On reduction, they yield amido-compounds which form crystalline hydrochlorides. If the α-compound be reduced and treated in an aqueous solution with 3 mols. of hydrochloric acid and 1 mol. of sodium nitrite, a grey precipitate separates out, which, on boiling with alcohol and animal charcoal, yields a colourless body. Recrystallised from glacial acetic acid, it can be obtained in needles 1 cm. long (m. p. 233°) of the composition $C_{10}H_{13}N_3O_2$. The body is similar to that obtained by Hofmann by treating nitrophenylenediamine with nitrous acid, and that by Ladenburg from various orthodiamines. It has scarcely any basic properties, being precipitated by water from its solution in hydrochloric acid. It behaves with alkalis like a weak acid, and forms salts which are decomposable by carbonic anhydride.

Trinitro-diethylquinol, $C_6H(NO_2)_3(OEt)_2$, is best prepared by adding the mononitro-compound gradually to a well cooled mixture of H_2SO_4 and HNO_3. It crystallises from alcohol in long yellow needles melting at 130°. It is more soluble in alcohol, ether, and benzene than the dinitro-compounds. When heated with alcoholic ammonia for some hours under pressure at 110—120°, it yields red crystalline scales. One of the ethoxyl- and one of the nitro-groups are replaced by ammonia groups. If trinitro-diethylquinol is acted on by aniline instead of ammonia, the nitro-groups alone are attacked. In addition to amidoazobenzene, a body crystallising from alcohol in red needles (m. p. 133°) is obtained. It is a diethoxy-dinitrodiphenylamine, $C_{16}H_{17}N_3O_6$. On boiling it with alcoholic potash, the aniline-group is separated and probably replaced by a HO-group. The product is a monobasic acid, and crystallises from alcohol in golden-yellow needles melting at 152°. The potassium salt has the composition $C_6H(NO_2)_2(OEt)_2.OK$.

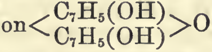
Hydrotoluquinone.—Toluquinone is easily reduced if suspended in water through which a current of sulphurous anhydride is passed. When all is dissolved, the hydrotoluquinone is shaken out with ether. It is purified by crystallising from high-boiling benzene, from which it separates out in mother-of-pearl plates melting at 124°. It forms a diacetyl-derivative melting at 52°. Hydrotoluquinone can be obtained by the oxidation and subsequent reduction of orthotoluidine.

Methyl Ethers of Hydrotoluquinone and their Condensation-products (comp. Abstr., 1878, 868).—The dimethyl ether, $C_7H_6(OMe)_2$, is a colourless liquid boiling at 214—218°, and solidifies to colourless crystals which melt at 15°. By the action of chromic acid it yields the quinone of a dioxymethylditolyl of the composition $C_{16}H_{16}O_4$,



$$\text{or} \left< \begin{matrix} C_7H_5(OMe).O \\ C_7H_5(OMe).O \end{matrix} \right>.$$

It is almost insoluble in water, but dissolves easily in alcohol, ether, benzene, and glacial acetic acid. On reduction, it yields the corresponding quinol (*loc. cit.*).

On heating this compound for several hours at 180—190°, with concentrated hydrochloric acid in a sealed tube, a crystalline mass is obtained, mixed with small quantities of a black substance which dissolves in alcohol with a violet colour. The latter is formed in larger quantities when the tube is heated to a higher temperature or for a longer period. On opening the tube, methyl chloride is evolved. The black substance crystallises from benzene in long needles (m. p. 232°); the author considers them to be an anhydride of tetroxy-ditoluyl, probably having the constitution  $\left< \begin{matrix} C_7H_5(OH) \\ C_7H_5(OH) \end{matrix} \right> O$. When distilled with zinc-dust it yields a semi-liquid hydrocarbon.

Xyloquinone, $C_8H_8O_2$.—The conversion of xylidine into the quinone is performed in two ways, either by the direct oxidation of the base or by decomposition of the amidazo-compound. On oxidation with chromic mixture, xylidine behaves differently from its homologues. The intermediate product which is of a light brown colour, does not exhibit the characteristics of aniline-black: on further oxidation, a precipitate always remains suspended in the liquid. The quinone resembles its homologues in most of its properties, but differs from them in its sparing solubility in hot water, as well as in being less readily reduced by sulphurous anhydride. Like tolu- and benzoquinone it is very volatile, and sublimes in golden-yellow needles at 125°. It can be reduced to a quinol. With hydrochloric acid, it yields a chloroquinol.

Xyloquinol, $C_8H_{10}O_2$.—Xyloquinone is best reduced by heating it at 100° in a closed flask with an aqueous solution of sulphurous anhydride. The quinol thus obtained is very slightly soluble in cold, but readily in hot water, and crystallises from it in plates with a pearly appearance (m. p. 212°). It oxidises rapidily, even by standing in the air, and becomes re-converted into xyloquinone. J. I. W.

Action of Melting Potassium Hydroxide on Benzoic Acid. By L. BARTH and J. SCHREDER (*Monatsh. Chem.*, **3**, 800—818).—The experiments described in this paper confirm and extend the results obtained by Barth in 1872 (*Annalen*, **144**, 138; and this Journal, 1872, 1013), showing that the products obtained by fusing benzoic acid at a high temperature with potash are much more complex than those produced in like manner with soda, and that the action consists of— (1.) *Direct oxidation* (or *hydroxylation*), whereby parahydroxybenzoic acid is obtained, together with a small quantity of salicylic acid. (2.) *Hydroxylation* and *carboxylation*, resulting in the formation of α-hydroxy-isophthalic acid, $C_6H_3(OH)(COOH)(COOH)$ [1 : 2 : 4]. (3.) *Reduction* and *condensation*, resulting in the formation of two diphenylcarboxylic acids, $C_{13}H_{10}O_2$ or $C_{12}H_9.COOH$, together with yellow and brown condensation-products.

Of the two diphenyl-carboxylic acids thus obtained, one forms a soluble, the other an insoluble barium salt. To separate them, the mixture was dissolved in dilute ammonia, the excess of the latter driven off by heat, the cooled and diluted solution precipitated with barium chloride, and the precipitate decomposed by hydrochloric acid. The organic acid thereby separated and purified by repeated crystallisation from alcohol, crystallises in tufts of anhydrous needles melting at 216—217°, yields diphenyl when heated with lime, and exhibits all the properties of *p*-diphenylcarboxylic acid.

The second diphenyl-carboxylic acid, separated by hydrochloric acid from the filtrate of the barium *p*-diphenylcarboxylate, forms a flocculent crystalline precipitate, and is obtained by repeated crystallisation from alcohol in dazzling white leaflets, likewise anhydrous, and melting at 160—161°. Heated with lime, it yields a large quantity of diphenyl. As it is distinct from the *p*-acid, and does not agree in its properties with the *o*-acid described by Fittig and Ostermayer, it must be *meta*-diphenylcarboxylic acid, and is probably identical with the acid which Fittig and Schultz obtained (*Annalen*, **203**, 132) by oxidation of isodiphenylbenzene.

m-Diphenylcarboxylic acid is easily soluble in ether, benzene, xylene, light petroleum, and glacial acetic acid, sparingly in water. Its aqueous solution, like that of the para-acid, gives a white precipitate with lead acetate. Its *ethylic ether*, $C_{13}H_9O_2Et$, is a colourless somewhat viscid non-crystallising oil, boiling at a rather high temperature. The *barium salt*, $(C_{13}H_9O_2)_2Ba,3\frac{1}{2}H_2O$, forms tufts of needles. The *calcium salt*, $(C_{13}H_9O_2)_2Ca$, is a white powder, containing in the air-dried state 3 mols. water, which is given off at 200°. The *copper salt* is a light greenish-blue flocculent precipitate; the *silver salt*, a white flocculent precipitate, not very sensitive to light. The *ammonium salt* is very unstable. The *sodium salt* is obtained as an indistinctly crystalline mass, drying up in the air to a white powder, containing 2 mols. water, which is given off at 130°; it is partly decomposed on agitating its aqueous solution with ether, the solution afterwards exhibiting a strongly alkaline reaction. The *sodium salt* of *p*-diphenylcarboxylic acid is decomposed by ether in the same manner.

The diphenylcarboxylic acids obtained as above were accompanied by very small quantities of two other bodies, one having the composition of a diphenylcarboxylic anhydride, but not agreeing in properties therewith, inasmuch as it was precipitated unaltered by acids from its solution in potash-lye, even after prolonged boiling; the other melting at 187°, and apparently consisting of di-diphenyl, $C_{24}H_{20}$, isomeric with benzerythrene and triphenyl-benzene.

The other condensation-products above mentioned, as resulting from the action of melting potash on benzoic acid, were not obtained in sufficient quantity for satisfactory examination. H. W.

Monobromopseudocumic Acid and Dibromomesitylenic Acid. By H. Süssenguth (*Annalen*, **215**, 242—252).—*Preparation of Monobromopseudocumene*, $C_6H_2BrMe_3$.—Monobromopseudocume (m.p. 72°) was first obtained by Beilstein and Kögler from coal-tar oil. In order to purify the crude oil, the author shakes it with tolerably strong soda-solution, and then pours off the upper layer of liquid, thus removing the phenol. After drying the liquid, it is fractionated, and the portion which boils constantly between 161° and 169° is treated with the theoretical quantity of bromine; the product, when washed with dilute soda-solution and distilled, yields a fraction which boils at 220—240°, and contains large quantities of monobromopseudocumene. On cooling the distillate by ice, it partially solidifies, and the crystals, after being drained and crystallised from alcohol, melt at 72°. *Monobromopseudocumic acid*, $C_6H_2BrMe_2.COOH$, is obtained by warming bromopseudocumene dissolved in acetic acid with twice its weight of chromic acid. It is easily soluble in alcohol, and dissolves in water on continued boiling, crystallising from the solution, on cooling, in small needles, melting at 172—173°; it can be sublimed. The author has not succeeded in obtaining salts of the heavy metals in a crystalline state. The *calcium salt*, $(C_6H_2BrMe_2COO)_2Ca + 2H_2O$, is obtained by boiling an aqueous solution of the acid with finely-powdered Iceland spar. It crystallises in fine colourless needles, soluble in water. The *barium salt*, $(C_6H_2BrMe_2.COO)_2Ba + 6H_2O$, crystallises in groups of needles, soluble in water. The *potassium salt*, $C_6H_2BrMe_2.COOH$, crystallises in fine concentric groups of needles or prisms, which effloresce in dry air.

Preparation of Bromomesitylenic Acid from Bromomesitylene.—On treating monobromomesitylene dissolved in acetic acid with chromic mixture, it readily undergoes oxidation. Bromopseudocumic acid differs from its isomerides in its easy solubility in alcohol and boiling water. Its salts are also more easily soluble than those of the corresponding bromomesitylenic acid, whose melting point is 212°. The *calcium salt*, $(C_6H_2BrMe_2.COO)_2Ca + 5H_2O$, forms long needles. The author has not obtained salts of the heavy metals, as they undergo decomposition in a hot solution.

Dibromomesitylene from Coal-tar Oil.—In preparing monobromopseudocumene, a large quantity of a substance boiling at 250° was obtained. On fractionally distilling it, a portion boiling constantly at 277—278° was isolated, which solidified on cooling. After purification from alcohol, it was obtained in colourless crystals 1 inch long, having all the properties of dibromomesitylene. The boiling point, 277—278° and melting point, 64°, differed greatly from former observations. In order to decide whether the body was a derivative of mesitylene or of pseudocumene, or of the third possible trimethylbenzene, the author prepared dibromomesitylene from pure mesitylene, and found that it exhibited the greatest similarity (b. p. 276—278°, m. p. 64°) to the brominated compound obtained from coal-tar oil.

Dinitro-monobromomesitylene, $C_6Br(NO_2)_2Me_3$.—On boiling dibromomesitylene with fuming nitric acid, an oily and a solid compound are formed. The solid body, after repeated crystallisation from alcohol, is obtained in colourless needles, melting at 194°. One bromine-atom is replaced by a nitro-group.

Dibromomesitylenic acid, $C_6HBr_2Me_2.COOH$.—The author finds that chromic acid acts too violently on dibromomesitylene; the temperature rises rapidly, and the compound is destroyed and bromine liberated. Hoogewerff observed a similar phenomenon with dichloromesitylene. In the case of the bromine compound, a third atom of bromine enters into combination, as the product of the reaction on crystallisation from alcohol yields large quantities of tribromomesitylene. By employing potassium dichromate and acetic acid, the oxidation proceeds well, and on adding water to the mixture when the reaction is complete, the dibromomesitylenic acid is precipitated. On recrystallisation from water, it is obtained in small colourless glittering needles, melting at 194—195°. They are soluble in alcohol, and can be sublimed between watch-glasses. The calcium and barium salts are easily soluble in water, and crystallise well; the salts of the heavy metals decompose in a warm solution. The *calcium salt* crystallises in needles and in rectangular tables. The *barium salt* forms short prisms, which are soluble in water.

The author has not succeeded in obtaining oxidation-products of the tribromo-derivative of the isomeric trimethylbenzene. Chromic acid and potassium permanganate in weak solutions have no action, and, when concentrated, decompose the compound. J. I. W.

Guaiaconic and Guaiaretic Acids (Preliminary Notice). By J. Herzig (*Monatsh. Chem.*, **3**, 822—824).—The author has already shown that guaiaconic acid, treated with hydrochloric acid, yields methyl chloride and catechol—together with bodies not yet examined —and has hence inferred that the guaiacol given off in the dry distillation of guaiacum resin pre-exists therein (Abstr., 1882, 593). This conclusion, however, is by no means unassailable, since we cannot be sure that the methyl evolved as chloride was directly connected with the catechol. Subsequent experiments have, however, distinctly shown the existence of a guaiacol residue in guaiaconic acid. In fact, when this acid dissolved in ether is treated with nitrous acid, and the resulting solution is shaken up with ice-cold water, there remains dissolved in the ether a body which, after repeated crystallisation from alcohol, melts at 122—123°, and exhibits the composition and properties of dinitroguaiacol, $C_7H_6(NO_2)_2O_2$.

Guaiaretic acid, treated in like manner with hydrochloric acid, likewise yields methyl chloride and catechol, together with a body which resembles pyroguaiacin in melting at 183—185°, but differs from that compound in not subliming readily under ordinary pressure, in immediately turning brown in contact with potash, and in not turning blue with sulphuric acid. Guaiacol is likewise resolved by the action of hydrochloric acid into methyl chloride and catechol.

The author is continuing his experiments. H. W.

Phenylhydroxypivalic Acid. By R. FITTIG and H. W. JAYNE (*Annalen*, **216**, 115—119).—When a mixture of sodium isobutyrate, isobutyric anhydride, and benzaldehyde is heated at 100° for four hours, *phenylhydroxypivalic acid*, $CHPh(OH).CMe_2.COOH$, is produced. This acid crystallises in glistening needles (m. p. 134°), soluble in alcohol and ether. At a temperature slightly above the melting point, it splits up into carbonic anhydride and butenylbenzene, $C_{10}H_{12}$. This property of the acid accounts for the fact that Perkin (this Journal, Trans., 1879, 136) only obtained butenylbenzene by the action of benzaldehyde on a mixture of sodium isobutyrate and isobutyric anhydride. W. C. W.

Ethoxymetatoluic Acid. By P. H. BROUN (*Amer. Chem. J.*, **4**, 374—377).—Remsen and Kuhara have shown that the nitrotoluic acid obtained by the oxidation of ordinary nitroxylene with chromic acid has the constitution $C_6H_3(\overset{1}{N}O_2)\overset{2}{Me}(\overset{4}{COOH})$ Abstr., 1882, 607). The corresponding diazo-compound is easily converted into the hydroxy-acid by boiling with water; but when boiled with alcohol, it yields, not metatoluic acid, as might be expected, but another acid, described as insoluble in cold and only slightly soluble in hot water, crystallising from alcoholic solution, volatilising with steam, and subliming in light flakes. The analysis of this acid did not yield satisfactory results, on account of the smallness of the quantity obtained; but the author of the present paper has succeeded in preparing it in larger quantity and in determining its constitution.

In preparing the amido-acid from the nitro-acid, it is advisable to use as little hydrochloric acid as possible; and the nitric acid used in converting the amido-acid into the diazo-acid must be very dilute. On boiling the dried diazo-compound with nearly absolute alcohol (99 p. c.) and diluting the product with water, the acid under investigation is thrown down with all the properties ascribed to it by Remsen and Kuhara. The analysis of its calcium salt gave numbers agreeing with the formula $(C_{10}H_{11}O_3)_2Ca,2H_2O$ or

$$[C_6H_3Me(OEt)COO]_2Ca,2H_2O,$$

showing that the acid in question is *ethoxymetatoluic acid*. Its formation may be represented by the equation $NO_3.N \colon N.C_6H_3Me.COOH + EtOH = NO_3H + N_2 + \overset{1}{EtO}.C_6H_3\overset{2}{Me}.\overset{4}{COOH}$. H. W.

Coumarin. By G. EBERT (*Annalen*, **216**, 139—161).—Coumarin dissolves in boiling baryta-water forming an unstable compound, which has not been isolated. Coumarin is also dissolved by a hot solution of potassium carbonate; an unstable compound is produced which is soluble in alcohol and water. A hot alcoholic solution of sodium ethylate also has the power of dissolving coumarin.

The properties of *ethylcoumarinic acid*, $EtO.C_6H_4.CH \colon CH.COOH$

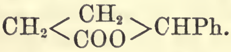
(α-ethylorthoxyphenylacrylic acid), have been previously described by Perkin (this Journal, Trans., 1881, 409). The calcium salt, $(C_{11}H_{11}O_3)_2Ca + 2H_2O$, crystallises in glistening needles. 100 grams of the saturated solution at 21° contain 2·15 grams of the anhydrous salt. Calcium ethylcoumarate also forms needle-shaped crystals containing 2 mols. H_2O. 100 grams of the saturated solution at 21° contain 0·43 gram of the anhydrous salt. Barium ethylcoumarinate is deposited from an alcoholic solution in silky needles containing 2 mols. H_2O. Barium ethylcoumarate forms crystals containing 4 mols. H_2O. It is very soluble in alcohol, but is left as a gummy mass on evaporating the solution. Both ethylcoumarinic and ethylcoumaric acids yield ethylsalicylaldehyde and ethylsalicylic acid on oxidation with potassium permanganate. These acids are both converted into ethylmelilotic acid, $EtO.C_6H_4.(CH_2)_2.COOH$, by the action of sodium amalgam on their aqueous solutions. The author also finds that the bromide, $C_{11}H_{12}Br_2O_3$ (m. p. 155°), obtained by the action of bromine on a solution of ethylcoumarinic acid in carbon bisulphide, is identical with the bromine-compound derived from ethylcoumaric acid. This statement does not agree with Perkin's observations (*loc. cit.*).

Coumaric acid stands in the same relation to coumarinic acid that angelic acid bears to tiglic acid. W. C. W.

Phenylbutyrolactone and Phenylparaconic Acid. By H. W. JAYNE (*Annalen*, **216**, 97—114).—A mixture of phenylparaconic acid and isophenylcrotonic acid is obtained by heating equivalent proportions of sodium succinate, benzaldehyde, and acetic anhydride at 125—130° for four hours in a flask fitted with an upright condenser. The product of the reaction is dissolved in water and extracted with ether. The extract is treated with sodium carbonate, and on adding hydrochloric acid to the alkaline liquid isophenylcrotonic and paraconic acids are precipitated. After the precipitate has been dried, it is treated with carbon bisulphide, which dissolves out isophenylcrotonic acid, and leaves phenylparaconic acid undissolved. A further yield of phenylparaconic acid is obtained by adding hydrochloric acid to the aqueous solution of the crude product after it has been treated with ether.

Isophenylcrotonic acid, $CHPh : CH.CH_2.COOH$, crystallises in needles or prisms, which dissolve freely in alcohol, ether, and carbon bisulphide. The acid melts at 86°, and boils at 302°.

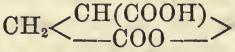
Barium isophenylcrotonate, $Ba(C_{10}H_9O_2)_2 + 3H_2O$, forms large crystals, freely soluble in water. $Ca(C_{10}H_9O_2)_2 + 3H_2O$ is also very soluble.

Isophenylcrotonic acid unites with hydrobromic acid, yielding *phenylbromobutyric acid*, $C_{10}H_{11}BrO_2$ (m. p. 69°). This acid is decomposed by a dilute solution of sodium carbonate, forming *phenylbutyrolactone*,  $CH_2<{}^{CH_2}_{COO}>CHPh$. This compound crystallises in rhombic needles ($a : b : c = 0·6106 : 1 : 0·426$) soluble in alcohol, ether, carbon bisulphide, and hot water. It melts at 37°, and boils at 306°, but begins to volatilise at 100°. It is converted into a salt of phenylhydroxybutyric acid by boiling with an alkali.

Barium phenylhydroxybutyrate, $Ba(C_{10}H_{11}O_3)_2$, is an amorphous body, soluble in water and in alcohol. The free acid, $C_{10}H_{12}O_3$, forms transparent crystals (m. p. 75°), soluble in alcohol, ether, and carbon bisulphide. It also dissolves in water, but at 80° the solution decomposes yielding the lactone.

Isophenylcrotonic acid unites with bromine to form phenyldibromobutyric acid (m. p. 138°), which is converted into phenylbutyrolactone or sodium phenylhydroxybutyrate by the action of sodium amalgam on its aqueous solution.

Phenylbutyric acid, $CH_2Ph.(CH_2)_2.COOH$, obtained by treating the isophenylcrotonic acid with nascent hydrogen, resembles benzoic acid in appearance. It melts at 47·5°, boils about 290°, and dissolves in ether, alcohol, and water. The barium salt of this acid is crystalline, the calcium salt amorphous.

Phenylparaconic acid,  $CH_2<\begin{matrix}CH(COOH)\\ \text{---}COO\text{---}\end{matrix}>CHPh$, crystallises in glistening needles containing $\frac{1}{4}$ mol. H_2O melting at 99°, soluble in ether, alcohol, chloroform, and hot water. The melting point of the anhydrous acid is 109°. At 150°, the acid begins to decompose into phenylbutyrolactone, carbonic anhydride and isophenylcrotonic acid. *Barium phenylparaconate*, $Ba(C_{11}H_9O_4)_2 + 3H_2O$, forms colourless crystals soluble in water. The *calcium* salt contains 2 mols. H_2O. It is converted into calcium isophenylcrotonate by heating at 140°.

Phenyl itamalates are produced when paraconic acid is boiled with an alkali.
W. C. W.

Phenylhomoparaconic Acid. By S. L. Penfield (*Annalen*, **216**, 119—127).—*Phenylhomoparaconic acid*,  $CHMe<\begin{matrix}CH(COOH)\\ \text{---}COO\text{---}\end{matrix}>CHPh$, is obtained by heating a mixture of equivalent quantities of benzaldehyde, sodium pyroracemate, and acetic anhydride at 130° for nine hours in a flask provided with an upright condenser; the contents of the flask are then dissolved in hot water and extracted with ether. The extract contains small quantities of phenylhomoparaconic and cinnamic acids. A third acid is also present. On adding hydrochloric acid to the aqueous solution from which these acids have been extracted by ether, phenylhomoparaconic acid is precipitated. The pure acid forms glistening needles melting at 177°, soluble in hot water, alcohol, and ether.

Silver phenylhomoparaconate, $C_{12}H_{11}O_4Ag$, forms small crystals soluble in water. By the action of calcium carbonate on a hot solution of phenylhomoparaconic acid, *calcium phenylhomitamalate*,

$$C_{12}H_{12}O_5Ca + 3H_2O,$$

is obtained in sparingly soluble needle-shaped crystals. $BaC_{12}H_{12}O_5 + 2H_2O$ resembles the calcium salt in its properties. $Ag_2C_{12}H_{12}O_5$ is insoluble in water.

Phenylhomoparaconic acid does not combine with bromine, but it dissolves slowly in strong hydrobromic acid, forming the unstable compound $C_{12}H_{13}BrO_4$. This body melts with decomposition at 149°. It is soluble in alcohol and ether. On warming the aqueous solution, carbonic anhydride is evolved, and crystals of an acid having the composition $C_{11}H_{12}O_2$ are deposited on cooling.

Phenylhomoparaconic acid is decomposed by heat at a temperature slightly above its melting point, yielding phenylbutylene (b. p. 177°), benzaldehyde, and other products. The phenylbutylene appears to be identical with the hydrocarbon which Aronheim (*Annalen*, **171**, 219) obtained by the action of allyl iodide on benzyl chloride.

W. C. W.

Coumarilic Acid. By R. Fittig and G. Ebert (*Annalen*, **216**, 162—171).—*Coumarilic acid*, $C_9H_6O_3$, prepared by the action of alcoholic potash on coumarin dibromide, melts at 190·5°, boils between 310° and 315° with very slight decomposition, and possesses the properties ascribed to it by Perkin (this Journal, 1870, 360; 1871, 37). The barium salt, $Ba(C_9H_5O_3)_2 + 4H_2O$, crystallises in plates, soluble in boiling water, whilst the calcium salt, $Ca(C_9H_5O_3)_2 + 3H_2O$, is deposited from a hot aqueous solution in needles. The crystalline silver salt is sparingly soluble in hot water.

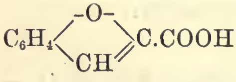
Coumarilic acid is not attacked by bromine. On fusion with potash, it yields salicylic and acetic acids. It unites directly with nascent hydrogen to form *hydrocoumarilic acid*, $C_9H_8O_3$, which crystallises in pearly leaves, soluble in alcohol, ether, and water. This acid melts at 116·5°, and boils about 299° with decomposition. The formation of hydrocoumarilic acid shows that coumarilic acid is not *hydroxyphenylpropiolic acid*, as stated by Beilstein. *Barium hydrocoumarilate*, $Ba(C_9H_7O_3)_2 + 2H_2O$, forms tabular crystals, which dissolve freely in water. The *calcium salt* bears a close resemblance to the barium salt. It readily forms supersaturated solutions. $AgC_9H_7O_3$ is very slightly soluble in water. *Ethyl hydrocoumarilate*, $C_9H_7O_3Et$ (m. p. 23°, b. p. 273°), is insoluble in water.

Coumarilic acid splits up into coumarone, C_8H_6O, and carbonic anhydride when distilled over lime. Coumarone is a colourless oil, heavier than water. It remains liquid at −18°, and boils at 169°. It is insoluble in water and soda-lye. It is not attacked by nascent hydrogen, but it unites with bromine, yielding a dibromide, $C_8H_6Br_2O$ (m. p. 86°), which slowly decomposes at the ordinary temperature.

Hydrocoumarilic acid does not yield a hydrocoumarone on distillation with lime, but is decomposed with formation of phenol.

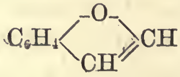
From the result of these experiments the authors propose the following formulæ:—

Coumarilic acid.



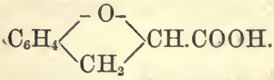
$$C_6H_4\left\langle\begin{matrix}-O-\\CH\end{matrix}\right\rangle C.COOH$$

Coumarone.



$$C_6H_4\left\langle\begin{matrix}-O-\\CH\end{matrix}\right\rangle CH$$

Hydrocoumarilic Acid.



$$C_6H_4\left\langle\begin{matrix}-O-\\CH_2\end{matrix}\right\rangle CH.COOH.$$

W. C. W.

Action of Sulphuric Acid on Cinnamic Acid. By E. Erdmann (*Annalen*, **216**, 179—199).—Cinnamic acid is completely decomposed by prolonged boiling with dilute sulphuric acid, splitting up into distyrenic acid, distyrene, and carbonic anhydride.

The relative yield of hydrocarbon and acid varies with the strength of the sulphuric acid employed, the more dilute the acid the larger being the yield of hydrocarbon. Good results are obtained by boiling cinnamic acid for 3½ hours with five times its weight of strong sulphuric acid diluted with an equal volume of water. The mixture of distyrenic acid and distyrene forms an oily layer on the surface of the liquid. This is collected, diluted with ether, and repeatedly shaken up with a solution of sodium carbonate. The ethereal solution contains the hydrocarbon, and the alkaline liquid distyrenic acid, which is precipitated on adding hydrochloric acid. The acid is best purified by conversion into the insoluble calcium salt. The pure acid, $C_{17}H_{16}O_2$, is amorphous, and forms amorphous salts. It is freely soluble in ether, alcohol, and glacial acetic acid. It melts about 50°, and boils without decomposition. The acid is monobasic. On oxidation with chromic mixture, it yields benzoic acid, but it is neither attacked by bromine nor by nascent hydrogen.

Distyrene, $C_{16}H_{16}$, is a colourless liquid exhibiting a blue fluorescence, which gradually disappears. The hydrocarbon has no action on polarised light. Its sp. gr. at 15° is 1·016, and it boils at 311°. On oxidation with chromic mixture, benzoic acid is produced. The crystalline dibromide, $C_{16}H_{16}Br_2$ (m. p. 102°), obtained by the addition of bromine to a mixture of distyrene and carbon bisulphide, is freely soluble in ether, benzene, carbon bisulphide, and in hot alcohol, glacial acetic acid, and light petroleum.

Distyrene is decomposed by prolonged boiling, yielding toluene, styrene, and isopropylbenzene. W. C. W.

Imides of Bibasic Acids. By M. LANDSBERG (*Annalen*, **215**, 172—213).—The author has endeavoured in his research to obtain a more complete knowledge of the imides of bibasic acids, in order to be able to determine their real constitution. His principal object has been to ascertain whether a hydrogen-atom in these imides can be replaced by metals other than silver or mercury, and, if possible, starting from the imides themselves, to prepare ethyl derivatives which yield ethylamine with elimination of water. The present paper is limited to an investigation of the properties of phthalimide and succinimide.

Phthalimide.—The phthalimide employed was prepared by Laurent's method, viz., by subliming ammonium phthalate. The sublimate was a snow-white mass consisting of very small plates melting at 228—229°. Phthalimide is precipitated from solutions of its metallic derivatives on adding an acid. *The potassium derivative*, $C_8H_4O_2NK$, is precipitated from an alcoholic solution of phthalimide, when it is treated with the theoretical quantity of potash in alcohol. It forms white plates which are almost insoluble in alcohol and ether. *The sodium derivative*, $C_8H_4O_2NNa$, is prepared in a similar manner. It is precipitated on adding ether. *The barium derivative*, $(C_8H_4O_2N)_2Ba + 4H_2O$, is prepared by decomposing the potassium compound with barium chloride. It forms a glittering white precipitate, which decomposes when heated to 100°. *The magnesium derivative*, $(C_8H_4O_2N)_2Mg$, is formed when the potassium compound is decomposed by magnesium sulphate. It is obtained as a white powdery precipitate easily soluble in water. *The silver derivative* is a white cheese-like precipitate which, when dried over sulphuric acid, has the composition $C_8H_4O_2NAg + \frac{1}{2}H_2O$. After drying at 100° for several days it is obtained in an anhydrous state. Laurent prepared the silver derivative by treating an ammoniacal solution of phthalimide with silver nitrate. He states that he obtained three different precipitates consisting of silver phthalimide, silver ammonium phthalimide, and silver amidophthalate. The author finds on repeating the experiments, that the powdery precipitate described by Laurent consists of silver phthalimide, and he considers the compound crystallising in needles to be a mixture of silver phthalimide and phthalimide. *The mercury derivative*, $(C_8H_4O_2N)_2Hg$, is prepared by decomposing the potassium compound with mercuric chloride. *The copper salt* is obtained as a bluish-white precipitate on mixing equivalent quantities of potassium phthalimide and copper sulphate. The author was unable to obtain the salt free from sulphate. Assuming that the salt obtained was a mixture of copper phthalimide and copper sulphate in varying proportions, and deducting the latter, from calculations based on the determinations of sulphuric acid, he obtains the formula $(C_8H_4O_2N)_2Cu + H_2O$ for the copper salt. He endeavoured to prepare the salt from copper chloride, but was equally unable to obtain it free from chloride. The salt obtained from the chloride crystallises with 2 mols. H_2O. On precipitating lead nitrate with potassium phthalimide a mixture of lead phthalimide with varying quantities of phthalimide is obtained.

Ethyl-phthalimide is obtained by treating anhydrous silver phthalimide with the theoretical quantity of ethyl iodide and a small quantity of anhydrous benzene, and allowing it to stand for some days; on evaporating, phthalimide separates at first, but from the last mother-liquors, well-formed plates melting at 90° are deposited, which, after repeated crystallisation from alcohol, melt at 90—94°, and have the composition $C_{10}H_{13}NO_4$. The author had not sufficient material to make further investigations of its properties.

Salts of Amidophthalic Acid.—The potassium salt,

$$CONH_2.C_6H_4.COOK,$$

is obtained when potassium phthalimide is boiled with water. It crystallises from an aqueous solution in clear rhombic plates. *The silver salt* is obtained in pearly-white flakes on adding silver nitrate to an alcoholic solution of potassium amidophthalate. On treating the silver salt with the theoretical amount of hydrochloric acid and filtering, a solution of the free acid is obtained. On evaporation in the cold, they are decomposed yielding nothing but ammonium phthalate. *The barium salt* is easily soluble in water, and, on addition of acids, yields no phthalimide. The author endeavoured to obtain the free acid from this salt, but only obtained ammonium phthalate.

Succinimide, $C_4H_5O_2N$.—The succinimide employed was obtained by distilling ammonium succinate. The metallic derivatives are all more or less soluble in water, and, on treatment with acids, yield succinimide. They possess the characteristic property of forming the corresponding salt of amidosuccinic acid by taking up water. *The potassium derivative* is obtained by treating an alcoholic solution of succinimide with the theoretical quantity of potassium hydroxide dissolved in alcohol, and then adding ether; it consists of small needle-shaped crystals, or a pure white powder, according to the amount of ether added. The crystalline form is anhydrous, whilst the powder contains half a molecule of water, $C_4H_4O_2NK + \frac{1}{2}H_2O$. Both forms are easily soluble in water and alcohol. *The sodium derivative*, $C_4H_4O_2NNa$, crystallises in small needles. It is very hygroscopic. *The barium derivative* is obtained by acting on a solution of succinimide in absolute alcohol with barium ethylate; the compound, which is easily soluble in water, crystallises with 2½ mols. H_2O. *The silver derivative* can be prepared either by decomposing potassium succinimide with silver nitrate, when it is obtained as a white powdery crystalline precipitate, $C_4H_4O_2NAg + \frac{1}{2}H_2O$, becoming anhydrous at $-80°$, or by adding ammonia to an alcoholic solution of succinimide, boiling, and then adding the theoretical quantity of silver nitrate. On cooling, the salt crystallises in long silky needles containing water. If only a trace of ammonia be present, the compound is obtained anhydrous, but the whole is not precipitated. Silver succinimide is very slightly soluble in cold water and alcohol. *The mercury derivative*, $(C_4H_4O_2N)_2Hg$, is obtained by dissolving mercuric oxide in a hot alcoholic solution of succinimide, and is deposited on cooling in small glittering needles which are easily soluble in water and alcohol: it can also be obtained by decomposing sodium succinimide with mercuric chloride. A *basic copper derivative* is obtained when sodium succinimide is treated with copper acetate. It is easily soluble in water. When dried at 100°, it has the composition $C_8H_8O_4N_2Cu,CuO_2H_2,2H_2O$.

Ethyl-succinimide.—The author dissolved succinimide in absolute alcohol, and treated the solution with the theoretical amount of sodium ethylate and ethyl iodide. As soon as a considerable amount of sodium iodide was formed, carbonic anhydride was passed into the mixture until no further precipitate was obtained. The solution was then filtered and the filtrate distilled. On fractionating, a portion was isolated which boiled constantly between 232—234°, and remained liquid at $-12°$. When distilled with potassium hydroxide, it yields ethylamine. Menschutkin found the boiling point of ethyl succinimide, obtained by distilling ethylamine succinate, to be 234°.

J. I. W.

Constitution of some Azobenzenedisulphonic Acids. By P. Rodatz (*Annalen*, **215**, 125—172).—The methods employed for preparing these acids are:—1. By reducing nitro-acids with sodium amalgam or zinc-dust and sodium. 2. By oxidising amido-acids with potassium permanganate. 3. By dissolving azobenzene in fuming sulphuric acid. The first two methods yield azo-acids whose composition may be known with certainty, provided that the nitro- or amido-acids employed be known. The third method, on the other hand, gives azo-acids of unknown constitution.

By heating azobenzene with fuming sulphuric acid, two azobenzenedisulphonic acids are formed—α and β. The former probably has the composition $SO_3H.C_6H_4.N_2.C_6H_4.SO_3H$ [$SO_3H : SO_3H = 4 : 4$], as it is also obtained by oxidising paramidobenzenesulphonic acid with potassium permanganate. This is confirmed by its behaviour when treated with hydrochloric acid at 150°, when it yields an amido-acid. On heating the potassium salt or the chloride (m. p. 222°) with hydrochloric acid at 150° in a sealed tube, paramidobenzenesulphonic acid is obtained. When the chloride of β-azobenzenedisulphonic acid (m. p. 120°) is heated with hydrochloric acid in a similar manner, it yields paramido- and metamido-benzenesulphonic acids. The former is the less soluble. The latter separates from an aqueous solution in thin white needles containing water of crystallisation and effloresce on exposure to the air; their solution becomes red when evaporated. When treated with bromine, it yields dibromamidobenzenesulphonic acid: with excess of bromine, it forms bromaniline. The acid, therefore, which is formed along with paramidobenzenesulphonic acid must be metamidobenzenesulphonic acid, and the composition of the azobenzenedisulphonic acid probably

$$SO_3H.C_6H_4.N_2.C_6H_4.SO_3H\ [SO_3H : SO_3H = 3 : 4].$$

The same acid is formed by the oxidation of a mixture of equal parts of the potassium salts of meta- and para-amidobenzenesulphonic acids. In the same manner other similarly constituted azo-acids can be prepared. The author, from want of material, was unable to make experiments with the ortho-acid. J. I. W.

Brominated Azobenzenedisulphonic Acids. By P. RODATZ (*Annalen*, **215**, 217—227).—The acids were prepared from brominated amidobenzenesulphonic acids of known constitution by oxidation with potassium permanganate.

Tetrabromazobenzenedisulphonic acid, $C_{12}H_4Br_4N_2(SO_3H)_2 1\frac{1}{2}H_2O$ $[SO_3H : Br : Br : SO_3H : Br : Br = 3 : 4 : 6 : 3 : 4 : 6]$. The dibromamidobenzenesulphonic acid from which it was prepared was obtained by acting on metamidobenzenesulphonic acid with bromine. Its constitution is $C_6H_2Br_2(NH_2).SO_3H$ $[NH_2 : SO_3H : Br : Br = 1 : 3 : 4 : 6]$. A dilute aqueous solution of the potassium salt was gradually mixed with a 5 per cent. solution of potassium permanganate at 45°. In order to convert the amido-acid into the azo-compound it is necessary to employ about four times the theoretical amount of potassium permanganate, a part of the amido-acid undergoing further oxidation.

Tetrabromazobenzenedisulphonic acid, prepared by decomposing the barium salt with sulphuric acid, separates from the concentrated solution in thin red needles which are soluble in water and alcohol. *The potassium salt*, $C_{12}H_4Br_4N_2(SO_3K)_2,3H_2O$, forms small regular hexagonal plates of a red colour, easily soluble in hot water. *The barium salt*, $C_{16}H_4Br_4N_2(SO_3)_2Ba,H_2O$, is precipitated from a solution of the potassium salt on adding barium chloride as a heavy flesh-coloured insoluble mass of small needles. *The calcium salt*,

$$C_{12}H_4Br_4N_2(SO_3)_2Ca,4H_2O,$$

is prepared in a manner similar to the barium salt; it forms yellowish-red plates. *The lead salt*, $C_{12}H_4Br_4N_2(SO_3)_2Pb,2\frac{1}{2}H_2O$, forms a heavy red crystalline precipitate insoluble in water.

Tetrabromazobenzene disulphochloride, $C_{12}H_4Br_4N_2(SO_2Cl)_2$, is prepared by heating the potassium salt with phosphorus chloride and treating the mass with water. The chloride remains undissolved as a red powder, which is slightly soluble in ether, but more soluble in benzene, from which it crystallises in fine red needles melting at 233°.

Tetrabromazobenzenedisulphamide, $C_6H_4Br_4N_2(SO_2NH_2)_2$, is prepared by digesting the chloride for some time with concentrated ammonia. The amide is very slightly soluble in water. It crystallises from alcohol in yellowish-red microscopic needles.

Tetrabromazobenzenedisulphonic acid loses its colour when heated with stannous chloride solution, and yields slender white needles of the dibromamidosulphobenzoic acid from which the azo-acid was prepared. A hydrazo-acid could not be obtained in this manner.

Tetrabromhydrazobenzenedisulphonic acid has been prepared by Jordan by treating hydrazometabenzenedisulphonic acid with bromine and water. The author finds that when treated with potassium permanganate solution, it yields the potassium salt of tetrabromazobenzenedisulphonic acid. The barium salt and the chloride cannot be obtained in a crystalline form.

By oxidising *dibromorthamidobenzenesulphonic acid* the author was unable to obtain the potassium salt crystalline, resinous matters being formed.

Tetrabromazobenzenedisulphonic acid, $C_{12}H_4Br_4N_2(SO_3H)_2,2H_2O$.—The acid obtained by Schmidt from paramidobenzenesulphonic acid whose composition is $C_6H_2Br_2(NH_2).SO_3H$ [$SO_3H : Br : NH_2 : Br = 1 : 3 : 4 : 5$], yields the above acid on oxidation. Its structure is

$$SO_3H.C_6H_2Br_2.N_2.C_6H_2Br_2.SO_3H \ [Br : SO_3H : Br = 2 : 4 : 6].$$

The free acid prepared from the barium salt crystallises in glittering red plates, soluble in water and alcohol. *The potassium salt*,

$$C_{12}H_4Br_4N_2(SO_3K)_2,2H_2O,$$

forms long plates of a dark red colour, slightly soluble in cold water, more freely in hot. *The barium salt*, $C_{12}H_4Br_4N_2(SO_3)_2Ba,3H_2O$, forms a heavy flesh-coloured precipitate consisting of fine microscopic needles, insoluble in water. *The calcium salt*, $C_{12}H_4Br_4N_2(SO_3)_2Ca,4H_2O$, prepared by treating a solution of the potassium salt with calcium chloride solution, crystallises in red rhombic plates easily soluble in hot water. *The lead salt*, $C_{12}H_4Br_4N_2(SO_3)_2Pb$, forms a brownish-red precipitate consisting of small groups of crystals.

Tetrabromazobenzene disulphochloride, $C_{12}H_4Br_4N_2(SO_2Cl)_2$, is obtained by melting the potassium salt with phosphorus chloride. It forms a brown powder which is slightly soluble in ether, but freely soluble in benzene, from which it crystallises in yellowish-brown plates melting at 258—262°.

Tetrabromazobenzenedisulphamide, $C_{12}H_4Br_4N_2(SO_2NH_2)_2$, is obtained by heating the chloride with concentrated ammonia for some time. It crystallises from ammonia and alcohol in long silky violet needles. On boiling the tetrabromazobenzenedisulphonic acid with stannous chloride, a dibromamidobenzenesulphonic acid is obtained. A hydrazo-acid could not be detected.

Hexbromazobenzenedisulphonic acid, $C_{12}H_2Br_6N_2(SO_3H)_2,H_2O$, is prepared from tribromamidobenzenesulphonic acid (derived from metamidobenzenesulphonic acid). It therefore has the constitution [Br : Br : SO_3H : Br = 2 : 4 : 5 : 6]. Potassium permanganate only acts on a solution of the potassium salt of the amido-acid at 70—80°. The free acid prepared from the barium salt forms thin yellow needles extremely soluble in water and alcohol. *The potassium salt*,

$$C_{12}H_2Br_6N_2(SO_3K)_2,3H_2O,$$

crystallises in silky lemon-yellow thin needles which are slightly soluble in cold water and easily dissolve in hot water and alcohol. *The barium salt*, $C_{12}H_2Br_6N_2(SO_3)_2Ba,2H_2O$, forms large yellowish-red prisms, slightly soluble in hot water. *The calcium salt*,

$$C_{12}H_2Br_6N_2(SO_3)_2Ca,7H_2O,$$

crystallises in red-pointed plates slightly soluble in cold water. *The lead salt*, $C_{12}H_2Br_6N_2(SO_3)_2Pb,4H_2O$, is prepared by neutralising the acid with lead carbonate. It forms yellow hexagonal pyramids slightly soluble in cold water.

Hexbromazobenzene disulphochloride, $C_{12}H_2Br_6N_2(SO_2Cl)_2$, is prepared by acting on the potassium salt with phosphorus chloride. It forms a red powder which crystallises from benzene in deep violet plates (m. p. 222—224°). *Hexbromazobenzene disulphamide*,

$$C_{12}H_2Br_6N_2(SO_2NH_2)_2,$$

forms yellowish-brown crystalline masses, slightly soluble in hot water and alcohol. On boiling it with stannous chloride solution, the acid is converted into an amido-acid. A hydrazo-acid could not be obtained.

J. I. W.

Jafferabad Aloes. By W. A. SHENSTONE (*Pharm. J. Trans.* [3], **13**, 461—462).—The author has found the aloïn extracted from Jafferabad aloes to be similar to Tilden's zanaloïn, the crystalline form and most of the reactions being alike. The author suggests a scheme for naming aloïns. Thus he divides them into two classes: 1. *Nataloïns*, like that obtained from Natal aloes, which yield only picric and oxalic acids by treatment with nitric acid and are not reddened even on heating with it. 2. *Barbaloïns*, which yield chrysamic, aloetic, picric, and oxalic acids, and are reddened by nitric acid. *α-Barbaloïns* from Barbary aloes are reddened in the cold by ordinary strong nitric acid. *β-Barbaloïns* from Socotrine, Zanzibar, and Jafferabab aloes are coloured only on heating by ordinary, but in the cold with fuming nitric acid.

D. A. L.

Certain Substances obtained from Turmeric. By C. L. JACKSON and A. E. MENKE (*Amer. Chem. J.*, **4**, 360—368).—In a former paper (Abstr., 1882, 1107) the authors described the preparation and properties of curcumin, the yellow colouring matter of turmeric, and showed that it may be represented by the formula

$$C_{14}H_{14}O_4 = C_6H_3(CH.\overset{1}{C}_5H_5.COOH)(\overset{3}{O}Me)(\overset{4}{O}H).$$

In the present paper they describe the products obtained from it by the action of nascent hydrogen and of bromine.

Curcumin Dihydride, $C_{14}H_{16}O_4$, obtained by the action of sodium-amalgam and water on curcumin, is a brownish-white powder, melting near 100°, insoluble in water, freely soluble in alcohol and glacial acetic acid, slightly in ether, insoluble in benzene and light petroleum. It dissolves in strong sulphuric acid with reddish-brown colour, in caustic soda and sodium carbonate on warming; the latter solution, however, depositing a brown precipitate as it cools.

An Anhydride of Curcumin Dihydride, $C_{28}H_{30}O_9 = (C_{14}H_{15}O_4)_2O$, obtained by heating curcumin with acetic acid of 85 per cent. and a large quantity of zinc-dust, at a temperature below the boiling point of the acetic acid, is a dirty white powder closely resembling the dihydride, and melting gradually near 120°. It is nearly insoluble in ether, light petroleum, and benzene, slightly soluble in chloroform, more soluble in alcohol and glacial acetic acid, from which it is deposited on evaporation as a varnish. It dissolves with yellow colour in aqueous potash, and with brown colour in a boiling solution of the carbonate, but without forming a definite potassium salt.

When diethylcurcumin, obtained as described in the authors' former paper, is treated with acetic acid and zinc-dust, it yields a mixture of *di-* and *mono-ethylcurcumin dihydride*, which is slowly oxidised by potassium permanganate, yielding ethylvanillic acid, together with a small quantity of ethylvanillin, indicated by its characteristic smell.

Tetrabromocurcumin, $C_{14}H_{10}Br_4O_4$, is formed by the action of bromine in excess on curcumin dihydride dissolved in acetic acid. The liquid left over night turns black, and on addition of water yields the tetrabromo-compound, as a red amorphous precipitate which does not melt below a red heat, but seems to decompose without melting. It is insoluble in water, light petroleum, and benzene, very slightly soluble in alcohol and ether, more freely in glacial acetic acid; not acted on by strong sulphuric acid, but vigorously attacked by boiling aqueous potash, forming a red solution, from which acids precipitate a black tarry body nearly free from bromine, whence it may be inferred that all the bromine in the original substance is situated in the side-chain.

Curcumin Tetrabromide, $C_{14}H_{14}Br_4O_4$, is formed on leaving curcumin suspended in carbon sulphide in contact with excess of bromine for some hours, and is left, as the solvent evaporates, as a whitish amorphous substance, melting with decomposition near 185°, insoluble in water, soluble with decomposition in alcohol and glacial acetic acid, very slightly soluble in ether, chloroform, and carbon bisulphide, insoluble in light petroleum and benzene. Potassium hydroxide and silver oxide convert it into vanillin; aniline and metallic zinc act upon it, the former with considerable evolution of heat.

Pentabromocurcumin Dibromide, $C_{14}H_9Br_7O_4$, is obtained by treating curcumin dissolved in glacial acetic acid with excess of bromine, or the solid tetrabromide with bromine, as a red amorphous substance melting near 120°, insoluble in water and in light petroleum, soluble in alcohol, ether, and glacial acetic acid, slightly soluble in benzene. Strong sulphuric acid acts on it but slowly. When heated alone, it gives off bromine and hydrobromic acid, leaving a black tar from which alcohol extracts a yellow substance containing bromine. Sodium hydroxide, sodium carbonate and water, and sodium ethylate and water all act upon it, but no smell of vanillin has been observed in either case. The same is true of the action of several oxidising agents, and this would seem to indicate the presence of part of the bromine in the benzene-ring. It is remarkable that this substance is but very slowly attacked by chromic acid mixture and by potassium permanganate, both of which act vigorously on curcumin. H. W.

Turmeric Oil—Turmerol. By C. L. Jackson and A. E. Menke (*Amer. Chem. J.*, **4**, 368—374).—This oil, to which turmeric (and therefore curry-powder) owes its aromatic taste and smell, was extracted from Bengal turmeric with light petroleum, and after being freed from the higher-boiling portion of that solvent by heating to 150° in a flask, formed a thickish oily yellow liquid having a pleasant aromatic odour. It was purified by fractional distillation under diminished pressure, and was thereby separated into three portions, the first boiling below 193°, the second at 193—198°, and the third consisting of a viscous semi-solid residue. The middle portion consisted of nearly pure turmerol; the first, of that compound contaminated with hydrocarbons from the petroleum. The middle fraction, after further purification by distillation in a vacuum, gave, as a mean result of several analyses, 83·62 per cent. carbon and 10·42 hydrogen, agreeing nearly with the formula $C_{19}H_{28}O$, which requires 83·81 C and 10·29 H.

Turmerol is a pale yellow oil having a pleasant, moderately strong aromatic smell, and a density of 0·9016 at 17°. It is optically dextrogyrate, $[\alpha]_D = 33·52$. Under ordinary pressure it boils at 285—290°, but decomposes at the same time, yielding a substance of lower boiling point. Under 60 mm. it boils at 193—198°, still however with slight decomposition. It is essentially insoluble in water, but mixes readily with all other ordinary solvents. It does not unite with acid sodium sulphite.

Turmerol is an alcohol, and is converted by heating at 150° with strong hydrochloric acid into turmeryl chloride, $C_{19}H_{27}Cl$, which is a pale brownish fragrant oil decomposed by distillation. The same compound is formed, but less definitely, by treating turmerol with phosphorus trichloride; the pentachloride appears to act partly in the same manner, but at the same time to add chlorine. By treating turmeryl chloride with boiling water, and with alcoholic solution of sodium acetate, potassium cyanide, or ammonia, substances are obtained having the characteristic odours of the classes to which they belong, but they have not yet been obtained pure. Turmerol treated with sodium yields a semi-solid mass having the composition of *sodium turmerylate*, $C_{19}H_{27}ONa$.

Isobutyl turmerylate, $C_{19}H_{27}.OC_4H_9$, prepared by boiling the sodium compound with isobutyl iodide in a reflux apparatus, is a heavy yellowish fragrant oil. The *ethylic ether* is a similar substance.

Oxidation of Turmerol.—By the action of a hot aqueous solution of potassium permanganate in excess, turmerol is oxidised to terephthalic acid. With a cold solution of the same salt, not in excess, it appears to yield some new acids, with the study of which the authors are at present occupied. H. W.

Hypochlorin and its Formation. By A. B. Frank (*Bied. Centr.*, 1882, 856).—Certain observations made go to prove that hypochlorin is the result of the action of acids on the decomposition products of chlorophyll; and Pringsheim's reaction may always be obtained in an acidified alcoholic extract of dead green plants. E. W. P.

Nature of Pringsheim's Hypochlorin Crystals. By A. Meyer (*Bied. Centr.*, 1882, 857).—The author agrees in the conclusions arrived at by Frank (preceding abstract); he considers hypochlorin to be identical with Hoppe-Seyler's chlorophyllan. Perfectly dry glacial acetic acid is a better reagent than hydrochloric acid for hypochlorin, as it dissolves chlorophyll more readily. E. W. P.

Researches on Pyridine. By H. Weidel and M. Russo (*Monatsh. Chem.*, **3**, 850—885).—Anderson, by heating pyridine with sodium, obtained a base which he regarded as *dipyridine*, $C_{10}H_{10}N_2$, together with other products. The authors of the present paper, following Anderson's process, with some modifications, for which we must refer to the original paper, have also obtained dipyridine, but they find that the chief products are: a base, $C_{10}H_8O_2$, isomeric with the dipyridyl which Skraup and Vortmann obtained by distilling dipyridyl-carboxylic acid, $C_{12}H_8N_2O_4$, with lime (p. 85 of this volume), and isonicotine, $C_{10}H_{14}N_2$.

The base, $C_{10}H_8N_2$, thus obtained is distinguished by the authors as "γ-dipyridyl."* It may be purified by crystallisation from boiling light petroleum, from which it separates in crystals on cooling; and distilling it in a current of steam. It dissolves very readily in alcohol, ether, benzene, and chloroform, somewhat less in ether, and is nearly insoluble in cold, but easily soluble in hot water. When heated, it melts and sublimes in long needles. Small quantities of it volatilise with vapour of water. The aqueous solution has a faintly alkaline reaction. The base has a bitter taste, no smell at ordinary temperatures, but when heated it gives off faintly odorous cough-exciting vapours. It melts at 114° and boils at 304·8° (bar. 760 mm.).

These are the properties assigned by Anderson to his dipyridine, $C_{10}H_{10}N_2$. The authors, however, find that the base in question gives, as a mean of several closely agreeing analyses, 76·87 per cent. C, 5·18 H, and 17·95 N, leading to the formula $C_{10}H_8N_2$, which requires

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* The designation of an organic base by a name ending in *yl* (a termination usually applied to alcoholic or acid radicles) is somewhat anomalous; a better name would perhaps be *dehydrodipyridine*.—H. W.

76·92 C, 5·13 H, and 17·95 N. This formula has further been confirmed by the analysis of several salts.

The anhydrous crystals of γ-dipyridyl absorb water from the air with great avidity, the melting point of the hydrated substance thus formed, sinking, according to the time of exposure, to 107°, 104°, 96°, and finally to 73°, which last is the melting point of the crystals deposited from aqueous solution. The hydrate, $C_{10}H_8N_2,2H_2O$, thus obtained, gives off the greater part of its water at 100°, the remainder only on distillation.

γ-Dipyridyl Methiodide, $C_{10}H_8N_2,2MeI$, is formed on adding methyl iodide in excess to a solution of the base in methyl alcohol; and separates on evaporation over sulphuric acid, in large, yellow-red, highly lustrous, monoclinic crystals, $0P . \infty P$. Treated with potash-lye or silver oxide, it does not yield the corresponding base in definite form. The reaction above described shows that γ-dipyridyl has the character of a tertiary amine.

Oxidation of γ-Dipyridyl.—This base in the free state offers great resistance to the action of oxidising agents, but in the form of sulphate it is easily oxidised by potassium permanganate, yielding *pyridine-monocarboxylic* or *isonicotinic acid*, according to the equation $2C_{10}H_8N_2 + 23O = 2(C_5H_4N.COOH) + 8CO_2 + 3H_2O + N_2$. This acid, after purification, forms a white crystalline mass melting at 307°, and identical in every respect with that which Weidel and Hübner obtained by oxidation of nicotine (this Journal, 1873, 508).

Action of Nascent Hydrogen.—γ-Dipyridyl treated with tin and hydrochloric acid takes up 6 at. hydrogen, and is converted into isonicotine: $C_{10}H_8N_2 + 3Sn + 6HCl = 3SnCl_2 + C_{10}H_{14}N_2$. This base, separated from the product in the usual way, and purified by drying in a vacuum at 150°, and subsequent distillation in hydrogen, forms a colourless oil, which solidifies on cooling to a mass of slender needles, and turns yellow in the air, especially in the fused state. It is extremely hygroscopic, deliquesces in water, alcohol, or wood-spirit, and dissolves readily in ether, light petroleum, and benzene. It has a strongly alkaline reaction, and cauterises the skin like caustic potash. When pure, it is nearly scentless at ordinary temperatures, but when gently heated, it emits a faint odour somewhat like that of commercial opium; at higher temperatures, it emits a pungent vapour. It has an acrid alkaline taste, and acts on the animal economy as a poison, like nicotine, but much less strongly. In aqueous solution, and especially when neutralised with sulphuric acid, it is easily oxidised by potassium permanganate to isonicotinic acid. Its salts are deliquescent, and crystallise with difficulty, even from the most concentrated solutions. The *methiodide*, $C_{10}H_{14}N_2,2MeI$, crystallises from its solution in methyl alcohol by spontaneous evaporation, in monoclinic or triclinic crystals.

Isonicotine, as already observed, is also found among the products obtained by the action of sodium on pyridine; and its formation, together with that of γ-dipyridyl and dipyridine, is supposed by the authors to take place by two stages, the first consisting in the formation of sodium-pyridine, C_5H_4NaN, and certain products formed therefrom by addition of hydrogen; the second in the action of the air on these products. This series of actions may, perhaps, be represented by the following equations:—

$$\begin{aligned} \text{I. } & 2C_5H_5N + 2Na = 2C_5H_4NaN + H_2 \\ & C_5H_4NaN + H_2 = C_5H_6NaN \\ & C_5H_4NaN + H_6 = C_5H_{10}NaN. \end{aligned}$$

$$\text{II. } 2C_5H_4NaN + O = Na_2O + \underset{\gamma\text{-Dipyridyl.}}{C_{10}H_8N_2}$$

$$C_5H_6NaN + C_5H_4NaN + O = Na_2O + \underset{\text{Dipyridine.}}{C_{10}H_{10}N_2}$$

$$C_5H_{10}NaN + C_5H_4NaN + O = Na_2O + \underset{\text{Isonicotine.}}{C_{10}H_{14}N_2}.$$

Certain resinous and oily products of no decided basic character, formed at the same time, are probably due to the further action of the sodium on the dipyridyl or on the sodium-pyridine. H. W.

The Trapezohedral Hemihedry of Strychnine Sulphate. By H. Baumhauer (*Jahrb. f. Min.*, 1882, **2**, Ref., 30).—Although the crystals show circular polarisation, yet they show no trapezohedral faces; on the basal planes, water or alcohol produces etching figures, formed by the primary pyramid; but dilute hydrochloric acid produces a series of furrows crossing each other at right angles, and inclined 16° to the edges 0P : P; on the opposite basal plane the furrows are similar, but inclined in the opposite direction. This behaviour proves the trapezohedral hemihedral nature of the crystals.

H. B.

Hydropiperic and Piperhydronic Acids. By E. Buri (*Annalen*, **216**, 171—179).—When the action of nascent hydrogen on potassium piperate takes place in a strongly alkaline solution, β-hydropiperic acid is produced, but if care is taken to keep the solution nearly neutral, only α-hydropiperic acid is obtained. The β-acid forms needle-shaped crystals (m. p. 130°), which are somewhat less soluble in water, ether, chloroform, alcohol, and carbon bisulphide than the crystals of the α-acid (m. p. 78°). To separate the two acids, the greater solubility of the ammonium salt of the β-acid is made use of; α-hydropiperic acid is converted into its isomeride by solution in warm soda-lye.

α-Hydropiperic acid unites with bromine, yielding a dibromo-addition-product, $C_{12}H_{12}Br_2O_4$, but when the β-acid is treated with bromine it forms a monobromo-substitution-product, $C_{12}H_{11}BrO_4$ (m. p. 170°).

Piperhydronic acid, $C_{12}H_{14}O_4$, obtained by the action of sodium-amalgam on a warm aqueous solution of β-hydropiperic acid, or preferably its monobromo-derivative, is deposited from an alcoholic solution in colourless plates (m. p. 96°) soluble in the solvents for hydropiperic acid.

When *calcium piperhydronate*, $(C_{12}H_{13}O_4)_2Ca + H_2O$, is treated with hot water, a portion dissolves, and the remainder melts.

W. C. W.

Action of Invertin. By A. Mayer (*Bied. Centr.*, 1882, 850).—There seems to be no relation between the action and the amount of invertin in a solution. Invertin is not destroyed by its own action. Temperatures which have no effect on invertin when active, are destructive to it when it is alone and quiescent. Neither bacteria nor light have any influence on this ferment. E. W. P.

Physiological Chemistry.

Behaviour of Ozone with Blood. By C. Binz (*Chem. Centr.*, 1882, 810).—Traces of ozone introduced into the blood give rise to the formation of metahæmaglobin, the ozone being itself quickly and completely destroyed by admixture with blood; this is the accepted view, which is now disproved by the author's experiments.

When a continual current of ozonised air, strong enough to produce irritation of the throat and chest within a minute, is passed through 400—500 c.c. of defibrinated calf's or sheep's blood, after one hour the blood has undergone no apparent change, either spectroscopically or microscopically. Its alkalinity, however, is greater than that in a check sample acted on by air alone. By prolonging the action the colour corpuscles are ultimately attacked. The ozonised blood very quickly undergoes the usual changes incident to blood. Smaller quantities (5—30 c.c.) of blood, treated in a similar manner, soon become dark, and after an hour resemble strongly reduced blood, whilst air alone does not change the colour. In the spectrum there are oxygen bands, along with which, on the following day, are metahæmoglobin bands, similar to those seen in blood treated with iodine. The microscope reveals, amongst other things, fragments of red corpuscles, all of them being puffed up and globular. Fresh dog's blood (30 c.c.) mixed with 30 c.c. of a 7 per cent. salt solution, and subjected to the ozonised air treatment is not coagulated after 90 minutes, but dark red oxygen bands are evident; the corpuscles are distended. With further treatment, the blood becomes thick as treacle, red-brown in colour, and metahæmoglobin bands develope. After a day, the corpuscles disappear and the metahæmoglobin increases. A specimen of this ozonised blood kept in a closed vessel had no putrid odour even after some weeks. The blood which does not come in contact with the current of gas remains red. Solutions of crystalline oxygenated hæmoglobin treated with ozonised air become turbid and brown in less than 10 minutes, and finally separate into a yellowish liquid with acid reaction, and a dirty grey fibrous albumin. Soda retards the decomposition of the hæmoglobin. Ozonised air was passed through 350 c.c. of blood in a column 15 cm. high, and also through another 300 c.c. of blood 42 cm. high; in both cases ozone could be distinguished by odour and by starch paper when the bubbles on the surface were pricked, or even when they were left to burst by themselves, being thus enclosed in the blood film for some minutes. These tests were continued an hour with the same results; no hydrogen peroxide is formed. The blood was changed in the same way as described above. The author estimates the ozone by a new method. A measured quantity of the ozonised air is shaken with mercury, which becomes oxidised at the expense of the ozone; the mercuric oxide is dissolved out with acetic acid, converted into chloride, precipitated with sulphuretted hydrogen, and weighed as sulphide. From this weight, the amount of ozone is easily calculated. D. A. L.

Digestibility of Caseïn from Warmed Milk. By M. HOFFMANN (*Chem. Centr.*, 1882, 811).—Rennet precipitates caseïn in compact masses, both from raw and warmed (short time at 50—70°) milk. Slight concentration of the rennet solution or the previous warming of the milk simply retards the curdling. If, however, the milk is boiled, or kept for two hours at 70° (Becker's method of milk preservation), a fine flocculent curd forms. Digestion experiments were tried with artificial gastric juice, and the amount of peptones formed determined colorimetrically show that Becker's preparation yields most, boiled milk comes next, and raw milk least in quantity of peptones. Becker's milk does not turn sour, but after a few days decomposes with an unpleasant odour. D. A. L.

The Digestive Fluids and Digestion of the Horse. By ELLENBERGER and HOFMEISTER (*Bied. Centr.*, 1882, 805—810).—In a previous communication (Abstr., 1882, 1119), the properties of the various fluids which form saliva were stated. In the present article the physiological action is more extensively considered and examined experimentally. The mixed saliva contains a powerful diastatic ferment, which completely converts a small quantity of starch into achroodextrin and sugar within a quarter of an hour, also the action commences immediately; but if coarsely powdered starch is used, then a short time elapses before the commencement of the conversion. Potato-starch is not converted into sugar in the mouth, yet a small portion of the starch of oats and barley is there converted. Both the parotid and submaxillary fluids contain a saccharifying ferment, and the action of these fluids when mixed is equal to the sum of their action when alone. A small amount of a diastatic ferment is found in the blood, in most of the organs, and in the watery portion of the excrement. Slightly acidifying the saliva, and mixing it with artificial acid gastric juice does not destroy its power, although a large addition of acid causes the action to cease, without, however, destroying the ferment; in fact the action is stronger when the fluids are acid than when neutral. Cane-sugar is but slowly altered. The parotid secretion contains a trace of a peptonising ferment; the mixed salivas have no effect on cellulose, nor on fat, save that with it they produce an emulsion, especially the parotid secretion. So far these statements refer only to the reactions in the mouth, the next portion of the experiments dealt with the changes occurring in the stomach. The digestion of horses continues from one feeding time to another, for if a feed is omitted, the digestion still goes on, but slowly, and food may be found in the stomach even when 24 hours have elapsed between the feeds.

The contents of the stomach, when oats are supplied, is a crumbly mass containing 60—70 per cent. water; with hay the contents contain 75—80 per cent. water, and at all times have an acid reaction, the percentage of the acid in the liquid portion seldom exceeding 0·2 per cent., being lowest, 0·08 per cent., immediately after eating; thus it appears that the acidity of the stomach of the horse is below that of the Carnivora. The acids present are lactic acid, followed by hydrochloric acid, the former never failing, and being most abundant with oats, whilst, with hay as fodder, hydrochloric is the principal. There is likewise found in the stomach an albuminous and lactic ferment, also a ferment which dissolves starch, and one which coagulates milk. The conversion of the starch occurs for the most part in the stomach; if food has been freely given, the conversion is but slow, and lasts longer; this happens because at least two-thirds of the fluids present consist of alkaline saliva, and so a considerable time must elapse before sufficient acid is secreted to prevent the conversion; the percentage of sugar present is 0·2—1·0. Vegetable albumin is rapidly digested, and converted into peptone; the process commences slowly, and increases rapidly, but the intensity is dependent on the amount of food given, for frequently there will not be enough pepsin and acid present to convert a large feed. In such a case, if another feed is given, the first is in part lost, as it is passed on into the intestines in an undigested state. After oats, 0·3 per cent. of peptone is present, which later on increases to 1·5; the absolute quantity may be at times 40 grams, but after hay the quantity is much less, being only 0·26 per cent., or 5 grams. E. W. P.

Hygienic Action of Maize as Fodder. By M. CHATIN (*Bied. Centr.*, 1882, 803).—This article was written in consequence of a notice published by Fua, on the raising of a large-grained early-ripening variety of maize. By reason of its pleasant-tasting oil, and easy digestibility, maize forms a valuable food for man and beast; and where it is much eaten by men, diseases of the bladder, epilepsy, and phthisis are unknown. But maize may at times be harmful, and then it will be found to be a bearer of *penicillium*, *aspergillus*, &c. Diseased grains contain a reddish oil, and also a neutral alkaloïd; where cheap and therefore probably diseased maize is used, pellagra is prevalent, but this disappears if the grain be previously dried in ovens.

E. W. P.

Alkalinity and Diastatic Action of Human Saliva. By R. H. CHITTENDEN and J. S. ELY (*Amer. Chem. J.*, **4**, 329—333).—The authors' experiments were made upon saliva obtained from 14 different persons, all, with one exception, being men between the ages of 20 and 30. The secretion of the saliva was accelerated by chewing a piece of pure india-rubber. The saliva was collected generally an hour or two after breakfast, and was at once filtered through paper in an atmosphere free from ammonia. A portion of the filtered liquid was then at once neutralised with standard acid, to determine the alkalinity, while another portion was used to determine the diastatic action of the saliva by its power of converting starch into sugar. The experiments, the numerical results of which are given in tables, led to the following conclusions:—

1. Saliva from different individuals may show a constant difference in alkalinity, although in the majority of cases the alkalinity varies only within narrow limits.—2. Saliva secreted by the same individual at different times has within certain limits a constant degree of alkalinity.—3. While saliva from different individuals shows in several cases a decided and constant difference in alkalinity, there is no corresponding difference in diastatic action which is at all constant. Hence it appears that the variations of alkalinity are comprised within limits too narrow to exercise any appreciable influence on the diastatic action of the saliva. H. W.

Chemistry of Vegetable Physiology and Agriculture.

The Test for Life. By L. KRETZSCHMAR (*Bied. Centr.*, 1882, 830).—Löew and Bokorny's reagent (alkaline silver solution), which they recommend as a test for living or dead albumin, is untrustworthy; the protoplasma of living or dead *spirogyra* is blackened by the silver, so that no distinction could be drawn between the two. Also cells which had been exposed to the solution containing no silver became grey, and the alkali itself kills the protoplasma. The author finds no difference between the actions of strong and dilute silver solutions. Löew states that living cells are only slightly blackened by the strong solutions, for the cells are rapidly killed.

E. W. P.

Influence of Oxygen on Fermentation. By F. HOPPE-SEYLER (*Bied. Centr.*, 1882, 860).—Cane-sugar in the presence of ferment and oxygen is inverted, but not fermented to alcohol; acid is formed at the same time, and the microscope shows the presence of much micrococcus and mycelium.

Animal matter in the presence of oxygen is readily altered, and the more easily, the larger the supply of oxygen, reduction-products such as sulphuretted hydrogen being formed. E. W. P.

Contributions to the Dissociation Hypothesis. By W. DETMER (*Bied. Centr.*, 1882, 831).—The action of dilute phosphoric acid and of chloroform on diastase and on germination has been studied, and it appears that certain substances, such as chloroform, do not destroy the action of the ferment, but do destroy plant cells; on the other hand, some substances, such as phosphoric acid, arrest the power of the ferment, but do not destroy the plant cells.

From these observations, the author infers that the fermentation theory as a starting point for the explanation of the origin of life processes is untenable. E. W. P.

Effect of Steeping and Drying on the Germination of Seeds, as also the Value of Sprouted Grain for Seed. By H. Will (*Bied. Centr.*, 1881, 821—826).—Samples of the usual agricultural seeds of Swedish origin were steeped for 12 and 24 hours, and then dried. Another set of samples were soaked for 12 hours, and then allowed to germinate between sheets of moist paper, and these latter were then sown at different stages of germination. The observations made show that steeping for 12 hours has no effect, whilst soaking for 24 hours is detrimental to germination. Some seeds are unable to endure the interruption in the germination, but in this case adventitious roots and axillary buds are formed; the further germination has proceeded, the more prone are the seeds to rot during their subsequent growth. Monocotyledons are more hardy than dicotyledons. Of the first, barley and oats are the most delicate; of the second, buckwheat and peas, and especially maize. E. W. P.

Part played by Lime in the Germination of Seeds. By A. v. Liebenberg (*Chem. Centr.*, 1882, 806—809).—Previous experiments in this direction have been made by Böhm and by Raumer and Kellermann; the experiments were, however, only made on one kind of plant, *phaseolus multiflorus*, the result indicating that lime is actually necessary for the growth of the young plant. The author has set himself to answer the questions: Are these experiments on *phaseolus multiflorus* correct? Is lime necessary for other plants also? Are not other minerals also useful to the young plant? What function does lime perform in the growth of the plant?

To this end several series of cultivations of seeds of various plants were very carefully conducted in distilled water, in well water, in water containing lime, in Knop's nutritive solution, and in many other solutions of single salts, the concentration being always equal to that of Knop's nutritive solution. The apparatus employed consists of glass vessels, which had been boiled in water for some days, covered with a piece of tulle, previously washed with hydrochloric acid; the germinated seed when the young roots were 10 to 20 mm. long are placed upon the net. The results arrived at are as follows:—1. In order to effect the consumption of the reserve nutritive matter of the seed during the germination, an addition of lime is alsolutely necessary in the following cases:—*Phaseolus multiflorus*, *Phaseolus vulgaris*, *Pisum sativum*, *Vicia sativa*, *Ervumlens*, *Ervum ervilla*, *Medicago sativa*, *Ricinus africanus*, *Soja hispida*, *Cucurbita pepo*, *Cucumis sativa*, *Brassica oleracea*, *Cannabis sativa*, *Helianthus annuus*, *Zea mays*, 2. The addition of lime is not necessary with *Brassica napus oleifera*, *Sinapis alba*, *Papaver somniferum*, *Carum carvi;* it is, however, advantageous to *Polygonum fagopyrum*, *Linum usitatissimum*. 3. Complete foods favour the development of the very young plant of *Polygonum fagopyrum*, *Brassica oleracea*, *Brassica napus oleifera*, *Ricinus africanus*, *Cucurbita pepo*, *Sinapis alba*, *Papaver somniferum*, *Helianthus annuus*, *Zea mays*, *Carum carvi*. 4. Nutritives without lime promote the development for a short time of *Polygonum fagopyrum* and *Zea mays*. 5. *Medicago sativa* requires other substances besides lime. The greater number of the cultivations were conducted in the dark in order to avoid assimilation; some few were conducted by light as check experiments. From time to time, the distilled water or solutions were changed.

From these results, it is evident that some plants do require lime in order that the reserve nutritive matter in the seed may become useful. Some experiments have been conducted on plants requiring lime to see if it is the root or the plant which is injured by the absence of lime. In the absence of lime, the roots appear to grow all right, but the stems attain a certain height and then die off. The roots suffer partial plasmolysis both in solutions free from and containing lime. If the roots are cut off, the young plant thrives in solutions containing lime until all reserve food is exhausted, whilst it dies in solutions free from lime. Again, if the seeds are first soaked in water containing lime, and are then cultivated in distilled water, the resulting plants are much stronger, and the reserve food is better utilised than when they are not steeped. From these facts, it is manifest that the roots are not injured by the absence of lime. The author is of opinion that seeds of some plants do not contain sufficient lime for the growth of the young plant, although after the plant is dead, lime can still be found in the seed; it is, however, not enough, and not easily assimilable.

With regard to the function of lime, the author has come to no positive decision. He, however, observes that when the plant becomes sickly lime is always wanting in the parts immediately affected, and if these parts be treated with dilute lime solution the death of the plant is avoided, and the whole of the reserve food is utilised.

Moreover, the falling off commences in all cases at those parts of the plants where the growth has been most vigorous, that is, where the cells have become stretched; it would seem from this that lime has something to do with the formation of the cells. D. A. L.

Researches on the Growth of the Maize Plant. By R. HORNBERGER and E. V. RAUMER (*Bied. Centr.*, 1882, 837—844).—Each separate portion of a maize plant, viz., roots, leaves, &c., was examined for ash, nitrogen, &c., plants of different ages being employed in each case. In preparing the ash, Strecker's method for the prevention of the formation of pyrrophosphate by means of baryta was made use of, and Stutzer's directions for the estimation of nitrogen in the forms of albumin and amides were followed. The percentages given are on 100 grams of dry matter in each portion of the plant, also the absolute quantities calculated on 1000 plants are referred to. In the original (*Landw. Jahrbûcher*, 1882, 359) these figures are given in full, as well as tables of curves representing the increase of each component as affected by growth.

During the first two weeks of germination, the seed suffers loss principally in mineral matter (phosphoric acid and potash), whilst of the organic matter only fat and nitrogen are lost. During the second week, amides are produced from the albuminoïds, but in the third week the loss in nitrogen, organic matter, phosphoric acid, is greatest, whereas but little potash is removed. The greatest increase of the plant occurs immediately after blossoming, and ceases some weeks before the grain is ripe; the maximum increase occurs 14 weeks after sowing, a second maximum occurring also three weeks earlier, at the commencement of the formation of the spadix. From the period of blossoming and onwards, the stems increase in weight sevenfold, whilst the leaves alter but little, and at the time when the grains fill most rapidly, the stems and leaves lose dry matter. As regards crude fibre, the increase goes side by side with the production of dry matter, being for the first 14 weeks one-fourth of the dry matter, but in the 15th week only one-thirteenth.

The highest relative amount of fibre is in the roots, then the blossom, and lowest in the grain, the greatest absolute quantity being found before blossoming in the leaves, later on in the stems. Before the completion of the setting of the grain, the plant is relatively poor in fat, after which an increase is observed; the seed contains the greatest amount of fat, the stems less than the leaves, but both stems and leaves finally yield up this fat to the seed. The non-nitrogenous extractive matter increases with the fat up to the time of ripening; it is present in the stems to the amount of 50 per cent., migrating afterwards to the grain. The total nitrogen decreases gradually during the whole period of growth, being at ripening time only one-third of what was present during the fourth week; up to blossoming, the leaves contain the principal quantity, later on the stems. The relation to one another of the two forms in which nitrogen appears is very varying, but generally they, like the total nitrogen, diminish in percentage up to the penultimate week of growth. In the last (16th) week, the amides diminish largely owing to an increase in albuminoïds, at the same time, because of the absolute diminution of nitrogen, albuminoïds are formed from amides. The highest relative amount of amides, 43 per cent. of the total nitrogen, was found in the 14th week of the observations, viz., at the time when the maximum absorption of nitrogen occurred; albumin is found principally in the leaves, stems, and seeds, whereas the spadix and stalk contain for the most part amides. The maximum absolute increase in proteïn takes place when the grain is forming (10th and 11th week); there is also a second maximum during the 14th week, but at this period amides are produced. It is evident that the subsidiary organs draw their supplies of nitrogen from the stem in the form of non-albuminoïd matter, which is only transformed into albumin by the increased energy of the later stages of growth. The author also considers that amides are first formed from the assimilated nitrogen, then the albuminoïds.

In the young plant, the percentage of ash is higher than in the old. The leaves are richest in ash, which becomes more siliceous with age; this statement is also true for the stems. All the organs of the plant, except blossom and spadix, are relatively poor in sulphuric acid; phosphoric acid likewise decreases with age, and the highest absolute amount is found in the grain and spadix, but it continues to be absorbed even after the dry matter no longer increases. The leaves contain most lime where it increases during blossoming, whereas it decreases in all the other parts.

There seems to be a definite relation between the lime and the carbohydrates, for after the first assimilation maximum (11th week) a reduction of both occurs in the 12th week, which is followed by a rise in the 13th.

Magnesia resembles lime in many points, but is present in largest quantities in the stem and grain, and not in the leaves. Potash appears up to the blossoming period principally in the stem, and is absorbed up to the time of maximum production of dry matter; the largest relative quantity is found in the young spadix. The observations show that there is in the plant during its later stages a less quantity of potash than was originally present, which seems to indicate a downflow of this substance back to the soil. The leaves contain nearly all the soda, whilst in the stems is found the greatest amount of the iron, whose assimilation seems to be irregular.

Attention is called to certain analogies between the various constituents: at the time of setting the ratio of phosphoric acid to potash is 1 : 3, from that date the ratio is widened. Potash to nitrogen from the 9th week onwards bears a ratio of 1 : 1·25 to one another. Lime and magnesia bear a constant proportion towards each other, and it seems probable that these two bases are indispensable for the formation of cellulose and carbohydrates. E. W. P.

Development of Wheat. By P. P. DÉHÉRAIN and MEYER (*Ann. Agron.*, 1882, 23—43).—This paper contains the authors' first year's (1881) observations on the development of wheat, intended to be supplementary to the researches of Pierre. They give detailed proximate analyses of the entire plant, the roots, the stems, and the heads at different phases of development, paying more attention to the distribution of the organic constituents than to that of the ash constituents. Their results are embodied first in a series of tables of percentage composition of the various parts at the various dates, and then in tables giving the weight in kilograms per hectare of the substances determined. The latter series of tables is reproduced here.

Entire Plant (excluding Roots).

	31st May.	13th June.	16th July.	23rd July (harvest).	30th July.
	kilos.	kilos.	kilos.	kilos.	kilos.
Mean total weight ...	10,200	12 937	10,400	7,425	5,090
Mean total dry weight	3,223	3,872	5,598	5,974	4,311
Water	6,977	9,065	4,802	1,451	779
Nitrogenous substances	382	387	391	399	306
Fat, chlorophyll, &c. ..	164	78	108	86	48
Cane-sugar	10	298	143	30	39
Glucose	135	55	55	52	8
Starch	268	333	1,157	1,847	1,374
Cellulose	783	1,270	1,428	1,911	1,228
Ash	288	248	279	289	241
Nitrogen	61	62	62	64	49
P_2O_5	25	15	28	28	24

Stems.

	31st May.	13th June.	16th July.	23rd July (harvest).	30th July.
	kilos.	kilos.	kilos.	kilos.	kilos.
Mean total weight....	10,567	11,016	5,655	4,481	3,085
Mean dry weight	3,223	3,403	3,207	3,735	2,634
Water..............	7,344	7,213	2,448	746	451
Nitrogenous substances	382	310	184	156	134
Cane-sugar..........	10	279	71	none	none
Glucose	135	51	26	8	none
Fat, chlorophyll, &c...	164	66	51	48	29
Starch..............	268	279	546	622	415
Cellulose...........	782	1,127	1,191	1,565	1,074
Ash	288	223	167	202	167
Nitrogen............	61	49	29	25	21
P_2O_5	25	15	14	9	7

Ears.

	31st May.	13th June.	16th July.	23rd July (harvest).	30th July.
	kilos.	kilos.	kilos.	kilos.	kilos.
Mean total weight....	—	1,792	4,645	3.063	1,944
Mean dry weight.....	—	467	2,389	2,207	1,676
Water..............	—	1,125	2,256	856	268
Nitrogenous substances	—	53	211	243	178
Fat, chloropyhll, &c...	—	13	57	43	34
Cane-sugar..........	—	24	70	30	15
Glucose	—	4	24	44	8
Starch..............	—	54	1,031	1,220	953
Cellulose...........	—	143	236	251	154
Ash	—	25	102	86	74
Nitrogen............	—	80	34	39	28
P_2O_5	—	15	12	16	14

It was of course impossible to ascertain the total weight of roots per hectare, but the percentage composition is given in the annexed table :—

Roots (per cent. of Dry Matter).

	31st May.	13th June.	16th July.	23rd July (harvest).	30th July.
	kilos.	kilos.	kilos.	kilos.	kilos.
Nitrogenous substances	6·31	4·87	3·18	2·50	2·12
Fat	0·50	0·97	0·72	0·63	0·47
Cane-sugar	2·60	2·10	1·90	1·03	0·90
Glucose	traces	0·21	none	none	none
Starch	9·31	10·71	10·36	9·87	9·25
Cellulose	38·24	36·80	36·65	38·24	40·40
Ash	13·50	7·29	7·66	7·80	7·86
Nitrogen	1·01	0·78	0·51	0·40	0·34
P_2O_5 per cent. of ash	6·41	4·71	2·07	1·39	1·43
P_2O_5 „ roots	0·86	0·34	0·15	0·11	0·11

The authors sum up thus:—(1.) In 1881, at Grignon, the total dry matter of the wheat increased in weight up to the harvest. It was only in those plots which were allowed to stand after the harvest that a loss in dry matter was observed. This loss was considerable, and demonstrates the advisability of reaping as soon as possible after maturity. (2.) The gain in dry weight from 31st May to 23rd July consisted of starch and cellulose, the albuminoïds and ash remaining stationary during these last two months of growth. (3.) The cessation in the assimilation of nitrogen and minerals appears to have been due to the peculiarities of the season. Bright days favoured the assimilation of carbohydrates, whilst drought hindered the assimilation of nitrogen and minerals by the roots. J. M. H. M.

Comparative Effect of two Metameric Bodies on the Growth of Nicotiana Longiflora. By J. E. Reynolds (*Chem. News*, **46**, 271).—In this paper, experiments and results thereof are described, the subject being the action of ammonium thiocyanate and its metameride, thiocarbamide, respectively on the growth of a variety of the tobacco plant (*Nicotiana longiflora*). For the experiments, several sets of three healthy plants were selected, the members of each set being alike as regards height, number of leaves, and strength of stem. The plants, potted singly in rather poor very sandy mountain loam, were under glass, and so placed as to receive equal light and to prevent excessive drawing up or splinding. Each set received the following treatment:—No. 1 plant was watered, when necessary, with Vartry water only. No. 2 was watered twice a week with a 0·2 per cent. solution of pure thiocarbamide; at other times was treated similarly to No. 1. No. 3 was sometimes watered twice a week with a 0·2 per cent. solution of ammonium thiocyanate. Following the changes of one set, it was observed that No. 3 was the first to be visibly affected; for after the third treatment, not only was the growth checked and development stopped, but the plants shrank in a curious manner, the leaves began to droop, and became sickly in colour. A fourth application made matters worse; therefore the thiocyanate treatment was stopped, and the soil well washed out by percolation with pure water. The plant recovered somewhat; the treatment and washing were repeated and continued for nearly three months. Plants have been killed by continued doses of thiocyanate. No. 2 plant was soon affected, but in a very different manner to No. 3; the stem did not elongate much, but the leaves developed in length, breadth, and substance, and had a healthy deep-green hue. This development was less satisfactory when the thiocarbamide was used alone, than when the soil was washed with water between the doses, which is easily accounted for from the fact that some of the thiocarbamide becomes converted into thiocyanate, which then exerts its deleterious effect. No. 1 plant soon outstripped the others in height, but its stem and leaves were poor and thin as compared with No. 2. The condition of each of the plants, after three months' (1st December, 1881) treatment, is here tabulated:—

	Plant No. 1.	Plant No. 2.	Plant No. 3.
Total height in inches from surface of soil.	31	23	12
Number of leaves......................	15	14	13
Maximum length of leaf in inches........	9½	15¼	8
Maximum breadth of leaf in inches	4¼	6	2½
Number of seed pods in any stage of development	9	15	none
Number of seed pods well developed	1	11	none

Corresponding results were obtained with the other sets. The quantity of nicotine is to be estimated on some future occasion, when more material is at hand. Thus it is evident that the ammonium thiocyanate is a plant-poison; whilst its metameride thiocarbamide is a distinct plant-food, and were it not for its tendency to revert to the thiocyanate, might be regarded as a good organic manure for tobacco. The author concludes—(1.) That the particular elements of which bodies are composed exert less influence on their physiological activity than the extra-molecular grouping of the component atoms. (2.) That, in some instances at least, differences of physiological activity between metameric bodies can be easily detected by the aid of plants.

D. A. L.

Growth of Plants under Special Conditions. By A. B. GRIFFITHS (*Chem. News*, **47**, 27).—A patent manure, consisting chiefly of animal charcoal, phosphates, and ferrous sulphate, having shown remarkable properties in aiding the growth of plants, the author undertook experiments to find out the reason, &c., of this. For the experiments three very young Savoy cabbages, all nearly of the same weight and in healthy condition, were chosen. No. I cabbage was planted on a piece of land, and not manured. No. II cabbage was planted on the same piece of land near to No. I, and received a weighed quantity of the manure. No. III cabbage was placed on a different piece of land, received the same quantity of manure as No. II, but grew more in the shade. All the plants were placed in the ground on the same day, and grew from February to December. They were then taken up with their roots attached, and after removal of all adhering soil by washing, were weighed. No. 1 weighed 4 lbs. $2\frac{1}{2}$ ozs.; No. II weighed 9 lbs. 3 ozs.; No. III 8 lbs. 6 ozs. Leaves and stems of each plant were carefully burnt, and the ashes analysed with the following results:—

	No. I.		No. II.		No. III.	
	Leaves.	Stalk.	Leaves.	Stalk.	Leaves.	Stalk.
Potash	33·951	41·231	31·634	39·223	31·521	38·929
Lime	15·665	13·601	14·210	13·583	14·310	13·621
Soda	2·523	4·296	1·825	2·360	1·917	1·813
Iron (Fe_2O_3)	8·323	1·502	12·290	3·521	11·832	3·005
Magnesia	4·936	6·210	3·128	6·000	2·921	5·942
Phosphoric acid	12·931	14·463	16·210	18·944	16·123	18·891
Sulphuric acid	8·613	9·619	7·641	8·916	7·592	8·922
Chlorine	7·994	6·781	7·310	4·200	7·400	4·319
Silica	4·999	2·294	5·631	3·121	6·265	4·468
	99·935	99·997	99·879	99·868	99·881	99·910

The conclusions the author draws from these experiments are:— (1.) That plants, when grown in a soil containing iron and phosphoric acid in a soluble form, are healthier and larger than if they are grown in a soil wanting in these soluble compounds. (2.) The plants grown in soils containing this manure appear to absorb larger quantities of soluble iron and soluble phosphates than when not so treated. (3.) Sunshine and rain appear to favour the absorption. The author attributes the superiority of Plants II and III over Plant I to the presence of the soluble iron salt and phosphates, and he therefore considers a fairly large proportion of soluble iron and soluble phosphates in a soil favourable to the growth of plants which develop a large amount of chlorophyll cells, like the varieties of cabbage.

D. A. L.

Chlorine as a Plant Food. By Farsky (*Chem. Centr.*, 1882, 809).—Chlorine is a very important plant-food, and to all appearances potassium chloride in this respect is more valuable than potassium nitrate, provided only that a certain quantity is not exceeded. Too much potassium chloride reduces the quantity of chlorophyll, makes the plants ripen sooner, and developes oxalic acid. This effect is well marked when hydrochloric acid is used. D. A. L.

Contribution to the Knowledge of the Interchange of Material in Amylaceous Plant Organs. By H. Müller (*Bied. Centr.*, 1883, 832—836).—The generally accepted idea concerning the freezing of potatoes is, that during that process a portion of the starch is converted into sugar. This subject has been carefully studied, and at the outset it was found that the sweetening of potatoes has nothing to do with the actual freezing of the tuber, but rather that the low temperature exerts a peculiar influence on the interchange of material in the tuber. The most important results are as follows:—By rapid freezing, no formation of sugar occurs; but if the tuber is slowly frozen, then sugar appears. Before the formation of ice occurs in the potato, its temperature must sink to −3°; when slowly frozen, a considerable time elapses before the temperature sinks from 0° to −2°. Sweetening is not caused by freezing, because the temperature remains for some time at 0°; thus potatoes which were not frozen, but whose temperature was for 15 days at −1° and −2°, contained 2 per cent. sugar. The percentage of sugar does not increase in potatoes when frozen and kept in the frozen state. At low temperatures, more sugar is formed by fermentation than the protoplasma present requires; consequently, the proportion of sugar increases. The increase of sugar is at first slow, gradually increasing, but finally decreases. A high percentage of moisture in the potato is advantageous to the formation of sugar. In other parts of a plant containing starch the greatest change occurs at 0°. The storage of sugar being greater at 0° than at 20° is not to be attributed solely to the less expiration which occurs at lower temperatures, but the change is also induced by a ferment. If potatoes which are sweet at 0° be warmed, the sugar rapidly disappears, and this is because at high temperatures expiration is more energetic. Potatoes exposed to the open air rapidly cool; but if the temperature rises before they have cooled to −2°, then they are not frost-bitten nor sweet; but should the temperature sink below −3°, then they are frozen hard, but at the same time not sweet; this is because the cooling down is rapid. It is otherwise when potatoes are kept in cellars, when the change is but gradual. A long time is required for the fall from +5° to −2°. During this time sugar accumulates, and they become sweet, not frozen hard; when the temperature has reached −3°, they are sweet and frozen hard. This sweetening is a loss, as a portion of the starch is first converted into sugar and then expelled as gas, but the whole of the albuminoïds remain. To enable sweetened potatoes to be eaten, they must be kept warm for several days, so that the sugar may be lost by expiration. Washing does no good, for all the sugar is not removed, and some of the albuminoïds are. Sweet potatoes can germinate. E. W. P.

Respiration of Plants. By E. Godlewski (*Ann. Agron.*, **9**, 37—43, from *Jahrb. f. Weis. Bot. de Prinsheim*, **13**, 3).—By a modification of Mayer's apparatus (which is, however, unfavourably criticised by the translator), the author has observed the proportion between the volume of oxygen absorbed and carbonic anhydride emitted during the germination of certain oily seeds.

During the first stage, that of swelling, which (at 15—20°) lasts about two days, the proportion $CO_2 : O$ is nearly 1, showing that at first it is the small quantity of carbohydrates contained in these seeds which is oxidised. During the second stage the proportion of oxygen increases, and about the fourth day the proportion is $CO_2 : O = 60 : 100$; this proportion remaining nearly constant up to the eighth or tenth day in the case of radish, hemp, flax, and lucerne seeds. It is during this stage that the greater part of the oil is consumed, the complete combustion of olein, *e.g.*, requiring the proportion $CO_2 : O = 57 : 80$. From the constancy of the proportion $CO_2 : O = 60 : 100$, the author constructs the following alternative equations, showing a transitory conversion of part of the oil into starch:—

$$\text{(1.)}\ C_{57}H_{104}O_6 + 56O_2 = 4C_6H_{10}O_5 + 33CO_2 + 32H_2O$$
$$CO_2 : O = 59 : 100.$$

$$\text{(2.)}\ (C_{18}H_{33}O_2)_3C_3H_5 + 3H_2O = 3C_{18}H_{34}O_2 + C_3H_8O_5$$
$$3C_{18}H_{34}O_2 + 52\tfrac{1}{2}O_2 = 4C_6H_{10}O_5 + 30CO_2 + 31H_2O$$
$$CO_2 : O = 57{\cdot}1 : 100.$$

During the third stage of germination a part of the starch is converted into cellulose, and another part is burned, the proportion $CO_2 : O$ again becoming unity. The respiration of seeds containing a large amount of starch is characterised by the constancy of the proportion $CO_2 : O = 1$.

The effect of reducing the pressure of oxygen is to render the respiration less active, but the proportion of carbonic anhydride is not disturbed until the oxygen present falls below a certain minimum, when intramolecular respiration takes place, some of the proximate principles of the seeds absorbing oxygen at the expense of others.

During the ripening of oleaginous seeds, the proportion $CO_2 : O$ is greater than unity (128 : 100 in the case of castor-oil seeds), showing that the oil is formed by reduction of the carbohydrates.

J. M. H. M.

Composition of Ivy Berries. By A. Jandous (*Chem. Centr.*, 1882, 806).—The fleshy part of the fruit contains 70 per cent. of water; also a dark red colouring matter soluble in alcohol and water, and turned greenish by ammonia, light red by hydrochloric acid; besides this, grape-sugar is present and a resinous substance of greenish-yellow colour, sweet at first, but afterwards sharp and bitter; hydrochloric acid turns it a beautiful green; and finally gum, albumin, and mineral matters. The seed contains albumin, inorganic matter, and a fat oil, with a characteristic herbaceous and irritating taste, only slightly soluble in water, precipitated by lead acetate, and slightly by lime water, and coloured green by ferric chloride. The poisonous properties of this fruit are neither due to the resinous matter in the flesh nor to the oil in the seeds.

D. A. L.

The Ice Plant ("Mesembrianthemum Crystallinum"). By H. Mangon (*Compt. rend.*, **96**, 80—83).—The author has analysed the leaves of this plant cultivated by himself under various conditions. He finds that of the *dried* plant about 43 per cent. on an average consists of salts of potassium and sodium. Calculating from the mean yield per square meter, the author finds that a *hectare* would give 588 kilos. of potash capable of yielding 863 kilos. of potassic carbonate. He therefore raises the question whether the plant might not be profitably cultivated, under certain conditions, as a source of potassium, and whether it might not be employed to remove from the saline soils of the Mediterranean coasts the excess of alkaline salts which render those soils so barren.

E. H. R.

Influence of Fallen Snow on the Temperature of the Air. By R. BILLWILLER (*Bied. Centr.*, 1882, 851).—Meteorological observations are quoted to show that when the ground is covered with snow, the temperature of the lower strata of the atmosphere is lower than when there is no snow, because this snow cuts off all communication of heat from the soil to the air. It follows that the soil in winter being always warmer than the air, when snow is on the ground, the air is deprived of its source of heat. E. W. P.

Influence of the State of Aggregation on the Temperature of and Moisture in a Soil. By E. WOLLNY (*Bied. Centr.*, 1882, 793—795).—A soil which has laid long uncultivated, or has never been cultivated, finally assumes a condition in which the particles lie too closely together; on the other hand, in a soil which has been fairly treated, the particles do not lie evenly side by side, but being bound together by clay, humus, &c., into lumps, interstices are formed sufficient for the free passage of air and water.

Experiments as to the effect of these two conditions on the temperature and moisture have been made in zinc boxes placed in the open air, with the following results:—The proportion of water increases with the fineness of division, and consequently is highest in a soil in a very fine state of division, because a greater number of capillaries are formed which draw up the bottom water, and prevent the downward flow of atmospheric water. Evaporation is greatest from finely divided soils; permeability is in a direct ratio with the size of the particles; it may happen that evaporation and permeability stand in indirect proportion to one another in a soil whose particles are of very varying size, so that a balance is maintained, and the amount of water present remains the same.

During the warm season, the coarse-grained soil is the warmest, but only up to a certain extent, for a further increase in the size of the grains causes a fall in temperature; the cause of this is the specific heat of the water present. Moreover, the cooling of the soil at night by the entrance of cold air is greater, and the conductivity for heat is so much less the larger the particles.

The differences in the temperatures of the two kinds of soil is so much the less the smaller the amount of water present; it is also lower when the evaporation is reduced, consequently during cold seasons, when the air is still and moist, this difference is at its minimum. E. W. P.

Irrigation of Meadows by Waste Water from Beet-sugar Factories. By TEUCHERT (*Bied. Centr.*, 1882, 851).—Crops irrigated by the above waste waters were greatly improved, nearly all the organic matter being removed from the water, which afterwards contained neither algæ, bacteria, nor vibrios. E. W. P.

Manurial Value of "Dissolved Wool." By A. PETERMANN (*Ann. Agron.*, 1882, 77—86).—"Dissolved wool" is made by treating woollen refuse with high pressure steam, evaporating the resulting liquid to dryness, and powdering the residue. It is a dark brown, hygroscopic powder, with an odour like that of caramel, and almost entirely soluble in water. It contains nitrogen as ammonia, as soluble organic compounds, and a very little in the insoluble condition in which it exists in wool. The author has made comparative trials of its manurial value against crude woollen refuse and nitrate of soda, with and without the addition of precipitated phosphate of lime. His trials were made with wheat plants growing in pots in a greenhouse, and upon a field crop of beet growing in the loamy soil of Gembloux. Experiments were also made on plants growing in earthenware cases holding a cubic metre of soil, to ascertain whether any loss of the soluble nitrogenous compounds of the dissolved wool occurred by drainage.

The action of the dissolved wool was very favourable on both wheat and sugar-beet, raising the yield of the former by 25 per cent., and of the latter by 30 per cent. It was more efficacious than crude woollen refuse, but less than nitrate of soda. No sensible loss of nitrogen by drainage occurred. J. M. H. M.

Chemical Manures and Farmyard Manure. By L. GUILLAUME (*Ann. Agron.*, 9, 30—37).—Having previously shown that the addition of phosphates to the soil of Haraucourt and Villepreux, a soil naturally very poor in phosphoric acid, does not produce remunerative results, the author has now extended his experiments to the use of superphosphates, and has also instituted a comparison between chemical manures and farmyard manure. All the results are summed up in the annexed table (p. 502), the chief points of interest being the following:—

Haraucourt.—Superphosphate gave better results than phosphate with wheat and oats; both raised the produce, but not to a sufficient extent to pay the cost of the application. The summer of 1882 being wet, the yield of green maize was very large, and the superiority of superphosphate over insoluble phosphate is strikingly shown. Potatoes succeeded best without any manure; farmyard manure in wet seasons seems to encourage disease. On beet, superphosphate produced better results than mineral phosphate.

Villepreux.—The soil is slightly calcareous, effervescing with acid, and contains 0·204 per cent. N. Phosphate and superphosphate alone produced good results with potatoes and sogina; farmyard manure and nitrate of soda with maize and mangold. The sogina seed was imported from Italy, and succeeded very well.

Haraucourt farm.	Bordeaux wheat per hectare.		Yellow oats, Flemish, per hectare.		Maize cut green, Aug. 15.	Potatoes.		Silesian wheat.
Kilos. per hectare.	Straw, kilos.	Grain, hectolitres.	Straw, kilos.	Grain, hectolitres.	Kilos.	Gross kilos.	Diseased, kilos.	Kilos.
Unmanured	5,050	19·43	5,000	61·35	37,200	18,000	none	38,400
15,000 farmyard manure	5,200	20·14	5,850	72·50	55,200	19,000	1,000	40,400
Ditto + 1,000 phosphate.	5,800	21·18	6,000	74·25	55,200	18,200	1,200	41,200
Ditto + 1,000 superphosphate	6,000	23·96	6,300	75·00	61,200	18,200	350	45,000

Villepreux School of Horticulture.	Wheat.		Black oats.		Green maize.	Mammoth mangold.	Potatoes.		Sogina.
Kilos. per hectare.	Straw, kilos.	Grain, hectolitres.	Straw, kilos.	Grain, hectolitres.	Kilos.	Kilos.	Gross kilos.	Diseased, kilos.	Kilos.
Unmanured	4,050	32·20	3,600	53·55	55,000	80,000	26,700	4,610	80,000
15,000 farmyard manure	4,500	33·25	4,200	55·75	100,000	100,000	26,500	4,450	100,000
1,000 phosphate	4,600	33·75	5,000	56·00	65,000	111,000	27,750	3,000	111,000
1,000 superphosphate	4,850	33·85	5,050	55·33	67,000	110,000	32,279	2,520	111,000
500 nitrate of soda	4,200	33·00	5,150	55·10	82,000	155,000	18,530	2,800	90,000

J. M. H. M.

Reduction of Nitrates in the Soil. By P. P. DÉHÉRAIN and MAQUENNE (*Ann. Agron.*, 9, 7—21).—Schloesing, in 1873, found that when 12 kilos. of soil mixed with 7·5 grams nitre were placed in a flask with a confined portion of air, the whole of the nitrate disappeared, a part of the nitrogen being converted into ammonia, and the rest being evolved as free nitrogen.

The following experiments and observations of the authors appear to show that this reduction of nitrates by soil is due to a fermentation carried on by *Anäerobia*.

A handful of garden soil is placed in a litre flask, the flask is then filled with a 7 or 8 per cent. solution of sugar, fitted with a delivery tube dipping into mercury, and maintained at 35° in a water-bath. In about 15 hours fermentation sets in, and an evolution of gas is produced which lasts about 30 hours; the action then slackens, but may be renewed by adding a little chalk to neutralise the acidity of the solution. The evolved gases consist of carbonic anhydride and hydrogen, and the solution contains butyric acid. The fermenting liquid contains vibrios similar to the butyric ferment discovered by Pasteur, but the authors have reason to believe that the *Bacillus amylobacter* of Van Tieghem is present also, perhaps in greater quantity than the butyric vibrio. In order to connect the existence of this anäerobic ferment in the soil with the reduction of nitrates, the authors cite the following observations:—

(1.) The reduction of nitrates takes place only in atmospheres deprived of oxygen. If some garden mould and a little saltpetre are placed in a sealed tube, the air of the tube will after a time be found to contain no oxygen, and at the same time no nitrate will be detected in the soil. The nitrogen contained in the tube is found to have increased.

(2.) The reduction of nitrates takes place only with soil rich in organic matter. A soil poor in organic matter (containing 0·1 per cent. nitrogen) may, however, be rendered active by adding to it glucose which has been treated with potash.

(3.) If the saltpetred soil be heated in the sealed tubes at 120—125° for some hours, and afterwards kept for a month, the nitrate does not disappear.

(4.) The addition of a few drops of chloroform to the contents of the tube also prevents the reduction of the nitrate, even when kept for several months; the oxygen of the enclosed air nevertheless disappears, being replaced by carbonic anhydride.

(5.) Soil which has been heated at 120° for some hours regains its power of reducing nitrates when it is mixed with a very small quantity of fresh soil and placed in another tube. Often the mere transference from one tube to another is sufficient, without any addition of fresh soil.

(6.) In an experiment with a saltpetred soil in contact with a solution of sugar, the gas evolved during fermentation was found to consist of CO_2, 67·3; H, 31·5; N, 1·2. When the sugar is omitted, or when the fermentation is less active, the reduction of the nitrate is not so complete, and *nitrous oxide* is evolved as well as nitrogen; in two cases cited by the authors, the nitrogen was mixed with 11·5 and

9·5 per cent. of nitrous oxide. In another case, when saltpetred soil and sugar solution were used, the gas consisted of CO_2, 85·5; N_2O, 8·2; N, 11·3.

The authors consider that the reduction of the nitrate is a secondary action, effected by the nascent hydrogen resulting from the butyric fermentation, and they compare the evolution of nitrous oxide in this case with its production when zinc is dissolved in dilute nitric acid. In connection with these results, the authors discuss the impoverishment in nitrogen of arable land bearing cereal crops, and the comparative richness in nitrogen of pasture land—some of the Rothamsted pasture soil, for instance, contains 0·25—0·28 per cent. N, whilst the wheat-growing plots, although receiving more nitrogen in manure than the pasture, contain only 0·12—0·18 per cent. N.

Well-worked arable soils, freely äerated, lose nitrogen by nitrification, the produced nitrates being carried away in the drainage water. In the soil of a pasture, however, the nitric fermentation proceeds very slowly because of the deficient supply of oxygen; on the other hand, there is probably always enough oxygen present in the soil to prevent the occurrence of the anäerobic fermentation, which would give rise to reduction of nitrates and loss of free nitrogen and nitrous oxide. Incidentally, the authors remark that the only certainly known causes of the continuous *enrichment* of soil in nitrogen are: (1) the fixation of free nitrogen observed by Berthelot, and (2) the fixation of ammonia observed by Schloesing. Both of these processes require a soil rich in organic matter, and in order that the gain of nitrogen may be permanent, the supply of oxygen and consequent nitrification must be limited. J. M. H. M.

Analysis of Materials used in the Preparation of Composts.

By A. PETERMANN (*Ann. Agron.*, 1882, 135—140).

	Water, p. c.	Organic matter.	Organic nitrogen.	P_2O_5.	K_2O.	CaO.	Remarks.
1. Mud from washing beetroot .	23·22	—	0·25	0·18	—	—	From entrance of settling pits.
2. „ „ „ .	26·56	—	0·14	0·78	—	—	„ „ „
3. „ „ „ .	1·36	6·81	0·20	0·12	0·35	0·62	From end of settling pits. Air dried.
4. „ „ „ .	2·54	9·83	0·29	0·18	0·39	0·25	„ „ „
5. „ „ „ .	42·45	12·20	0·59	1·09	—	—	Mixed with one-half scum from defecation.
6. „ „ „ .	23·12	—	0·16	0·11	0·41	—	Mixed with one-half lime.
7. Mud from mill pond	9·25	3·90	0·15	0·15	0·48	—	Air dried,
8. Pond mud	2·56	4·54	0·05	0·14	—	—	„
9. „	41·14	3·77	0·21	0·61	0·44	—	Fresh.
10. „	8·15	7·20	0·13	—	—	—	Air dried.
11. „	8·76	40·47	0·23	0·20	0·28	—	From coal washing.
12. Wool washing mud	48·92	13·08	0·58	0·15	0·39	—	
13. Paper makers' waste........	52·29	13·26	0·26	0·15	0·96	—	Mud from causticiser. 7·12 per cent. sand,
14. „ „	46·57	8·22	none	traces	0·16	16·1	„ „ 4·70 „ „
15. „ „	13·92	38·08	0·70	1·68	0·34	21·68	Mud from rag washing,
16. „ „	4·63	4·75	0·47	0·41	0·49	—	„ „ „
17. Gas lime	21·09	—	0·29	—	—	—	N as ammonia,
18. „	—	—	0·05	—	—	—	
19. „	—	—	0·41	0·09	—	—	
20. Waste from salt works	16·32	4·46	—	traces	traces	12·40	40 p. c. sand; 1 p. c. NaCl. Lime as $CaCO_3$.
21. „ soap „	36·81	—	—	0·54	1·22	—	Lime as $CaCO_3$.
22. „ „ „	39·93	—	—	0·17	traces	29·50	A little Na_2CO_3 and NaCl.
23. Mill sweepings	14·76	76·36	1·93	0·94	0·61	—	6·33 per cent. sand.
24. Tanners' waste	18·98	21·48	0·95	0·24	—	—	23·18 per cent. sand.
25. Ashes from tannery	—	—	—	0·74	1·17	36·00	
26. „ „	—	—	—	1·19	1·46	—	
27. Coal ashes	—	—	—	0·99	1·28	—	
28. Mixture of ashes, coal, soot..	—	—	0·24	0·90	0·49	—	
29. Compost	10·09	44·94	1·03	0·55	5·08	—	Earth, lime, wool refuse, wood ashes, potash salts.
30. „	16·48	23·33	1·88	0·19	1·77	—	Sugar refining cloths, straw, earth, lime; watered with liquid manure.

J. M. H. M.

Artificial Manuring of Sugar-canes. By G. Riffard (*Bied. Centr.*, 1882, 797—803).—An average crop of canes (50,000 kilos. canes, and 10,000 kilos. leaves) removes per hectare, of nitrogen 41·3 kilos., phosphoric acid 27·7, sulphuric acid 34·4, lime 50·0, magnesia 35·9, and potash 72·2. Of this ash, but very little is returned to the soil in any form; the leaves are used as fodder, as is also the scum from the pans, but the rest is lost to the ground. As manures, guano, farmyard manure, and Villes' No. 5 have been employed, but no marked difference in the yields was noticed; the canes absorb alkaline chlorides readily, as much as 42·7 of the ash of the cane, and 26 per cent. of the ash of the leaves may consist of potash if they are manured with potassium chloride, which has a bad effect on the plants the canes gradually becoming yellow.

The author has made experiments, using 12 per cent. superphosphate, saltpetre, guano, potassium chloride, and ammonium sulphate, and finds that stable manure produces the best results; although the yield is not the best, yet the amount of uncrystallisable sugar per 100 kilos. juice is the lowest. It still remains to be proved whether the use of potassium sulphate in preference to the chloride is to be recommended or not, as lowering the percentage of uncrystallisable sugar. E. W. P.

Analysis of Gas-lime. By A. Mayer and F. Clausnitzer (*Bied. Centr.*, 1882, 852).—Water = 30·1, calcium hydroxide 32·6, carbonate 17·5, sulphate and sulphite 20·2, sulphide traces; thiocyanate traces; ammonia 0·01. Total = 100·4.

Gas-lime must therefore be used as if it were slaked lime, and not as sulphate; it cannot be used in manure heaps or on moor or sandy soils, but must be long exposed to the air before use. E. W. P.

Analytical Chemistry.

Asbestos Filters. By P. Casamajor (*Chem. News*, 1883, 17).—The author recommends the following method for the preparation of asbestos filters.

Of the different kinds of asbestos, the Australian is the best for rapid filtration; it is first rubbed through a brass sieve (10 openings to the inch), and the dust and fine particles are removed from the sifted material by washing it with water and stirring well in a No. 25 or No. 30 sieve until the water comes through clear; the washed asbestos is then boiled for half an hour with a solution of hydrochloric acid, 1 part of fuming acid to 4 parts of water; after this treatment, the pulp is well washed until free from acid and then strongly heated in a platinum dish. It may be kept in a wide-mouth bottle until required for use, when it is made into a thin paste and poured on to the perforated platinum disc. D. A. L.

Influence of Hygroscopic Condensation in Glass Vessels on the Determination of the Density of Aqueous Vapour. By D. Macaluso and G. Grimaldi (*Gazzetta*, **12**, 535—543).—If an unsaturated vapour conformed to the laws of Boyle and Gay-Lussac, its density, as compared with that of air or any permanent gas, would remain constant for all pressures and temperatures. With regard to aqueous vapour, Regnault found (*Études sur l'Hygrométrie*) that, although its density may be calculated according to these laws for pressures and temperatures remote from the point of saturation, its value becomes much greater as the vapour approaches that point, in consequence either of abnormal condensation, or of a deposition of liquid on the inner surface of the vessel, which can be prevented only by keeping the vapour far above the point of saturation. It therefore becomes of interest to determine whether such deposition really takes place, and, if so, to what amount. Regnault suggested, as an approximative method of determining this point, the use of glass vessels of different forms, so that the ratios of their surfaces to their capacities might also be different; and this suggestion was adopted by Wüllner and Grotrian in their memoir on the density and tension of saturated vapours (*Wied. Ann.*, **11**, 545); they found, however, no appreciable difference in the results of their experiments with different vessels, and thence inferred that the surface-condensation in question does not take place. Macaluso and Grimaldi, on the other hand, consider that these experiments are not conclusive, inasmuch as the ratios of surface to volume in the vessels employed in them differed but little from each other. They have, therefore, endeavoured to determine the matter by the use of vessels to which this objection does not apply, and they infer from their experiments that a condensation of water on the surface of the glass vessels really takes place, which, although small at the temperature of 108°, is plainly appreciable, and would probably be much greater at temperatures nearer to the point of saturation. They consider, however, that this surface-condensation is not the sole cause of the difference between the experimental value of the vapour-density and the values calculated according to the laws of Boyle and Gay-Lussac. H. W.

A Modified Process for the Estimation of Chlorine in Bleaching-powder. By J. W. C. Harvey (*Chem. News*, **47**, 51).—The original process is that in which the chlorine in bleaching-powder is determined from the number of c.c. of a bleaching solution of known strength required to convert a solution of ferrous chloride containing a weighed quantity of pure iron into ferric salt. The modification proposed does away with the weighing of the iron and the making of ferrous chloride from it. The basis of the method consists in adding a measured quantity of a dilute solution of stannous chloride to excess of a solution of ferric chloride, the amount of ferrous salt thus formed being determined by standard potassium dichromate; by this means, therefore, a known quantity of ferrous chloride can be formed immediately. The estimation is thus worked: the same quantity of stannous chloride as in the test experiment is added to excess of ferric chloride; and the diluted solution is titrated with the bleaching-powder solution until all the ferrous is converted into ferric chloride. The amount of chlorine is calculated from the ferrous iron found by the dichromate, &c., &c. Required solutions are: 1. Stannous chloride, dissolve 60 grams in hydrochloric acid, and make up to 1 litre: 5 c.c. of this solution suffice for an experiment. The amount of ferrous chloride to which it corresponds should be determined before each series of estimations. 2. Ferric chloride, which must be free from ferrous salt. 3. Standard dichromate, 30 grams in 2 litres.

D. A. L.

Estimation of Chlorides, Bromides, or Iodides in Presence of Sulphuretted Hydrogen. By H. Topsöe (*Zeits. Anal. Chem.*, **22**, 5—10).—By the addition of an excess of potassium permanganate solution acidified with nitric acid, the sulphuretted hydrogen is oxidised to sulphuric acid, the liberated bromine or iodine converted into the corresponding hydro-compound by aqueous sulphurous acid. the excess of permanganate being reduced by the same agent, and in the solution now free from sulphuretted hydrogen the haloïds are determined by the usual methods.

O. H.

Modification of Scheibler's Azotometer. By K. Sonden (*Zeits. Anal. Chem.*, **22**, 23—27).—The author describes an apparatus for the measurement of gases, the *volume* being constant and the *pressure* of the gas being variable.

O. H.

Estimation of Nitric Oxide and Nitric Acid. By C. Boehmer (*Zeits. Anal. Chem.*, **22**, 20—23).—The author has some time ago (*ibid.*, **21**, 212) pointed out that chromic acid absorbs nitric oxide with great facility. He now utilises this fact in the gravimetric estimation of nitric oxide (and of nitric acid) in Schlösing's method, by passing the gas through Liebig's bulbs filled with strong chromic acid solution, and ascertaining the increase of weight.

O. H.

Estimation of "Half Soluble" Phosphoric Acid. By H. v. Ollech (*Bied. Centr.*, 1882, 853).—Instead of employing $\frac{1}{4}$ per cent. solution of citric acid, a $\frac{5}{4}$ per cent. solution was used; the phosphates examined were in various states of aggregation, finely-powdered, coarse, and medium-grained; also in one set of experiments, the phosphoric acid was precipitated directly, in the other only after the organic matter had been destroyed. But little difference was noticed whether the phosphates had been ignited or not; the more finely divided the substance, the higher was the percentage of dissolved acid; the concentrated citric acid dissolved less than the diluted; it matters not how magnesia mixture is added to the solution from which phosphoric acid is to be thrown down, so long as the mixture is not in too great excess.

E. W. P.

Separation of Strontium and Calcium. By D. Sidersky (*Zeits. Anal. Chem.*, **22**, 10—14).—The principle upon which the method is based consists in the observation, that if a mixture of ammonium sulphate and oxalate is added to a solution containing both strontium and calcium, the whole of the strontium is precipitated as sulphate, and the whole of the calcium as oxalate.

The author extracts the mixed precipitate with dilute hydrochloric acid, weighing the residue as sulphate, and precipitating the calcium oxalate from the solution by ammonia.

Satisfactory test experiments are quoted. O. H.

Detection of Strontium. By F. Ransom (*Pharm. J. Trans.* [3], **13**, 626—627).—Solutions of strontium nitrate varying from 1·25 per cent. upwards are precipitated or rendered turbid by the addition of a 5 per cent. solution of potassium chromate. A 1·25 per cent. solution does not alter until boiled, when a precipitate forms: boiling accelerates precipitation in all cases. Descending to weaker solutions and applying heat, turbidity is obtained until, with a 0·25 per cent. strontium solution, only a slight cloudiness can be observed. Free acetic acid prevents this precipitation in the cold, for even a 20 per cent. solution is not affected until boiled, and then is merely rendered turbid. This state of things is not altered by neutralising the free acid with ammonia, for, even then, strontium nitrate solutions are only rendered turbid by the potassium chromate instead of being precipitated as they are when the strontium salt is pure. Calcium salt solutions, even when strong, are not precipitated by 5 per cent. potassium chromate solution; sometimes, however, a turbidity may be obtained; the small precipitate causing calcium turbidity remains diffused in the liquid, whilst that of strontium nitrate turbidity aggregates in circular discs adhering to the glass. From these facts, it is evident that potassium chromate may be used to detect strontium; further, it should be observed that plenty of free acetic acid ought to be used when barium is to be separated with potassium chromate previously to testing for strontium. D. A. L.

Weil's Method for the Determination of Copper, Iron, and Antimony. (*Chem. News*, **46**, 284.)—The necessary solutions are:—(1.) Normal copper solution, 19·6675 grams of pure powdered crystalline copper sulphate, which has been dried between white blotting-paper, are dissolved in water and made up to half a litre. (2.) Is a similar solution containing 7·867 of copper sulphate. (3.) Standard tin solution, 4·5 to 5 grams of tin crystals (stannous chloride), dissolved in water, and 30 grams of hydrochloric acid, are made up to half a litre, with water acidified with about 40 per cent. hydrochloric acid. This solution is standardised with solution No. 1. 10 c.c. of solution No. 1 are mixed with 25 c.c. hydrochloric acid, boiled, and the tin solution to be standardised is run in until the green colour disappears.

Estimation of Copper.—5 grams of substance are dissolved in hydrochloric or sulphuric acid, and made up to 250 c.c. 10 c.c. of this solution are taken, 25 c.c. hydrochloric acid added, and then titrated as above.

Estimation of Iron.—When there are 2½ vols. of free hydrochloric to 1 vol. of the ferric solution, no indicator is necessary, and the standard tin solution is run in until the iron solution is colourless; in this way the quantity of iron is obtained in terms of copper. Of solutions containing 2 grams of the sample in 250 c.c., 10 c.c. are evaporated in a porcelain capsule, with 10 c.c. of the copper solution (No. 2); to the concentrated mixed solution large excess (about 75 c.c.) of hydrochloric acid is added, and this is titrated with the tin solution as before; of course the tin required for the copper used must be deducted. The copper is used as an indicator, and is not required with substances containing more than 2 per cent. of iron.

Estimation of Iron and Copper.—5 grams of ore in 250 c.c. Titrate as above. In another, 10 c.c. of solution, precipitate the copper with zinc, filter, reconvert the ferrous into ferric salt by means of potassium permanganate, and titrate the iron again.

Estimation of Antimony.—In making up the 250 c.c. in this case, it is necessary to use aqueous solution of tartaric acid to prevent precipitation of antimony. The solution of antimonic chloride is mixed with normal copper solution, and a large excess of hydrochloric acid then titrated; the c.c. standard tin solution used indicates the sum of the copper and antimony. If the mixed solution of cuprous and antimonious chloride is allowed to remain some time, the copper becomes reoxidised, but the acid does not, therefore a second titration gives the quantity of copper only; this is scarcely required when strength and quantity of copper solution added is known. *Antimony, copper,* and *iron,* when together in same sample, are thus determined. 5 grams substance is dissolved in nitric acid, evaporated down, and filtered. The filtrate contains iron and copper, which are determined as above directed. The precipitate contains all the antimony; it is dissolved in hydrochloric acid, treated with potassium permanganate, and the antimonic chloride determined as directed.

This process depends on the reducing action of stannous chloride. It is therefore necessary to get rid of extraneous oxidising influences, such as free chlorine, nitric acid, or excess of permanganate, &c., before titration; this is effected by evaporating to dryness, taking up with hydrochloric acid, and repeating, until the solution or vapour evolved on boiling ceases to turn starch-paper blue. D. A. L.

The Thiocyanate Reaction for Iron. By H. WERNER (*Zeits. Anal. Chem.*, **22**, 44).—Chlorides, and to a less extent nitrates, of the earth-metals are said to interfere with the above reaction.

O. H.

Analysis of Iron. By A. TAMM (*Chem. Centr.*, 1882, 766).—In this paper the various methods of iron analysis at present in use in different countries are discussed.

The total *carbon* is determined in England, Sweden, and many parts of Germany, by dissolving the iron in ammonium copper chloride, collecting undissolved carbon on an asbestos filter, and finally burning, and weighing as carbonic acid. In Freiberg the carbon is not burnt, but oxidised with chromic acid. In France this iron is dissolved in mercuric chloride (Boussingault's method). The English method is quicker than the Swedish iodine method. For *graphite* determination, at Dowlais the iron is dissolved in nitric acid, the graphite and silica remain undissolved; the first is burnt, the second weighed. Daily tests of the furnace metal are universally made by Eggertz's colorimetric method. *Silica* is generally determined in England by dissolving the iron, either in aqua regia or in hydrochloric acid, diluting with sulphuric acid; others dissolve in nitric, diluted with sulphuric acid. At Creusot and Terrenoir the pulverised iron is moistened with nitric acid, ignited, and oxidised in a muffle, heated in oxygen, and then converted with dry hydrochloric acid into ferric chloride, which is volatilised, leaving pure silica behind. *Phosphoric acid* is mostly weighed in the form of the ammonium molybdate precipitate. The iron is dissolved either in nitric acid, with subsequent addition of hydrochloric acid, or in a mixture of the two acids, or seldom in nitric acid alone; the first is the best solvent. Pattinson works on 3 grams of iron; Stead with 2. At Creusot 1 gram is used. The precipitation is conducted in acid, alkaline, or neutral solution. Thus Eggertz's acid solution is in use in the Lowther Works, in Landore, and at Creusot. Ammoniacal solution (Snelus's method) is in vogue at Dowlais, and is used by Pattinson, whilst Stead uses a neutral solution, and Riley employs the magnesium method. Altogether the acid method is the best, and is in fact the only one available for iron containing arsenic. *Sulphur* is estimated in various ways. At Dowlais, Snelus, Stead, and others dissolve the iron in aqua regia, turn the sulphur into sulphuric acid, and precipitate with barium chloride, &c. In other methods, the sulphur is converted into hydrogen sulphide. In Freiberg, the gas is passed into solution of bromine in hydrochloric acid, and the sulphuric acid determined with barium chloride. Pattinson passes the gas into an ammoniacal cadmium chloride solution, and oxidises the precipitated sulphide with bromine, and then treats with barium chloride, &c. In other places, the gas is passed into lead acetate, or sulphate of copper or silver nitrate solutions. Rollet at Creusot ignites the pulverised iron in a stream of gas, consisting of three-fourths of hydrogen and one-fourth carbonic acid; the gas is led into silver nitrate solution, and when only small quantities of sulphur are present, the gas is passed through a series of flasks, each flask containing silver solution representing 0·01 per cent. of sulphur, thus the number of flasks precipitated gives directly hundredths per cent. of sulphur. *Manganese* is determined in England and Belgium with ammonium acetate; in France, Germany, and Sweden by means of sodium acetate. Pattinson's titration method only gives approximate results. Various colorimetric systems are in use: thus, Osmond's, in Devain and Creusot; Dehayes, in Terrenoir. These methods are not very good. Särnström's volumetric method is very good. *Iron* is determined in England with potassium dichromate; in France, Belgium, and Germany, with permanganate. At Landore, when titanic acid is present, reduction is effected with sodium sulphide. D. A. L.

Reduction of Ferric Salts. By P. T. AUSTIN and G. B. HURFF (*Chem. News*, **46**, 287).—The authors suggest the use of a saturated solution of sodium sulphite for the reduction of ferric to ferrous salts previous to titration of the iron with permanganate. The sodium sulphite solution is added to the acid ferric solution in small quantities at a time, until it is colourless; the reduced solution is then boiled out of contact with the air, until all the sulphurous anhydride is driven off. Satisfactory results have been obtained by this method.

D. A. L.

Estimation of Sulphur in Iron and Steel. By G. CRAIG (*Chem. News*, **46**, 272).—In answer to Rocholl (next Abstract), the author states that he has, in test-experiments with magnesium sulphate, obtained all the sulphur precipitated as barium sulphate in presence of large quantities of ferric and potassium chlorides. Rocholl was under the impression that such a precipitation was not possible under the given conditions. Several experiments have also been made with the hydrogen peroxide evolution process, all the sulphur being given off, not a trace of sulphur being found in the residue by Rocholl's process. On two occasions, however, when the residue was fused with potassium nitrate and sodium carbonate, a small quantity of sulphur was found, thus:—

	Cu in iron.	S evolved.	S in residue.		Per cent. S evolved.
			Liquid.	Solid.	
1.	0·50	0·063	0	0 *	100·0
2.	0·50	0·065	0	0·002†	97·0
3.	0·50	0·064	0	0·003†	95·4

The author suggests that the difference between his and Rocholl's results is probably due to the fact that he (the author) boils his solution for about 15—20 minutes after the evolution of gas has become sluggish. D. A. L.

Estimation of Sulphur in Pig-iron. By H. ROCHOLL (*Chem. News*, **46**, 236).—The author does not approve of Craig's method (this vol., p. 121); neither does he agree with the statement "that the residue *left* on dissolving pig-iron in strong hydrochloric acid is free from sulphur, even when the metal contains much copper."

The author has dissolved several samples of iron in hydrochloric acid in the usual way, passing the hydrogen evolved through a 5-bulb tube containing weak ammoniacal silver nitrate. The silver sulphide is oxidised with bromine-water, filtered, and precipitated with barium chloride; results obtained are given in table below under "Sulphur A." The residue in the flask is filtered, and the solid portion washed into a basin, evaporated, and successively heated with nitric and hydrochloric acids, dried, redissolved, and filtered. From the filtrate, barium chloride always produces a precipitate representing a second portion of "Sulphur B." No other precipitate with this reagent is obtained. The following are the results:—

* Rocholl's process. † Fusion process.

Name of iron.	Copper.	Total S.	Sulphur A.	Sulphur B.	Sulphur B per cent. of total sulphur.
1. Cleveland pig-iron....	None	0·075	0·069	0·006	8
2. Ordinary Bessemer pig	0·02 (about)	0·045	0·041	0·004	9
3. „ „ „	0·02 (about)	0·026	0·021	0·005	19
4. Cupriferous „ „	0·02	0·065	0·050	0·015	23
5. „ „ „	0·23	0·017	0·011	0·006	35
6. „ „ „	0·26	0·061	0·029	0·032	52
7. „ „ „	0·26	0·064	0·027	0·037	58
8. „ „ „	0·26	0·026	0·009	0·017	65
9. „ „ „	0·27	0·041	0·026	0·015	36
10. „ „ „	1·09	0·071	0·046	0·025	35

D. A. L.

Volumetric Estimation of Manganese Dioxide. By J. W. C. HARVEY (*Chem. News*, 1883, 2).—The requisite solutions are:—1. Standard potassium dichromate, 30 grams of pure salt in 2 litres; so that 1 c.c. = 0·017 Fe = 0·013205 MnO_2. 2. Stannous chloride solution: dissolve 180 grams in hot hydrochloric acid, and, when clear, make up to 1 litre with water. 3. Ferric chloride solution containing 60 grams of iron per litre. To work the process, 1 gram of the finely powdered manganese dioxide is warmed with 10 c.c. of the stannous chloride solution and 15 c.c. hydrochloric acid until the oxide is dissolved; excess of ferric chloride is now added, and the whole heated again; finally the amount of ferrous chloride formed by the residual stannous chloride is determined with potassium dichromate. This being done, 10 c.c. of stannous chloride solution are heated with excess of ferric chloride, and the amount of ferrous salt is determined with the dichromate. From the difference between this and the former determination, the manganese can be calculated. An analysis occupies 15 minutes. The stannous chloride should be tested against the dichromate if any length of time elapses between the determinations. The method has been tested against Fresenius and Will's process, and has always yielded better results. D. A. L.

Separation of Vanadic Acid from Metals. By W. HALBERSTADT (*Zeits. Anal. Chem.*, **22**, 1—4).—The hydrochloric solution is evaporated to dryness and the residue extracted with a saturated ammonium oxalate solution to which a few drops of acetic acid have been added. The solution thus obtained is, while hot, very gradually mixed with acetic acid as long as oxalates are precipitated. The filtrate is evaporated, the residue ignited, heated in a current of oxygen, and weighed as vanadic pentoxide.

The method is applicable to the separation of vanadium from barium, calcium, zinc, and lead, but not suited to that from cobalt, nickel, manganese, magnesium, bismuth, copper, or cadmium. O. H.

Test for Arsenic. By W. A. H. NAYLOR and J. O. BRAITHWAITE (*Pharm. J. Trans.* [3], **13**, 464—465; compare this vol., p. 381).—In this paper, a series of experiments is described, intended to clear up the question whether oxalic acid, when boiled with a solution of sodium arsenate, exercises a reducing action upon it, either alone or with sulphuric acid or hydrogen sulphide. To this end, 1 gram of sodium arsenate and $\frac{1}{2}$ gram oxalic acid or ammonium oxalate were dissolved in 50 c.c. of water and boiled for half an hour; no reduction was observed. Moreover, a mixture of oxalic acid and sodium oxalate solutions may be boiled for some time without the evolution of carbonic acid; thus oxalic acid alone exerts no reducing action on arseniates. With regard to any reduction which takes place when oxalic acid and sulphuretted hydrogen act simultaneously on sodium arsenate, the authors found that sulphuretted hydrogen, when passed through a solution of oxalic acid, gave rise to a powerful reducing agent, probably formic acid, which substance, however, does not reduce sodium arsenate to arsenite. The authors conclude that oxalic acid cannot be credited even indirectly with the reduction of arsenates. D. A. L.

Examination of Water and Air for Sanitary Purposes, with Remarks on Disinfection. By R. Hitchcock (*Chem. News*, 1883, 7).—The author points out that although it is not possible to ascertain by chemical means whether a water contains contagious disease-germs or not, nevertheless chemical analysis is very valuable, for by it the source of any impurity may be traced, and the possibility of the water becoming a vehicle of disease may be indicated. In the same way with air, although the bad gases alone would not produce disease, nevertheless disease-germs would grow and multiply better in gases from decomposition of animal matter than in pure air; and, besides, the germs will be very readily disseminated by the rising gases. Air charged with germs can be filtered through gun-cotton, which can be dissolved in ether, when the germs remain behind and can be microscopically examined. The author attaches great importance to this point. He considers ordinary aërial disinfection utterly useless; the only efficient plan for purifying a sick room is to immediately disinfect all refuse, and to have thorough ventilation. D. A. L.

Ammonia-process for Water Analysis. By C. W. Marsh (*Chem. News*, 1883, 19—20).—In this paper, a statement made by Remsen is confirmed, to the effect that when free ammonia and albuminoïd ammonia are determined by Wanklyn's process, the amounts of the two added together are found to be much smaller than the total ammonia found when the oxidising mixture is added without previous boiling. Results obtained from the analysis of 26 samples of various waters (well, cistern, canal, distilled, spring, surface) tend thus; the analysis for free and albuminoïd ammonia being made as Wanklyn directs: in *one* case only did the sum of the free and albuminoïd ammonia exceed the total ammonia, and this result the author attributes to error from the high colour of the solution Nesslerised; in *three* cases, the amounts were identical, due to the fact that no volatile nitrogenous substances escaped during the distillation part of the process; in the remaining *twenty-two* the sum of the free and albuminoïd ammonia was less than the total ammonia. These results prove conclusively that some volatile substance escapes conversion into ammonia; and from a series of ten experiments out of which six support the view, the author comes to the conclusion that the volatile substance is a condensable nitrogenous organic compound which passes over and is condensed along with the "free" ammonia distillate. The experiments consist in redistilling the "free" ammonia distillate with potassium permanganate, so that the free ammonia is obtained plus the ammonia produced by the decomposition of the nitrogenous organic compound; for example, in experiments Nos. 2 and 3:—

	1. Free ammonia.	2. Albumin. ammonia.	3. Sum of 1 and 2.	4. Total ammonia.	5. Sum of free and regained ammonia.	Sum of 2 and 5.
2. Well water	0·05	0·10	0·15	0·16	0·06	0·16
3. ,, ,,	0·05	0·08	0·13	0·17	0·09	0·17

The results of all the experiments are tabulated. D. A. L.

Determination of Nitrites. By E. W. Davy (*Pharm. J. Trans.* [3], **13**, 466—468).—The proposed method is based on the reaction which takes place between nitrous acid or soluble nitrites and gallic acid, of the nature represented by the equation:—

$$\underset{\text{Gallic acid.}}{C_7H_6O_5} + 2HNO_2 = \underset{\text{Tanno-melanic acid.}}{C_6H_4O_3} + CO_2 + 2NO + 2H_2O.$$

This change is always accompanied by a coloration of the solution. The colouring matter thus formed is unaffected by dilute sulphuric, nitric, and hydrochloric acids, or even by concentrated solutions of organic acids, oxalic, acetic, and tartaric; moreover, the coloration is not affected by the presence of saline and earthy salts, or small quantities of organic matter or of nitrates. The intensity of the colour produced is in direct proportion to the amount of nitrite reacting on the gallic acid; the process can therefore be applied quantitatively in a manner similar to the Nessler test. Thus it would only be necessary to compare the colour produced in the liquid under examination with that produced with a definite quantity of standardised nitrite solution. The standard nitrite recommended has double the strength of that described by Frankland for use with Griess's test; the gallic acid test solution is a concentrated aqueous solution of the acid which, if coloured, can be decolorised by treatment with animal charcoal; this solution is made strongly acid, so as to prevent the very rapid change of colour which gallic acid generally undergoes. The process is well adapted for water analysis; its application is very simple: 25 to 50 c.c. of the water are boiled with 1 or 2 c.c. of the gallic solution and a few drops of sulphuric or hydrochloric acid; the colour produced is then compared with the standard in the usual way. If iron salts are present, they should first be removed by ammonia and filtration. The author has been able to detect 1 part of nitrous acid in 20,000,000 parts of water. Compared with Griess's method this process does not give so deep a colour when there are large quantities of nitrites present, but with smaller quantities it is equally efficient, and, from an economical point of view, has a decided advantage. D. A. L.

Preparation of Alkaline Potassium Permanganate Solution for Water Analysis. By J. STAPLETON (*Chem. News*, **46**, 284).—The great difficulty has been to prepare alkaline potassium permanganate solution free from ammonia; the author considers that most likely the potash is the cause of this difficulty. The process now recommended by him consists in (1) the purification of the potash by a sort of "Clarke's process," and (2) the distillation by steaming of the mixed solutions of alkali and permanganate. It has been used for two years and has proved satisfactory. It is thus worked: the potash is dissolved in a hard water containing dissolved calcium carbonate, and the precipitate of calcium carbonate is allowed to subside 24 hours or so, carrying down with it a large proportion of the nitrogenous organic matter. The clear potash-solution is now mixed with the solution of potassium permanganate; the mixed solution is warmed by a Bunsen, and is subjected to a current of steam from water free from ammonia; the vapours are condensed; and the steaming is continued until the distillate, when Nesslerised, shows only 0·005 mgrm. per litre of ammonia; this occupies about one hour, and the solution is practically free from ammonia. It is advisable to have the neck of the retort inclined slightly upwards, to fill it only to one-third, to put in some small pieces of pumice, and to support it on wire-gauze on a tripod in such a manner as to be able to syphon off the liquid. D. A. L.

Preparation of a Volumetric Solution for Determining the Hardness of Water. By C. R. C. TICHBORNE (*Chem. News*, **46**, 235).—Since the time of its introduction, Clarke's process for determining the hardness of water has undergone, with the exception of some minor changes, no improvement. As the preparation and standardising of the soap-solution is troublesome, the author thought the usual method might be improved. It was thought that by taking a definite fatty acid (oleic) and neutralising with standard soda, a trustworthy soap-solution could be obtained in which the sodium would represent its equivalent of the calcium constituting the hardness. When soda is added to oleic acid, it gives a neutral reaction with phenol-phthalein as indicator, when the quantity required for the formula $M'C_{18}H_{33}O_2$ has been added, assuming the sp. gr. of oleic acid as 0·915; if another equivalent of soda be now added, the aqueous solution of the sodium oleate becomes a solid jelly, and, if the action of the soda be pushed further, additional compounds are formed. The mono- and di-sodium oleates are permanent compounds, and, as the fatty acid is the measure of hardness, either can be used for the determination.

Method of preparation:—5 c.c. oleic acid are dissolved in 50 c.c. alcohol, 2 drops of phenol-phthalein are now added, and a volumetric solution of soda is run in until a pink tinge is produced. If gelatinous salt is required, another equal quantity of soda is run in. The author prefers this salt when it can be easily prepared, which is not always the case. The sodium oleate is made up to the required strength by the addition of equal parts of rectified spirit and water. Each 15·5 c.c. of soda used in the first neutralisation equals 820 c.c. of volumetric soap solution. Such a solution is in Clarke's original scale; it is not necessary to titrate against a calcium solution, as the soda is quite as definite. The author has always found that 5 c.c. of oleic acid (pure or commercial) require 15·5 c.c. of soda: 32 c.c. of the solution when operating on 100 c.c. water represent 16° hardness per gallon by Clarke's scale. The advantages claimed are that the soap-solution may be made in five minutes, requires no titration against a standard water, and is more permanent than those made from ordinary soaps.

D. A. L.

Estimation of the Fertility of a Soil. By A. Vogel (*Bied. Centr.*, 1882, 852).—If a sample of a soil treated with acetic acid gives no indication of phosphoric acid after having been in contact with ammonium molybdate for 24 hours, the percentage of phosphates is abnormally low.

Organic matter may be roughly estimated by boiling 10 grams of the soil with water, and adding to the solution potassium permanganate until a permanent coloration is produced. E. W. P.

Determination of the Flashing Point of Petroleum. By J. T. Stoddard (*Chem. News*, 1882, 297).—The author suggests a modified form of Liebermann's flashing point apparatus. It consists of a cylinder 2 to 3 cm. in diameter, and 10 to 12 cm. long, closed at the bottom by means of a cork through which just passes a small tube drawn out to a jet. This tube is bent round and up along the outside of the cylinder, and is connected with a supply of compressed air by means of india-rubber tubing, which is furnished with a screw clip for regulating purposes. To use the apparatus the cylinder is filled to about one-third with oil; it is then plunged into a water-bath up to the level of the oil, and can be secured in this position by means of a clamp. Air is admitted through the tube at a rate sufficient to keep about 0·5 cm. of foam on the surface. A small flame or match is used to test for the flashing point. D. A. L.

Estimation of Coke and Volatile Products in Coal. By R. Galloway (*Chem. Centr.*, 1882, 767).—About 500 grains of the powdered coal are weighed in a tared porcelain crucible, which is then placed in a larger clay crucible, the bottom of which is covered with powdered wood-charcoal, the space round and above the smaller crucible is filled up with lumps of wood-charcoal, and after the cover is on, the whole is heated at a bright red heat in a furnace. This done, it is allowed to cool, and the porcelain crucible is weighed. The total weight, less weight of crucible, is coke, whilst the loss represents the volatile products. Previous methods have always given the amount of coke too low, because part is generally burnt away by the air. The charcoal in this process prevents access of air, and also keeps the smaller crucible in the proper position. D. A. L.

Estimation of Alcoholic Liquors. By J. NESSLER and M. BARTH (*Zeits. Anal. Chem.*, **22**, 33—43).—A considerable number of various brandies (cherry, plum, &c.) have been examined by the authors, and tested specially for copper and hydrocyanic acid. The metal was found in varying amounts, up to 18 mgrm. per litre, in most, and the hydrocyanic acid in the whole of the samples in quantities from 3 to 17 mgrms. per litre. O. H.

Relation between the Glycerol and Alcohol in Wine. By E. BORGMANN (*Zeits. Anal. Chem.*, **22**, 58—60).—From a number of experiments, the author concludes that the proportion of glycerol to alcohol is never less in pure wines than 7·8 : 100. O. H.

Analyses of Pure Wines. By R. FRESENIUS and E. BORGMANN (*Zeits. Anal. Chem.*, **22**, 46—58).—The results may be tabulated as follows:—

100 *c.c. contain Grams.*

		Red Main wines.	White Main.	Hocks.	White French.	Red French.	Moselle.
Alcohol ...	Maximum.	9·51	10·15	10·39	9·84	9·32	8·72
	Minimum .	9·49	8·90	6·42	9·05	7·99	7·04
	Average...	9·50	9·52	8·77	9·44	8·56	8·08
Extractives	Maximum.	3·30	2·78	3·00	2·62	2·67	2·44
	Minimum .	2·70	2·16	1·86	2·47	2·17	1·92
	Average...	3·00	2·43	2·32	2·54	2·44	2·11
Mineral matter	Maximum.	0·35	0·20	0·30	0·28	0·27	0·20
	Minimum .	0·29	0·17	0·16	0·24	0·21	0·15
	Average...	0·32	0·19	0·22	0·26	0·25	0·18
Acidity ...	Maximum.	0·62	0·80	1·01	0·71	0·58	0·95
	Minimum .	0·54	0·54	0·48	0·54	0·48	0·64
	Average...	0·58	0·69	0·66	0·62	0·54	0·79
Glycerol ..	Maximum.	1·23	1·34	1·28	1·00	0·99	0·85
	Minimum .	1·16	0·86	0·64	0·88	0·75	0·66
	Average...	1 19	1·10	0·92	0·94	0·86	0·73
Sulphuric acid	Maximum.	0·082	0·069	0·050	0·019	0·027	0·018
	Minimum .	0·070	0·027	0·045	0·015	0·006	0·006
	Average...	0·076	0·044	0·047	0·017	0·013	0·012
Phosphoric acid	Maximum.	0·065	0·051	0·048	0·046	0·037	0·056
	Minimum .	0·065	0·033	0·026	0·023	0·023	0·039
	Average...	0·065	0·039	0·040	0·034	0·027	0·047

The mutual relations of the different constituents are on the average as follows:—

Alcohol : glycerol = 100 : 10·5
Extract : acidity = 1000 : 16·6
Acidity : mineral matters = 10 : 3·4
Mineral matters : extractives = 1 : 11·2
Phosphoric acid : mineral matters = 1 : 6·8.

O. H.

Estimation of Sugar by Alkaline Copper Solutions. By P. Degener and F. Allihn (*Bied. Centr.*, 1882, 845—847).—Because of the uncertainty which exists in the usual process for the estimation of sugar, Degener proposes a solution consisting of 80·2 grams copper tartrate, 400 c.c. solution sodium hydroxide made up to 500 c.c. with water; 12·5 c.c., 25 c.c., or 50 c.c. of this are then mixed with a solution of Rochelle salt, and boiled with the sugar solution for half an hour. The author states that only 6 mols. cuprous oxide will be formed for every molecule of grape-sugar, whether the copper be in excess or not. Allihn, on the contrary, finds that the quantity reduced varies, so that there is no advantage gained by the use of this method.

E. W. P.

Pyroleïn. By J. Arbos (*Pharm. J. Trans.* [3], **13**, 624—626).—When certain fixed oils are distilled with glycerol, both substances undergo decomposition, the distillate being in two layers, the lower one consisting of acroleïn, whilst the upper is generally an oily, limpid, acid liquid, insoluble in water, greasy to the touch; this contains what the author calls *pyroleïn.* It is completely soluble in a small quantity of alcohol, but on adding more alcohol an oil separates out, which is soluble in ether and in excess of pyroleïn. The alcoholic solution forms an emulsion with lead acetate, and a precipitate with copper sulphate. Results obtained by distilling separate mixtures containing (1) 2 parts of glycerol and 1 of olive oil; (2) 20 parts glycerol, 9 parts olive oil, and 1 of oil of sesame; (3) 20 glycerol, 10 olive oil, and 1 of cotton-seed oil, along with observations, are tabulated below:—

Reactions.	Pyroleïn from		
	Olive oil.	Olive and Sesame oil.	Olive and Cotton-seed oil.
The mixture during distillation	Does not foam	Foams	Does not foam.
Odour	Faint	Inoffensive	Penetrating, irritating the throat.
Crystallises at 54·5° F. after	96 hours, m. p. crystals 61·2° F.	40 hours, m. p. 70·2° F.	24 hours, m. p. 77° F.
Colour of liquid by reflected light	Dark brown	Dark greenish	Buff coloured.
by transmitted light	Red	Dark red	Reddish-yellow.
Alcoholic solution	Reddish-yellow	Reddish	Golden-yellow.
Treated with ammonia	Much oil separates, but slightly coloured and turbid, after 24 hours, remains so 48 hours	Very small quantity of solid yellowish oil separates after 48 hours	Very small quantity of solid yellowish oil after 48 hours.
With nitric acid, liquid becomes	Brown	Reddish, and then blackish	Blackish.
,, ,, the oil which separates is	Dark brown	Black	Black.
,, ,, after 24 hours liquid is	Reddish	Light yellowish	Yellowish.
,, ,, ,, ,, oil is by reflected light	Blackish	Cherry-red	Bright carmine.
by transmitted light	Deep red	Scarlet	Bright scarlet.
$PtCl_4$ produces two layers, the denser is	Muddy red	Red	Dark yellowish-brown.
Ditto after 24 hours by transmitted light	Deep red	Dark red; greenish by reflected light	Reddish.
With copper sulphate the supernatant liquid is by reflected light	Dark greenish	Bottle-green	Greenish.
by transmitted light	Dark buff-red	Very dark reddish-brown.	Olive-brown.

The author is of opinion that these reactions will be useful in the examination of fixed oils. D. A. L.

Milk Analysis. By E. PFEIFFER (*Zeits. Anal. Chem.*, **22**, 14—20).—The author's remarks as to the estimation of caseïn and albumin contain nothing new. He points out, as Hoppe-Seyler and others have done long ago, that milk contains a considerable amount of nitrogenous matter apart from the caseïn and albumin, this albuminous matter being precipitable by tannin. In human milk it varies between 0·3 and 0·5 per cent., in cow's milk it is about 0·7 per cent. O. H.

Adulteration of Butter. By E. SCHMITT (*Ann. Agron.*, **8**, 544—555).—The conflicting evidence of analysts in a case of suspected butter adulteration led the author to examine the different published processes for the analysis of butter.

The density of butter is, according to the author, too variable and too difficult to determine exactly either by sp. gr. flask or by the *margarimeter*, so as to allow of definite conclusions being drawn. It is moreover easy to imitate exactly the density of genuine butter. The same remarks apply to the fusing and solidifying points, which vary according to the method adopted to determine them, and with the quantity of water contained in the butter.*

The microscopical examination proposed by Juillard yielded results which were untrustworthy, and discordant from those of the chemical examination.

The proximate analysis (water, fat, caseïn, ash) does not distinguish between pure butter and mixtures of butter with oleomargarin. Husson's process (*Jour. Chim. Pharm.*, 1878, 100), depending on the relative solubilities of the natural fats in glycerol, alcohol, and ether under special conditions, was also tried. This gave, for a butter subsequently proved to be genuine, margarin 36, oleïn 46, butyrin and caprin 3, = 85; these figures are at variance with the composition of genuine butter. Lechartier's process (*Ann. Agron.*, **1**, 456), based on saponification with alcoholic potash, distillation of the soap with tartaric acid, and estimation of the distilled volatile acids by titration or conversion into barium salts, did not give concordant results. The same sample of butter gave 83·84, 82·25, 89·70, and 85·54 per cent. of fixed insoluble fatty acids.

Hehner and Angell's process was the only one found to give correct and concordant results; three independent determinations by different operators giving 88·25, 88·00, and 88·13 per cent. of fixed fatty acids in the same butter-fat. The author recommends the determination of the melting point of the fixed fatty acids separated by this process; for genuine butter-fat this should be 36—38°. Some analyses made in this way are subjoined:—

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* *Note by Abstractor.*—Some of the uncertainty which the author complains of in his determinations of density and fusing point, appears to be due to the fact that he operated on crude butter, and not upon butter-fat, as is customary in England.—J. M. H. M.

	M. p. butter.	Per cent. fixed fatty acids.	M. p. fixed fatty acids.
1. Butter seized by Public Prosecutor (genuine)	33·5°	88·25	39·5°
2. Flemish butter (warmbrüchig)	37·5	88·80	39·5
3. Best Lille butter	36·0	88·89	39·0
4. Butter (Saint Amand)	36·0	88·72	40·2
5. Oleomargarin	37·0	94·0	41·0
6. "Dutch butter" (2 fr. 60 per kilo.)	37·0	94·32	41·5
7. Lard	31·5	95·17	42·5
8. Butter 75 per cent., lard 25 per cent.	37·0	90·25	40·5
9. Maize oil (sp. gr. 0·919)	—	94·67	26·0

The standard proportion of fixed acids contained in genuine butter-fat has been variously fixed by different chemists. Hehner and Angell give 87·5 per cent., Pierre Apery 88—89·5 (for Siberian butter), Bischoff 88—88·36; Fleischmann and Vieth from analyses of 185 German butters give 89·73 as maximum, Russian chemists adopt 90·00 as maximum, Ralli 85·5, and Girard 87·96. J. M. H. M.

Estimation of Salicylic Acid in Milk and Butter. By A. Rémont (*Bull. Soc. Chim.* [2], **38**, 547—548).—20 c.c. of milk are taken, two or three drops of sulphuric acid added, and the whole agitated so as to break the coagulum and produce a nearly homogeneous mass, which is then agitated with 20 c.c. of ether and left at rest for a time; 10 c.c. of the ethereal solution are then decanted and evaporated in an ordinary test-tube, marked to indicate a volume of 10 c.c. The residual butter is then boiled with 10 c.c. of alcohol and left to cool. A solution is thus obtained equal in volume to the milk, and containing all the salicylic acid originally in it. 5 c.c. are filtered off into a graduated tube of 15 mm. diameter, and two or three drops of a 1 per cent. solution of ferric chloride added; the intensity of the colour is then compared with that given by a pure milk to which 0·1 to 0·2 gram of sodium salicylate per litre has been added.

Butter is examined in a similar manner, 10 grams being taken and boiled with 50 c.c. of alcohol, and the liquid tested colorimetrically.

E. H. R.

Genesis of Ptomaïnes. By F. Coppola (*Gazzetta*, **12**, 511—520).—These bases were originally regarded by Selmi (*Rendiconti dell' Accad. di Bologna*, 1874), and afterwards by Schwanert (*Ber.*, 1874, 1332), as exclusively products of cadaveric putrefaction. Selmi, however, afterwards modified his opinion so far as to admit that, in cases of serious pathological alterations, they might be produced in the animal organism during life, a conclusion fully confirmed by Spica (Abstr., 1881, 294). Finally the question was further modified by the experiments of Paternò and Spica (Abstr., 1882, 741) on blood and on egg-albumin, and by those of Gautier on normal urine, all of which showed that reactions similar to those above alluded to may be exhibited by perfectly healthy animal fluids.

To throw further light on this question, the author has made a series of experiments on the physiological action of bases extracted from the blood of a healthy dog; and his conclusions are that alkaloïds extracted from healthy animal fluids, carefully protected from putrefactive alteration, may exhibit strong toxic properties, and that consequently whatever idea may be formed of the nature of the putrefactive process, the albuminoïds must be capable of undergoing certain transformations, which may give rise to the formation of poisonous alkaloïds. This being the case, it becomes a question whether among these transformations should be included those which albuminoïdal substances undoubtedly undergo in the extraction of alkaloïds by Dragendorff's process; for if this be the case, it might be alleged that the ptomaïnes are merely products of the decomposition of the albuminoïds, brought about either by chemical reagents or by putrefaction, either during life or after death; and until some process of extraction shall have been devised, incapable in itself of giving rise to the production of such alkaloïds, no satisfactory proof can be given of their presence in the normal animal organism. H. W.

New Method of Detecting Dyes in Yarns or Tissues. By J. Joffre (*Chem. News*, **46**, 211, 250, and 260).—The reagents which serve to distinguish the various dyes are nitric acid, potassium hydroxide, hydrochloric acid, ammonia, ferric sulphate, and stannous chloride. Full details of the effects produced by these reagents on a very large number of dyes are given, but for these reference must be made to the article itself. E. W. P.

Technical Chemistry.

Flameless Combustion. By T. Fletcher (*Dingl. polyt. J.*, **246**, 293—295).—In experimenting with gas and air burners, the author found that the smaller the flame produced, the greater the heating effect which could be obtained from the consumption of a given quantity of gas. This result led him to reduce the flame as much as possible, and ultimately it was proved that under the most favourable conditions the flame would disappear entirely. If, for instance, a ball of iron wire be heated in the flame of a gas blowpipe, and the supply of air be gradually increased, the jet of flame will become shorter and the temperature will gradually rise. Then if after the ball has become heated, the gas tube be pinched for an instant so as to extinguish the flame, it will be found that there is a sudden increase of heat, and that the iron will be melted. A similar increase of heat during the flameless combustion is shown if a lump of fireclay be substituted for the iron wire, and petroleum vapour may be used in the place of coal-gas. The author's experiments are still in their infancy; it is hoped, however, that they will be the means of effectually utilising much of the heat at present wasted. D. B.

Removal of Fixed Glass Stoppers. (*Chem. News*, **46**, 286.) To remove these, tap and then unscrew with a wooden wrench, made of a piece of wood about 3·5 inches long and 1 inch in breadth and depth, with a piece morticed out large enough to admit the flat part of the stopper. If this and all ordinary means fail, soak the neck of the bottle and stopper in water. D. A. L.

Explosion of a Zinc Gasometer containing Oxygen. By L. Pfaundler (*Ann. Phys. Chim.* [2], **17**, 176).—On testing with a spill a sample of oxygen gas which had been kept for six months in a zinc gasometer, a violent explosion took place. As the introduction of hydrogen or coal-gas was precluded by the column of water within the gasometer, the author considers that this water gradually absorbed the acid vapours of the laboratory, which thus acted upon the zinc, and liberated hydrogen. This view was confirmed by the observed corrosion of the zinc. In order to prevent this, the author suggests that the surface of the zinc should be preserved by a coating of varnish.

V. H. V.

Recent Progress in the Soda Industry. By G. Lunge (*Dingl. polyt. J.*, **246**, 334—343, 383—390, 416—423, and 520—532).—In the introduction to this extensive paper, the author mentions that although most of the subjects have already been published elsewhere, the information is in many cases so imperfect, that it was thought desirable to discuss this important question more minutely. In the first place attention is called to the want of uniformity in specific gravity tables, a question which affects, not only the soda industry, but almost all other branches of technical chemistry. Messel has compiled a table showing the wide differences in the specific gravity of sulphuric acid and ammonia obtained by various investigators. Squire calls attention to the fact that the tables published in books are drawn up for pure substances, and are therefore often useless for commercial products. The author cannot agree with Messel, who states that the differences can hardly arise from impurities in sulphuric acid made from sulphur.

Referring to gas generators, the author quotes as a novelty, Wilson's gas producer, used in England for steel furnaces, copper-smelting furnaces, glass and porcelain furnaces, and applied to Mactear's decomposing furnace.

As to the progress made in the manufacture of sulphuric acid from pyrites, it is mentioned that the so-called shelf-burners, which are generally used in Germany, are now coming into extensive use in England. The process of Benker and Lasne, based upon the introduction of sulphurous anhydride and steam into the chamber exit gases before they reach the Gay-Lussac tower, does not appear to have given satisfactory results. The use of potassium nitrate in the form of an aqueous solution has also been abandoned.

Lovett, in a paper on the testing of noxious vapours, describes a number of absorption-apparatus and several forms of aspirator (*J. Soc. Chem. Industry*, 1882, 209).

Referring to Hurter's dynamic theory of the manufacture of sulphuric acid, the author points out that it must be considered a most valuable research in pure chemistry. Hurter attempts to show, according to mathematical principles, the connection which exists between the dimensions of the chambers, the composition of the gases, the intensity of the reaction, and the consequent temperature in the chambers, as depending on the method of combining single chambers into sets. He thinks he has been successful in finding a law applicable to more complicated reactions, which he expresses in the following words:—"The rate of chemical change depends on and is proportional to the facility with which groups of molecules favourable to the particular change can form in the system in which the change occurs." Hurter does not give the deduction itself, but merely a differential equation based thereon, into which he introduces the amount of sulphurous anhydride, oxygen, water, and nitrogen compounds, in order to find the dynamic equation representing the rate of the formation of sulphuric acid in the chambers. He obtains the following results:—

1. As the chamber space is increased in arithmetic progression, the amount of sulphurous anhydride not converted into sulphuric anhydride decreases in geometric progression.

2. The chamber space for a given fixed loss of sulphur is proportional directly to the velocity of the gas, or, what is the same thing, to the amount of sulphur burnt.

3. The chamber space is inversely proportional to the nitrogen compounds and aqueous vapour present.

Hurter's conclusions as to temperature show that the excess of temperature of the chambers over the surroundings for successive chambers decreases in geometric progression, and that the temperature of the leading chamber depends on the number of chambers which are connected into one system.

In discussing the manufacture of sodium sulphate, Lunge mentions that the substitution of machine power for manual labour is becoming more and more of an accomplished fact. In England the processes of Jones and Mactear are competing with each other. Since the construction of the furnace devised by Jones and Walsh has been altered, this furnace is said to work satisfactorily, although it is less generally employed than Mactear's salt cake furnace. In general construction this furnace is very similar to Mactear's carbonator, there being, however, no central opening, but a central division or pot, into which the salt and acid are continually fed. This pot serves as a mixing vessel, from which the thin pasty mass flows over into the first division of the bed, where the first stage of the process is completed. It then passes successively through the other division until it reaches the outer circumference of the furnace, where it passes into the delivery trough which runs all round the furnace, and is luted to prevent escape of gas. The materials are mixed by means of an agitator placed between the two flues, through which the acid vapours mixed with the products of combustion pass away to the condensers. The heating of the furnace may be carried out as most convenient, care being taken to obtain thorough combustion, so as to prevent soot being passed on into the condensers. The great advantage of this continuous system of decomposing salt is to be found in connection with the condensation of the hydrochloric acid. The salt-cake as it is withdrawn is almost entirely free from smell or acid vapour; there is no difficulty in making sulphate of 97 per cent. from common white salt. The advantages may be summarised as follows:—Reduced cost of labour and fuel, and economy of sulphuric acid. Complete condensation without wash-towers, no weak acid being produced. Hydrochloric acid formed of greater strength than by an open furnace, and equal to the best form of close furnace. Complete removal of nuisance caused by escapes of acid vapours during the working or discharging. Small amount of wear and tear, and low cost for repairs. Better quality of salt cake, rendering it specially suitable for glass-making purposes. Ability to use rock salt alone. Less outlay for plant to decompose a given amount of salt and condense all the acid. Referring to the decomposition of salt in hand-furnaces, Deacon's furnace has been introduced into most works using muffle furnaces.

According to Weldon, the preparation of anhydrous sodium sulphate from crystallised Glauber salt by Pechiney's process, is effected on a large scale in the following manner:—At the salt-work of Giraud, the mother-liquor left after the salt has crystallised from the salt water when subjected to cooling, deposits large quantities of sodium sulphate, associated with 10 atoms of water. Pechiney adds to Glauber salt a certain proportion of "sels mixtes," *i.e.*, a mixture of sodium chloride and magnesium sulphate, which is deposited during the concentration of the mother-liquor to 35° B. by sun heat. The mixture is then introduced into iron cylinders, and heated to 70—80°. When a temperature of 35° has been attained, the contents of the cylinders are found to have become a mixture of anhydrous sodium sulphate with a saturated solution of "sel mixte," the latter having dissolved in what was the water of hydration of the sodium sulphate. The whole is then machined at a temperature not under 35° (hence Pechiney's object in heating to 70—80°), when the full quantity of anhydrous sulphate corresponding to the hydrated sulphate treated is obtained. The whole process is performed in a very short time, and its only cost is for a small amount of labour and steam. The solution filtered from it is employed for the production of more hydrated sulphate.

Parnell has made a series of trials on the action of potassium nitrate in the manufacture of caustic soda, the results of which confirm the conclusion previously arrived at, namely, that the ammonia evolved from the boiling liquors in the Leblanc process is due to cyanide, and does not arise from the decomposition of the nitrate.

Referring to the improvements in the manufacture of chlorine, Lunge mentions Strype's process of purifying hydrochloric acid from sulphuric acid by means of calcium chloride. This method, which is worked successfully at Wicklow, consists in adding to the hydrochloric acid in the cold about 20 per cent. of its volume of the solution of calcium chloride, obtained as a bye-product in the Weldon process. Thus almost the whole of the sulphuric acid originally present in the hydrochloric acid is precipitated, and may be separated by filtration.

In the manufacture of potassium chlorate, as at present ordinarily conducted, there is a loss of from 15—25 per cent. of the total chlorate produced. According to Pechiney's improved method, this loss is reduced to below 5 per cent. The improvement in question was devised for the purpose of reducing the cost of preparing sodium chlorate, now extensively used in the printing of aniline-black. Pechiney, in investigating the solubility of a mixed solution of sodium chlorate and chloride, found that, not only does the solubility of sodium chlorate increase with the temperature, but it increases to such an extent that mere concentration by evaporation of a mixture of these salts will cause practically the whole of the sodium chloride to fall down, leaving sodium chlorate alone in solution. The disadvantages of this process are: the large amount of sodium sulphate required by the reaction $CaCl_2O_6 + 5{\cdot}5CaCl_2 + 6{\cdot}5Na_2SO_4 = 2NaClO_3 + 2NaCl + 6{\cdot}5CaSO_4$; the unavoidable loss of sodium chlorate; its separation from the large amount of calcium sulphate; and the expense of evaporating the wash waters. The presence of so large a proportion of sodium chloride was a further cause of loss of chlorate. Pechiney surmounted these difficulties by removing the 5·5 molecules $CaCl_2$, which are unavoidably formed in the preparation of 1 molecule $CaCl_2O_6$, and thereby reducing the quantity of calcium sulphate and sodium chloride considerably. The method consists in evaporating the crude chlorate liquor until its density is 48° B. The liquor is then cooled to 12°. Of its 5·5 mols. of calcium chloride, 4·3 mols. are thus caused to crystallise out as $CaCl_2,2H_2O$. The concentrated solution must be cooled to at least 12°, or this proportion would not be separated; it must not, however, be cooled below 10°, or calcium chlorate would be deposited as well. The crystals obtained between these limits of temperature are free from calcium chlorate, and are of a nature permitting them to be separated completely from their mother-liquor by means of the hydro-extractor. The mother-liquor consists of 1 mol. $CaCl_2O_6$, and 1·2 mol. $CaCl_2$. It is diluted with its own volume of water, treated with three times 1·2 mol. lime, and heated to 80°, to determine the formation of calcium oxychloride. It is then cooled and filtered. The filtrate consists of a solution of 1 mol. calcium chlorate and only 0·3 mol. calcium chloride, and thus contains one-eighteenth of the proportion of calcium chloride originally present, so that the above-mentioned loss is considerably reduced.

In conclusion, the author discusses the recovery of sulphur from soda-waste. At Salindres, Pechiney simply injects air into the liquor by the aid of a Körting's injector, and then when oxidation has just reached the point at which treatment of the product by an acid would not cause evolution either of sulphuretted hydrogen or of sulphurous anhydride, he decomposes the product by hydrochloric acid. During the operation of oxidising the liquor, there occurs a considerable precipitation of lime, in a peculiarly dense state, and readily separable. Owing to this separation, the quantity of hydrochloric acid is appreciably reduced. Kingzett recommends to dry the soda-waste in the air, then grind it, and finally melt it with coal-tar pitch, for the purpose of asphalt-making. After referring to Mond's sulphur recovery, Lunge describes and discusses at length the process invented by Schaffner and Helbig, as recently reviewed by Weldon (*J. Soc. Chem.*

Industry, 1882, 45), and Chance (*J. Soc. Arts*, 1882, 727; and *J. Soc. Chem. Industry*, 1882, 264). D. B.

Improvements in the Preparation of Alkalis. (*Dingl. polyt. J.*, **246**, 279—285.)

Analytical Methods.—In dissolving iron pyrites or similar sulphur ores, Lunge uses nitric acid of a density not exceeding 1·42, and to avoid the separation of sulphur and facilitate the oxidation, $\frac{1}{3}$ vol. of hydrochloric acid is added to the mixture. The same investigator recommends the use of phenacetolin instead of the barium chloride method for determining carbonated in the presence of caustic alkalis. The barium chloride method was found to give satisfactory results when the quantity of carbonic anhydride present was small; in the case of caustic liquors, however, inaccurate results were obtained; phenacetolin is preferable, although there is a certain amount of doubt in determining the end reaction. With crude soda-liquors containing much sodium carbonate, and only a small amount of caustic soda, the barium method is almost useless. When phenacetolin is used, the titration should be continued until a red colour is produced, which indicates the complete saturation of the sodium hydroxide. Sodium sulphide does not interfere with the reaction, so that solutions containing it can be titrated direct for alkalinity; ammonia, however, behaves differently, giving a red colour immediately after its addition. For titrating the oxidisable sulphur compounds in crude soda-liquors with iodine, Lunge recommends to dilute 5 c.c. to 200 c.c., then add starch solution, acidify with acetic acid, and titrate as rapidly as possible with iodine solution. In titrating alkaline ferrocyanides with copper sulphate according to Hurter's method (*ibid.*, **243**, 489), depending on the oxidation with calcium hydrochlorite, it is better to add a concentrated solution of calcium hypochlorite or bromine-water from a burette, until the mixture ceases to give a blue colour with iron chloride. A second portion is then treated with the same quantity and titrated with copper sulphate, until a distinct pink coloration is produced, with a dilute solution of ferrous sulphate. In calculating the results according to Schæppi's formula, only 84·1 per cent. of the quantity actually present is obtained, due to the fact that Schæppi, instead of basing his calculation on the molecular weight of cupric oxide (79), assumed the atomic weight of copper (63).

Combined Process of Leblanc and Ammonia-Soda Manufacture.—According to Schaffner and Helbig, the soda residues obtained in the Leblanc process are treated with magnesium chloride. The magnesium hydroxide formed and that precipitated by the addition of slaked lime or dolomite to the magnesium chloride are used to evolve ammonia from the ammonium chloride liquors of the ammonia-soda manufacture, magnesium chloride being again formed. According to Solvay the bicarbonate obtained in the ammonia-soda process always contains water, and on heating becomes pasty, forming troublesome deposits in the apparatus used. This difficulty is overcome by adding a certain quantity of calcined soda to the bicarbonate. It is further recommended to utilise the natural basic phosphates in the manufacture of soda and potash by the ammonia process. The crude phosphates are ground, washed with water, in order to remove the calcium carbonate, burnt, and used for the recovery of ammonia from the ammonium chloride.

Korndorff has patented a process for recovering potassium chloride by means of calcium chloride or solutions containing it, in dissolving carnallite raw salts, instead of using water, or solutions of magnesium chloride containing potash. Thus the magnesium sulphate is prevented from being dissolved, the result being that the solution on crystallisation yields a purer potassium chloride.

According to Meyer, potassium sulphate is prepared from schoenite in the following manner:—The separation of both salts is effected by boiling a hot saturated aqueous solution of schoenite with an excess of schoenite salt, potassium sulphate being separated, whilst a corresponding quantity of magnesium sulphate is dissolved. On evaporation, crystals of schoenite are obtained, and subsequently crystals of magnesium sulphate, which are separated from the mother-liquor at 25—30°. If allowed to cool below this temperature, the potassium sulphate contains schoenite.

Grüneberg extracts schoenite from kaïnite by means of a saturated solution of sodium chloride. The latter dissolves at 80—100°, nearly one-half its weight of schoenite from kaïnite. From this solution schoenite crystallises almost completely on cooling. The mother-liquor, if not too rich in magnesium chloride, may be used for a further extraction. It suffices to lixiviate the mass three times, or the process may be made to work continuously. The greater portion of the magnesium chloride is contained in the first extract, and is used either in the manufacture of potassium chloride or recovered on evaporation.

Wittgen and Cuno have patented a process for preparing potassium carbonate from potassium chloride by forming carbonate of zinc and potassium, and decomposing it with water. D. B.

New Mineral Manure Deposits. By P. GRIGORJEFF (*Chem. Centr.*, 1882, 809).—In many districts in Russia there are extensive deposits of the so-called Ancella-Schicht. The author has examined the green sandstone and the sand of this deposit from four places in the Rjazansehen Gubernie. The sandstone contains (besides a small quantity of clay) 57·91—62·59 per cent. of a cement consisting of calcium phosphate and carbonate and brown hæmatite; the sand contains 18·03—27·04 per cent. of the cement. The sandstone is composed of 47·13—50·41 per cent. calcium phosphate (which forms 75·49—86·63 per cent. of the cement.), 19·18—24·96 per cent. glaukonite, and 5·2—14·5 per cent. quartz. The sand contains 40·12—42·23 per cent. glaukonite. These are very valuable manures, especially the sandstone, which contains easily decomposible silicates containing 8 per cent. potash. D. A. L.

Production of Pozzolana. By L. DEMARCHI and O. FODERA (*Dingl. polyt. J.*, **246**, 540).—In the *Journal of Engineering and Mining*, **34**, 45, the occurrence and production of pozzolana at Rome and Naples is described. The following is the composition of pozzolana occurring near San Paolo:—

SiO_2.	Al_2O_3.	MgO.	Fe_2O_3.	CaO.	H_2O.	Alkalis and volatile substances.	Sand.	
47·66	14·33	3·86	10·33	7·66	7·03	4·13	5·00	= 100·00

From 15—45 per cent. of lime is added, the quantity depending on the subsequent application of the cement, *e.g.*, for the production of hydraulic cement, an addition of 18 per cent. lime is required.

D. B.

English Cement. (*Dingl. polyt. J.*, **246**, 539).—The following are analyses of samples of cement from the Folkestone (I and II, taken in March, 1880, and September, 1881, respectively) and Thames, (III, taken in 1881) Cement Works:—

	Insoluble.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.
I........	1·260	20·990	8·869	4·998	61·350	0·669
II........	2·566	18·917	8·763	4·412	62·472	0·841
III........	2·894	21·307	6·593	5·386	61·459	0·449

	SO_3.	K_2O.	Na_2O.		
I........	0·886	0·978	—	=	100·000
II........	0·929	1·100	—	=	100·000
III........	1·422	0·437	0·429	=	100·376

D. B.

Portland Cement and its Adulteration. By W. Michaëlis (*Dingl. polyt. J.*, **246**, 390—391).—The author has made a series of experiments as to the effect of additions of trass, Roman pozzolana, blast-furnace slag, glass and flint, on the tenacity and durability of cement, which show that these substances by no means always produce a beneficial effect, and that some of them only set very slowly with lime, and harden very gradually. How far such addition may be made depends on the composition of the cement itself, and on the body chosen for admixture with it.

The practice of German cement manufacturers to adulterate their finely powdered Portland cement with foreign and less valuable substances, such as blast-furnace slag, trass, chalk, or limestone, and to sell this mixture as Portland cement, having been carried too far, it was resolved, at a meeting of the Society of German Cement Manufacturers, to consider the sale of cement adulterated with foreign bodies of less value as a fraud on the buyers, unless the nature of the mixture be made clearly known on sale and delivery. Additions up to 2 per cent. of the weight which are made with the object of imparting especial properties to the cement, are not to be regarded as adulterations.

D. B.

Process for Rendering Cement and Lime less subject to Atmospheric Influences. By E. Puscher (*Dingl. polyt. J.*, **246**, 539).—The author recommends that the cement materials should be allowed to remain in a cold solution of 1 part ferrous sulphate in 3 parts of water for 24 hours, after which they are dried in the air. The compound of iron hydroxide formed renders the cement firmer and harder, and less subject to atmospheric influences.

D. B.

Tellurium in Copper. By T. EGLESTON (*Chem. News*, **47**, 51—52).—The author has examined a sample of copper which was "red-short," and in the process of refining gave off dense white fumes, which "poisoned" the furnaces, rendering them unfit for refining purposes. The cold metal is tough and malleable. The cause of this mischief is the presence of tellurium, of which substance the "matte" contained 0·12 per cent., the "black copper" 0·095 per cent., the "refined copper" 0·083 per cent. The copper as it comes from the mould has every appearance of being good, but if repeatedly heated and left to cool in the air, it becomes covered with tellurium oxide. This, the author thinks, is the first time tellurium has been detected in commercial copper, and he is surprised that such small quantities should make the metal red-short. D. A. L.

Novelties in the Iron Industry. (*Dingl. polyt. J.*, **246**, 433—438, 474—483, and 508—513).—At the meeting of the Iron and Steel Institute recently held at Vienna, a paper was read by G. J. Snelus "On the Chemical Composition and Testing of Steel Rails." The author refers to the investigations of Smith and Dudley, who conclude that soft steel rails, *i.e.*, rails with low tensile strength and considerable extension are the most durable. For such rails, Dudley gives the following composition:—Carbon, 0·300; silicon, 0·040; phosphorus, 0·100; manganese, 0·350. In spite of the apparently conclusive proofs as to the superiority of soft steel rails, the North Eastern Railway Company, among others, uses a harder material having the following composition:—Carbon not under 0·3 or over 0·45 per cent.; silicon, 0·06; phosphorus, 0·06; sulphur, 0·06. Besides these substances, the steel should contain only iron and manganese. The author is of opinion that as hard rails break more easily, it is best to use the softer kinds. He, however, objects to Dudley's formula as being difficult to work to and very expensive. He considers the production of sound castings free from porous and blistered places to be the most important point, and mentions that with the use of Dudley's formula it would scarcely be possible to obtain this result. Sound castings can be produced only by using more carbon, silicon, or manganese.

Referring to the question as to the presence of phosphorus in steel, all evidence shows that it is a most vital one.

The author recommends the following formula:—Carbon, 0·35; silicon, 0·10; phosphorus as low as possible, but not above 0·075; manganese, 0·75.

In conclusion, some remarks are made in connection with the testing of steel rails.

In a paper read by G. L. Bell on blast-furnace practice with coke and with charcoal, the author states that the comparison of blast-furnace statistics is a difficult matter, as there are so many quantities variable—ore, flux, fuel, and temperature—that it requires the greatest possible caution to enable the effect of any one single change to be really identified. Nevertheless, it is clearly proved that Austrian charcoal furnaces are worked with much less fuel per ton of pig iron made than coke furnaces in England. Whereas also in Cleveland a blast furnace produces about 30 tons of grey iron per week per 1,000 cubic feet capacity, and in Luxembourg with similar ore about 50 tons, and in England with hæmatite 50—55 tons; in Vordernberg, the charcoal furnaces are driven so as to produce 73 to 93·5 tons white iron, and in America even still more heavily. The paper examines minutely the probable causes and effects of these different methods of working.

The most notable paper read during the meeting at Vienna was that by J. Gjers, on the rolling of steel ingots with their own initial heat without the use of fuel, by means of the so-called soaking pits. Bessemer in 1856 showed that it was possible to produce malleable steel direct from liquid cast iron without the expenditure of any fuel except that which already existed in the fluid metal. The author has supplemented this work by devising a method which enables him to roll such steel into a finished bar with no further expenditure of fuel. It is known that the fluid metal poured into the mould contains a larger amount of heat than is required for the purpose of rolling or hammering. This heat is composed not only of the high temperature of the fluid metal, but also the store of latent heat in the same, which is liberated when solidification takes place. All attempts hitherto made with a view of utilising this heat of the ingot have proved failures. The difficulty depends on the fact that a steel ingot when newly stripped is far too hot in the interior for the purpose of rolling, and if it be allowed to cool the exterior becomes too cold to enable it to be rolled successfully. The author introduced his new mode of treating ingots at the Darlington Steel and Iron Company's works in June, 1882.

It is carried out in the following manner. A number of upright pits are built in a mass of brickwork sunk in the ground below the level of the floor. These pits are in connection with an ingot crane. Each pit is covered with a lid at the floor level, and after having been well dried and heated to redness, is ready for operation.

As soon as the ingots are stripped they are transferred one by one and placed separately, by means of the crane, in the previously heated soaking pits and covered with the lid to exclude the air. In these pits, the ingots are left to stand and soak, *i.e.*, the excessive heat of the interior becomes uniformly distributed throughout the metallic mass. Comparatively little heat being able to escape, as the ingot is surrounded by red-hot brickwork, the surface-heat of the ingot is greatly increased, and after the lapse of from twenty to thirty minutes, the ingot is lifted out of the pit and swung round to the rolls by means of the crane. The advantage gained is that the ingot is always certain to be at least as hot in the centre as it is on the surface. Every ingot when cast contains a considerably larger store of heat than is necessary for the rolling operation; this surplus from successive ingots going into the brickwork of the soaking pits tends continually to keep the pits at the intense heat of the ingot itself.

During the soaking operation, a quantity of gas exudes from the ingots and fills the pit, thus entirely excluding the air. This gas being composed of hydrogen, nitrogen, carbonic oxide, and carbonic anhydride, protects the ingots from oxidation. D. B.

Tungsten Steel. (*Chem. Centr.*, 1882, 783).—When tungsten is mixed with steel during the final stage of preparation, a very characteristic alloy is obtained. Steel with 10 to 12 per cent. tungsten is so hard that it cannot be worked at the lathe nor can it be filed; it may, however, be forged and polished. Steel with 5 to 6 per cent. is still hard, but can be worked. Tungsten steel can be highly magnetised, and magnets made from it show extraordinary power. Muchet's patent steel contains tungsten. Tools made from tungsten steel are forged into form and then ground, and are extremely hard. Steel is improved by the addition of small quantities of tungsten.

D. A L

Composition of Firwood Charcoal. By L. RINMAN (*Dingl. polyt. J.*, **246**, 472).—One gram of the charcoal contained 0·053 water. Composition:—

C.	CO_2.	CO.	CH_4.	H.	H_2O.	Ash.
81·5	4·8	4·9	1·8	0·7	5·3	1·0

About 0·5 per cent. nitrogen and air may be considered as adhering to the charcoal. By excluding the water and ash we obtain for 100 parts of charcoal the following numbers:—

		C.	O.	H.
C..........	87·0	87·0	—	—
CO_2.......	5·1	1·4	3·7	—
CO........	5·3	2·3	3·0	—
CH_4.......	1·9	1·45	—	0·45
H.........	0·7	—	—	0·70
	100·0	92·15	6·7	1·15

D. B.

Examination of Galician Petroleum. By A. NAWRATIL (*Dingl. polyt. J.*, **246**, 328—334, and 423—429).—The author has investigated 18 varieties of Galician petroleum, obtained direct from the springs. The following are the properties of the samples analysed:—

1. Petroleum from Klenczany. Colour light reddish-yellow, with green fluorescence, transparent. Sp. gr. at 15° 0·779.

2. Petroleum from Ropa. Brownish-red with green fluorescence, transparent. Sp. gr. 0·808.

3*a*. Petroleum from Ropa. Transparent, reddish-brown with green fluorescence. Sp. gr. 0·800.

3*b*. Petroleum from Ropa. The same as 3a. Sp. gr. 0·853.

4. Petroleum from Wojtowa. Non-transparent, greenish-black. Sp. gr. 0·820.

5. Petroleum from Wojtowa. The same as 4. Sp. gr. 0·836.
6. Petroleum from Libusza. Greenish-black. Sp. gr. 0·837.
7. Petroleum from Senkowa. Greenish-black. Sp. gr. 0·837.
8. Petroleum from Libusza. Greenish-black. Sp. gr. 0·842.
9. Petroleum from Starunia. Greenish-black. Sp. gr. 0·845.
10. Petroleum from Siary. Blackish-brown. Sp. gr. 0·847.
11. Petroleum from Pagorzyn. Brownish-black. Sp. gr. 0·849.
12. Petroleum from Lipiniki. Greenish-black. Sp. gr. 0·850.

13. Petroleum from Siary. Brownish-black. Sp. gr. 0·853.
14. Petroleum from Mencina. Greenish-black. Sp. gr. 0·853.
15. Petroleum from Klenczany. Dark green. Sp. gr. 0·870.
16. Petroleum from Kryg. Brownish-black. Sp. gr. 0·876.
17. Petroleum from Harklowa. Brownish-black. Sp. gr. 0·898.
18. Petroleum from Harklowa. Brownish-black. Sp. gr. 0·902.

These oils were subjected to fractional distillation, and the results are tabulated. The table, which is too long for insertion here, gives the sp. gr. of the fractions obtained at 50° to 100°, 100° to 150°, 150° to 200°, 200° to 250°, 250° to 300°, 300° to 350°, 350° to 400°, and above 400°, with the percentage proportions of gum, coke, and loss. The following table, which is a condensation of the first, gives the percentages of the products separated, including coke and loss:—

Sample.	Light oils, distillates up to 150°.	Petroleum distillates from 150°—300°.	Heavy oils, distillates above 300° + gum.	Coke and loss.
1......	43·5	33·5	22·85	0·15
2......	26·6	42·0	30·40	1·00
3*a*	27·5	34·2	37·00	1·30
3*b*.....	11·4	39·8	46·50	2·30
4......	12·4	43·6	41·50	2·50
5......	13·5	50·3	34·30	1·90
6......	19·0	29·2	47·10	4·80
7......	22·0	37·4	30·10	2·50
8......	13·3	32·8	49·40	4·00
9......	10·9	34·9	50·90	3·30
10......	20·0	31·2	43·3	5·5
11......	9·8	45·4	40·6	4·2
12......	20·9	30·3	44·0	4·8
13......	11·3	31·9	52·3	4·5
14......	19·6	33·1	42·9	4·4
15......	3·4	38·6	54·5	3·5
16......	8·0	32·6	53·2	6·2
17......	6·7	28·2	58·2	6·9
18......	5·7	29·1	56·7	7·5

D. B.

New Source of Benzene, Naphthalene, and Anthracene. (*Dingl. polyt. J.*, **246**, 429—432).—According to Liebermann, the manufacture of benzene, naphthalene, and anthracene, from petroleum residues, is worked on a large scale by Nobel Brothers, of Baku. Although the quality of the anthracene and naphthalene compares favourably with the same products derived from coal-tar, the benzene boiling between 80° and 85° contains large quantities of foreign hydrocarbons, and is not suitable for the preparation of nitrobenzene. It is proposed to purify it by freezing out the benzene. The residues at Baku are heated in red-hot iron retorts filled with pumice stone, the gas produced being used for heating and lighting purposes. As byeproduct, a tar resembling coal-tar, is obtained. 1000 kilos. naphtha residues yield about 500 cubic meters of gas, and 300 kilos. tar containing 4—5 per cent. benzene and toluene, and 0·6 per cent. crude anthracene. D. B.

Carbon Bisulphide. By L. H. Friedburg (*Chem. News*, **47**, 52).—The author gives some facts in addition to those already published (*Ber.*, **8**, 1016). *Dinitrobenzene* (m. p. 84°) is formed amongst other products when bisulphide of carbon, charged with nitric peroxide, is mixed with pure benzene. When this same mixture is exposed to direct sunlight, the inside of the glass above the liquid becomes covered with small white crystals, which decompose when brought in contact with the air, yielding nitric peroxide and benzene. The author suggests that they are possibly nitro-addition products of the character of benzene hexchloride, $C_6H_6(NO_2)_4$ or $C_6H_6(NO_2)_6$. When carbon bisulphide charged with sulphurous anhydride, and the same medium charged with nitric peroxide (not free from nitrous acid), are brought together in a cool dry beaker, white crystals form in considerable quantities; these are nothing but lead-chamber crystals of the sulphuric acid works. Carbon bisulphide which has been cleansed with fuming nitric acid, has sp. gr. 1·266 at 15°, and b. p., at 760 mm., 47·4°. The author has always detected nitrobenzene as one of the products of this treatment of crude bisulphide with nitric acid: he therefore considers that benzene is one of the products formed during the manufacture.

The author recommends that, in extracting oils with bisulphide, excess of the latter should be avoided, and that a mixture of oils and bisulphide should never be run into a still containing oil freed from this substance. D. A. L.

Preservation of Wine by Salicylic Acid. By D. Denucé (*Bied. Centr.*, 1882, 859).—The addition of 10—40 grams of salicylic acid to every hectolitre of wine is not deleterious. E. W. P.

Amount of Carbonic Acid in Beer. By T. Langer (*Dingl. polyt. J.*, **246**, 487).—Beer, rich in carbonic acid, is obtained by using a wort rich in maltose, and containing a small amount of peptones. It is also necessary to work with strong yeast, a proportionate quantity being introduced into the casks: the fermentation should not be allowed to go too far, whilst the temperature should be kept as low as possible. The brewer's task therefore is to produce, absorb, and preserve, carbonic acid in beer, whilst the publican's business is to handle the beer with the utmost care, to avoid all possible loss of gas. D. B.

The Ferment of Chica Beer. By Griessmayer (*Bied. Centr.*, 1882, 861).—The formation of this beer from maize in South America, is due to a ferment situated on the epidermis of the grain (comp. this vol., p. 365). The ferment can affect unripe starch, and resists a temperature of 95°. When the grains germinate, the vibrio developes in its interior. Eurotium belongs to the same category of ferments, being capable of saccharifying and fermenting. E. W. P.

The Strontia Process for the Separation of Sugar from Molasses. By C. SCHEIBLER (*Bied. Centr.*, 1882, 848).—This is a more detailed account of the process previously described. Molasses are dissolved in water with 3 mols. crystallised strontium hydroxide per 1 mol. sugar. After heating, the strontium saccharate,

$$C_{12}H_{22}O_{11},2SrO,$$

is thrown down; this precipitate, after filtration and washing with 10 per cent. strontium hydroxide solution, is treated with water, whereby it is decomposed, and the filtrate after evaporation yields crystalline sugar. To prepare the crystallised hydroxide, the carbonate is ignited at a somewhat higher temperature than that required for calcium carbonate, and then boiled with water, from which on cooling $Sr(OH)_2,8H_2O$ crystallises. The deficiency of strontianite in the market is a bar to this process, but it is hoped that cælestin, of which there is a large supply obtainable from Sicily, may in time be made use of. E. W. P.

Action of Dibromonaphthol on Amines. By R. MELDOLA (*Chem. News*, **47**, 27).—The dibromonaphthol (m. p. 111°), obtained by the action of bromine on α-naphthol, acts as a powerful oxidiser when heated with certain amines; thus it converts diphenylamine into diphenylamine blue. The author has tried its action with various other amines. Thus when dibromo-α-naphthol is dissolved in aniline and heated at 140° for about 30 minutes, an orange colour is developed, and on adding alcohol a basic substance separates out in large orange needles. Similar bases are obtained from paratoluidine and β-naphthylamine. These bases are soluble in hot dilute acids with a crimson colour; they form well characterised salts and bronzy crystalline platino- and zinco-chlorides.

In the course of the author's present research, he has observed the following colour-reactions with dibromonaphthol and other haloïd derivatives of phenols. With α-naphthylamine and with cumidine dibromonaphthol gives colours dissolving in alcohol with magenta-red; with resorcinol, it gives a reddish-brown. When monobromo-β-naphthol is heated with α-naphthylamine, it gives a red; tetrabromo-β-naphthol readily gives diphenylamine blue; and with α-naphthylamine a violet. Tribromophenol gives diphenylamine-blue with diphenylamine; with α-naphthylamine a red, with β-naphthylamine a violet. Some of these compounds are now being investigated. D. A. L.

Luting for Conduct-pipes. (*Chem. Centr.* 1882, 784.) The material recommended can be used for steam, water, or gas, for pipe-joints, and is much cheaper and more efficient than red lead. It consists of equal quantities of burnt lime, cement, potter's clay, and loam. These are well dried, ground, sifted, and intimately mixed and kneaded up with linseed-oil varnish. For water-pipes, it is well to use more cement, in order to make the material still more resisting.

D. A. L.

General and Physical Chemistry.

Photometric Intensity of the Lines of the Hydrogen Spectrum. By H. LAGARDE (*Compt. rend.*, **95**, 1350—1352).—The relative intensity of the various lines in the spectrum of a gas is not constant, but varies with the temperature and pressure. The author has determined the intensity of the lines of the hydrogen spectrum under varying conditions by means of Crova's spectrophotometer (*Compt. rend.*, **93**, 512). The results obtained up to the present are given in the following table. R is the length of resistance-wire introduced into the circuit to vary the tension, and therefore temperature of the electric spark: *p* is the pressure of the gas expressed in mm. of mercury. The numbers are only relative, being compared with the intensity of the corresponding parts of the spectrum of the particular lamp used by the author, taken arbitrarily as 1000.

		Line.		
p.	R.	H_α.	H_β.	H_γ.
6·5 mm.	14	3·6	5·5	17·2
	10	6·2	7·5	18·1
	6	7·5	12·4	19·6
	2	9·5	22·6	36·7
0·542 mm.	14	8·8	25·8	65·8
	10	12·9	34·2	86·1
	6	28·3	72·5	140·2
	2	49·4	152·1	240·9
0·010 mm.	14	12·6	39·3	110·9
	10	17·8	55·0	133·8
	6	38·5	94·9	176·4
	2	76·1	183·2	289·6

L. T. T.

Stokes's Law of Fluorescence. By E. HAGENBACH (*Ann. Phys. Chem.* [2], **18**, 45—56).—By former experiments, the author established the universality of Stokes's law of fluorescence, but his results have been criticized by Lommel and Lubarsch. In the course of the present paper the author elucidates the following points:—

(1.) An oblique instead of a normal position of the spectrum apparatus to the surface of the fluorescent liquid does not cause an increase of intensity of light within the apparatus.

(2.) The intensity of light in the field of the spectroscope is independent of its distance from the fluorescent liquid, provided that the illuminated surface fills the angle of aperture of the collimator.

(3.) As regards the dependence of the colour of the light on the degree of concentration of the fluorescent liquid, the author objects to Lommel's view that with increase of concentration the more strongly absorbed constituents are more refracted than those which are less strongly absorbed.

The author has repeated his experiments and those of Lommel and Lubarsch, using sunlight, the electric light, and sodium light, and has confirmed his former results in every way. V. H. V.

Dependence of Molecular Refraction of Liquid Carbon Compounds on their Chemical Constitution. By H. Schröder (*Ann. Phys. Chem.* [2], **18**, 148—175).—This paper is an enlargement of a preliminary communication (Abstr., 1882, 910—911), and contains in a series of tables the values deduced according to Lorenz's formula of the molecular refraction for the lines H_α and H_γ, and for a ray H of infinite wave-length. These values confirm the results noted in the former paper.

I. *The Refraction equivalent in the case of Homologous Substances increases with Molecular Weight.*—An increase of CH_2 causes an increase of about 4·5, of O about 1·5, and of chlorine replacing hydrogen about 4·7.

II. *Metameric Substances at the same Temperature have not identical, but only approximately, equal Molecular Refraction.*—Thus, according to Lorenz's formula, the molecular refraction of the acids of the acetic series is somewhat less than the ethereal salts metameric with them, but according to the old empirical formula of Landoldt the reverse is the case. Again, the normal compounds possess a somewhat smaller refraction-equivalent than the isomeric iso-compounds, and this relation is also reversed by the adoption of the old formula.

III. *The Atom Refraction of the Elements Carbon, Hydrogen, and Oxygen stand in a simple relation.*—(1.) In every compound CO has the same effect as CH_2. Thus the molecular refractions of propionic acid and propyl alcohol, of butyric acid and butyl alcohol, &c., are identical. (2.) In acids and ethereal salts O_2, and in alcohols HOH, have the same effect on the molecular refraction as CH_2. (3.) The atom-refraction of O in OH has one-third the effect of CH_2. (4.) The doubly-bound carbon-atom has an atom-refraction twice as great as the singly-bound carbon-atom.

For examples the reader is referred to the former abstract (*vide supra*).

IV. *Aromatic Compounds.*—The peculiar dispersive power of the aromatic compounds has been noticed by Brühl and others. The author shows that on comparing aromatic compounds containing the same number of hydrogen- and oxygen-atoms, but differing from one another by four carbon-atoms, differ by ten refraction steres thus:—

	Mr.A².
Phenol, $C_6^{12}H_6^6O_1^1$	26·72 = 19 × 1·4
Ethyl alcohol, $C_2^2H_6^6O_1^1$...........	12·47 = 9 × 1·386
Benzoic aldehyde, $C_7^{13}H_6^6O_1^2$......	30·29 = 21 × 1·442
Acetone, $C_3^3H_6^6O_1^2$	13·71 = 11 × 1·428
Ethyl benzoate, $C_9^{15}H_{10}^{10}O_2^3$........	40·72 = 28 × 1·455
Methyl butyrate, $C_5^5H_{10}^{10}O_2^3$	26·29 = 18 × 1·46
Ethyl hydrocinnamate, $C_{11}^{17}H_{14}^{14}O_2^3$	50·85 = 34 × 1·495
Ethyl valerianate, $C_7^7H_{14}^{14}O_2^3$......	35·98 = 24 × 1·499

Again, on comparing the molecular refraction of the aromatic hydrocarbon and the paraffinoid alcohols containing the same number of hydrogen-atoms, a difference of molecular refraction of nine steres is observed.

	Mr.A^2.
Benzene, $C_6^{12}H_6^6$	$24{\cdot}99 = 18 \times 1{\cdot}388$
Ethyl alcohol, $C_2^2H_6^6O_1^1$	$12{\cdot}47 = 9 \times 1{\cdot}386$
Mesitylene, $C_9^{15}H_{12}^{12}$	$39{\cdot}05 = 27 \times 1{\cdot}446$
Amyl alcohol, $C_5^5H_{12}^{12}O_1^1$	$26{\cdot}09 = 18 \times 1{\cdot}449$

These values show that six carbon-atoms of the phenyl grouping have a refraction constitution C_6^{12}, but that the refraction-equivalent increases with decrease of refrangibility of the ray.

Chlorine.—A chlorine-atom combined with a carbon-atom has the same effect on molecular refraction as the grouping CH_3. Thus ethyl chloracetate has the same refraction-equivalent as the ethereal salts of the formula $C_5H_{10}O_2$, and ethylene chloride as propyl chloride.

The author proposes in a future communication to bring out further relationships between the molecular refractions of the carbon compounds.

V. H. V.

Luminosity of Flame. By W. SIEMENS (*Ann. Phys. Chim.* [2], **18**, 311—316).—The luminosity of burning gases is a secondary phenomenon dependent on the separation and incandescence of solid particles suspended in the flame. Gases from which no such particles are separated, burn with a feebly luminous flame, and this luminosity is assigned to the incandescence of the gases themselves. No experiments have hitherto been made to ascertain whether pure gases heated to a high temperature really emit light. In order to examine this point, the author's brother made a series of observations with a Siemens regenerative oven of the form used in the hard glass manufacture, whereby a temperature of the melting point of steel, 1500—2000° C., could easily be attained. By a suitable contrivance the interior of the oven could be examined, and it was thus found that, provided the experimental room was kept perfectly still, the heated air in the oven emitted no light. The introduction of a luminous flame into the oven caused its interior to be only feebly illuminated. As a result of these experiments, it follows that the supposition that the luminosity of the flame is due to the incandescence of the gas is incorrect. In order to determine the temperature at which luminous flames become non-luminous, the author suggests a repetition of the above experiments with a more refined apparatus.

The author further demonstrates that the heat-rays emitted from hot gases are very small in number as compared with those emitted from equally hot solid bodies.

Observations on the behaviour of flames themselves prove equally that the luminosity of flames is not due to the incandescence of the products of combustion. If the gases to be burnt are more quickly mixed, the flame becomes shorter, since the process of combustion is accelerated, and hotter, since less cold air is mixed with the burning gas. The same phenomenon occurs if the gases are strongly heated before they are burnt; but since the ascending products of combustion are maintained for a short time only at the temperature of the flame, the above phenomenon would be reversed were the gases self-luminous. The luminous part of the flame is separated by a line of demarcation from the products of combustion, and is coincident with the termination of chemical action, which is probably the cause of the emitted light. If it be assumed that the gas molecules are surrounded with an envelope of ether, then a chemical combination between two or more of these molecules will cause a vibration of the ether particles, which becomes the starting point of the light and heat waves. The luminosity of gases when an electric current is passed through them can be explained in a similar manner, and the author has already observed that all gases are conductors of electricity when their point of so-called polarisation maximum has been reached. V. H. V.

Constitution of Electrolytes. By A. BARTOLI (*Gazzetta*, **13**, 27—34).—A theoretical paper not admitting of abstraction.

Electrolysis of Water and of Solutions of Boric Acid. By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, **13**, 35—37).—The authors find, contrary to Bourgoin (*Ann. Chem. Phys.* [4], **15**, 56 [1868]), that pure water and pure aqueous boric acid are both capable of electrolytic conduction. Bartoli showed (*Nuovo Cimento*, 1879) that pure water may be decomposed by the current of a single Daniell's element, and from experiments mentioned in the present paper it appears that a solution of boric acid saturated at 80° conducts better than water, and exhibits easily visible decomposition with a battery of a small number of Bunsen's elements. H. W.

New Experiment in Electrolysis. By E. SEMMOLA (*Compt. rend.*, **96**, 336—337).—The apparatus consists of a voltameter having three electrodes arranged in the form of an equilateral triangle, with a tube over each electrode. One of the electrodes, *c*, is connected with the positive pole of the battery, the other two, *a* and *b*, being connected with the negative pole by means of a commutator, which is so arranged that the current can be sent entirely through *a* or *b*, or can be bifurcated and sent partly through *a* and partly through *b*. The sum of the volumes of hydrogen collected in the two tubes, when the current is thus bifurcated, is equal to the volume collected in a single tube when the current is sent entirely through one of the electrodes *a* or *b*, thus proving by means of a single voltameter that the same quantity of electricity always produces the same amount of chemical decomposition. C. H. B.

Thermoelectric Properties of Minerals belonging to Various Systems. By W. G. HANKEL (*Ann. Phys. Chem.* [2], **18**, 421—428). An examination of the thermoelectric properties of the topaz has convinced the author that Hauy's view, according to which only hemimorphous crystals show a difference of potential with change of temperature, is too restricted, since experiment shows that most minerals, provided that they may be obtained in sufficiently well crystallised individuals, possess this property, and in the present communication the author describes the position of the thermoelectric poles in relation to the crystallographic axes in minerals belonging to various systems.

(I.) Regular System. *Helvin* crystallises in tetrahedrons; on cooling, the large tetrahedral faces are positively, the small faces negatively, electrified. This polarity is opposite to that observed in boracite, which crystallises in the same form. In helvin, the larger faces are more glistening than the smaller, the reverse being the case with boracite: hence it appears that the more glistening face becomes electrified positively, the less glistening face negatively.

(II.) Tetragonal System. *Mellite* resembles apophyllite and idocrase in its thermoelectric behaviour; for the ends of the primary axes become electrified positively, and the terminal edges and prismatic side-faces negatively.

(III.) Hexagonal System. *Pyromorphite* and *Mimetesite* resemble apatite, which is isomorphous with them in that the ends of the primary axes are electrified positively, whilst their prism-faces are negatively electrified. But in individuals of mimetesite, if the prism faces are overgrown, they frequently show an electropositive potential. The author formerly observed a similar reversed polarity in specimens of the beryl.

Phenacite crystallises in the rhombohedric tetratohedral modification of the hexagonal system; the terminations of the primary axes and the rhombohedral faces are electrified positively, the prismatic side-faces negatively. The reverse is, however, the case with pennine. Some specimens of *dioptase* resemble phenacite in their thermoelectric poles, whereas others resemble pennine, but observations were rendered difficult from the imperfect form of the crystals.

(IV.) Rhombic System. *Strontianite*, *Luthenite*, and *Cerussite*. The ends of the primary and brachydiagonal axes become the positive poles, but those of the macrodiagonal are the negative poles.

(V.) Monoclinic System. *Euclase* resembles gypsum in its thermoelectric properties; the ends of the vertical and clinodiagonal axes are the positive, the ends of the orthodiagonal axes the negative poles. The same position of the poles is observed in *titanite;* in this mineral the surfaces $0P$, and part of the surfaces $\frac{1}{2}Ᵽ\infty$ and $Ᵽ\infty$ are positively, and the remaining portions of the surfaces $\frac{1}{2}Ᵽ\infty$ and $Ᵽ\infty$ are negatively electrified. The author observed in 1840 that the electric polarity of crystals of titanite as of boracite undergo reversal at 112°. This phenomenon can best be observed by heating the crystals to 210°; at the commencement of cooling the ends of the orthodiagonal axis have an electronegative potential which reaches a maximum, then diminishes, and finally undergoes reversal. V. H. V.

Specific Heat of Water. By F. NEESEN (*Ann. Phys. Chem.* [2], **18**, 369—386).—The author begins his communication with a comparison of the relative value of the methods available for determination of specific heat. Of the three methods, (I) the method of mixture, (II) the method of melting of ice, (III) the method of cooling, the latter involves a source of error in the supposition that all sides of the cooling body, at every moment of time, are at the same temperature, a supposition which is never fulfilled. The author has devised a form of apparatus to obviate this source of error, and in order to render the results of observation by it more exact, he has made a series of experiments on the dependence of the specific heat on the temperature. As regards the variation of the specific heat of water with the temperature, Regnault and others observed a small increase of specific heat with rise of temperature, whilst Pfaunder and Platten found a decrease under the same circumstances, and Rowland observed a decrease from 0—30°, and from that point an increase.

In the present paper the author has re-examined this question with the aid of a Bunsen's ice calorimeter; full details are given of the form of apparatus, method of observation, determination of the specific heat of platinum and glass. It appears as a result of the experiments that the mean specific heat of water at first increases, and then decreases, but the maximum point varies according as the temperature was observed by mercury or air thermometer; with the former, the maximum is at 12°, with the latter at 20°. The author endeavoured to reduce his observations in terms of the formula $D = a(b - t)^c$, but the values deduced from this formula did not agree satisfactorily with the observed values; he puts forward with reserve the empirical formulæ $D = 14 + 8{\cdot}063(t - 2)$, from 0—20°, and $D = 167 + 7{\cdot}77(t - 21)$ above. The results of the author's observations agree qualitatively with those of Rowland obtained by the method of mixture, and a table is given in which the observations are compared. V. H. V.

Measurement of Pressures developed in Closed Vessels by the Explosion of Gaseous Mixtures. By VIEILLE (*Compt. rend.*, **95**, 1280—1282).—The author has made experiments to show that the manometric results calculated from the displacement of a piston of known diameter and mass, inserted in the wall of the vessel, gives results as good as those obtained with the usual static manometers, and is more suitable for the measurement of pressures of very short duration. L. T. T.

Momentary Pressures produced during the Combustion of Gaseous Mixtures. By MALLARD and LE CHATELIER (*Compt. rend.*, **95**, 1352—1355).—In a former communication (this vol., 148) the authors, during the combustion of gaseous mixtures, noticed the production of pressures of exceedingly short duration, but of much greater intensity than would normally be expected. They have now very carefully measured, by means of Depretz's plan of registering the displacement of a piston, the pressures produced in closed vessels. With mixtures of hydrogen and oxygen, momentary pressures of 20 atmospheres have been obtained, the normal pressure calculated relative to the temperature of combustion being but 11 atmospheres. The authors propose the following explanation. The first portion of the mixture in exploding compresses the adjoining layer. If now the velocity of propagation of ignition is sufficiently rapid, this adjoining layer of the explosive mixture will be ignited before an equalisation of pressure can take place, and hence the pressure due to this explosion will be superimposed on that derived from the first portion of the mixture. This will be repeated, the pressure in each succeeding wave becoming greater, and the momentary pressure due to one of these explosive zones will be that registered by the piston. This hypothesis is supported by the fact that the excess of pressure above the normal increases with the velocity of propagation of ignition of the mixture experimented with. This hypothesis would also explain the formation of the explosive wave discovered by Berthelot and Vieille: for supposing the pressure to increase from layer to layer, a point would be reached where the rise in temperature due to the compression would be sufficient in itself to cause ignition of the mixture, and this would then be propagated with the velocity of the propagation of the pressure. The fact that the velocity of this explosive wave is greater than that of sound under ordinary circumstances, is probably due to the intensity of compression and temperature in the exploding mixture. The duration of these excess pressures is less than one ten-thousandth of a second, and it is therefore probable that the *observed* excess pressure is much below the actual, since the motive action of even very large pressures acting on a piston for so short a time is exceedingly small. A pressure of 100 atmospheres acting for one-thousandth of a second on a piston 1 gram in weight and of 1 cq. section would displace the piston only $\frac{1}{2000}$ mm.

L. T. T.

Thermochemical Investigation on the Chlorides of Iodine. By J. Thomsen (*Ber.*, **15**, 3021—3022).—When a molecule of solid iodine unites with a molecule of gaseous chlorine to form liquid iodine chloride, the heat of combination is 11650 cal. The heat evolved by the union of a molecule of iodine monochloride with a molecule of chlorine to form the solid trichloride is 15660 cal. The heat of formation of the trichloride $I + Cl_3 = ICl_3$ is 21490 cal.

W. C. W.

Thermochemical Investigation on the Chlorides of Sulphur, Selenium, and Tellurium. By J. Thomsen (*Ber.*, **15**, 3023—3025).—The heat of formation of sulphur chloride, S_2Cl_2 (from rhombic crystals of sulphur), is 14260 cal.; of selenious chloride ($Se_2 + Cl_2$) 22150 cal., and selenic chloride, $SeCl_4$, from amorphous selenium, 46160 cal.; of telluric chloride, $TeCl_4$, from metallic tellurium, 77380 cal. The heat of formation increases therefore with the molecular weight.

W. C. W.

Method of Estimating the Heat of Formation of difficultly combustible Volatile Carbon-compounds. By J. Thomsen (*Ber.*, **15**, 2996—3000).—The heat of formation of compounds of carbon and chlorine, or of carbon, hydrogen and chlorine, may be determined by mixing the vapour of the substance with hydrogen, and burning the mixture in oxygen. The volume of hydrogen used is measured, and the weight of hydrochloric acid, water, and carbonic anhydride produced is also determined. The operation is conducted in an apparatus described by the author in his recently published book on "Thermochemical Investigations," **2**, 339. W. C. W.

Heat of Formation of the Chlorides of Phosphorus and Arsenic. By J. Thomsen (*Ber.*, **16**, 37—39).

Reaction.	Heat.	Explanation.
P,Cl_3	75300 cal.	Direct formation of chlorides from phosphorus.
P,Cl_5	104990 „	
PCl_3,Cl_2	29690 „	PCl_5 from PCl_3 and Cl_2.
$PCl_3 : Aq$	65140 „	Heat of solution.
$PCl_5 : Aq$	123440 „	
As,Cl_3	71390 „	Direct combination of arsenic with chlorine.
$AsCl_3 : Aq$	17580 „	Heat of solution.

A. K. M.

Heat of Formation of the Chlorides and Oxides of Antimony and Bismuth. By J. Thomsen (*Ber.*, **16**, 39—42).

Reaction.	Heat.	Explanation.
Sb,Cl_3	91390 cal.	Heat of formation.
Sb,Cl_5	104870 „	
$SbCl_3,Cl_2$	13480 „	$SbCl_5$ from $SbCl_3$ and Cl_2.
$SbCl_3 : Aq$	7730 „	Complete decomposition.
	8910 „	Formation of $Sb_4O_5Cl_2$.
$SbCl_5 : Aq$	35200 „	Complete decomposition.
$Sb_2,O_3,3H_2O$	167420 „	Production of SbO_3H_3.
Sb,O_2,H,H_2O	117890 „	
$Sb_2,O_5,3H_2O$	228780 „	Production of SbO_4H_3.
Sb,O_3,H,H_2O	148570 „	
SbO_3H_3,O	·30680 „	
Bi,Cl_3	90630 „	Heat of formation.
Bi,O,Cl,H_2O	88180 „	
$BiCl_3 : H_2O,Aq$	7830 „	Formation of $BiOCl,H_2O$ from $BiCl_3$.
$BiCl_3 : 3H_2O,Aq$	− 6350 „	„ BiO_3H_3 from $BiCl_3$.
$BiO_3H_3,HClAq$	+ 14180 „	„ $BiOCl,H_2O$ from BiO_3H_3.
$Bi_2,O_3,3H_2O$	137740 „	Production of BiO_3H_3.
Bi,O_2,H,H_2O	103050 „	

A. K. M.

Heat of Formation of Carbon Tetrachloride and Ethylene Perchloride. By J. Thomsen (*Ber.*, **15**, 3000—3002).—The heat evolved by the union of an atom of amorphous carbon with four atoms of chlorine gas to form a molecule of carbon tetrachloride vapour, is 21030 cal., and for liquid carbon tetrachloride 28320 cal.

The heat of formation of methane is 21750 cal., and of carbon oxide

29000 cal. Hence it appears that the affinity of chlorine and hydrogen for carbon is equally strong. The heat of formation of ethane is −2710 cal., and of gaseous ethylene perchloride −1150 cal. For liquid ethylene perchloride the heat of formation is + 6000 cal.

W. C. W.

Volume-change of Metals on Fusion. By F. NIES and A. WINKELMANN (*Ann. Phys. Chem.* [2], **18**, 364—365).—The results of the experiments made by Roberts and Wrightson show that the density of most metals is less in the liquid than in the solid state. These results are apparently in direct contradiction to those of the authors, which show that metals when liquid at their point of fusion occupy a smaller volume than when solid at the same temperature. This discrepancy is, however, only apparent, for in Roberts and Wrightson's experiments the density of the metals in the solid state were taken at the ordinary temperature, whereas those of the metals in the liquid state were taken at their point of fusion. The values so obtained are not directly comparable. But some results of Wrightson, in the case of iron and steel, agree with those of the authors. For the former physicist found that in the conversion of iron from the solid state the density of the solid metal 6·95 decreases to 6·5, the density of the plastic metal, and then suddenly increases to 6·88, the density of the liquid metal.

V. H. V.

Distillation in a Vacuum. By A. SCHULLER (*Ann. Phys. Chem.* [2] **18**, 317—325).—The author at the outset calls attention to the advantages of the automatic mercury pump; by its aid he has devised a form of apparatus to study fractional distillation and sublimation in a vacuum, and the separation of metals from impurities with which they are contaminated. In the course of his experiments the author arrives at the conclusion that sufficient attention is not paid to the substance used for lubrication, and to the so-called anhydrous phosphoric acid used as a desiccating agent; the latter contains phosphoric anhydride, P_2O_5, which sublimes at 50° in large translucent crystals. The author considers that the best substance for lubrication is a mixture of wax and vaseline, and for desiccation metaphosphoric acid. Of the elements examined, selenium, tellurium, cadmium, zinc, magnesium, arsenic, and antimony, are easily sublimed, but the fusible metals, bismuth, lead, and tin, distil only with difficulty. The author's observations on this point differ from those of Demarçay, but he explains this discrepancy by supposing that the metals used by Demarçay were contaminated with impurities, which, according to his observations, caused the volatilisation of the metals in question; but if the distillation be frequently repeated, these impurities are separated. Secondly, it is found that sodium, selenium, tellurium, cadmium, zinc, arsenic, and antimony, distil so readily in a vacuum that this process may be used for their purification. Thirdly, during the first distillation of these metals, there is an evolution of gas, but this ceases after the process has been repeated. Fourthly, it is found that many metals require to be heated slightly above their point of sublimation to effect their distillation; this phenomenon the author attributes to the slight difference of pressure caused by the rise of temperature, which causes a more or less mechanical impulse to the metallic vapour. Fifthly, organic substances, as tallow, wax, colophony, distil in a vacuum without decomposition, and can thus be separated from impurities; but crude sugar, dry grape-sugar, and quinine sulphate, decompose during or even before distillation. Caoutchouc distils in two separate layers, of which the more volatile has the smell of caoutchouc, whilst the less volatile has but little smell, and is of the consistency of fresh caoutchouc. In conclusion, the author recommends this process of fractional distillation in a vacuum for purification of organic substances. V. H. V.

Velocity of Solidification of Bodies in a State of Superfusion. By D. GERNEZ (*Compt. rend.*, **95**, 1278—1280).—The experiments were made with columns of melted phosphorus 60—70 cm. long, enclosed in **U**-tubes of diameter 1·4—2·7 mm., the walls of which did not exceed 0·2 mm. in thickness. The surface of the phosphorus was protected from the air by a thin layer of water. The tube was plunged for a short time into a bath of a temperature above the melting point of phosphorus, and then suspended in a bath of water kept at a constant temperature and agitated by a current of air. The solidification was caused by touching the surface of the phosphorus in one limb of the tube with a piece of solid phosphorus, and registering the time taken before solidification reached the surface in the other limb. The solidification proceeds quite uniformly, and the author calls the length of the column solidified in one second the *velocity of solidification.* He has heated the phosphorus to 100°, 140°, 200°, and 215° before cooling, but the velocity of solidification was not influenced.

The following are a few of the numbers obtained, reduced to a column of phosphorus at its melting point, 44·2° :—

Temperature	43·8°	43·5°	42·9°	42·1°	41·4°	40·6°	39°	38°
Velocity of solidification in mm.	1·16	2·63	8·78	24·1	56·9	88·3	159·7	243·1
Temperature..	36°	34·2°	33°	31·2°	29°	27·4°	24·9°	
Velocity of solidification in mm.	353·35	538·9	628·9	675·7	800·0	952·4	1030·9	

L. T. T.

Dissociation of Chlorine and Bromine. By C. LANGER and V. MEYER (*Ber.*, **15**, 2769—2775).—Previous experiments in this direction have been successful only with iodine, the diminution of pressure reducing the density from 8·8 to 4·4, or half the theoretical numbers, below which it could not be brought by reduction of pressure and increase of temperature. With both the other halogens, it has only been proved that their molecules are dissociated under a higher temperature than iodine, but the lowest density obtained for chlorine was 2·05 instead of the normal 2·45: no constant figure has yet been obtained for bromine.

The authors instituted a fresh series of experiments in order to try if they could reduce the figures to one-half their normal value, as in the case of iodine, using V. and D. Meyer's apparatus for removal of gas pressure, and discarding platinum chloride and bromide, using the halogens themselves in a state of the greatest possible purity. Hitherto the heat obtained was limited by the yielding of the Bayeux porcelain employed; and platinum was considered unsuitable; the authors, therefore, instead of raising the temperature, decided on diluting the heated vapour with an indifferent gas. The apparatus was that used by V. Meyer for estimating the density of permanent gases. A horizontal tube with capillary openings in both ends is brought to the temperature of the experiment, filled with the gas under examination (in the present case chlorine or bromine) mixed with a large excess of air or nitrogen; when the mixture has reached the required temperature, it is forced by a current of pure carbonic anhydride, introduced through one of the capillary openings, into an absorption apparatus containing potassium iodide solution, and from thence into a gas-measuring tube containing an alkaline solution. The halogen remains in the iodide, and is estimated volumetrically; the gas mixture used for dilution is measured, the operation is checked by the measurement of air, without the halogen, before and after the actual experiment; the presence of such active bodies as chlorine and bromine necessitated certain precautions which are detailed. The temperatures at which the work was carried out were 14°, 100°, 900° with Fletcher's oven not using blast, 1200° with the same oven using blast. Some of the results with chlorine are given—

Undiluted at 100°	2·50				
Diluted with 5 vols. of air	2·51				
Diluted with 15 ,, ...	2·46				
Undiluted at 900°	2·49	2·46	2·41	2·46	
Undiluted at 1200°	2·41	2·42	2·45	2·47	2·44

These figures agree tolerably well with the normal value of Cl_2, 2·45.

The behaviour of bromine at a low temperature and greatly diluted is interesting—at the ordinary temperature, 50° under its boiling point; when diluted with 10 volumes of air, its density is closely that of Br_2, namely, 5·52.

1	part Br	vapour	10·5	parts air,	temp.	13·5°,	density	5·51.
1	,,	,,	10·1	,,	,,	13·5	,,	5·54.
1	,,	,,	10·1	,,	,,	14·0	,,	5·45.
1	,,	,,	10·3	,,	,,	14·0	,,	5·46.

The authors promise further information on other experiments at high temperature and greater dilution. J. F.

Dissociation Heat of the Water Molecule and the Electric Luminosity of Gases. By E. Wiedemann (*Ann. Phys. Chem.* [2], **18**, 509—510).—In former researches, the author has shown the quantity of heat derivable from an electric discharge, which is necessary to convert the band into a line-spectrum, is independent of the

pressure of the gases and the cross section of the tube; its value is about 128,300 cal. From theoretical considerations, the author, starting with the view that the band-spectrum arises from an oscillation of the molecule, and the line-spectrum from a similar motion of the dissociated atoms, shows that a gram of water requires 126,000 cal. in order to effect its decomposition into its atoms. Thomsen in his "Thermochemische Untersuchungen" has put forward the probability that the atoms of nitrogen are firmly attached to one another. The author has established experimentally that if the same capillary tube be filled under the same pressure successively with hydrogen and nitrogen, and the gases subjected to the same discharge of the same intensity, then the line-spectrum is revealed in the hydrogen, but not in the nitrogen. In order to bring out the line-spectrum in nitrogen, a condenser must be included in the circuit. Hence it follows that the molecule of nitrogen requires a greater dissociation heat than the molecule of hydrogen. Siemens (this vol., p. 540), as well as the author, has observed the luminosity of gases under the influence of the electric discharge. The author has established that in charging the electrodes, a dielectric polarisation is induced, so that the ethereal envelopes of single gas molecules are distorted, and undergo an orientation: if a discharge takes place, the ethereal envelope is set into motion, and there is a passage of free electricity from the electrodes from molecule to molecule. The author has more fully examined this motion, and has proved that it can be so powerful as to effect the resolution of the molecules into the atoms. Siemens would explain the luminosity of gases by this oscillation of the ethereal envelope.
V. H. V.

Ammonium Hydrogen Sulphide. By ISAMBERT (*Compt. rend.*, **95**, 1355—1358).—The author has examined the vapour of ammonium hydrogen sulphide in order to determine whether this substance volatilises unchanged or splits up into ammonia and hydrogen sulphide. Dialysed by means of a porous porcelain tube, the gas which passes through contains more than its proper proportion of ammonia; thus proving at least partial dissociation. The author then made determinations of the compressibility of its vapour at 35—40°, and under pressures varying from 720 mm. to 1030 mm. Regnault's determinations gave for ammonia $\frac{p_0v_0}{pv} = 1·01881$, and for hydrogen sulphide $\frac{p_0v_0}{pv} = 1·01083$. For a mixture of equal volumes of the two gases, this ratio would therefore be a little less than 1·01482, or at 40° about 1·01, whereas that of the vapour of an easily condensible gas has been shown by Herwig to be about 1·1. The author obtained numbers varying between 1·007 and 1·008, showing that no appreciable quantity of the undissociated compound could be present.

He has also determined the heat of liquefaction, and found it to be 23, a number far above the average, but almost identical with the heat of formation of ammonium hydrogen sulphide. He therefore concludes that in the form of vapour complete dissociation has taken place, and that in liquefying a reformation of the sulphide is brought about. L. T. T.

Constant of Capillarity of Liquids at their Boiling Points. By R. Schiff (*Ber.*, **15**, 2965—2975).—The apparatus employed by the author in this research consists of a capillary **U**-tube, the two limbs having different diameters. The apparatus containing some of the liquid to be examined is suspended in a glass vessel, which is filled with the vapours given off by boiling some of the same substance; when the temperature of the apparatus is constant, the height the liquid in each limb of the tube, and the height of the meniscus is read off by means of a cathetometer. From these data the constant C can be calculated.

Let $d =$ the diameter of the narrow limb and d' the diameter of the wider limb of the **U**-tube, $h =$ the observed difference in the height of liquid in the two tubes, $hc =$ the height corrected for the meniscus, $n =$ the rise in a normal tube of 1 mm. diameter, $r =$ the radius of the narrow, and R of the wide tube, let f and F represent the height of the menisci, ρ and ρ' the radius of the curves of the menisci, S_t the specific gravity of the liquid at $t°$, and $C = ns_t = 2a^2s$. C also = Quinke's $\alpha \times 4$.

The correction for the meniscus is made by means of the following formula: $hc = h + \dfrac{\frac{r}{3} + \frac{f}{3}}{2}$. If m and m' represent the corrections for the meniscus, then $hc = h + m - m'$,

$$\text{and } n = \frac{dd'}{d' - d}\left(\frac{h + \frac{r}{3} - \frac{R}{3} + \frac{f}{3} - \frac{F}{3}}{2}\right).$$

The following values for C were obtained:—

Methyl alcohol, 7·636; ethyl alcohol, 7·059; propyl alcohol, 7·002; isopropyl alcohol, 6·808; chloroform, 9·121; carbon tetrachloride, 8·160; ethylene chloride, 9·719; benzene, 8·646; toluene, 7·383; xylene (chiefly ortho), 6·698; metaxylene (pure), 6·718; paraxylene, 6·662; paracymene, 5·586. W. C. W.

Passage of Alcoholic Liquids through Membranes. By H. Gal (*Compt. rend.*, **96**, 338—340).—The degree of dilution which alcohol experiences when exposed to a moist atmosphere in contact with a membrane (this vol., p. 279), is independent of the temperature; but the rate at which dilution takes place is materially affected by the temperature, and is much more rapid at 30° and 50° than at − 10°. Dilution takes place whether the membrane is in contact with the liquid or with its vapour. The latter fact is explained by the difference between the vapour-tensions of water and alcohol at all temperatures, and by the fact that the alcohol vapour diffuses out into the atmosphere, which contains only a trace of alcohol vapour, whilst the water vapour diffuses into an atmosphere already more or less saturated. Dilution takes place whether the membrane be goldbeater's skin, bladder, or parchment, but is much more rapid with the first and much slower with the last, than it is when bladder is used. The author's previous results are confirmed by Bidaud. C. H. B.

Mutual Displacements of Bases of Neutral Salts in Homogeneous Systems. By Menschutkin (*Compt. rend.*, **96**, 348—350). An aqueous solution of triethylamine gives a purplish-violet coloration with a few drops of phenolphthalein solution, but the colour is destroyed by alcohol even in presence of a large excess of triethylamine. On addition of one drop of a solution of an alkali, the colour is restored, but is not so intense, and has a bluer tinge.

A standard aqueous solution of potassium hydroxide, and a standard alcoholic solution of sodium hydroxide respectively were added to solutions of triethylamine chloride and acetate, the above reaction being used to indicate the presence of free alkali. When the potassium hydroxide was used, the liquid was mixed with a volume of alcohol equal to four times the volume of the potash solution. It was found that triethylamine is entirely displaced from its salts by an equivalent of sodium or potassium hydroxide.

The chemical mass of the triethylamine exerts no influence on its displacement, for if that were the case, the displacement would not be complete in presence of the liberated triethylamine.

These facts are contrary to the law of Berthollet; but in perfectly homogeneous systems the chemical mass of the triethylamine may exert influence, and the law of Berthollet may or may not be true.

C. H. B.

Nature of Solution. By W. L. Goodwin (*Ber.*, **15**, 3039—3051). —The author draws the following conclusions from his experiments on the solubility of chlorine in water:—The chlorides of calcium, cobalt, iron, magnesium, and strontium prevent the formation of solid chlorine hydrate. The solubility of chlorine in water is increased by the presence of hydrochloric acid or lithium chloride. With mixed chlorides, the solubility is generally the mean of that for the separate salts. The influence of chlorides on the solubility of chlorine is chemical at low and mechanical at higher temperatures.

W. C. W.

Inorganic Chemistry.

Crystallisation of Chlorine Hydrate. By A. Ditte (*Compt. rend.*, **95**, 1283—1284).—Chlorine hydrate containing excess of water is introduced into a long bent tube and strongly sealed. The limb containing the hydrate is then heated, when the chlorine evolved becomes condensed in the cold limb by the pressure of its own vapour. If the whole apparatus be now allowed to cool slowly, chlorine hydrate reforms on the surface of the water in fine fern-like crystals.

If the limb containing the hydrate and water be immersed in water and the whole allowed to rest for some time, the crust of hydrate crystals gradually increases until it entirely shuts off communication between the water and chlorine. Chlorine then gradually condenses above the hydrate, which thus is enclosed between a layer of water and one of chlorine. On standing some time, the fern-like shapes disappear, and isolated crystals about 2—3 mm. long are formed of a greenish-yellow colour, highly refracting, and belonging apparently to the regular system. L. T. T.

Variation in the Amount of Oxygen in the Air. By C. A. Vogler (*Bied. Centr.*, 1882, 851).—The author considers that at meteorological stations the percentage of oxygen in the air should be regularly determined, as he believes that the percentages of oxygen are closely connected with some of the barometric changes.

E. W. P.

Oxidation of Sulphur in the Air. By A. Basaroff (*Jour. Russ. Chem. Soc.*, 1882, 396—398).—In order to suppress the vine-disease caused by *Oïdium Tuckeri*, flowers of sulphur are often dusted over the plants; but although this method has been used for more than 20 years, the mode of action of the sulphur has not yet been clearly ascertained.* The author has investigated the question anew, by passing about 250 litres of air, collected about 1½ meter over the vineyard ground which was treated with flowers of sulphur, first through cotton wool, and subsequently through a solution of pure soda. After oxidation by chlorine, $BaSO_4$ was obtained, corresponding with 9·6 c.c. of SO_2. The air contained, therefore, 0·004 per cent. by volume, or 0·009 per cent. by weight of sulphurous anhydride, and this quantity of so strong a disinfectant is, in the author's opinion, quite sufficient to produce the effect mentioned above.

B. B.

Reactions between Sulphur, Sulphur Oxides, Carbon, and Carbon Oxides. By Berthelot (*Compt. rend.*, **96**, 298—304).—*Carbonic oxide* is decomposed into carbon and carbonic anhydride at a bright red heat, and even at the softening point of glass, but the amount of decomposition is very small. *Sulphurous anhydride*, as Buff and Hofmann have stated, is decomposed by the electric spark into sulphuric anhydride and sulphur. No oxygen is set free; part of the sulphur unites with the platinum electrodes; the remainder combines with the sulphuric anhydride to form a viscous liquid, which absorbs a certain quantity of sulphurous anhydride. This is the intermediate product of the reaction. It is decomposible in the reverse direction, and the tensions of the sulphuric and sulphurous anhydrides which it gives off limit the decomposition of the sulphurous anhydride. When sulphurous anhydride is passed over purified charcoal heated to redness in a porcelain tube, carbonic oxide,

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* The author is evidently unaware of Pollacci's experiments (this Journal, 1876, ii, 540), who found that sulphured grapes gave off hydrogen sulphide, and that this gas rapidly kills the *oïdium*.—C. E. G.

carbon oxysulphide, and carbon bisulphide are formed in proportions indicated by the equation $4SO_2 + 9C = 6CO + 2COS + CS_2$, and a small quantity of sulphur is set free. Probably the carbon combines with the oxygen of the sulphurous anhydride, liberating sulphur which then unites partly with carbon, and partly with the carbonic oxide formed. When electric sparks are passed for a long time through a mixture of equal volumes of carbonic anhydride and sulphurous anhydride, the residual gas has the composition SO_2, 31; CO_2, 30; CO, 20; decrease, 19 = 100. Each gas decomposes independently, and the oxygen liberated from the carbonic anhydride combines with sulphurous anhydride to form sulphuric anhydride, which condenses. The sulphurous anhydride is apparently somewhat more stable than the carbonic anhydride. When a mixture of equal volumes of sulphurous anhydride and carbonic oxide is passed through a narrow porcelain tube heated to redness, the issuing gas has the composition SO_2, 37; CO_2, 20; CO, 43 = 100. Sulphur is liberated, but neither carbon oxysulphide nor carbon bisulphide is formed in notable quantity. The carbonic oxide evidently reduces the sulphurous anhydride, thus $2CO + SO_2 = 2CO_2 + S$, but the reduction is not complete. If a mixture of 2 vols. carbonic oxide with 1 vol. sulphurous anhydride is subjected to the action of electric sparks, the sulphurous anhydride is partially reduced, but a portion of it decomposes independently without giving up oxygen to the carbonic oxide, and forms a compound of sulphur, sulphurous and sulphuric anhydrides, which condenses on the sides of the tube. In presence of mercury, the sulphurous anhydride is completely decomposed, and the residual gas has the composition CO_2, 24; CO, 75; O, 1. The mercury absorbs the sulphuric anhydride produced, forming a basic sulphate. Sulphurous anhydride has no action on potassium sulphate at a bright red heat, but at a red heat it converts the carbonate into sulphate, with a trace of sulphide. If the current of the gas is slow, the proportion of sulphide increases.

A slow current of dry carbonic anhydride has no action on boiling sulphur, but if sulphur vapour and carbonic anhydride are passed through a porcelain tube heated to redness, a slight but distinct reaction takes place. The issuing gas contains 2·5 per cent. of a mixture of 1 vol. carbon oxysulphide, 1 vol. carbonic oxide, and 0·5 vol. of sulphurous anhydride. The carbonic anhydride probably does not directly attack the sulphur, but first dissociates into carbonic oxide and oxygen. Carbonic anhydride has no action on potassium sulphate at a bright red heat. When it is passed over the sulphite, the latter is converted into sulphate and polysulphide, with a small quantity of carbonate. The acid sulphite gives the same products, but this salt dissociates even when heated in a current of an inert gas, such as nitrogen. Carbonic anhydride acts on potassium polysulphide at a red heat, sulphur being liberated and a mixture of carbonic oxide, sulphurous anhydride, and carbon oxysulphide being formed, together with a small quantity of carbonate. This reaction is probably due to the dissociation of the carbonic anhydride.

Sulphur can be distilled off potassium sulphate below a red heat without any reaction taking place, but in a porcelain tube heated to redness sulphur vapour reduces the sulphate, forming sulphurous anhydride and a polysulphide, thus: $K_2SO_4 + 5S = K_2S_3 + 2SO_2$. The action of sulphur on potassium carbonate is well known.

The importance of these reactions in the study of the decomposition of gunpowder is evident. C. H. B.

Pyrosulphuryl Chloride. By D. KONOVALOFF (*Compt. rend.*, **95**, 1284—1286).—Ogier (Abstr., 1882, 694) obtained for this body the anomalous vapour-density 3·72. The author has repeated these experiments with chloride prepared very carefully according to Schützenberger's directions (*Compt. rend.*, **69**, 352). Thus obtained, *pyrosulphuryl chloride* boils at 153° at 752 mm. pressure, and is a colourless liquid, fuming in the air, of sp. gr. 1·872 at 0°, and having a high coefficient of expansion. In contact with water, it decomposes very slowly at ordinary temperatures, very rapidly at high temperatures. The vapour-densities were made by V. Meyer's method. At the temperature of aniline vapour (183·7°), the numbers obtained varied between 7·23 and 7·41, with nitrobenzene vapour (210°), 7·27. Theory for $S_2O_5Cl_2 = 7·43$. The author believes the previous low numbers obtained to be due to the presence of impurities, probably $SO_2(OH)Cl$ (differing only slightly in percentage composition). A mixture of $S_2O_5Cl_2$ and $SO_2(OH)Cl$, boiling at 140—146°, gave $\Delta = 4·01$. Pure $S_2O_5Cl_2$ heated with about 4 per cent. of water gave a liquid boiling at 139—140°, and giving $\Delta = 4·7$. L. T. T.

Crystalline Form, Specific Heat, and Atomicity of Thorium. By L. F. NILSON (*Compt. rend.*, **96**, 346—348).—Brögger finds that the hexagonal crystals of thorium obtained by reducing the double chloride of thorium and potassium by means of sodium are really a combination of the regular octohedron and tetrahedron, and are therefore identical in form with the crystals of silicon. The density of pure crystallised thorium is 11·230; that of the amorphous form is 10·968; mean = 11·099. It follows, therefore, that the atomic volume of thorium is 20·94, a value approaching that of zirconium, cerium, lanthanum, and didymium. The atomic heat of the oxygen in thoria is equal to 4·08, a value almost identical with the atomic heat of the oxygen in the oxides of zirconium, cerium, titanium, and tin, and in zircon and manganese dioxide. The specific heat of thorium is 0·02757, and its atomic heat is therefore 6·41 (Th = 232·4).

These facts, together with facts and analogies previously observed, show conclusively that thorium is quadrivalent and that thoria is a dioxide, ThO_2. C. H. B.

Atomic Weight of Lanthanum. By P. T. CLEVE (*Bull. Soc. Chim.* [2], **39**, 151—155).—About 1·5 kilos. of the mixed oxides of lanthanum and didymium obtained from cerite, gadolinite, orthite, and keilhauite, were converted into nitrates, the nitrates partially decomposed by ignition, and the residue extracted with water. The solution, which was free from cerium and thorium, was fractionally precipitated with ammonia. The first fraction consisted of didymium oxide, almost pure, the seventh and last fraction of almost pure lanthanum oxide. The lanthanum oxide was then converted into sulphate, which was purified and separated into fractions by repeated crystallisation, and the amount of lanthanum oxide in the sulphate was determined by ignition. The mean of 12 determinations gave 57·480 ± 0·00395 per cent. of La_2O_3. If $SO_3 = 80$, then $La = 138·22$; or if $O = 15·9633$, and $S = 31·984$, then $La = 138·019 \pm 0·0246$. These results confirm those of Brauner (*Monats. Chem.*, **3**, 493); the difference between them and earlier determinations is probably due to the difficulty of expelling all free sulphuric acid from the sulphate without causing decomposition, and to the fact that lanthanum oxide absorbs a small quantity of oxygen at a dull red heat, but gives it off again at bright redness; the oxide is, moreover, somewhat hygroscopic. No element intermediate between didymium and lanthanum could be detected. C. H. B.

Allotropic Arsenic. By R. Engel (*Compt. rend.*, **96**, 497—499).—Hittorf and Berzelius observed that in the condensation of the vapour of arsenic in an inert gas, three forms of the metal are obtained, viz.: (1) crystalline arsenic in the warm part of the apparatus; (2) black amorphous arsenic; and (3) in the cooler part a grey powder. This latter modification is more readily oxidised by nitric acid than either of the former, but it is generally considered that this property is due to a difference of cohesion. Bettendorf found that both black and grey amorphous arsenic have a density of 4·7, and that when heated to 360° they are transformed into crystalline arsenic (sp. gr. 5·7). He regarded these forms as three distinct allotropic modifications, and he suspected that the yellow powder which precedes the deposition of the grey arsenic was a further modification, but he was unable to isolate it.

The author has examined the form of arsenic precipitated by various reducing agents from solutions of arsenious acid. Whatever be the precipitant employed, the resultant metal was of a velvety brown or black colour; its sp. gr. was 46—47°, and on heating to 360° it is converted into ordinary crystalline arsenic. The author considers that Bettendorf's yellow coloration was due to the yellow vapour of arsenic, and not to any solid form. The grey powder results from the sudden, and the black powder from the slow, solidification of the vapour. There are thus only two well-defined allotropic modifications: 1st, the amorphous form obtained in the dry way, or in the wet way of precipitation; 2nd, the crystalline form obtained by the condensation of vapour of arsenic at 360°, or slightly higher temperature.

V. H. V.

Reduction of Tungsten Compounds. By O. v. Pfordten (*Ber.*, **15**, 2975—2976).—A question of priority.

Chemistry of the Chromammonium Compounds. By S. M. Jörgenson (*J. pr. Chem.* [2], **25**, 398—430).—A continuation of the author's researches on this subject (Abstr., 1880, 10; 1882, 468, 1169).

VI. Normal Erythrochromium Salts.—Erythrochromium nitrate, $HO(Cr_2,10NH_3)5NO_3,H_2O$, is prepared by treating 5 grams of the rhodo-chloride with 50 c.c. of water and 35 c.c. dilute ammonia; the solution, at first deep blue, changes to deep crimson, and contains basic erythrochromium chloride; on addition of 4—5 volumes of dilute nitric acid, a crimson precipitate of impure erythrochromium nitrate is obtained, and may be purified by repeated treatment with dilute nitric acid, solution in water, reprecipitation with nitric acid, and washing with alcohol, and is finally dried in the dark. It forms a crimson powder, composed of microscopic octahedrons; it is not very stable, undergoing slow spontaneous decomposition, even in the dark. At 100° it decomposes, becoming first dark green, and finally black. On ignition, it decomposes rather violently, red fumes being evolved, and a greenish-black voluminous residue of chromium oxide left. It is insoluble in alcohol, but moderately soluble in cold water with a crimson colour; on boiling the solution, chromium hydroxide separates. On boiling a solution acidulated with a few drops of nitric acid, it is converted into roseochromium nitrate. The erythro-nitrate is insoluble in dilute nitric acid, but dissolves slowly in strong acid to a violet liquid, and after a time is resolved into chromium and ammonium nitrates. On boiling the solid erythro-nitrate with dilute hydrochloric acid, it is converted into chlorpurpureochromium chloride. An aqueous solution of the erythro-nitrate gives the following reactions:—Dilute nitric acid precipitates the salt; dilute hydrochloric acid gives no precipitate; concentrated acid after some time precipitates chlorpurpureo-chloride; concentrated hydrobromic acid precipitates red needles of the erythrobromide; hydrofluosilicic acid a rose-red non-crystalline precipitate; hydrogen platinochloride gives no precipitate, but on adding alcohol a crystalline chocolate-brown precipitate is produced; hydrogen platinochloride and magnesium sulphate give a red precipitate of microscopic needles; potassium ferricyanide, a precipitate of long dark-red needles; potassium ferrocyanide, a voluminous violet-red precipitate, which slowly becomes crystalline; mercuric chloride gives no precipitate, but sodium mercuric chloride and potassium mercuric bromide give voluminous precipitates of pale violet-red needles; hydrogen aurochloride and stannous chloride give no precipitates; solid potassium iodide, a brownish-red crystalline precipitate; sodium pyrophosphate, a clear violet precipitate, soluble in excess of the reagent; potassium chromate, no precipitate; potassium dichromate, a reddish-yellow precipitate, even from dilute solutions.

Erythrochromium bromide, $HO(Cr_2,10NH_3)Br_5,H_2O$, is prepared by the action of concentrated hydrobromic acid on an ammoniacal solution of the rhodo-chloride. It crystallises in microscopic crimson needles, loses 1 mol. H_2O over sulphuric acid, but suffers no further loss on heating at 100°; after 24 hours, however, it is found to be nearly completely converted into rhodochromium bromide. It is very readily soluble in cold water with crimson colour and neutral reaction; the solution gives similar reactions to those of the nitrate, except that it is readily precipitated by hydrogen platinochloride; the salt is precipitated unaltered on adding 2 vols. of concentrated hydrobromic acid; boiling the aqueous solution with a few drops of hydrobromic acid converts it into the roseo-bromide, whilst on heating a mixture of the salt with concentrated hydrobromic acid at 100°, it is rapidly converted into bromopurpureochromium bromide. Addition of silver nitrate in the cold precipitates all the bromine, and on shaking with freshly precipitated silver chloride, all the bromine is replaced by chlorine; from this all the bromine-atoms would seem to be of equal value; solution in ammonia, however, and precipitation with alcohol, gives basic erythro-bromide, in which one-fifth of the bromine has been removed. A xantho-salt could not be obtained by addition of sodium nitrite to the erythro-bromide, subsequent addition of hydrobromic acid gives an orange-yellow crystalline precipitate, apparently a perbromide. The erythro-bromide when shaken with silver oxide and water, gives a red alkaline liquid containing *erythrochromium hydroxide*, which, however, was not isolated.

Erythrochromium sulphate, $(HO,Cr_2,10NH_3)_25SO_4$, is obtained as a pale crimson precipitate on adding dilute sulphuric acid and alcohol to a concentrated solution of erythrochromium bromide.

Erythrochromium chloriodide, $HO(Cr_2,10NH_3)ClI_4,H_2O$, is obtained in short microscopic prisms on adding concentrated hydriodic acid to an ammoniacal solution of the rhodochloride. It loses 1 mol. H_2O over sulphuric acid, and on then heating at 100° is converted into the rhodo-salt. A corresponding bromiodide is obtained by the action of potassium iodide on a concentrated solution of the erythro-bromide.

Erythrochromium platinochloride, $HO(Cr_2,10NH_3)_2,PtCl_6,10H_2O$, is obtained by the addition of hydrogen platinochloride and a little alcohol to a solution of the erythro-nitrate as a chocolate-brown precipitate of very small thin needles; it is nearly insoluble in cold water. The erythro-chloride behaves differently with hydrogen platinochloride, being precipitated without addition of alcohol in cinnabar-red crystals, which when washed with water, are slowly converted into the chocolate-coloured needles of the platinocyanide. The red precipitate is in all probability a double chloride and platinocyanide.

VII. BASIC ERYTHROCHROMIUM SALTS.—*Basic erythrochromium bromide*, $HO(Cr_210NH_3)Br_4(OH),H_2O$, is prepared by dissolving erythrochromium bromide in ammonia, and adding alcohol, when the basic salt slowly crystallises out. It forms violet-red plates, loses 1 mol. H_2O on standing over sulphuric acid, and decomposes at 100°. It dissolves very readily in water, with crimson colour and faintly alkaline reaction. It is converted into the normal bromide by treatment with hydrobromic acid, but not by ammonium bromide, thus differing from the basic rhodo-salts, which expel the ammonia from ammonium salts. An aqueous solution of the basic erythro-bromide gives the following reactions:—It is precipitated by alcohol; is nearly completely precipitated as dithionate by sodium dithionate; is completely precipitated as a lilac-red crystalline powder by potassium ferrocyanide; gives no reaction with potassium ferricyanide alone, but on addition of dilute ammonia gives a reddish-yellow crystalline precipitate; it does not react with potassium chromate; with potassium mercuric bromide, it gives a thick precipitate of lilac-coloured needles, and with sodium platinochloride a cinnabar-red granular precipitate.

Basic erythrochromium nitrate, $HO(Cr_210NH_3)4NO_3(OH),3\frac{1}{2}H_2O$, prepared in a manner similar to the bromide, forms long crimson six-sided rhombic tables. When kept it slowly decomposes, with loss of ammonia.

Basic erythrochromium dithionate, $HO(Cr_210NH_3)2S_2O_6(OH),2H_2O$, is obtained by adding sodium dithionate to normal or basic erythrochromium nitrate or bromide. It crystallises in brilliant dark violet needles, united in fan-shaped groups. At 100°, the air-dried salt loses 2 mols. H_2O and 2 mols. NH_3, without change of shape; the product dissolves in cold dilute hydrochloric acid, and the violet-red solution deposits the tetraminechromium chloride of Cleve on standing.

VIII. BASIC ROSEO-SALTS.—*Basic roseocobalt dithionate*,

$$Co_2 10NH_3(OH)_2(S_2O_6)_2,4H_2O,$$

is prepared by boiling nitratopurpureocobalt nitrate with dilute ammonia, mixing with sodium dithionate, and adding two drops of alcohol (of 90° Tr.) to 10 c.c. of this liquid, when a crystalline precipitate of the basic dithionate is obtained; this is now returned to the main portion, when after brisk stirring, and about one hour's standing, the dithionate separates as a crimson-red precipitate, consisting of rhomboïdal tables or monoclinic octahedrons. It is sparingly soluble in water, the solution having a violet-red colour, and is converted into normal roseo-salt by dilute hydrochloric acid; it dissolves in solution of ammonium chloride in the cold with evolution of ammonia.

Basic roseochromium dithionate, $Cr_2 10NH_3(OH)_2(S_2O_6)_2 + 4H_2O$, is prepared in manner similar to the above, which it closely resembles in appearance and properties.

The remainder of the paper consists of speculations as to the probable constitution of the chromammonium compounds.

A. J. G.

Ammoniocobalt Compounds. By MAQUENNE (*Compt. rend.*, **96**, 344—345).—When ozonised oxygen is passed through an ammoniacal solution of cobalt sulphate, the liquid first becomes brown, then green, and finally deposits deep green microscopic prismatic plates on the sides of the vessel. If the chloride is used, the crystals are slender needles. These compounds can be more easily obtained by passing a rapid current of air through a mixture of 100 c.c. ammonia with 10 c.c. of a saturated solution of cobalt sulphate for about two hours. The precipitated crystals are collected, dried rapidly between filter-paper, and thrown, in small portions at a time, into 25 c.c. of a cooled mixture of equal volumes of sulphuric acid, alcohol, and water, when the brown substance becomes rose-coloured. On adding an excess of chlorine-water, the rose-coloured compound becomes green, and the liquid, if heated to boiling and left to cool, deposits prismatic crystals which are sometimes as much as 5 mm. long, and can be obtained larger by recrystallisation from dilute (5 per cent.) sulphuric acid. These crystals are dark green, almost black, quadratic prisms, of the composition $Co_2O_2(SO_4)_2(NH_3)_{10},SO_4H_2 + H_2O$. They are but slightly soluble in water, by which they are decomposed with evolution of oxygen, but they dissolve easily in dilute acids without sensible decomposition, even at 100°, if the operation is conducted rapidly. By prolonged ebullition with acids, this compound is converted into a roseocobalt salt. It is entirely decomposed by the fixed alkalis, with evolution of oxygen and precipitation of black cobaltic oxide.

If this salt is dissolved in boiling dilute hydrochloric acid, and the solution mixed with strong hydrochloric acid, green shining plates, with a greasy and somewhat nacreous lustre, are precipitated. They have the composition $Co_2O_2Cl_4(NH_3)_{10},HCl + 3H_2O$, are somewhat stable, and dissolve in water, or better, in water acidulated with hydrochloric acid. If the acid solution of the sulphate is mixed with alcohol instead of with strong hydrochloric acid, a pale green magma of interlaced slender needles is precipitated. This compound is a chloride undoubtedly identical with that obtained by treating an ammoniacal solution of cobalt chloride with ozone. It is far less stable than either of the other compounds; it is decomposed rapidly by cold water, and, if left to itself after drying, is transformed in a day or two into a red mass which consists mainly of roseocobalt chloride.

These compounds may be regarded as the acid salts of the oxycobalt-ammonium of Fremy. The nitrate is somewhat unstable, and crystallises in green microscopic needles. With solutions of these compounds, especially on agitation, ammoniacal sodium phosphate gives a green crystalline precipitate, which is deposited more readily on the rubbed portions of the sides of the vessel, like ammonio-magnesium phosphate. C. H. B.

Manganese Sulphite. By A. Görgeu (*Compt. rend.*, **96**, 341—343).—Manganese sulphite, $MnSO_3,3H_2O$, can be obtained in monoclinic crystals by the evaporation at ordinary temperatures of a solution of manganese sulphite in a concentrated aqueous solution of sulphurous acid, or of a solution obtained by adding an alkaline sulphite to a large excess of a solution of a manganese salt until a permanent precipitate just begins to form. This salt has a pale rose colour; dissolves in 10,000 parts of cold or 5,000 parts of hot water; is rather more soluble in strong solutions of manganous salts; and dissolves somewhat easily in a strong aqueous solution of sulphurous acid. It oxidises slowly in dry air, more quickly in ordinary air, and rapidly in moist air or in contact with aërated water, especially if finely powdered. In presence of water, chlorine, bromine, and iodine convert it into sulphate.

Another hydrate, $MnSO_3,H_2O$, is obtained by precipitating the manganese sulphite at 100°. It forms rose-coloured crystals belonging to the rhombic system, and does not lose its water below 150°. It rapidly takes up water in the cold, especially in presence of sulphurous acid, forming the hydrate $MnSO_3,3H_2O$.

The trihydrated salt begins to lose water at 70°, and oxidises somewhat rapidly. When calcined at a bright red heat, it leaves a residue of trimanganese tetroxide. Both hydrates when heated out of contact with air give off sulphurous anhydride and leave a residue of manganese monoxide, sulphate, and sulphide. Heated gradually to redness in a current of hydrogen, manganese sulphite leaves a residue of 87 parts manganese monoxide and 13 parts manganese sulphide.

Manganese sulphite combines easily with the alkaline sulphites, forming double salts which crystallise well. C. H. B.

Mineralogical Chemistry.

Occurrence of Smaltite in Colorado. By. M. W. ILES (*Jahrb. f. Min.*, 1883, **1**, Ref., 194).—Smaltite and erythrite occur with a little iron pyrites, native silver, and calcite, in a mineral vein near Gothic, Gunnison Co., Colorado. A sample of smaltite from the surface croppings gave—

Co.	Fe.	As.	SiO_2.	Pb.	S.	Bi.	Cu.
11·59	11·99	63·82	2·60	2·05	1·55	1·13	0·16

Ni and Ag traces. Total = 94·89

A purer sample yielded 15 per cent. cobalt. B. H. B.

Brazilian Specimens of Martite. By O. A. DERBY (*Jahrb. f. Min.*, 1883, **1**, Ref., 194).—The opinion has recently been advanced that the octohedral crystals of martite are due to the transformation of pyrites, but a recent examination of a great number of crystals from various Brazilian localities indicates that they should rather be considered as produced by the alteration of magnetite. B. H. B.

Analysis of a Variety of Siderite. By E. CLASSEN (*Jahrb. f. Min.*, 1883, **1**, Ref., 194).—This variety of siderite occurs on hæmatite, in the Lake Superior district, either in crusts or in single crystals. It is often associated with calcite, and has a light green colour. It contains—

FeO.	CaO.	MgO.	MnO.	CO_2.	Total.
41·115	15·883	2·567	trace	40·428	99·993

B. H. B.

Silica and Lithium Silicates. By P. HAUTEFEUILLE and J. MARGOTTET (*Jahrb. f. Min.*, 1883, **1**, Ref., 195—196).—The authors have succeeded in obtaining artificially three lithium silicates, of which two are analogous to the magnesium iron silicates; Li_4SiO_4 and Li_2SiO_3, resembling $(Mg,Fe)_2SiO_4$ (olivine) and $(Mg,Fe)SiO_3$ (hypersthene) respectively: they agree in many points, but with regard to $Li_2Si_5O_{11}$ no natural mineral is known resembling it. All these compounds were obtained by the action of lithium chloride on silicates.

Li_4SiO_4 behaves like olivine before the blowpipe. It is somewhat soluble in hot water; the angle of the rhombic prism measured 119°.

The salt Li_2SiO_3, analogous to hypersthene, has the same angle and crystal system as the preceding. It is not attacked by dilute acid.

The most acid salt, $Li_2Si_5O_{11}$, belongs also to the rhombic system. Quartz and tridymite were also formed by means of lithium chloride, the former at the melting point of silver, the latter at a bright red heat. The formation of these bodies is explained by the theory that lithium chloride contains an oxychloride which renders the crystallisation of the silicic acid possible. B. H. B.

Relation between the Optical Properties and Chemical Composition of Pyroxene and Amphibole. By F. J. WIIK (*Jahrb. f. Min.*, 1883, **1**, Ref., 187—188).—The author measured the clinopinakoid angle of a great number of pyroxenes and amphiboles from Finland, and investigated the relation to the percentage of FeO in the former and Al_2O_3 in the latter. The results are given in the annexed table.

		Angle.	FeO per cent.	Analyst.
	A. *Pyroxene Group.*			
1	Malacolite (dark)............	36° 30′	1·08	H. Rose.
2	„ (yellow).........	37°	0·99	Bonsdorff.
3	„ (light coloured) ...	38°	2·52	F. Lemströn.
4	„ (greyish-green)....	39°	2·68	E. Moberg.
5	Diopside (green)............	38—40°	4·81	Castren.
6	Malacolite (grey)............	39° 30′	4·00	Hjelmman.
7	„ (green)...........	39° 30′	4·97	Hjelt.
8	„ (green)...........	41°	6·00	Landzétt.
9	„ (green)...........	42° 30′	10·38	Castren.
10	Pyroxene (green)...........	42° 30′	12·29	Wiik.
11	Augite (black)..............	43—44°	12·04	Kudernatsch.
12	„ (black)..............	43° 30′	15·75	Fagerlund.
13	„ (black)..............	45° 30′	17·31	Sjögren.
14	Malacolite (red)............	46°	20·44	Berzelius.
15	„ (black).........	48°	27·50	Castren.
		Angle.	Al_2O_3 per cent.	
	B. *Amphibole Group.*			
16	Actinolite (green)...........	16—18°	2·83	Aakerstedt.
17	„ (green)...........	17°	1·69	Michaelson.
18	„ (dark green)......	18° 30′	5·10	Hoffrén.
19	Hornblende (black)..........	18° 30′	4·98	Wasz.
20	Amphibole, anthophyllite.....	20°	7·9	Tammelin.
21	Hornblende (black)..........	24° 30′	11·92	Rammelsberg.
22	„ (green)..........	26° 30′	15·37	Kajander.
23	„ (green)..........	27° 30′	20·10	Nylander.

The increase of a degree in the angle, with pyroxene, represents an increase of about 2 per cent. of FeO, or of 10 per cent. of the silicate $(Ca,Fe)SiO_3$.

B. H. B.

Artificial Production of Wollastonite. By L. BOURGEOIS (*Jahrb. f. Min.*, 1883, **1**, Ref., 196—197).—*Wollastonite* was obtained by melting together the required amounts of lime and silica at a bright red heat, and slowly cooling for two days in the furnace. A mass of acicular crystals was obtained which appeared transparent and colourless under the microscope. As the optical properties do not coincide with those of the natural mineral, the author is of opinion that the compound is dimorphous. He regards the artificial crystals as biaxial with an extremely small axial angle.

Meionite.—The constituents were melted together at a bright red heat, in the proportions indicated by the formula—

$$5CaO,Na_2O,4Al_2O_3,9SiO_2.$$

In order to obtain a meionite free from soda, the materials $6CaO$, $4Al_2O_3$, $9SiO_2$, were melted together. The mixture became fluid at a dark red heat. The author believes that the product thus obtained is not meionite but anorthite. B. H. B.

The so-called Ersbyite from Pargas. By F. J. WIIK (*Jahrb. f. Min.*, 1883, **1**, Ref., 189).—The author contradicts his former statements with regard to ersbyite (*Naumann's Mineralogie*, 1881, p. 672), and he now, after an exhaustive investigation, determines the genuine ersbyite to be microcline, the analysis being as follows:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	Total.
66·18	19·52	0·36	13·03	0·91	100

Sp. gr. = 2·57

The colourless felspar formerly mistaken for ersbyite is a variety of andesine, the analytical results being as follows:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	Loss on ignition.	Total.
59·59	26·44	6·23	7·12	0·61	99·99

Sp. gr. = 2·67. B. H. B.

Emerald from Paavo, in Finland. By F. J. WIIK (*Jahrb. f. Min.*, 1883, **1**, Ref., 189).—The emerald was surrounded by a zone of radiated red albite, this again by a thin layer of muscovite. The analyses gave the following results:—

	SiO_2.	Al_2O_2.	GlO.	Total.
I.	66·37	19·29	14·01	99·67
II.	66·10	18·59	14·18	99·87

B. H. B.

Diorites of Montreal. By B. J. HARRINGTON (*Jahrb. f. Min.*, 1883, **1**, Ref., 247—248).—Numerous dykes of diorite occur near Montreal. Their character is very variable; their colour is light to dark grey, and sp. gr. 2·92—3·00. The analysis of a typical specimen gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	TiO_2.	CaO.	MgO.
40·95	16·45	13·47	0·33	3·39	10·53	6·10

K_2O.	Na_2O.	P_2O_5.	Loss on ignition.	Total.
1·28	4·00	0·29	3·84	100·63

B. H. B.

Monazite and Zircon from the Quarries of Nil-St. Vincent. By A. RENARD (*Jahrb. f. Min.*, 1883, **1**, Ref., 183—184).—Monazite occurs in this locality in the form of small tabular crystals with a greasy lustre and amber-yellow to red colour. The forms of the crystals are + P, Ꝑ∞, $\infty\bar{P}\infty$, ∞P, − Ᵽ∞. The measurement of the angles gave the following results: Ꝑ∞ : P = 141° 20′ 21″, $\infty\bar{P}\infty$: Ꝑ∞ = 100° 16′. The chemical analysis gave 28—29 per cent. P_2O_5 as usual. The metals cerium, lanthanum, and didymium were qualitatively determined. Together with monazite, crystals of zircon 0·5 mm. long were formed, which gave on analysis 32·56 per cent. SiO_2 and 67·29 per cent. ZrO_2. B. H. B.

Vanadium in the Leadville Ores. By M. W. ILES (*Jahrb. f. Min.*, 1883, **1**, Ref., 194).—At the Evening Star and Ætna Mine an orange-coloured substance was discovered, which gave the following analytical results:—

SiO_2.	PbO.	ZnO.	V_2O_5.	Fe_2O_3.	H_2O.	CO_2.	Total.
36·86	38·51	9·07	9·14	2·59	2·41	0·48	99·06

The author thinks it probable from these results that the mineral is a dechenite. B. H. B.

Occurrence of Aërenite. By J. MACPHERSON (*Jahrb. f. Min.*, 1882, **2**, 98).—This mineral, described by v. Lasaulx, has been found in the Pyrenees associated with ophite, at Tartaren, in Catalonia, and at Caserras, in Aragon. It occurs in the rock in small veins. The sections on being heated become opaque through loss of water, but transparent again on moistening with that liquid. H. B.

Serpentine from the Alps. By E. HUSSAK (*Jahrb. f. Min.*, 1883, **1**, Ref., 252—253).—The serpentine rocks investigated have been partly described by Drasche (*Jahrb. f. Min.*, 1872, 322). They prove to be altered slate rocks rich in augite. Salite and diallage were the original constituents, and have not, as Drasche states, yielded bastite, but antigorite, which, as a rule, is accompanied by talc.

Analyses were made of the green serpentine slate from Sprechenstein (I); of the compact serpentine from the same locality (II); of the antigorite isolated from the slate by means of Thoulet's solution (III); and of the chlorite rock resembling serpentine (IV).

The analyses (I—III) agree very well with Drasche's analyses of serpentine from Heiligenblut and Windisch-Matrei.

	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	40·90	7·68	2·08	0·30	37·45	12·15	100·56
II.	40·55	10·40	2·70	4·40	33·59	9·32	100·96
III.	41·14	3·01	3·82	0·40	39·16	11·85	99·38
IV.	29·62	41·92		0·30	18·23	10·34	100·41

B. H. B.

Metamorphism of Massive Crystalline Rocks. By J. D. DANA (*Jahrb. f. Min.*, 1883, **1**, Ref., 242—245).—The rocks investigated occur at Cortland, in Westchester county, New York. The facts observed appear to sustain the following conclusions. These rocks, although they include soda-granite, norite, augite, diorite, hornblendite, pyroxenite, and different chrysolitic rocks, are not independent igneous rocks erupted from great depths. They are metamorphic in origin, and differ from the other Westchester county rocks, because the metamorphic process had to do with sedimentary beds that differed in constitution.

These rocks underwent an upheaval through subterranean movements, and in the course of it they became metamorphosed. The number of these rocks does not imply widely different ingredients in the original strata, for they are all alike in containing the same bases in nearly the same proportion. B. H. B.

Melaphyres of Lower Silesia. By A. P. Coleman (*Jahrb. f. Min.*, 1883, **1**, Ref., 248—250).—The melaphyres investigated occur in the neighbourhood of Waldenburg and Lähn. They consist principally of triclinic felspar, probably oligoclase. The presence of orthoclase is doubtful. Augite occurs in all, and with it is frequently found a rhombic pyroxene, generally altered to bastite. Brown hornblende occurs in the rocks from Waldenburg; the melaphyre from Guckelberg also contains biotite. Olivine occurs in variable quantity, and in many specimens is entirely absent. The melaphyre from Rosenthal contains round granules of quartz.

Analyses were made of the rock from Rosenthal near Johannisberg (I), from Lower Schönau (II), and from Kunzendorf near Lähn (III), the results being as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
I.	58·93	15·47	7·71	—	5·84	3·14	3·17
II.	52·49	15·52	10·99	—	7·26	4·82	3·31
III.	55·12	14·43	—	9·11	6·60	5·88	4·03

	Na_2O.	Loss on ignition.	Ti.	Total.	Sp. gr.
I.	4·97	2·34	—	101·57	2·7166
II.	3·62	3·36	trace	101·38	2·7492
III.	3·64	1·85	trace	100·66	2·7052

B. H. B.

Analysis of a Mineral Spring at Salzbrunn. By T. Poleck (*J. pr. Chem.*, **27**, 45—48).—The "Kronenquelle" at Salzbrunn in Schlesien proceeds from a basin 75 cm. in diameter and 3·3 meters deep. Its flow is at about the rate of 530 litres per hour. The water which was collected by the author was 10·5° when the temperature of the air was 17·3°, and was colourless and without smell.

It possessed a slight chalybeate taste, and was slightly alkaline. Its sp. gr. was 1·00216.

In 1000 grams of the water there were found the following:—

	grams.		grams.	Carbonates as bi-carbonates. grams.
Sodium chloride	0·05899	calculated as sulphate	0·07160	0·05899
Potassium sulphate ..	0·04086	„ „	0·04086	0·18010
Sodium sulphate	0·18010	„ „	0·18010	0·04085
Sodium carbonate	0·55060	„ „	0·73763	0·87264
Lithium carbonate ...	0·00620	„ „	0·00922	0·01140
Calcium carbonate....	0·43990	„ „	0·69826	0·71264
Magnesium carbonate	0·23288	„ „	0·33268	0·40477
Strontium carbonate..	0·00198	„ „	0·00246	0·00280
Manganese carbonate.	0·00118	„ „	0·00155	0·00181
Alumina	0·00047	„ „	0·00156	0·00913
Ferrous carbonate	0·00595	„ ferric oxide	0·00370	0·00036
Aluminium phosphate.	0·00036	„ as such ...	0·00036	0·00047
Silicic acid	0·03460	„ as such ...	0·03460	0·03460
Total.....	1·55407		2·01458	2·33057
Residue on evaporation dried at 180°	1·56300	sulphate found direct	2·01500	

Traces of bromine, iodine, boric acid, barium and nickel were detected. The free carbonic anhydride in 1000 c.c. water was found to be 849·4 c.c. at 10·5° and 740 mm. J. I. W.

Organic Chemistry.

Chlorination of Hydrocarbons from Caucasian Petroleum. By W. MARKOWNIKOFF and W. OGLOBLIN (*Jour. Russ. Chem. Soc.*, 1882, 354).—On chlorinating the hydrocarbons of the series C_nH_{2n} from the above source, they give chlorides $C_nH_{2n-1}Cl$, several *isomerides* being formed simultaneously. Some of these are easily decomposed, with formation of hydrocarbons of the general formula C_nH_{2n-2}. They resemble the chlorides of saturated hydrocarbons, in giving ethereal salts of acetic acid by double decomposition. The presence of aromatic hydrocarbons in crude Caucasian petroleum has been confirmed, and diethyltoluene and pseudocumene were identified, in addition to those mentioned in previous communications. B. B.

Formation of Dibromodinitromethane and of Villiers' Tetranitroethylene Bromide. By S. M. LOSANITSCH (*Ber.*, **16**, 51—52). The author has shown (Abstr., 1882, 954) that dibromodinitromethane is produced by the action of nitric acid on tribromaniline. He has since observed that it is also formed from other bodies belonging both to the aromatic and fatty series (and amongst these ethylene bromide) when they are heated with concentrated nitric acid. According to Villiers (Abstr., 1882, 815), the action of fuming nitric acid on ethylene bromide yields tetranitroethylene bromide, forming an explosive potassium salt, $C_2(NO_2)_4Br_2,2KOH$. The author finds that

Villiers' compound is identical with dibromodinitromethane, the potassium derivative having the formula $CBrK(NO_2)_2$. The latter explodes at 147—150° (according to Villiers at 145°).

A. K. M.

Conversion of the Propyl into the Isopropyl Group. By G. GUSTAVSON (*Jour. Russ. Chem. Soc.*, 1882, 354—355).—Normal propyl bromide is converted into isopropyl bromide not only on boiling it with aluminium bromide, as observed by Kekulé and Schröter, but the conversion takes place at the ordinary temperature. This conversion, however, does not take place during the synthesis of hydrocarbons by Friedel's and Craffts' method. B. B.

Direct Combination of Hydrogen with Ethylene. By BERTHELOT (*Bull. Soc. Chim.* [2], **39**, 145).—The author has previously shown that at a dull red heat hydrogen combines directly with hydrocarbons, especially with ethylene, the combination being limited by the dissociation of the hydrides formed. This dissociation varies rapidly with the temperature, and at the softening point of glass, about 550°, only 51 per cent. of the ethylene is converted into ethane. At a lower temperature, however, with longer time, as much as 70 per cent. of the ethylene is converted into ethane, and probably at a still lower temperature, with sufficient time, the conversion would be complete. C. H. B.

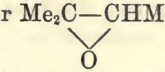
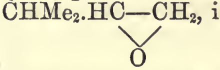
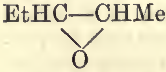
Stability of Trimethylcarbinol. By B. PAWLESKI (*Ber.*, **15**, 3034—3036).—Trimethylcarbinol boils at 83° under a pressure of 760 mm. At the temperature of its critical point, viz., 234·9°, it is perfectly stable. A determination of the density of the vapour of this substance at 337°, which was conducted in an atmosphere of carbonic anhydride, agreed with the theoretical results. W. C. W.

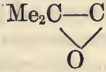
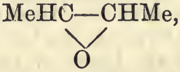
Schwarz's Process for preparing Pure Grape-Sugar. By WORM-MÜLLER and J. OTTO (*Bied. Centr.*, 1883, 68).—An excess of crude sugar is slowly introduced into a mixture of 600 c.c. 80 per cent. alcohol, and 20 c.c. fuming hydrochloric acid at 25°, then filtered and set aside to crystallise. Purification is further attained by washing and by recrystallisation from alcohol. The alkaline mercuric cyanide process for estimating dextrose is accurate when the solution is diluted with 3 vols. water and the sugar solution contains about 1 per cent. sugar. E. W. P.

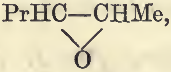
Saccharin and Saccharic Acid. By H. KILIANI (*Ber.*, **15**, 2953—2960).—Saccharin is most conveniently prepared by treating a solution of 1 kilo. of invert cane-sugar in 9 litres of water with 100 grams of slaked lime. After the liquid has remained 14 days in a closed vessel, 400 grams of slaked lime are added, and the mixture is preserved for one or two months until the clear liquid exerts only a feeble reducing action on an alkaline solution of copper sulphate. After the mixture has been filtered, the filtrate is saturated with carbonic acid, and the lime which remains in solution is exactly precipitated by oxalic acid: on evaporating the filtrate, saccharin is slowly deposited. Saccharin in aqueous solution slowly changes into saccharic acid, the presence of free oxalic acid is favourable to this reaction. On the other hand, saccharic acid is partially converted into its anhydride by boiling the aqueous solution.

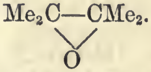
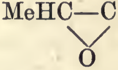
Potassium saccharate, $C_6H_{11}O_6K$, crystallises in thick monoclinic plates, $a : b : c = 1·2893 : 1 : 1·8861$, $\beta = 85° 25'$. The *calcium* and *zinc salts* are amorphous. *Copper saccharate*, $Cu(C_6H_{11}O_6)_2 + 4H_2O$, forms blue crystals. By the action of nitric acid (sp. gr. 1·375) at 35°, saccharin is slowly converted into oxalic acid and a new acid, $C_6H_{10}O_7$; after removing the oxalic acid by boiling with calcium carbonate, the new acid is obtained in rhombic plates or prisms [$a : b : c = 0·6903 : 1 : 0·528$] which closely resemble crystals of citric acid in appearance. The crystals are soluble in water and warm ether, and the aqueous solution is feebly lævogyrate. This body acts not only as a monobasic acid but also as a lactone. W. C. W.

Some Oxides of the Ethylene Series and their Action on Water. By A. ELTEKOFF (*Journ. Russ. Chem. Soc.*, 1882, 355—396). —In the present paper the author gives an account of some of the known compounds of the formula $C_nH_{2n}O$.

Amylene or *Trimethyl-ethylene oxide*, $C_5H_{10}O$, or  $\underset{O}{Me_2C{-}CHMe}$, was first obtained in 1861 by Bauer (*Annalen*, **115**, 91) by the action of hydrochloric acid on amylene glycol and subsequent treatment of the product with potash. On repeating Bauer's experiments with pure amylene glycol (b. p. 176—177°) the author obtained a compound, $C_5H_{10}O$ (b. p. 94—95°), which, however, was found to be no "oxide," but pure *methyl-isopropyl ketone*, formed apparently by the dehydrating action of hydrochloric acid on the glycol. According to Carius (*Annalen*, **126**, 199) a compound, identical with Bauer's, is obtained by the action of potash on the corresponding chlorhydrin; this, however, the author finds to be the true *amylene oxide*. It boils at 75—76°, and has a sp. gr. of 0·8293 at 0°. It enters into direct combination more readily than the lower oxides of the same series, for it is completely converted into the glycol by the action of water, even at the ordinary temperature, in half an hour. *Isopropyl-ethylene oxide*, $C_5H_{10}O$ or  $\underset{O}{CHMe_2.HC{-}CH_2}$, isomeric with the above compounds, was obtained in an analogous way. It boils at 82°, and combines very slowly with water, complete conversion into the glycol taking place only after the mixture has been heated for 50—60 hours at 100°. The third isomeric compound, *methyl-ethyl-ethylene oxide*, $C_5H_{10}O$ or  $\underset{O}{EtHC{-}CHMe}$, obtained from the corresponding hydrocarbon by the method described above, is a liquid (80°) which combines with water to form the glycol (b. p. 187—188°) only after continued heating at 100°. It is seen from the above that of the three isomeric compounds, one enters very readily into direct combination where the combination takes place on a "*tertiary*" carbon-atom. The behaviour of the isomeric oxides described below is analogous to this.

Isobutylene oxide,  $\underset{\diagdown O \diagup}{\mathrm{Me_2C—CH_2}}$, obtained by the action of potash on the chlorhydrin prepared by the direct union of isobutylene with hypochlorous acid in aqueous solution, is a colourless liquid of sp. gr. 0·8311 at 0°, boiling at 51—52°. It combines directly with water at the ordinary temperature with considerable development of heat, to form isobutylene glycol (b. p. 176—178°). The isomeric *butylene oxide* or *symmetrical dimethyl-ethylene oxide,*  $\underset{\diagdown O \diagup}{\mathrm{MeHC—CHMe}}$, was obtained from the corresponding hydrocarbon. A mixture of isobutylene and dimethyl-ethylene was first prepared by the action of sulphuric acid on isobutyl alcohol, and from this the first hydrocarbon was removed by agitation with dilute sulphuric acid ($1H_2SO_4 : 1H_2O$) in which it dissolves, leaving pure dimethyl-ethylene. Butylene oxide is a colourless liquid boiling at 56—57°, and having a sp. gr. of 0·8344 at 0°. It takes up the elements of water much less readily than isobutylene oxide, and is only completely converted into the glycol (b. p. 183—187°) by heating it at 100° for eight hours.

Methyl-propyl-ethylene oxide,  $\underset{\diagdown O \diagup}{\mathrm{PrHC—CHMe}}$, obtained in the same way from hexylene (from mannitol), boils at 109—110°. It is converted into the glycol (b. p. 206—207°) only when heated with water at 100—110° for a considerable length of time.

Hexylene oxide (tetramethyl-ethylene oxide),  $\underset{\diagdown O \diagup}{\mathrm{Me_2C—CMe_2}}$. The tetramethyl-ethylene, which formed the starting point for its preparation, was obtained by heating methyl iodide and lead oxide or amylene (trimethyl-ethylene) in sealed tubes at 220—230° for eight hours. In this reaction, some ethyl oxide is formed by the action of the lead oxide on the methyl iodide, some amylene remains unchanged, and the rest (about one-third) is converted into a mixture of hexylene (tetramethyl-ethylene) (b. p. 73°) and heptylene (unsymmetrical methyl-butyl-ethylene) $CMe_3.MeC \colon CH_2$ (b. p. 78—80°), as was shown by the reaction of the products of transformation of these hydrocarbons. After conversion into the chlorides, the two hydrocarbons were separated by fractional distillation and obtained in the pure state. The conversion of amylene into hexylene by the above method takes place thus: $CMe_2 \colon CHMe + MeI = CMe_2 \colon CMe_2 + HI$, but the author has hitherto been unable to understand the formation of the heptylene which takes place simultaneously. Hexylene, obtained as above, was first converted into the chlorhydride $CMe_2Cl.CMe_2.OH$ (m. p. 55°), and this, by the action of potash in presence of a *little* water, into hexylene oxide (b. p. 95—96°). It combines with water with the evolution of a considerable amount of heat forming the corresponding glycol, *pinacone.* This combination takes place so easily that, on distilling hexylene oxide with potash, no oxide at all is formed, but crystals of the hydrate of pinacone, $C_6H_{14}O_2 + 6H_2O$ (m. p. 46°), are formed in the receiver. The facility with which hexylene oxide becomes hydrated is explained by the circumstance that the oxygen is linked to *two tertiary* carbon-atoms. In contradistinction to this, *propylene oxide*,  $MeHC—CH_2$ (with O bridging), containing no tertiary carbon-atom, combines with difficulty with water, and cannot be converted completely into the glycol, even after being heated with it for eight hours at 100°. The author proceeds to investigate the mode of addition of different acids to the above oxides, the thermal phenomena taking place at the same time, and the heats of combustion of the oxides, as compared with those of the isomeric aldehydes and ketones. B. B.

Aldehyde-ammonium Bases. By G. MEYER (*Ber.*, **16**, 207—208).—By the action of sodium ethylate and methyl iodide at the ordinary temperature on a concentrated aqueous solution of acetaldehyde-ammonia, a crystalline mass of isocholine, $OH.CHMe.NMe_3.OH$, is produced. The salts of this base are very unstable, and act as powerful reducing agents. The iodide, $C_5H_{14}NOI$, forms needle-shaped crystals which are freely soluble in dilute alcohol. The platinochloride, $C_{10}H_{28}N_2O_2,PtCl_6$, is insoluble in ether. W. C. W.

Thiocyanopropimine. By J. TCHERNIAC and T. H. NORTON (*Compt. rend.*, **96**, 494—497).—By the action of monochloracetone on ammonium thiocyanate in alcoholic solution, thiocyanacetone is formed, which reacts with the excess of the ammonium salt to produce the thiocyanate of a new base, $C_4H_6N_2S$, which the authors propose to name *thiocyanopropimine.* The changes may be expressed thus:— $NH_4.SCN + MeCO.CH_2Cl = NH_4Cl + MeCO.CH_2.SCN$ and $MeCO.CH_2.SCN + NH_4.SCN = H_2O + (SCN.CH_2.CNHMe)HSCN$.

The *thiocyanate* of this base crystallises in bulky straw-yellow crystals melting at 114°, soluble in alcohol and hot water; the *nitrate*, $C_4H_6N_2S.HNO_3$, obtained from the preceding salt by the action of silver nitrate, crystallises in large colourless needles melting at 183°; the *acid sulphate* forms small white needles, the platinochloride a yellowish brown powder.

The base *thiocyanopropimine*, obtained from the thiocyanate by the action of concentrated potash, forms hygroscopic crystals which display in a most marked way the phenomenon of superfusion, for they melt at 42°, but solidify only at 28°. This compound boils at 136° under a pressure of 30—40 mm. mercury.

Acetylthiocyanopropimine, $SCN.CH_2.CMe\,\vdots\,N\overline{Ac}$, prepared by the action of acetic anhydride on the above base, crystallises in delicate silky needles, having a diamond-like lustre; it melts at 130°, but resolidifies at 91°.

Methylthiocyanopropimine hydroiodide, $SCN.CH_2.CMe\,\vdots\,NMe,HI$, from the free base and methyl iodide, forms transparent brown crystals melting at 157°, soluble in hot, sparingly soluble in cold water. V. H. V.

Isonitroso-compounds. By V. MEYER (*Ber.*, **16**, 167—170).—Since benzylhydroxylamine yields benzyl alcohol and not benzylamine on reduction, the benzyl-group in this compound must be attached to an oxygen, and not to a nitrogen atom. It will consequently have the formula $NH_2(OC_7H_7)$ and acetoxime will be $CMe_2\colon N.OH$.

It further appears that only bodies containing carbonyl, *e.g.*, acetones, aldehydes, yield isonitroso-compounds when acted on by hydroxylamine. Lævulic and pyroterebic acids form isonitroso-compounds, but ethylene oxide and glycidic acid do not.

This reaction is therefore capable of affording valuable aid in arriving at the constitution of certain compounds. W. C. W.

Aldoximes. By J. PETRACZEK (*Ber.*, **15**, 2783—2786).—The present paper is preliminary, and is in continuation of the researches of V. Meyer on the reactions of aldehyde with hydroxylamine, and the formation thereby of volatile nitrogenous products.

Ethylaldoxime, C_2H_5NO.—An aqueous solution of hydroxylamine chloride is decomposed by an equivalent of soda; to the cooled mixture, acetaldehyde, diluted with water, is added, the mixture is left for 12 hours, exhausted with ether, dried with calcium chloride, and the ether is expelled: a fluid remains which has a constant boiling point of 114—115°; it is miscible with water, alcohol, and ether in all proportions, and has a weak smell of aldehyde.

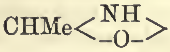
Propylaldoxime, C_3H_7NO, is prepared from propaldehyde by Przybytek's method (*Beilstein Org. Chemie*, p. 232), and very closely resembles the original aldoxime in its properties.

Isobutylaldoxime, C_4H_9NO, prepared by Fossek's method (*Monatsh. Chem.*, **11**) from isobutyl alcohol and chromic acid mixture; it is a colourless liquid not miscible with water, but partially soluble therein; its boiling point is about 139°.

Benzylaldoxime, C_7H_7NO.—Benzaldehyde is added to an aqueous solution of hydroxylamine chloride and excess of soda, and then sufficient alcohol to clear the solution; to prevent oxidation the vessel is filled with carbonic acid. After 24 hours the mixture is shaken with ether, which is driven off, and the residual oil dried over sulphuric acid. The product boils about 200° with partial decomposition; small portions may be distilled unaltered, but if a few grams are used, the mass assumes a brown colour, disengages ammonia, and deposits crystals which are either pure benzylaldoxime or an isomeric modification.

Solid benzylaldoxime forms white crystals similar to those of benzoic acid, slightly soluble in water, easily in alcohol and ether, and melting at 161·5°; prolonged boiling with hydrochloric acid decomposes it. The behaviour of benzaldehyde towards hydroxylamine does not differ from that of aldehydes of the acetic series.

As to the general constitution of aldoximes, ethylaldoxime for example, there are three possible formulæ:



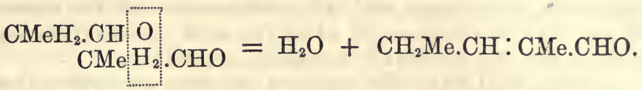
$$CMeH_2.NO\,;\ CHMe\colon N.OH\,;\ \text{and}\ CHMe\Big<\substack{NH\\ -O-}\Big>$$

J. F.

Condensation-products of Aldehydes and their Derivatives. By A. Lieben and S. Zeisel. (Second Memoir.) **Methylethylacroleïn and its Derivatives** (*Monatsh. Chem.*, 4, 10—87).—In a former memoir (Abstr., 1879, 615), the authors showed that the action of sodium acetate on propaldehyde gives rise to a condensation-product, $C_6H_{10}O = 2C_3H_6O - H_2O$; and the experiments described in the present paper lead to the conclusion that this body consists of *propylidenepropaldehyde* or *α-methyl-β-ethylacroleïn*

$$CMeH_2.CH : CMe.CHO,$$

and that its formation takes place by the union of the oxygen of one of the propaldehyde molecules with the H_2 of the other, the water thus formed being eliminated, thus:



$$\begin{array}{l} CMeH_2.CH\boxed{O} \\ \qquad CMe\boxed{H_2}.CHO \end{array} = H_2O + CH_2Me.CH : CMe.CHO.$$

Methylethylacroleïn is an unsaturated aldehyde, oxidising in the air, and forming with hydrogen sodium sulphite a crystalline compound, which is not decomposed by sodium carbonate, but combines directly with HCl or Br_2, the latter compound uniting readily with hydrogen sodium sulphite and forming a body having the composition

$$C_6H_{10}OBr_2,SO_3HNa + 3H_2O.$$

By reduction in alcoholic solution with zinc-turnings and sulphuric or hydrochloric acid, or better with iron and acetic acid, methylethylacroleïn is converted into caproic aldehyde, hexyl alcohol, and an unsaturated alcohol, $C_6H_{12}O$. The aldehyde and the hexyl alcohol yield on oxidation a hexoic or caproic acid, viz., *methylpropylacetic acid*, CHMePr.COOH, together with *methyl propyl ketone* and *hexyl caproate*, $C_5H_{11}.COOC_6H_{13}$.

The unsaturated alcohol, $C_6H_{12}O$, forms with bromine an unstable compound, $C_6H_{12}O,Br_2$, which is decomposed by heating under reduced pressure, and when boiled with water yields, as chief product, *hexenyl glycerol*, $C_6H_{11}(OH)_3$, and the unsaturated aldehyde $C_6H_{10}O$.

The *hexenyl-glycerol*,

$$C_6H_{11}(OH)_3 = CH_2Me.CH(OH).CMe(OH).CH_2(OH),$$

purified by conversion into the corresponding triacetin, and separated therefrom by boiling with baryta-water, agitation of the watery liquid with ether, and evaporation under reduced pressure, is a thick colourless liquid, slightly volatile at ordinary temperatures, and distilling under 53 mm. pressure between 170° and 176°. Heated with excess of hydriodic acid in a sealed tube at 100°, it yields a hexyl iodide, $C_6H_{13}I$, distilling at 154—160°. The *triacetin*, $C_6H_{11}(O\overline{Ac})_3$, is a colourless, thickish liquid, having a faint odour and aromatic taste, heavier than water, and not miscible therewith.

Oxidation of Methylethylacroleïn.—By oxidation with free oxygen, chromic acid mixture, or moist silver oxide, this aldehyde yields propionic, acetic, formic, and carbonic acids, a slightly soluble unsaturated acid, viz., methylethylacrylic acid, $C_6H_{10}O_2$, a soluble non-volatile crystalline acid, viz., dehydroxycaproic acid, $C_6H_{12}O_4$, accompanied by a non-crystalline acid, and finally methyl-propyl ketone, $CH_3.CO.C_3H_7$.

The formation of these bodies may be represented by the following equations, from which it will be seen that the oxidation takes place partly at the aldehyde-group, whereby methylethylacrylic acid is formed, partly at the double linking, whereby the molecule is split up, with formation of propionic, acetic, and formic acids, while the formation of dihydroxycaproic or methyl-hydroxypropyl-hydroxyacetic acid may be explained by oxidation at both these places simultaneously, and that of methyl propyl ketone by the successive action of water and oxygen :—

$$(1.)\ CH_2Me.CH\colon CMe.CHO + O = CH_2Me.CH\colon CMe.COOH$$

Methylethylacrylic acid.

$$(2.)\ CH_2Me.CH\colon CMe.CHO + O_4 + H_2O = CH_2Me\ COOH +$$

Propionic acid.

$$Me.COOH + H.COOH$$

Acetic acid. Formic acid.

$$(3.)\ CH_2Me.CH\colon CMe.CHO + O_2 + H_2O =$$
$$CH_2Me.CH(OH).CMe(OH).COOH$$

Dihydroxycaproic acid.

$$(4.)\ CH_2Me.CH\colon CMe.CHO + H_2O = CH_2Me.CH_2.CMe(OH).CHO$$

and $CH_2Me.CH_2.CMe(OH).CHO + O_2 = H_2O + CO_2 +$

$$CH_2Me.CH_2.COMe$$

Methyl propyl ketone.

Methylethylacrylic acid crystallises in large colourless monoclinic prisms, having the axes $a : b : c = 1{\cdot}4807 : 1 : 0{\cdot}3847$, and the angle $ac = 104° 38'$. Observed forms $\infty P . \breve{P}\infty$. Habit, prismatic in the direction of ∞P. Melting point 24·4°. Sp. gr. of fused acid at 25° (corr.) = 0·9812, referred to water at the same temperature. Boiling point 213° (corr.) under a pressure of 750 mm. reduced to 0°. The acid has a characteristic, rather agreeable, scarcely sour odour, quite different from that of the lower fatty acids, but somewhat resembling that of methylpropylacetic acid. The *calcium salt*, $Ca(C_6H_9O_2)_2 + 4H_2O$, is much more soluble in hot than in cold water or aqueous alcohol, and crystallises, sometimes in hard hemispherical nodules adhering to the sides of the vessel, sometimes in well-defined prisms or slender silky needles, often in radiate groups. The *silver salt*, $AgC_6H_9O_2$, obtained by digesting the free acid with a large quantity of water and excess of silver carbonate, crystallises on cooling in needles and laminæ. The solution of the calcium salt gives white precipitates with nitrate of silver or lead; with cupric acetate a sky-blue precipitate soluble in excess of calcium acetate; with zinc acetate a white, and with ferric chloride a red precipitate, oily when first separated.

By reduction with hydrobromic acid and zinc, or with hydriodic acid, methylethylacrylic acid is converted into a caproic acid, $C_6H_{12}O_2$, identical with that which is obtained by oxidation of the above mentioned hexyl alcohol and caproic aldehyde, that is to say, methylpropylacetic acid.

Methylethylacrylic acid unites directly with bromine, forming the compound $C_6H_{10}O_2Br_2$ = EtCHBrMe.COOH.CBr, which separates in large fine crystals, is reconverted by nascent hydrogen into methylethylacrylic acid, and is decomposed by excess of water at 100°, yielding hydrogen bromide, bromamylene, methylethylacrylic acid, methyl propyl ketone, dihydroxycaproic acid (apparently identical with that which is obtained by oxidation of methylethylacroleïn), and carbon dioxide. H. W.

Constitution of Nitroso-compounds. By V. MEYER and M. CERESOLE (*Ber.*, **15**, 3067—3074).—By the action of benzyl chloride on an alcoholic solution of the sodium compound of nitrosoacetone, a crystalline body is obtained which is isomeric with benzylnitrosoacetone (*Ber.*, **15**, 1876). It forms colourless plates melting at 45°, freely soluble in ether, chloroform, alcohol, and light petroleum. It is sparingly soluble in water, and insoluble in alkalis. The formation of this body instead of benzylnitrosoacetone (m. p. 81°) is further evidence in favour of the view that nitrosoacetone does not contain the NO-group, and that its constitution may be represented by the formula CH_3.CO.CH ⁚ N.OH.

The authors are of opinion that true nitroso-compounds are produced only by the action of nitrous acid on the CH-group, and that isonitroso-derivatives, C ⁚ NOH, are formed by the action of nitrous acid on the CH_2-group. W. C. W.

Nitrosoketones. By F. P. TREADWELL and B. WESTENBERGER (*Ber.*, **15**, 2786—2789).—Referring to previous communications on ketines by one of the authors (Abstr., 1881, 895; 1882, 166), they announce that in their experiments, occupied with preparation of nitrosoacetone, they allowed the prepared solution to remain unnoticed for the space of a week. On proceeding to extract it with ether, they found, instead of nitrosoacetone, the acetoximacid, NHO.CMe ⁚ CH.NHO, already obtained by V. Meyer and Janny by the action of dichloracetone on hydroxylamine. It melts at about 153°, gives colourless solutions with alkalis, and sublimes in white needles. The authors point out certain advantages of this mode of preparing the substance in question. A nitrosoisobutylketone was formed by a similar reaction; it crystallises in the form of white leaves, melting at 42°, and easily sublimed, soluble in ether and alcohol, easily in warm, but sparingly in cold water. The authors note the lowering of the melting point of the nitrosoketones in proportion as their molecular weights increase.

$C_4H_7O_2N$.	$C_5H_9O_2N$.	$C_6H_{11}O_2N$.	$C_7H_{13}O_2N$.
74°	54°	49·5°.	42°.

The primary nitrosoketone, $C_3H_5O_2N$, does not follow the rule, its melting point being 65°. J. F.

Isonitrosoketones. By C. SCHRAMM (*Ber.*, **16**, 177—180).—When isonitrosomethylketone, MeCO.CMe ⁚ N.OH, is decomposed by boiling with strong hydrochloric acid, the sole products are hydroxylamine hydrochloride, acetic acid, and a small quantity of *ethylmethylacetoximic acid*, OHN ⁚ CMe.CMe ⁚ NOH. This acid is easily prepared by the action of hydroxylamine hydrochloride on an aqueous solution of isonitrosomethylketone. It crystallises in white needles, which sublime about 215°, and are sparingly soluble in water. W. C. W.

Action of Nitric Acid on Ethyl Acetoacetate and Chloracetoacetate. By M. PRÖPPER (*Ber.*, **16**, 67).—According to a previous communication (Abstr., 1882, 1193), the author obtained ethyl nitrosoacetate and chloronitrosoacetate by the action of concentrated nitric acid on the abovementioned ethereal salts. A further study of these bodies has led him to infer that they are really oximido-bodies in accordance with the view of Meyer and Ceresole (*Ber.*, **15**, 3067). In support of this, he urges the fact that ethyl acetoacetate and chloracetoacetate yield oxalic acid and the two bodies $C_4H_7O_3N$ and $C_4H_6ClO_3N$ respectively, whilst ethyl dichloracetoacetate is not attacked; this being easily explained on the assumption of the *diad* oximido-group: whereas if the *monad* nitroso-group is present, a similar body should also be producible from the dichloracetoacetate. Boiling with hydrochloric acid decomposes ethyl oximidoacetate into hydroxylamine hydrochloride, oxalic acid, and ethyl chloride; whilst boiling with water decomposes the chloro-derivative into hydroxylamine hydrochloride, oxalic acid, and alcohol. A. K. M.

Brom-addition-derivatives of the Crotonic Acids and of Methacrylic Acid. By C. KOLBE (*J. pr. Chem.*, [2], **25**, 369—398).—The constitution of the isomeric crotonic, isocrotonic, and methacrylic acids being still uncertain, although it is known that the two former are derivatives of normal butyric acid, and the latter of isobutyric acid, the author in the hope of settling the question has investigated the brom-additive compounds of these acids.

Methacrylic acid was dissolved in carbon bisulphide, and the calculated quantity of bromine slowly added. The resulting *dibromisobutyric acid* crystallises in long prisms melting at 48°. On heating it with 10 parts of water in a vessel provided with a reflux condenser, decomposition commences at the boiling temperature, carbonic anhydride being copiously evolved. The solution then contains a small quantity of acetone, hydrobromic acid, ordinary bromomethacrylic acid, bromhydroxyisobutyric acid, and very small quantities of propaldehyde, and an oil whose amount was too small for further investigation. The same products are obtained with aqueous solution of sodium carbonate, but acetone is formed in large quantity, whilst the yield of bromomethacrylic acid and of hydroxybromisobutyric acid is very small.

Bromhydroxyisobutyric acid, $CMe(CH_2Br)(OH).COOH$, crystallises in groups of fine white needles melting at 100—101°, soluble in ether and benzene, insoluble in carbon bisulphide and chloroform; it does not distil with steam. No salts could be obtained, as in presence of bases it is decomposed with formation of metallic bromides; on heating it with water, a very slow decomposition ensues. By treatment with nascent hydrogen, it is converted into the ordinary hydroxyisobutyric acid.

On adding dibromisobutyric acid to a moderately concentrated solution of sodium hydroxide, it dissolves, with evolution of heat, and is completely converted into bromomethacrylic acid.

From these results, it follows that methacrylic acid must have the constitution $CH_2\colon CMe.COOH$, as originally suggested by Frankland; for by the formula $\equiv CH.CHMe.COOH$, proposed by Fittig, the dibromide would have the constitution $CHBr_2.CHMe.COOH$, and on boiling with water and treatment with nascent hydrogen, should yield, not the known hydroxyisobutyric acid, $CMe_2(OH).COOH$, but an isomeric acid of the formula $CH_2(OH).CHMe.COOH$.

Crotonic and isocrotonic acids, when treated with bromine, both yield the same dibromobutyric acid, which when boiled with water or solution of sodium carbonate, is decomposed into β-bromopropylene, monobromocrotonic acid and bromhydroxybutyric acid, together with carbonic anhydride and hydrobromic acid.

Bromhydroxybutyric acid was obtained as an oily substance, not solidifying on standing for many weeks under an exsiccator. Salts could not be obtained, as it is decomposed by bases, with formation of metallic bromides. On boiling it with water for eight hours, a *dihydroxybutyric acid* was obtained, whose barium salt, $[C_3H_5(OH)_2.COO]_2Ba$, was not crystalline. On treating dibromobutyric acid with sodium hydroxide, monobromocrotonic acid was alone obtained. In conclusion, the author entirely fails to confirm the statement of Erlenmeyer and Müller (Abstr., 1882, 598), that ordinary monobromocrotonic acid is a mixture of two isomeric acids. The acid was prepared by three methods, and in each case proved to be one substance only.

A. J. G.

New Method for preparing Carbonic Oxide. By E. NOACK (*Ber.*, **16**, 75—76).—When carbonic anhydride is passed over heated zinc-dust contained in a combustion tube, it is almost completely reduced to carbonic oxide, the last traces of carbonic anhydride being easily removed by passing the gas through soda solution.

A. K. M.

Carbonic Hydroxide. By M. BALLO (*Ber.*, **15**, 3003—3007).—Aqueous solutions of potassium and sodium bicarbonates, as well as solutions of carbonic anhydride, dissolve metallic magnesium with evolution of hydrogen. Solutions of the normal carbonates of sodium and potassium have no action on magnesium: hence the author concludes that in an aqueous solution, the carbon dioxide exists in the form of a hydroxide.

An aqueous solution of sulphur dioxide also has the power of dissolving magnesium with evolution of hydrogen. W. C. W.

Action of Acids on Acetamide. By W. OSTWALD (*J. pr. Chem.*, **27**, 1—39).—The author has studied the action of various acids on acetamide at certain temperatures, in order to determine the relative intensities of their chemical actions. By observing the amount of the amide decomposed in a given time, or *vice versâ*, he has obtained numbers which represent the rate of decomposition by the acids under examination. The intensity of the reaction was determined by estimating the amount of ammonium salt formed, the salt being decomposed by sodium hypobromite and the nitrogen measured. The author finds that the presence of acetamide along with the ammonium salt in the nitrometer yields free nitrogen, in excess of that which would be evolved; but he has made corrections for the amount of acetamide present. The observations were made at 65°, the boiling point of methyl alcohol, and at 100°. The rate at which the acetamide is decomposed is directly proportional to the strength of the acid present. The reaction commences quickly; but the further it proceeds, the smaller is the amount of decomposition in equal intervals of time. The author has tabulated the results obtained with solutions of acetamide of given strength in various intervals of time. From the different times required to decompose successive varying quantities of acetamide, the author has calculated the time in minutes at which the reaction would be half completed in the case of each acid. The results are shown in the following table:—

	65°.	100°.	Proportion.
1. Hydrochloric acid	72·1	4·98	14·48
2. Nitric acid..............	75·2	5·35	14·06
3. Hydrobromic acid	74·0	5·14	14·39
4. Trichloracetic acid	112·8	—	—
5. Dichloracetic acid	433·7	—	—
6. Monochloracetic acid.....	4570·0	—	—
7. Formic acid	28950·0	2138·0	13·55
8. Lactic acid	29340·0	2128·0	13·80
9. Acetic acid..............	—	—	—
10. Sulphuric acid	180·0	14·1	12·77
11. Oxalic acid	1516·0	118·6	12·80
12. Tartaric acid............	13660·0	929·0	14·71
13. Malic acid	35310·0	—	—
14. Succinic acid............	—	7976·0	—
15. Citric acid..............	44810·0	3088·0	14·53
16. Phosphoric acid	—	3880·0	—
17. Arsenic acid	—	4005·0	—

By dividing the intervals of time in the table of results by the above values at the respective temperatures, comparable figures are obtained. The author has drawn the curve representing the theoretical progress of the reaction, according to the formula $\frac{y}{a-y} = Ct$; where a is the substance taking part in the reaction, and y is the amount decomposed in time t, C being a constant. Alongside the curve are placed dots representing the results of experiments, and showing the amounts of ammonia formed in various intervals of time in presence of different acids.

The dots representing the reaction in presence of hydrochloric, nitric, and hydrobromic acids, show that during the decomposition there is an accelerating moment. Former researches (*ibid.*, **23**, 209) have shown that monobasic acids in certain cases have a more powerful action in the presence of their neutral salts. It is, therefore, evident that in this case the variation is due to the presence of the neutral ammonium salts. In the case of trichloracetic acid, however, a retarding action is evinced: it is possible that this is due to the tendency to form the corresponding amido-acid. The bibasic acids act less rapidly towards the end of the reaction. There is no doubt that this is due to the formation of the acid salt. In the case of the tribasic phosphoric and arsenic acids, the retarding effect is still more marked.

The curve representing experiments made at 65° is almost identical with that formed from those at 100°, except that in the case of bibasic and tribasic acids, towards the end of the reaction, the latter is lower than the former, showing that a rise in temperature promotes the formation of the acid salt. If the time for each acid of the semi-completion of the reaction be divided into that for hydrochloric acid, the *relative velocities* are obtained, referred to HCl = 1.

The author shows that the affinities of bodies vary as the 4th root of the velocity of the reaction in which they take part. The relative velocities and their 4th roots representing the relative affinities are given in the following table. Those under *a* are from experiments made at 65°, those under *b* from those at 100°, and those given under *c* are the results of former experiments (*ibid.*, **18**, 362) made by the method of equivalent weights:—

	Relative Velocities.				Relative Affinities.		
	65°.		100°.		*a.*	*b.*	*c.*
Hydrochloric acid	0·0000	100·0	1·0000	100·0	100·0	100·0	98·0
Nitric acid	0·9588	98·0	0·9327	97·0	98·0	97·0	100·0
Hydrobromic acid	0·9743	98·0	0·9690	98·0	98·0	98·0	95·0
Trichloracetic acid....	0·6393	80·0	—	—	80·0	—	80·0
Dichloracetic acid	0·1663	40·8	—	—	40·8	—	33·0
Monochloracetic acid..	0·01687	13·0	—	—	13·0	—	7·0
Formic acid	0·002663	5·1	0·002330	4·83	5·16	4·83	3·9
Lactic acid	0·002628	5·13	0·002340	4·85	5·13	4·85	3·3
Acetic acid	0·0005466	2·34	—	—	—	2·34	1·23
Sulphuric acid	0·4283	65·4	0·3532	59·4	65·4	59·4	66·7
Oxalic acid	0·05086	22·6	0·04199	20·5	22·6	20·5	—
Tartaric acid	0·0005644	7·51	0·005360	7·32	7·51	7·32	5·2
Malic acid	0·002184	4·67	—	—	4·67	—	2·82
Succinic acid	0·00065	2·55	0·0006244	2·50	2·55	2·50	1·45
Citric acid...........	0·001608	4·01	0·001612	4·01	4·01	4·01	—
Phosphoric acid......	—	—	0·001284	3·58	—	3·58	—
Arsenic acid	—	—	0·001244	3·53	—	3·53	—

J. I. W.

Action of Aluminium Chloride and Bromide on Hydrocarbons. By G. GUSTAVSON (*Jour. Russ. Chem. Soc.*, 1882, 354).—On shaking the compound $AlBr_3,3C_6H_6$ with toluene, the latter combines with a part of the aluminium bromide, and benzene is set free. In like manner cymene displaces some of the benzene from the same compound. Aluminium bromide is therefore distributed between aromatic hydrocarbons, and by this circumstance the great effect of reaction with only small quantities of halogen-compounds of aluminium is explained.

B. B.

Oxidation of the Nitro-toluenes by Potassium Ferricyanide. By W. A. NOYES (*Ber.*, **16**, 52—54).—The author has examined the action of an alkaline solution of potassium ferricyanide on ortho- and paranitro-toluene with the view to ascertain whether, with this oxidising agent, the *ortho*-nitro-group has the effect of hindering the oxidation of the methyl-group, as is the case when chromic acid is used, or whether both ortho- and para-groups are oxidised alike, as in the case of alkaline permanganate. He finds that *both* of these nitro-toluenes are oxidised to the corresponding nitro-benzoic acids.

A. K. M.

Derivatives of Mesitylene. By G. ROBINET (*Compt. rend.*, **96**, 500).—By the chlorination of mesitylene at a temperature not exceeding 215°, a *mono-* and a *di-chloromesitylene* are obtained. The former, $C_6H_3Me_2.CH_2Cl$, is a colourless liquid, which boils from 215—220°, and does not solidify at $-17°$ (the monochloromesitylene, already known, boils at 204—206°); the latter, $C_6H_3Me(CH_2Cl)_2$, crystallises in delicate white needles, which melt at 41° and distil at 260° (the dichloromesitylene of Kahn crystallises in prisms, melting at 59°, boiling at 243°). *Dibromomesitylene*, $C_6H_3Me(CH_2Br)_2$, prepared by treating the vapour of mesitylene with bromine, crystallises in delicate white needles melting at 66°, having a pungent odour, soluble in ether. The dibromomesitylene, $C_3HBr_2Me_3$, already known, melts at 60°. *Mesitylenic acetate* from monochloromesitylene and sodium acetate, is a colourless liquid, which distils in a vacuum at 242°; on heating a mixture of this compound with a further quantity of monochloromesitylene and concentrated nitric acid there are obtained mesitylenic acid and mesitylaldehyde. The latter, $C_6H_3Me_2.CHO$, is a heavy oil, forming a crystalline compound with sodium hydrogen sulphite.

V. H. V.

Benzoylmesitylene. By E. LOUISE (*Compt. rend.*, **96**, 490—500).—By the action of aluminium chloride on a mixture of benzoic chloride and mesitylene (Friëdel and Crafts' reaction), benzoylmesitylene, $C_6H_2Me_3\overline{Bz}$, is formed. This compound forms transparent, colourless, voluminous crystals, soluble in ether, alcohol, &c. It melts at 29°, but exhibits in a most marked way the phenomenon of superfusion, for it can be cooled to $-40°$ without a trace of crystallisation.

V. H. V.

Metanitriles. By O. WALLACH (*Ber.*, **15**, 6—7).—This is an answer to Staedel (*Ber.*, **15**, 2864) on the history of this class of bodies.

A. K. M.

Methylation and Ethylation of Aniline and Toluidine. By H. REINHARDT and W. STAEDEL (*Ber.*, **16**, 29—31).—When the hydrobromides and hydriodides of aniline and toluidine (see p. 579) are heated with methyl or ethyl alcohol, secondary and tertiary bases are formed. In the case of the hydrobromides, a temperature of 145—150°, continued for eight hours, is employed, in that of the hydriodides 125°, also for eight hours. In preparing the tertiary bases, an excess of alcohol is to be employed, viz., 5 per cent. of methyl alcohol, and 5—10 per cent. of ethyl alcohol. The following bases and derivatives have been prepared in this way:—Methylaniline (b. p. 192° at 754 mm.) and its acetyl derivative (m. p. 101°), which crystallises in prisms. Dimethylaniline (b. p. 192°) and its platinochloride,

$$(C_8H_9N)_2,H_2PtCl_6,$$

forming large, four-sided, reddish-yellow anhydrous plates, or deep ruby-red prisms, with 2 mols. H_2O. Ethylaniline (b. p. 202—204°) forming an acetyl-derivative which melts at 54·5°, and boils at 248—250°. It crystallises in splendid monoclinic prisms. Diethylaniline (b. p. 211—211·5°) gives a platinochloride in yellowish-red crystals. Methylorthotoluidine (b. p. 207°) yields an acetyl-derivative boiling at 250—251°. Dimethylorthotoluidine (b. p. 183°) forms a platinochloride crystallising in flat reddish-yellow needles. Ethylorthotoluidine (b. p. 213—214°) yields an acetyl-derivative boiling at 254—256°. Diethylorthotoluidine (b. p. 208—209°), the platinochloride of which forms large reddish-yellow rhombic plates. Dimethylparatoluidine (b. p. 208°) gives a platinochloride crystallising in sparingly soluble plates. A. K. M.

Hydrobromides and Hydriodides of Aromatic Bases. By W. STAEDEL (*Ber.*, **16**, 28—29).—Aniline hydrobromide and hydriodide have already been described by Hofmann. The following analogous compounds have been prepared by the author:—*Orthotoluidine hydrobromide*, C_7H_9N,HBr, crystallises in large rhombic prisms, and the *hydriodide*, C_7H_9N,HI, in thin rhombic prisms. The latter is partly decomposed by water, with separation of orthotoluidine. The *hydrobromide* and *hydriodide* of *paratoluidine* form white crystalline plates. From commercial *xylidine* two *hydrobromides* can be obtained, one of which is derived from the [Me : Me : NH_2 = 1 : 3 : 4] xylidine, and crystallises in slender needles, whilst the other forms large rhombs. The constitution of the latter has not yet been determined. *Metachloraniline hydrobromide*, C_6H_6ClN,HBr, crystallises in large bright-red shining plates, and *parabromaniline hydrobromide*, $C_6H_6BrN,HBr + \frac{1}{2}H_2O$, in large white efflorescent prisms. *Metanitraniline hydrobromide*, $C_6H_6(NO_2)N,HBr$ (?), forms yellow plates which rapidly effloresce and give off hydrobromic acid. *Ortho-* and *para-nitraniline* also dissolve in hydrobromic acid, the latter yielding a hydrobromide, crystallising in large prisms. *Metamidophenetoïl* forms a hydrobromide,

$$EtO.C_6H_4.NH_2,HBr\ (?),$$

crystallising readily in soluble plates. A. K. M.

Nitrotoluidines from Liquid Dinitrotoluene. By A. BERNTHSEN (*Ber.*, **15**, 3016—3019).—When the mixed bases obtained by the reduction of liquid dinitrotoluene are dissolved in hot dilute hydrochloric acid, the hydrochloride of a base melting at 91·5° first crystallises out. The benzoic derivative of this nitrotoluidine is deposited from an alcoholic solution in prisms melting at 167°. The mother-liquor from the hydrochloric acid solution just mentioned contains orthonitrotoluidine hydrochloride. The free base melts at 78°, and its benzoic derivative crystallises in flat prisms melting at 171·5°.

A complete separation of these nitrotoluidines may be effected by the action of benzoic chloride on the ethereal solution of the mixed bases, as the ortho-compound is attacked before its isomeride. The orthobenzoic derivative is separated from the hydrochloride of the other base by treatment with hot dilute hydrochloric acid, which dissolves the latter compound. The benzoic compounds may also be separated by recrystallisation from hot alcohol, in which the substance melting at 167° is more freely soluble than that melting at 171·5°.

These results differ in many respects from those obtained by Cunerth (*Annalen*, **172**, 223), who describes a nitrotoluidine melting at 94·5°, which forms a benzoic derivative melting at 145°.

W. C. W.

Ethylnitraniline. By A. WELLER (*Ber.*, **16**, 31—32).—Ethylacetanilide is treated with 4 parts of cold nitric acid (sp. gr. 1·52), and, when dissolved, the product is poured into cold water and well shaken. Ethylacetonitranilide, $C_6H_4(NO_2).NEt\overline{Ac}$, separates out in small white plates, and is easily purified by crystallisation from water, in which it is sparingly soluble. It is insoluble in light petroleum and carbon bisulphide, sparingly soluble in ether, readily in alcohol and benzene. It melts at 117·5°. When boiled with potash solution, it is converted into ethylnitraniline, $NO_2.C_6H_4.NEtH$, which can be purified by crystallisation from alcohol, and then melts at 95—95·5°. This body is very sparingly soluble in water, light petroleum, and carbon bisulphide, readily in warm alcohol, ether, and benzene. It crystallises from alcohol in large prisms. A. K. M.

Dimethylxylidines, Dimethylmetachloraniline, and Dimethylmetamidophenetoïl. By H. v. BAUR and W. STAEDEL (*Ber.*, **16**, 32—33).—On heating the two hydrobromides obtained from commercial xylidine (see p. 578) with methyl alcohol (2 mols.), two isomeric dimethylxylidines are obtained, one of which,

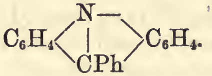
$$[Me : Me : NMe_2 = 1 : 3 : 4] \text{ (loc. cit.)},$$

boils at 203—205°. It is a colourless liquid, forming readily soluble salts. The isomeride obtained from the second hydrobromide boils at 200—202°, and is very similar to the former. *Dimethylmetachloraniline*, $C_6H_4Cl.NMe_2$, obtained from metachloraniline hydrobromide and methyl alcohol, is a colourless liquid boiling at 231—233°. Its salts crystallise well; the hydrobromide in plates, the oxalate in white plates, the hydrochloride in slender needles, and the platinochloride in delicate yellow needles. A nitroso-derivative has also been prepared, the hydrochloride of which crystallises in gold-coloured plates.

Dimethylmetamidophenetoïl, $OEt.C_6H_4.NMe_2$, can easily be obtained by the same reaction. It is a colourless liquid forming crystalline salts. Its nitroso-derivative also yields a hydrochloride crystallising in gold-coloured plates. A. K. M.

Preparation of the Base $C_{19}H_{13}N$ (obtained from Benzenylisodiphenylamidine) from Benzoyldiphenylamine. By A. Bernthsen (*Ber.*, **15**, 3011—3016).—When a mixture of benzonitril and diphenylamine hydrochloride is heated at 180—190°, benzenylisodiphenylamidine, $NPh_2.CPh \colon NH$, is produced; but at a higher temperature (230—250°) a totally different base is obtained, which has the composition $C_{19}H_{13}N$. The same compound is formed by the action of zinc chloride on benzoyldiphenylamine at 270°. It is deposited from benzene in yellow prisms, containing 1 mol. benzene, which effloresce on exposure to the air, and also in monoclinic plates (m. p. 180°), which are free from benzene. The *hydrochloride*, $C_{19}H_{13}N,HCl$, forms sparingly soluble golden-yellow prisms, which dissociate when brought into contact with pure water. The yellow-coloured platinochloride is almost insoluble in water.

The constitution of the base has not yet been definitely ascertained; its mode of formation seems to indicate that it is *nitrilotriphenylmethane*,



$$C_6H_4\left\langle\begin{array}{c}N-\\|\\CPh\end{array}\right\rangle C_6H_4.$$

W. C. W.

Acetoximes. By A. Janny (*Ber.*, **15**, 2778—2783).—*Dimethylacetoxime*, $CMe_2 \colon NHO$ (Abstr., 1882, 1047), is easily soluble in water, alcohol, and ether; melts at 59—60°, and boils unaltered at 134·8°; its formation from acetone and hydroxylamine is instantaneous.

Ethylmethylketone and hydroxylamine in aqueous solution left for 24 hours, yields *ethylmethylacetoxime*, which may be extracted by ether; it is purified by distillation, and boils between 152—153°; it does not solidify in a mixture of ice and salt; its sp. gr. is 0·9195 at 24°; it is miscible in all proportions with alcohol and ether, and dissolves in 10 times its volume of water; when decomposed with concentrated soda solution, it yields a crystalline sodium derivative; with hydrochloric acid, it yields hydroxylamine.

Methylpseudobutylacetoxime, $CMe_3.CMe \colon NHO$, is obtained from methylpseudobutylketone and hydroxylamine. The substance crystallises in fine colourless needles melting at 74—75°; they are easily soluble in alcohol and ether and the ordinary solvents, also in warm water, sparingly in cold water. It is volatile with steam, tastes of camphor, and sublimes unchanged.

Methylphenylacetoxime, $CMePh \colon NHO$, is formed from hydroxylamine and acetophenone. It forms colourless silky needles melting at 59°, easily volatile with steam; the vapour has a very agreeable smell, but attacks the eyes. It is easily soluble in the usual solvents, and also in acids and alkalis.

Diphenylacetoxime, $CPh_2 \colon NHO$, is obtained from benzophenone and hydroxylamine, but the mixture must be left at rest for a week before extracting the substance; the crystals melt at 139—140°, and are easily soluble in ether and acetone, less so in benzene, chloroform, and light petroleum, sparingly in cold water. It is soluble in alkalis, from whence it is precipitated by hydrochloric acid; it is also soluble in concentrated hydrochloric acid, but is precipitated on diluting with water. J. F.

Acetoximes. By A. JANNY (*Ber.*, **16**, 170—177).—*Dimethylacetoxime* decomposes into hydroxylamine and acetone when boiled with strong hydrochloric acid, $CMe_2 \colon NOH + H_2O = NH_3O + Me.CO_2Me$.

Acetic anhydride and acetic chloride readily attack acetoxime, but the product of the reaction was not investigated. On mixing benzoic chloride and acetoxime, a crystalline mass is produced, which on being heated gives off hydrochloric acid, and leaves a benzoic derivative, $C_{10}H_{11}NO_2$; this substance crystallises in transparent colourless plates (m. p. 41°), which dissolve freely in alcohol and ether. It is decomposed by heating with acids, with liberation of hydroxylamine.

Acetoxime hydrochloride, C_3H_7NO,HCl, prepared by passing dry hydrochloric acid gas over solid acetoxime or into a solution of acetoxime in absolute alcohol, is a white hygroscopic powder soluble in alcohol and water, but insoluble in ether. The aqueous solution slowly decomposes at the ordinary temperature, hydroxylamine being formed. The hydrochloride melts at 98—101°, and at a higher temperature splits up into hydrochloric acid and acetoxime. A platinochloride could not be obtained.

When ether is added to an alcoholic solution of acetoxime and sodium ethylate, a white crystalline salt is precipitated, which contains 19·49 per cent. Na, and probably has the composition $C_3H_6NONa + EtHO$. This compound is insoluble in alcohol and water. Acetoxime is not reduced by nascent hydrogen. It is completely destroyed by potassium permanganate or ferrocyanide.

Benzylacetoxime, $CMe_2 \colon NOC_7H_7$, is formed by the action of benzyl chloride on an alcoholic solution of acetoxime and sodium ethylate. The brown oil which separates out when the crude product is diluted with water is extracted with ether, and distilled in a current of steam. Pure benzylacetoxime is a colourless oil, soluble in alcohol and ether. It boils at 190° with decomposition. On boiling with hydrochloric acid, it splits up into acetone and benzylhydroxylamine. *Benzylacetoxime hydrochloride* is an oily liquid. It is decomposed by moisture, benzylhydroxylamine hydrochloride being deposited in crystalline scales, which are soluble in alcohol and water. On reduction with hydriodic acid, benzylhydroxylamine yields benzyl iodide, showing that the benzyl-group in this compound is attached to the oxygen- and not to the nitrogen-atom. The constitution of benzylacetoxime and benzylhydroxylamine may be represented by the formulæ $CMe_2 \colon N.OC_7H_7$ and $NH_2.OC_7H_7$. W. C. W.

So-called Nitrosomethylbenzene Compounds. By S. GABRIEL (*Ber.*, **15**, 3057—3064).—*Nitrosomethylorthonitrobenzene* or *orthonitrobenzylaldoxime* can be prepared by the action of hydroxylamine hydrochloride and sodium carbonate on an alcoholic solution of orthonitrobenzaldehyde. *Metanitrobenzylaldoxime* can be prepared by a similar reaction. By the action of methyl iodide in presence of methyl alcohol and potash on this compound, a methylated derivative, $C_6H_4(NO_2).CMe \colon NHO$, is obtained, which crystallises in colourless needles (m. p. 63°). This substance is freely soluble in most solvents. It is decomposed by hydrochloric acid at 160° into methyl chloride, metanitrobenzoic acid, and ammonia.

By the action of hydroxylamine on metanitroacetophenone, *metanitrophenylmethylacetoxime* is produced. This substance forms needle-shaped crystals melting at 131·5°, freely soluble in alcohol, ether, acetic acid, and chloroform, but sparingly soluble in carbon bisulphide and light petroleum. It yields a methyl-derivative, $C_6H_4(NO)_2.CMe \colon NMeO$, which crystallises in needles melting at 63°.

The fact that the methyl-derivative of metanitrobenzylaldoxime is not identical with the compound obtained by the action of hydroxylamine on metanitroacetophenone shows that the so-called nitrosomethylmetanitrobenzene is not a true nitroso-compound, and that it does not contain the group NO. W. C. W.

Phenacylethylanilide. By A. WELLER (*Ber.*, **16**, 26—27).—The action of bromacetophenone on dimethylaniline has been described by Staedel and Siepermann (Abstr., 1880, 639). By the action of bromacetophenone (phenacyl bromide) on diethylaniline, the author has obtained a new base to which he gives the name phenacylethylanilide. It crystallises from alcohol in slender needles of a pale greenish colour, melting at 94—95°. It is insoluble in water, sparingly soluble in alcohol, more readily in ether, benzene, and carbon bisulphide. In its reactions, it strongly resembles the alkaloïds. Its solution in hydrochloric acid gives white precipitates with potassium mercury iodide, and tannin, yellow precipitates with picric acid and phosphomolybdic acid, a yellowish-white precipitate with platinic chloride, and a brown precipitate with a solution of iodine in potassium iodide. The addition of a drop of dilute nitric acid produces a beautiful red coloration, or if enough base is present a red precipitate; this reaction strongly resembles that for brucine. On heating this new base with methyl iodide at 100°, the phenacyl-group is split off, forming iodacetophenone. A. K. M.

Action of Iodine on Mono- and Di-nitrodiphenylthiocarbamide. By S. M. LOSANITSCH (*Ber.*, **16**, 49—50).—When iodine is added to a hot alcoholic solution of metadinitrodiphenylthiocarbamide and the alcohol distilled off by a current of steam, a solid and an aqueous residue are obtained, the latter containing trinitrotriphenylguanidine hydriodide and metanitraniline, whilst the former consists of nitrophenylmonothiourethane and dinitrodiphenylcarbamide. From iodine and metanitrodiphenylthiocarbamide, nitraniline, pheny carbimide, metanitrophenylmonothiourethane, and metanitrotr guanidine are obtained. Metanitrophenylmonothiourethane,

$$EtO.CS.NH.C_6H_4.NO_2,$$

is also obtained, together with $CS(NH.C_6H_4.NO_2)_2$, by boiling nitraniline with a slightly alkaline alcoholic solution of carbon bis phide. It forms large yellow prisms melting at 115°, readily soluble in alcohol, but insoluble in water. Metadinitrodiphenylcarbamide, $CO(NH.C_6H_4.NO_2)_2$, crystallises from alcohol in bright yellow needles melting at 233°. Metatrinitrotriphenylguanidine,

$$C_6H_4(NO_2)N : C(NH.C_6H_4.NO_2)_2,$$

forms yellow shining plates melting at 189°, soluble in hot alcohol and in potash with decomposition. Metanitrotriphenylguanidine,

$$PhN : C(NHPh).NH.C_6H_4.NO_2 \text{ or } C_6H_4(NO_2)N : C(NHPh)_2,$$

crystallises from alcohol in yellow plates (m. p. 159°). (See also *Ber.*, **7**, 1236.) A. K. M.

Azo-derivatives. By C. GIRARD and A. PABST (*Bull. Soc. Chim.* [2], **39**, 119—120).—The diazo-derivative of sulphanilic acid yields with methylaniline, β-naphthol, diphenylamine, &c., compounds giving various shades of orange. The diazo-derivative of naphthylamine-sulphonic acid yields compounds giving various shades of red, and diazodinitrophenol yields compounds giving various shades of dark red and brown. It would appear that azo-compounds have less tinctorial power the greater their molecular symmetry. The introduction of a conjugate sulphonic group inclines the shade of the colour towards orange-yellow, whilst the addition of methyl in the phenol or amido-group slightly inclines the shade towards red.

C. H. B.

Azo- and Diazo-derivatives of Phenylenediamine. By O. WALLACH and E. SCHULZE (*Ber.*, **15**, 3020—3021).—*Monacetometaphenylenediamine hydrochloride*, $NH_2.C_6H_4.NH\overline{Ac},HCl$, is prepared by boiling phenylenediamine (1 mol.) with glacial acetic acid (2 mols.) for two hours, and treating the product with hydrochloric acid. The crystals (m. p. about 280°) are soluble in water, but insoluble in a mixture of alcohol and ether. The free base is obtained in crystalline scales by treating an aqueous solution of the hydrochloride with potassium bicarbonate, and extracting the mixture with ether.

Phenolazoacetometamidobenzene, $NH\overline{Ac}.C_6H_4.N_2 : C_6H_4.OH$, prepared by the method previously described by the author (*Ber.*, **15**, 2825), has a brick-red colour, and melts at 208°. On boiling with 10 parts of hydrochloric acid (25 per cent.) it is converted into *phenolazoamidobenzene hydrochloride*, $NH_2.C_6H_4.N_2.C_6H_4.OH,HCl$. The free base crystallises in brownish-yellow scales melting at 168°.

Benzene diazophenol, $C_6H_4(N_2.C_6H_4.OH)_2$, exists as a dark powder, soluble in soda-lye. W. C. W.

Parazophenol. By R. BOHN and K. HEUMANN (*Ber.*, **15**, 3037—3039).—*Parazophenol*, prepared by fusing potassium parazobenzene-disulphonate or potassium hydroxyazobenzene-sulphonate with potash, is identical with the parazophenol obtained by Jäger (*Ber.*, **8**, 1499) from paranitrosophenol, and by Weselsky and Benedikt (*Annalen*, **196**, 340) from paranitrophenol and also from diazophenol.

On nitration, parazophenol yields dinitrophenol [1 : 2 : 4], which melts at 112°. By the action of fuming sulphuric acid parazophenol is converted into a crystalline sulphonic acid,

$$HSO_3.C_6H_3(OH).N_2.C_6H_4.OH,$$

which has a golden-green metallic lustre. The barium salt of this acid forms brownish-red crystals. W. C. W.

New Azo- and Diazo-compounds. By O. Wallach (*Ber.*, **15**, 2825—2830).—Two methods have heretofore been used for obtaining these compounds, either by the consecutive introduction of two diazo-residues into a phenol, or by the action of a diazotised monamidoazo-compound with a phenol. If R be a carbohydrogen radicle, and Ph any phenol residue, the following formulæ will represent the bodies:—$N_2R.Ph.N_2R$ and $N_2Ph.R.N_2R$.

A new process would be found if one could diazotise successively the two amido-groups in a diamine and pair these diazo-derivatives with phenols, forming compounds of the type $N_2Ph.R.N_2Ph$, bodies which have no representative amongst the known azo-compounds. Efforts in this direction have not as yet been successful. The author has, however, made an attempt with the metadiamines, and describes the process.

Tolylenediamine (m. p. 99°) is transformed into the monacetyl-derivative by Tiemann's method, dissolved in 2 mols. of hydrochloric acid, and when carefully cooled with ice is treated with a solution of 1 mol. of sodium nitrite, and afterwards with an alkaline solution of 1 mol. of phenol. The solution becomes red, and on adding an acid deposits a flocculent yellow body, which may be purified by resolution and reprecipitation. It is sparingly soluble in alcohol, and very difficult to recover from its solution; sometimes it is obtained therefrom in crystals, sometimes in flakes, and appears to exist in two modifications. The crystals are in the form of golden- to red-yellow plates, melting at 252—253°. The analysis gave figures corresponding with the formula $NH\overline{Ac}C_6H_3Me.N_2.C_6H_4.OH$.

In order to remove the acetyl-group, the substance is boiled some time in a reflux apparatus with excess of 20 per cent. hydrochloric acid in connecion. As soon as a deep red clear solution is obtained the solution is cooled, when crystals of the hydrochloride of an amido-compound separate; these are collected and decomposed with sodium carbonate, when the free amido-compound $NH_2.C_6H_3Me.N_2 C_6H_4.OH$ is obtained as a yellow precipitate. It crystallises from dilute alcohol in fine yellow-brown needles melting at 172°, easily soluble in acids and alkalis, alcohol, and ether, but only sparingly in cold water.

J. F.

Compound of Phenol with Carbonic Anhydride. By A. Klepl (*J. pr. Chem.* **25**, 464).—By heating salicylic acid, paraoxybenzoic acid, or a mixture of the two, at 260° for two hours, they are decomposed into phenol and carbonic anhydride. During cooling the contents of the tube solidify in crystals resembling pyramids, with step-like faces of common salt. These crystals melt at 37°. On opening the tubes, much carbonic anhydride is evolved, and the crystals become white and opaque. On gently heating, or on covering with alcohol, ether, chloroform, or water, carbonic anhydride is copiously evolved and phenol remains. A. J. G.

Compound of Phenol with Sulphurous Anhydride. By A. HOLZER (*J. pr. Chem.* [2], **25**, 462—464).—This compound is prepared by heating sodium phenylate in sulphurous anhydride, or by passing the latter into dry phenol and distilling, when a yellow oil passes over at 140°, solidifying on cooling to large well-formed rhombic tables. It melts at 25—30° if precautions are taken to prevent loss of sulphurous anhydride. It readily loses sulphurous anhydride in a vacuum or on exposure to air, and is decomposed by heating in a stream of carbonic anhydride, whilst in a stream of sulphurous anhydride it can be distilled through tubes heated to dull redness without suffering much decomposition. The analytical results, although not very accordant, owing to the instability of the substance, show a compound of 1 mol. of sulphurous anhydride with 4—5 mols. of phenol.

A. J. G.

New Ethereal Derivatives of Phenols. By W. STAEDEL and others (*Annalen*, **207**, 40—49).—*Ethyl orthocresyl ether*, $C_7H_7.OEt$, is best prepared by heating on a water-bath a mixture of potassium cresolate, alcohol, and ethyl bromide, and after the removal of the potassium bromide and alcohol, the cresyl ether is extracted with ether, dried with calcium chloride, and rectified. Ethyl orthocresyl ether is a colourless liquid (b. p. 180—181° uncorr., sp. gr. 0·9577), with a pleasant ethereal odour. *Ethylene orthocresyl ether*,

$$(C_7H_7O)_2 : C_2H_4,$$

is prepared in a similar manner; it is a white crystalline mass melting at 79°. *Methyl α-naphthol ether*, $C_{10}H_7.OMe$, prepared from potassium α-naphtholate and methyl iodide, may be purified by steam distilling. It is a yellowish oily liquid (b. p. 258°, sp. gr. 1·0974), soluble in alcohol, ether, chloroform, and benzene. *Methyl β-naphthol ether* forms large white brilliant leaflets (m. p. 72°), of pleasant aromatic odour, soluble in ether, chloroform, and benzene, insoluble in water. It is volatile with steam. *Benzyl phenol ether*, $C_6H_5.OCH_2Ph$, from potassium phenylate and benzyl chloride. The phenol is converted by soda into phenylate, and together with the potassium chloride is dissolved out with water, the benzyl phenyl ether remaining undissolved. It crystallises in brilliant white plates (m. p. 39°), greasy to the touch, and when warmed evolving a pleasant aromatic odour. *Benzyl paracresyl ether*, $C_7H_7O.CH_2Ph$, from potassium paracresolate and benzyl chloride, separates from its alcoholic solution either in white scales and plates with silky lustre, or in colourless hexagonal transparent prisms. It melts at 41°, has a pleasant odour, is greasy to the touch, burns with a smoky flame, and is soluble in alcohol and benzene, but insoluble in water. *Benzyl orthocresyl ether* is a colourless viscid oil, gradually becoming yellow; it does not solidify in the cold. It boils at 285—290°, but does not distil without decomposition, and has an unpleasant candle-like odour. It is soluble in alcohol and ether, but not in water. *Benzyl metacresyl ether.*—The metacresol used was prepared from thymol. The ether forms white satiny tablets (m. p. 43°, b. p. 300—305° without decomposition), soluble in alcohol, ether, and benzene, insoluble in water. *Benzyl β-naphthyl ether*, $C_{10}H_7.OCH_2Ph$, crystallises in brilliant white odourless leaflets melting at 99°, soluble in alcohol, ether, benzene, and chloroform, insoluble in water, and not volatile with steam. *Benzyl α-naphthyl ether* could not be obtained pure, as the oily product decomposed when an attempt was made to distil it.

D. A. L.

Appendix to the Paper on Cholesterin. By E. SCHULZE (*J. pr. Chem.*, **25** [2], 458—462; comp. Abstr., 1882, 1202).—When paracholesterin and the two cholesterins obtained by the author from lupine shoots are shaken with chloroform and sulphuric acid of sp. gr. 1·76, they give the same colour reaction as ordinary cholesterin. Isocholesterin, even in considerable quantity, gives after 10—15 minutes only a faint red tinge to the chloroform layer (0·03—0·04 gram isocholesterin giving a less intense coloration than 0·002 gram cholesterin). After some hours, the coloration changes to intense brown, the sulphuric acid layer showing a brownish-yellow colour and a faint fluorescence. The author has repeated his experiments made to ascertain if isocholesterin is a single chemical substance or a mixture, and confirms his previous view as to its individual nature. A. J. G.

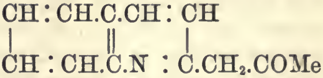
Isomeric Nitrobenzaldehydes. By F. TIEMANN and R. LUDWIG (*Ber.*, **15**, 3052—3057).—The γ-nitrometahydroxybenzaldehyde (m. p. 138°) described by the authors (this vol., 189) is found to be a mixture of α- and β-nitrometahydroxybenzaldehydes, which melt at 125° and 166° respectively. Both α- and β-nitrometahydroxybenzaldehyde are sparingly soluble in light petroleum; the former is precipitated in glistening plates on addition of light petroleum to its solution in benzene. A blue colouring matter closely resembling indigo in many of its properties is produced by the action of acetone and dilute soda-lye on β-nitromethylmetahydroxybenzaldehyde, but pure α-nitromethylhydroxybenzaldehyde does not exhibit this reaction. The α-compound is also less soluble in hot light petroleum and less volatile in a current of steam than its isomeride. The slender crystals of the α-derivative, obtained by distillation in a current of steam, melt at 104—105°, but more compact crystals of the same substance melt at 107°. W. C. W.

Bromacetophenone and Acetophenone Derivatives. By W. STAEDEL (*Ber.*, **16**, 22—26).—Bromacetophenone (see also Abstr., 1880, 659) crystallises from ether in splendid rhombs, apparently isomorphous with chloracetophenone. The formation of the base $NMePh.CH_2.COPh$, by the action of bromacetophenone on dimethylaniline has already been described (Abstr., 1881, 722). It can also be obtained from bromacetophenone and methylaniline, or from methyl bromide and acetophenone-anilide. New bases have been obtained by the action of ethyl- and diethyl-aniline on bromacetophenone (this vol., p. 582). By the action of bromacetophenone on quinoline a solid mass is formed, for the most part soluble in cold water; the aqueous solution yields, first long thick prisms, and subsequently short thick prisms. Solutions of both forms of crystals give splendid carmine-coloured precipitates with ammonia, soluble in hydrochloric acid. The author has also made experiments with some of the homologues of acetophenone. The bromine-derivative of phenylacetone reacts violently with ammonia, yielding a body crystallising in splendid thick prisms. The dibromide from phenylbenzyl ketone gives a body crystallising in long slender needles, which are very sparingly soluble in alcohol. The bromine-derivative of dibenzyl ketone (m. p. 47°) gives two compounds, one forming long silky needles soluble in alcohol, and the other six-sided plates sparingly soluble in alcohol. From the bromine-derivative of isopropyl phenyl ketone a body containing no nitrogen was obtained indirectly. It crystallises in splendid rhombic prisms. A. K. M.

Ethyl Orthonitrocinnamylacetoacetate. By E. Fischer and H. Kuzel (*Ber.*, **16**, 33—37).—Bonné (*Annalen*, **187**, 1) has shown that acetophenone is formed by the saponification of ethyl benzoylacetoacetate. This may be explained either by assuming that acetic acid and ethyl benzoylacetate are first formed, the latter then splitting up into carbonic anhydride, alcohol, and acetophenone, or that benzoylacetone is first formed, and then decomposed into acetic acid and acetophenone. In order to decide which series of reactions is correct, the authors have experimented with ethyl orthonitrocinnamylacetoacetate. On boiling this with dilute sulphuric acid, they have succeeded in obtaining the intermediate product, orthonitrocinnamylacetone, $NO_2.C_6H_4.CH : CH.CO.CH_2.COMe$, which by the continued action of the acid decomposes into acetic acid and orthonitrocinnamyl methyl ketone. The ethyl orthonitrocinnamylacetoacetate is obtained from orthonitrocinnamic acid by converting it into the chloride, which is then added, in ethereal solution, to ethyl acetosodacetate suspended in ether: the mixture is warmed to complete the reaction, the ether distilled off, and the residue after being washed with water is crystallised from boiling alcohol. The ethyl orthonitrocinnamylacetoacetate thus purified forms yellow prisms melting at 120·5°. It is readily soluble in chloroform, sparingly in hot alcohol and in ether. The saponification is effected by boiling 20—30 grams with five times its weight of 30 per cent. sulphuric acid. After five hours' heating, the product was allowed to cool, when it solidified to a crystalline mass, which was found to contain unaltered substance, nitrocinnamic acid, nitrocinnamylacetone, and nitrocinnamyl methyl ketone. On treating the mass, after filtration from the sulphuric acid, with an excess of cold soda solution, the orthonitrocinnamyl methyl ketone remains undissolved, and can be extracted by ether and purified by crystallising it from dilute alcohol. It forms long silky needles melting at 60°, and is identical with the body described by Baeyer and Drewsen (*Ber.*, **15**, 2858). The nitrocinnamylacetone is recovered from the soda extract by precipitation with hydrochloric acid, dissolving in carbon bisulphide, and finally crystallising from boiling alcohol, when it is obtained in yellow prisms, which soften at 105°, and melt at

112—113°. It is readily soluble in hot alcohol, sparingly in cold alcohol, carbon bisulphide, and ether. Boiling with dilute sulphuric acid converts it for the most part into nitrocinnamyl methyl ketone.

A. K. M.

Ethyl Orthocinnamylacetoacetate (Part II). By E. FISCHER and H. KUZEL (*Ber.*, **16**, 163—167).—The ethylic salt of orthonitrocinnamylacetoacetic acid splits up on boiling with dilute sulphuric acid, yielding alcohol, carbonic acid, and orthonitrocinnamylacetone. By the action of stannous chloride on a concentrated alcoholic solution of nitrocinnamylacetone, *acetonylquinoline*, 

$$\begin{array}{l} CH\colon CH.C.CH\colon CH \\ | \qquad\qquad \| \qquad\quad | \\ CH\colon CH.C.N\colon C.CH_2.COMe \end{array}$$

is produced. This base crystallises in golden needles (m. p. 76°), which are sparingly soluble in hot water, forming a yellow solution which dyes silk and wool yellow. On heating with strong hydrochloric acid at 160°, it yields methylquinoline, which forms a beautiful pink platinum salt $(C_9H_6NMe)_2H_2,PtCl_6$ (m. p. 226—230°), and a crystalline picrate sparingly soluble in alcohol and water. The same body is obtained by the reduction of orthonitrocinnamyl methyl ketone by stannous chloride, and it also appears to be identical with the quinaldine of Döbner and von Miller (*Ber.*, **15**, 3075).

An acid solution of stannous chloride slowly dissolves ethyl orthocinnamylacetoacetate, with evolution of carbonic acid and production of methylquinoline. Acetonylquinoline is not formed by this reaction.

Ethyl cinnamylacetoacetate forms pale yellow crystals melting at 40°, soluble in alcohol and ether. It is decomposed by boiling with dilute sulphuric acid into carbonic acid and the compound

$$C_6H_5.C_2H_2.CO.CH(COMe).COOEt.$$

W. C. W.

Conversion of Phenyl Ethers of Carbonic Acid into Salicylic Acid. By W. HENTSCHEL (*J. pr. Chem.*, **27**, 39—45).—The author shows that when sodium-phenol is acted on by carbonic anhydride, sodium phenyl carbonate is first formed; and in presence of another molecule of sodium-phenol this is decomposed with formation of the sodium salt of salicylic acid. The intermediate product is best prepared by passing dry carbonic anhydride into a solution of sodium phenol in absolute alcohol; the resulting body is a mixture of equal parts of ethyl and phenyl sodium carbonate. When heated with sodium-phenol it yields salicylic acid.

The author has prepared phenyl sodium carbonate in large quantities by passing carbonyl chloride into an aqueous solution of sodium phenol. After purification, it was obtained as a white crystalline mass which distilled at 301—302°. The mode of preparation is of general application. The author has likewise prepared the orthonitrophenyl-compound, which crystallises from alcohol in silky rhombic plates.

Ethyl phenyl carbonate obtained by the action of ethyl chloroformate on potassium-phenol, can also be converted into salicylic acid. Analogous methods of preparation yield a series of substituted ethyl ethers of phenyl carbonate. A parachlorophenyl, a tribrominated, an orthonitro-ether of phenyl carbonate, and finally the corresponding thymol compounds, have been obtained.

Conversion of Ethyl Phenyl Carbonate into Salicylic Acid.—On heating ethyl phenyl carbonate with sodium-phenol in equivalent proportions, the following reaction takes place :—

$$HO.C_6H_4.COOEt + C_6H_5.ONa = OH.C_6H_4.COONa + C_6H_5.OEt.$$

The author considers that carbonic anhydride in this case exerts first an etherifying action on sodium-phenol, and that the phenyl sodium carbonate thus formed only yields salicylic acid on coming into contact with a second mol. of sodium-phenol. In Kolbe's process, it is possible that the conversion of the phenyl salt into salicylic acid might be produced by some other method such as warming. The author was unable to obtain salicylic acid by digesting ethyl phenyl carbonate, or diphenyl carbonate, with sodium or an alcoholic solution of sodium.

The Conversion of Diphenyl Carbonate into Salicylic Acid is best performed by distilling the salt with dry sodium ethylate in a current of hydrogen gas. The reaction

$$CO(O.C_6H_5)_2 + EtO.Na = OH.C_6H_4.COONa + C_6H_5.OEt$$

takes place. When distilled with sodium hydroxide, the diphenyl carbonate yields sodium salicylate and phenol. The reaction proceeds so readily that the author suggests the possibility of a commercial process being made out of it. J. I. W.

Sulphamic Acids and Hydroxy-acids derived from Pseudocumol. By O. JACOBSEN and H. MEYER (*Ber.*, **16**, 190—193).—*Sulphonamidoxylylic acid*, $C_6H_2(COOH)Me_2.SO_2NH_2$ [1 : 2 : 4 : 5], prepared from pseudocumolsulphonamide by oxidation with potassium permanganate in dilute alkaline solution or by chromic acid mixture, crystallises in long needles melting at 268°, freely soluble in alcohol and sparingly soluble in hot water. The potassium salt forms rhombic plates containing 1 mol. H_2O, and freely soluble in water. The ammonium salt containing 2½ mols. H_2O crystallises in delicate needles. The acid is decomposed by strong hydrochloric acid at 210°, yielding xylylic acid and metaxylene. Xylylic acid is also produced when it is fused with potash. On further oxidation with potassium permanganate, sulphonamidoxylylic acid is converted into *sulphonamidoxylidic acid*,

$$C_6H_2(COOH)Me(COOH).SO_2NH_2\,[1:2:4:5].$$

The product of this reaction is filtered, and the filtrate after concentration acidified with hydrochloric acid to remove unaltered sulphonamidoxylylic acid. The filtrate is then evaporated to dryness, and the residue treated with strong hydrochloric acid and extracted with ether. The acid contained in the extract is purified by conversion into the barium salt $C_9H_5O_4Ba.SO_2NH_2$. From a hot solution, the barium salt is deposited as an anhydrous crystalline powder, but on evaporating the aqueous solution at the ordinary temperature prisms containing 2½ mols. H_2O are obtained. The free acid is exceedingly soluble in alcohol and ether. It is deposited from an aqueous solution in needles or prisms, which melt with partial decomposition between 295—300°. It is decomposed by strong hydrochloric acid at 250°, forming xylidic acid, and on fusion with potash yields *hydroxy-xylidic acid*, $C_6H_2(COOH)Me(COOH).OH$ [1 : 2 : 4 : 5]. This acid crystallises in prisms soluble in alcohol and ether. It melts at 285—290°, and even below this temperature slowly decomposes into paracresol and carbonic anhydride. The non-crystalline normal potassium hydroxyxylidate is very soluble. The acid salt is thrown down as a crystalline precipitate on the addition of acetic acid to the aqueous solution of the normal salt. The zinc salt is more soluble in cold than in hot water. Ferric chloride produces a dark red coloration with the free acid and also with its salts.

On further oxidation with potassium permanganate, sulphonamidoxylidic acid yields the potassium salts of sulphotrimellic acid and sulphonamidotrimellic acid. The precipitate thrown down on the addition of lead acetate to the solution of these two salts is decomposed by sulphuretted hydrogen. On evaporating the filtrate, *potassium sulphotrimellate*, $C_6H_2(COO)_3.SO_3K$, is deposited in transparent prisms. The mother-liquor contains free sulphonamidotrimellic acid. When the potassium salts of these acids are fused with potash, *hydroxytrimellic acid*, $C_6H_2(COOH)_3.OH$ [1 : 2 : 4 : 5], is produced. This substance forms transparent prisms containing 2 mols. H_2O. It is soluble in water, alcohol, and ether. The anhydrous acid melts at 240—245°. The barium salt, $(C_9H_3O_7)_2Ba_3 + 5H_2O$, crystallises in small transparent prisms. The silver and copper salts are sparingly soluble in hot water. The lead salt is insoluble. Hydroxytrimellic acid is decomposed by strong hydrochloric acid at 230°, forming carbonic anhydride and metahydroxybenzoic acid. On distillation with lime, phenol is produced. W. C. W.

Acetoximic Acids. By C. SCHRAMM (*Ber.*, **16**, 180—183).—*Methylpropylacetoximic acid*, $OHN\colon CMe.CEt\colon NOH$, is deposited in white needle-shaped crystals melting at 170°, when hydroxylamine hydrochloride is added to a hot aqueous solution of isonitrosoethylketone. *Methylbenzylacetoximic acid*, $OHN\colon CMe.C(C_7H_7)\colon NOH$, prepared by the action of hydroxylamine hydrochloride on a hot alcoholic solution of isonitrosobenzylketone, crystallises in needles which melt at 181°. Both these acids are soluble in alcohol and ether. They sublime at temperatures below their melting points. They dissolve with difficulty in ammonia, and they are soluble in strong solutions of potash and soda, forming colourless solutions. Isonitrosoketones dissolve in alkalis, producing an intense yellow coloration. Dimethylacetoximic acid forms a silver salt, $OHN\colon CMe.CAg\colon NOH$, but the homologous acids do not. Now, since all the acids of this series form sodium salts, it follows that the sodium must replace an atom of H in the NOH-group, whereas the silver-atom is directly attached to the carbon-atom. W. C. W.

Electrolysis of Solutions of Hydrofluoric Acid and of Potassium Antimonate, with Carbon Electrodes. By A. BARTOLI and G. PAPASOGLI (*Gazzetta*, **13**, 22—27).—(1.) *Electrolysis of Hydro-*

fluoric Acid.—When wood-charcoal or gas-retort carbon, after purification by chlorine, is used as the positive electrode in the electrolysis of aqueous hydrofluoric acid, it is partly disaggregated, swelling up in the immersed part, and becoming so brittle that after a while it splits up by its own weight into rather large fragments, whereas the carbon at the negative electrode remains quite unaltered. On repeatedly washing the altered carbon till the wash-water is no longer acid, then drying it at 100°, reducing it to impalpable powder, repeatedly boiling it with hydrochloric acid, and once more thoroughly washing it with water, it exhibits the following properties. 1. It dissolves partially, with dark-red colour, in strong sulphuric acid. 2. It is attacked by a hot solution of sodium hypochlorite, yielding sodium fluoride, mellic acid, and the usual derivatives of the latter. 3. In addition to carbon, hydrogen, and oxygen, it contains fluorine, amounting to about 3 per cent. of the disaggregated carbon, and not due to electrolysis of mineral matter, inasmuch as the carbon used in the experiment did not yield on ignition any perceptible quantity of ash.

When graphite is employed as positive electrode in the electrolysis of strong aqueous hydrofluoric acid, the immersed portion swells up, becomes pappy, and quickly disintegrates; and the disintegrated portion, when purified in the manner above described, forms a black powder, which swells up considerably when heated, is insoluble in all solvents, and contains carbon, oxygen, hydrogen, and fluorine.

(2.) *Electrolysis of Potassium Antimonate.*—When a solution of this salt, obtained by heating the acid antimonate in large excess with caustic potash-lye, is decomposed by a battery of eight Bunsen's elements, the positive electrode being formed of wood-charcoal or retort-carbon, large quantities of gas are evolved at the negative electrode, and only a small quantity at the positive, which at the same time is strongly attacked, while the electrolyte becomes deep black, and deposits a black sediment, Ω, soluble in a large quantity of water. On filtering the liquid, adding the black wash-waters of the precipitate Ω, then concentrating on the water-bath, and adding excess of hydrochloric acid, a copious precipitate, B, is formed, which, after washing and drying, contains only traces of antimony, and exhibits the following properties. 1. After drying at 100° it contains carbon, hydrogen, oxygen, and antimony. 2. It dissolves in water and in alkaline hydrates, forming deep black solutions, from which it is completely precipitated by mineral acids. 3. It dissolves with rise of temperature in aqueous potassium hypochlorite, forming mellic acid and other benzocarboxylic acids, together with potassium antimonate. This substance being analogous in modes of formation and in properties to mellogen, the authors distinguish it by the name *Stibiomellogen.*

When graphite is used as positive electrode in solutions of potassium antimonate, large quantities of gas are likewise evolved at the negative, and very little at the positive electrode. At the end of the experiment, the graphite is found to be much disintegrated, and a copious black deposit Ω is found at the bottom of the voltameter, surmounted by a nearly colourless liquid containing small quantities of mellic acid and its derivatives. The deposit Ω, after washing and drying, is found to consist of a mixture of graphite and a new compound of carbon, hydrogen, oxygen, and antimony, which the authors designate as *Stibiographic acid.* Its composition and properties will form the subject of a future investigation.

From the results obtained in this and in preceding investigations, the authors infer: (1.) That in the electrolysis of nitric, phosphoric, arsenic, and antimonic acids and their salts, the first and third yield with electrodes of wood-charcoal or retort-carbon, mellogen free from nitrogen and arsenic—whereas with graphite electrodes they yield graphite free from nitrogen or arsenic—and that the second and fourth give with charcoal or retort-carbon electrodes, phospho- and stibio-mellogen respectively,—whereas with graphite electrodes they give phospho- and stibio-graphitic acid. H. W.

Electrolysis, with Carbon Electrodes, of Solutions of Binary Compounds and of Various Acids and Salts. By A. Bartoli and G. Papasogli (*Gazzetta*, **13**, 37—55).—In this paper, the authors describe the results obtained by electrolysing (*α*) with electrodes of wood-charcoal or retort-carbon; *β* with electrodes of graphite,—solutions of the following compounds.

1. Hydrochloric, hydrobromic, and hydriodic acids and their potassium salts. 2. Potassium cyanide. 3. Sulphuric and nitric acids and their salts. 4. Arsenic acid. 5. Boric acid. 6. Alkaline hypochlorites, permanganates, bichromates, and chlorates of alkali-metals. 7. Chromic acid. 8. Mellic acid. 9. Oxalates, formates, acetates, &c. 10. Hydrogen and sodium sulphite. 11. Sodium pyrogallate.

Analyses are also given of mellogen obtained by electrolysis of sulphuric, mellic, and boric acids; of the benzocarboxylic acid obtained by oxidation of mellogen; of pyromellic acid obtained by electrolysis of potassium hydroxide with carbon electrodes; and of hydromellic and hydropyromellic acids.

From the results of these experiments, and of those detailed in the preceding, and in former papers relating to the same subject (Abstr., 1882, 58, 406, 850), the authors draw the following general conclusions:—

1. In liquids whose electrolysis is not accompanied by evolution of oxygen at the anode, wood-charcoal, retort-carbon, and graphite are not disintegrated, and do not suffer any appreciable loss of weight.

2. On the contrary, in liquids whose electrolysis gives rise to liberation of oxygen at the anode: wood-charcoal, retort-carbon, and graphite, employed as positive electrodes, are partly disintegrated and partly oxidised to CO and CO_2 (the relative quantities of which depend upon the strength of the current and the superficial area of the positive carbon) together with other products varying according to the nature of the carbon.

3. Graphite used as positive electrode in these liquids never colours the electrolyte, whereas retort-carbon and charcoal, previously purified by the action of chlorine at a high temperature, colour the liquid deep black, both in alkaline solutions and in those of certain acids and their salts.

4. Charcoal or retort-carbon employed as positive electrode in

solutions of acids or of neutral salts whose electrolysis gives rise to evolution of oxygen at that electrode, forms chiefly, or rather almost entirely (besides CO and CO_2), a black substance—called by the authors mellogen,—whose composition is represented by the formula $C_{14}H_2O_4$, or a multiple thereof, together with mere traces of benzocarboxylic acids; whilst in solutions of phosphoric acid, hydrofluoric and potassium antimonate, a substance is formed, analogous to mellogen in its properties, but containing phosphorus, fluorine, or antimony, according to the electrolyte employed.

Graphite, on the other hand, employed as positive electrode in the same liquids, produces—in addition to gaseous CO and CO_2—chiefly graphitic acid, $C_{14}H_2O_3$, or an analogous compound containing phosphorus, fluorine, or antimony according to the nature of the electrolyte.

5. Wood-charcoal and retort-carbon, as well as graphite, used as positive electrode in alkaline electrolytes, yield mellic acid, $C_{12}H_6O_{12}$, pyromellic acid, $C_{10}H_6O_8$, hydromellic acid, $C_{12}H_{12}O_{12}$, and another body, which is either hydropyromellic acid, $C_{10}H_{10}O_8$, or an acid isomeric therewith. H. W.

Amidometaxylenesulphonic Acid. By O. JACOBSEN and H. LEDDERBOGE (*Ber.*, **16**, 193—195).—Amidometaxylenesulphonic acid [1 : 3 : 4 : 6], prepared by the action of fuming sulphuric acid on commercial xylidine at 140—150°, crystallises in long flat prisms. One part of the acid dissolves in 362·3 parts of water at 0°, and in 136·3 at 100°. The crystals char without melting. The potassium salt, $NH_2.C_8H_8.SO_3K + H_2O$, and the sodium salt crystallise in large transparent rhombic plates, which dissolve freely in water. The barium salt, $(NH_2.C_8H_8.SO_3)_2Ba + H_2O$, forms very soluble microscopic needles.

On oxidation with potassium permanganate, metaxylenesulphonic acid is converted into *azo-xylenedisulphonic acid*,

$$N_2 : (C_6H_2Me_2.SO_3H)_2 \ [1 : 3 : 4 : 6].$$

The potassium salt, $N_2 : (C_8H_8.SO_3K)_2 + 4H_2O$, crystallises in rhombic plates, which resemble iodoform in appearance. On the addition of hydrochloric acid to the solution, the acid salt,

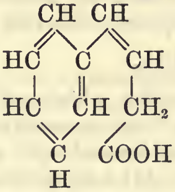
$$HSO_3.C_8H_8.N_2.C_8H_8.KSO_3 + 4H_2O,$$

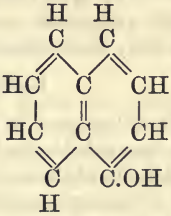
is precipitated in golden prisms. It is sparingly soluble in dilute mineral acids, but dissolves freely in pure water. Most of the salts of this acid are crystalline. The free acid crystallises in plates of a yellowish-red colour, which dissolve readily in water. By the action of stannous chloride, azoxylenedisulphonic acid is converted into amidoxylenesulphonic acid. W. C. W.

Glycocines, Glycocine Ethers, and Oxethylenecarbamides of the Toluyl and Xylyl Series. By A. EHRLICH (*Ber.*, **16**, 204—206).—The author confirms the accuracy of Staat's description Abstr., 1880, 387) of the properties of orthotolylglycocine. *Orthotolylglcocinetoluidide*, $C_7H_7.NH.CH_2.CO.NH.C_7H_7$, is obtained when a mixture of ethyl chloracetate (1 mol.) and toluidine (2 mols.) is heated in a flask with a reflux condenser, for half an hour. The contents of the flask are then heated with hydrochloric acid and poured into water. The crystalline deposit is washed with water, dried, and dissolved in the minimum amount of alcohol. It is reprecipitated by the addition of strong hydrochloric acid to the alcoholic solution. From dilute alcohol, this compound is deposited in long pointed crystals melting at 91°, soluble in alcohol and ether. *Ethylorthotolylglycocine* is an oily liquid (b. p. 272—278°) which does not solidify at −10°. *α-Metaxylylglycocine* is prepared by mixing ethereal solutions of α-metaxylydine (2 mols.) and chloracetic acid (1 mol.). The crystalline product is boiled with water for half an hour and the solution filtered; on cooling, xylylglycocine crystallises out in transparent prisms melting at 133°. It dissolves freely in alcohol, ether, hydrochloric and glacial acetic acids. *Ethyl-α-metaxylylglycocine* is a non-crystallisable oil resembling the corresponding derivative of orthotoluidine. *Xylylglycocinexylidide*, $C_8H_9.NH.CH_2.CO.NH.C_8H_9$, forms glistening needles (m. p. 128°), soluble in alcohol, ether, and glacial acetic acid. W. C. W.

Primary and Secondary Naphthylamines. By G. Benz (*Ber.*, **16**, 8—22).—Merz and Weith (Abstr., 1880, 813) have shown that the action of ammonia and aniline on the phenols is much assisted by the presence of a dehydrating agent, such as zinc chloride. From β-naphthol and ammonium zinc chloride they obtained principally dinaphthylamine mixed with a little mononaphthylamine. The author finds that on heating β-naphthol with calciammonium chloride, β-naphthylamine is the principal product, the best results being obtained (viz., 80 per cent.) when the mixture of naphthol (1 part) and calciammonium chloride (4 parts) is heated for two hours at 230—250°, and then for six hours at 270—280°). Dinaphthylamine is formed in much smaller quantities, the highest percentage (16) being obtained when anhydrous calciammonium chloride is employed, and the heating carried on for eight hours at 260—270°. Similar results were obtained from α-naphthol. When zinc ammonium chloride is employed, the yield of primary amine is much smaller, whilst a large yield of dinaphthylamine can be obtained, viz., 65 per cent. from α-naphthol, and 80 per cent. from β-naphthol. To obtain the dinaphthylamine, naphthol (5 grams), naphthylamine (5 grams), and calcium chloride (10 grams), are heated together for eight hours at 270—280° in the case of the β-compound, and at 260° in that of the α-compound. When α-naphthylamine (1 part), β-naphthol (1 part), and calcium chloride (2 parts), are heated for eight hours at 280°, α-β-dinaphthylamine is produced. It crystallises in prisms readily soluble in warm benzene, ether, and alcohol. It melts at 110—111°. This body is not obtained when β-naphthylamine and α-naphthol are employed. With picric acid, it forms a compound of the formula $NH(C_{10}H_7)_2 + 2[C_6H_2(NO_2)_3.OH]$, crystallising in groups of brownish-black needles, and melting at 172—173°. With acetic chloride, it forms the compound $(C_{10}H_7)_2N\overline{Ac}$, crystallising in needles melting at 124·5—125°. α-Dinaphthylamine forms with picric acid a compound melting at 168—169°, and crystallising in small black needles. The acetyl-derivative melts at 217°, and forms groups of yellowish needles. The picric acid compound from β-dinaphthylamine melts at 164—165°, and crystallises in groups of long slender needles. The acetyl-derivative crystallises in small colourless needles melting at 114—115°. A. K. M.

Synthesis of α-Naphthol. By R. FITTIG and H. ERDMANN (*Ber.*, **16**, 43—44).—By the action of heat on phenylparaconic acid, Jayne obtained isophenylcrotonic acid and phenylbutyrolactone. The authors find that on distilling phenylparaconic acid but little isophenylcrotonic acid is formed, the decomposition going further, whilst α-naphthol is produced. Experiment also shows that the action of heat on isophenylcrotonic acid is to decompose it into α-naphthol and water. The authors point out that this reaction is a further confirmation of the generally accepted formula for naphthalene.


Isophenylcrotonic acid.


α-Naphthol.

A. K. M.

α-Naphthoic Cyanide and its Derivatives. By P. BOESSNECK (*Ber.*, **15**, 3064—3066).—*α-Naphthoic cyanide*, $C_{10}H_7.COCN$, is prepared by the action of mercuric cyanide on naphthoic chloride. The crude product is treated with water and ether, and on evaporating the ethereal solution, the naphthoic cyanide is deposited in beautiful yellow needle-shaped crystals melting at 101°. By boiling with water or dilute alkalis it is decomposed into hydrocyanic and naphthoic acids. Ammonia or aniline converts it into naphthoylamide and naphthanilide respectively. The cyanide dissolves slowly in acetic acid which has been saturated with gaseous hydrochloric acid, and on pouring the solution into water, *α-naphthylglyoxylamide*,

$$C_{10}H_7.CO.CONH_2,$$

is deposited. This substance crystallises in long white needles (m. p. 151°), soluble in alcohol. By the action of alcoholic potash, it is converted into potassium *α-naphthylglyoxylic acid*, $C_{10}H_7.CO.COOH$. The free acid crystallises in colourless plates; the silver salt is amorphous. W. C. W.

α-Chloronaphthylsulphonic Acid. By K. E. ARNELL (*Bull. Soc. Chim.* [2], **39**, 62—63).—The action of sulphuric acid on α-chloronaphthalene apparently yields only one derivative, *α-chloronaphthalenesulphonic acid*, $C_{10}H_7.SO_2Cl$, which forms large crystals melting at 95°. When heated with excess of phosphorus pentachloride, this compound yields β-dichloronaphthalene melting at 68°. Since this β-chloronaphthalene is an α-derivative containing two chlorine-atoms in the same benzene nucleus, it follows that α-chloronaphthalenesulphonic acid has the constitution $SO_3H : Cl = 1 : 4$. The α-bromonaphthalenesulphonic acid, obtained by the action of fuming sulphuric acid on α-bromonaphthalene, has an analogous constitution. C. H. B.

Nitronaphthalenedisulphonic Acids. By J. E. ALEN (*Bull. Soc. Chim.* [2], **39**, 63—64).—When α-naphthalenedisulphonic chloride is treated at the ordinary temperature with a mixture of concentrated nitric and sulphuric acids, it yields a mixture of two nitro-derivatives which can be separated by taking advantage of the difference in their solubility in benzene. The first, *mononitro-naphthalenedisulphonic chloride*, $NO_2.C_{10}H_5(SO_2Cl)_2$, crystallises from benzene in large yellowish tabular crystals, which contain benzene but gradually give it off and become opaque. It crystallises from acetic acid in small yellowish needles which melt at 140—141°. The second compound, *dinitro-naphthalenedisulphonic chloride*,

$$C_{10}H_4(NO_2)_2(SO_2Cl)_2,$$

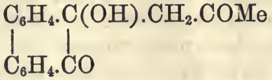
crystallises from benzene in flattened needles, which melt at 218·5—219·5°. It is less soluble in benzene than is the mononitro-derivative.

β-Naphthalenedisulphonic chloride, when treated with a mixture of concentrated nitric and sulphuric acids, yields a mononitro-derivative $NO_2.C_{10}H_5(SO_2Cl)_2$, which crystallises in short yellowish prisms melting at 185—187°.

The mononitro-derivative of naphthalene-α-disulphonic acid is obtained by digesting the chloride with water in sealed tubes at 150°. It is a very soluble compound and crystallises in flexible needles. The ammonium, calcium, and lead salts are very soluble; the barium salt is much less soluble.

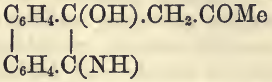
When the chloride is treated with aqueous ammonia, two products are obtained, viz., the amide, $NO_2.C_{10}H_5(SO_2NH_2)_2$, which is only slightly soluble and crystallises in almost colourless flattened needles melting at 285° with decomposition, and a somewhat soluble compound, probably $NO_2.C_{10}H_5(SO_2NH_2).SO_3NH_4$. C. H. B.

Addition of Acetone under the Influence of Caustic Alkalis. By F. R. JAPP (*Ber.*, **16**, 282).—In consequence of the appearance of a paper by Baeyer and Drewsen (*Ber.*, **15**, 2856; this vol., 341) in which the formation of an addition-product of acetone and orthonitrobenzaldehyde by the action of caustic alkalis is described, the author published a note stating that he has for some time past been engaged on the study of similar reactions, in which, by the action of caustic alkalis or ammonia, diketones may be made to combine directly with 1 or with 2 mols. of acetone. The first compound of this class, acetone-phenanthraquinone, described in a former communication (Japp and Streatfield, this Journal, Trans., 1882, 273), was prepared by decomposing acetone-phenanthraquinonimide (obtained by the action of ammonia on phenanthraquinone and acetone) with acids. The author now rejects the constitution ascribed to these compounds in the first paper, and prefers to formulate them—



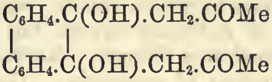
$$\begin{array}{l} C_6H_4.C(OH).CH_2.COMe \\ |\qquad | \\ C_6H_4.CO \end{array}$$

and



$$\begin{array}{l} C_6H_4.C(OH).CH_2.COMe \\ |\qquad | \\ C_6H_4.C(NH) \end{array}$$

By substituting potash for ammonia in the above reaction, diacetonephenanthraquinone,



$$\begin{array}{l} C_6H_4.C(OH).CH_2.COMe \\ |\qquad | \\ C_6H_4.C(OH).CH_2.COMe \end{array}$$

is obtained. By the spontaneous evaporation* of its acetone solution this compound is deposited in short oblique prisms, fusing with decomposition at 187°. The monacetone addition-product is also formed in small quantity in the reaction.

Benzil seems to react with acetone and potash in a similar manner.

The above reactions are still under investigation. F. R. J.

Action of Concentrated Sulphuric Acid on Dinitroanthraquinone. By C. Liebermann (*Ber.*, **16**, 54—58).—The action of concentrated sulphuric acid on dinitroanthraquinone has been described by Liebermann and Hagen (this volume, p. 72). In continuing his experiments, the author finds that the nitration of anthraquinone takes place with much greater difficulty than has hitherto been supposed, and that much mononitro-derivative is produced together with the dinitro-compound. It is probable therefore that the composition of the dye-stuff (*loc. cit.*) may vary with the amount of mononitro-derivative mixed with the dinitroanthraquinone, and hence the want of agreement between the author's analyses and those of Böttger and Petersen (*Annalen*, **160**, 147). Dinitroanthraquinone, as prepared by Böttger and Petersen, is also wanting in homogeneity, and so is the dye-stuff derived from it.

By the action of concentrated sulphuric acid on α-nitroanthraquinonesulphonic acid, Claus (*Ber.*, **15**, 1521) obtained two bodies to which he assigned the formulæ $[C_{14}H_4(OH)(NO_2)O_2.SO_3H]_2O$ or $O : C_{14}H_4(NO_2)O_2.SO_3H$, and $SO_3H.C_{14}H_4(OH)(NO_2)O_2.O.SO_3H$ or

$$SO_3H.C_{14}H_4(NO_2)O_2 : (OSO_3H)_2.$$

The author considers these formulæ by no means established, and assigns to the former compound the more simple formula

$$NH_2.C_{14}H_4(OH)_2O_2.SO_3H,$$

i.e., according to him the nitro-group, is reduced and hydroxyl introduced. A. K. M.

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* This paper was forwarded to Berlin in English. The words of the English manuscript "by spontaneous evaporation" have been transformed by the German translator into "unter freiwilliger Erwärmung" ("with spontaneous rise of temperature").—F. R. J.

Madder Colours. By A. Wurtz (*Compt. rend.*, **96**, 465—471).—This paper is a report drawn up by Wurtz on a memoir of Rosenstiehl on the colouring matters of the madder root. From this root five separate colouring substances can be extracted: alizarin, purpurin, madder-orange, pseudopurpurin, and purpuroxanthin. The researches of Graebe and Liebermann have fixed the constitution of the two former, whilst Rosenstiehl has studied more especially the three latter substances. He has shown that purpuroxanthin is isomeric with alizarin, and can be converted into purpurin by fusion with potash; and inversely purpurin can be reconverted into purpuroxanthin by the action of reducing agents, but if the action be prolonged, hydropurpuroxanthin is formed. Rosenstiehl has also devised a new method of formation of purpurin. On heating the madder root with sulphurous acid, Kopp obtained a product known as *commercial purpurin;* as this substance is useless for dyeing purposes, it has been customary to heat it to 180° with glycerol to convert it into *solid purpurin.* This *rationale* of the process Rosenstiehl has explained; the "commercial purpurpin" contains pseudopurpurin, which possesses no tinctorial properties, but is easily decomposed into carbonic anhydride and purpurin; this latter dyes a brilliant madder-red. Rosenstiehl has succeeded in separating the pseudopurpurin, and shows that it is a monocarboxyl-derivative of purpurin, thus: purpurin, $C_{14}H_5O_2(OH)_3$, pseudopurpurin, $C_{14}H_4O_2(OH)_3.COOH$.

This fact has thrown an unexpected light on the practical industry of the madder; for it has long been observed that madder of Avignon gave a more solid dye-stuff than the madder of Alsace. It is now shown that this fact is due to the greater quantity of lime in the Avignon soil, which serves to eliminate the pseudopurpurin as a lime compound, and prevents it being fixed to the tissue of the root.

It has also been customary in Alsace to add small quantities of chalk to the dye-baths; this also prevents the fixation of the pseudopurpurin which passes into the residues, where it may be decomposed by sulphuric acid and converted into useful purpurin. Rosenstiehl has also studied madder-orange, identical with the munjistin of Stenhouse, and has shown that it is a monocarboxyl-derivative of purpuroxanthin, bearing to it the same relation that pseudopurpurin does to purpurin. These researches also show that the madder root contains, besides alizarin existing as such, three glucosides, viz., one which gives pseudopurpurin or purpurincarboxylic acid, a second which gives alizarincarboxylic acid, and a third which gives munjistin or xanthopurpurincarboxylic acid. The memoir presented to the Academy contains a full account of the various substances obtained from madder, and their physical properties as absorption-spectra.

V. H. V.

Physical Isomerism of Monochloro-camphor. By P. Cazeneuve (*Compt. rend.*, **95**, 1358—1361).—From the mother-liquors of the monochloro-camphor obtained by the action of dry chlorine on an alcoholic solution of camphor (this vol., 214), the author has succeeded in isolating another *monochloro-camphor*, differing in physical properties from the first. This compound is soft, like camphor, whereas the *normal* body is hard and brittle, and is much more soluble in cold alcohol than the latter. It mixes with boiling alcohol in all proportions, and on cooling crystallises in microscopic needles. It is insoluble in water, and has an odour resembling that of camphor. It liquefies in contact with choral hydrate. Its specific rotatory power is $[\alpha]_j = +57°$. It softens at 95°, melts at 100°, and distils with very slight decomposition at 244—247°. It is not decomposed by alcoholic solution of silver nitrate; but on boiling with alcoholic potash, it is converted into the *normal* monochloro-camphor. Taking this latter reaction into account, the author believes this to be a case of physical and not chemical isomerism, and that the isomeride bears the same relation to the normal body as is the case with the dichlorocamphor previously described (Abstr., 1881, 738 and 1107).

L. T. T.

Products of the Distillation of Colophony. By A. Renard (*Compt. rend.*, **95**, 1386—1387).—The author has examined that portion of the product of the destructive distillation of "rosin" which passes over below 100°. Besides some aldehydes which he has not yet examined, he has obtained two principal fractions boiling at 30—40° and 67—70° respectively. The former consists of a mixture of ordinary and normal amylenes, together with small quantities of a pentane boiling at 33—38°. The fraction 67—70° consists principally of isomeric hexylenes, but contains a little hexane.

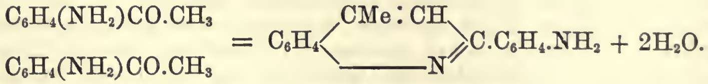
L. T. T.

Action of Cyanogen Chloride on Potassium Pyrroline. By G. L. Ciamician and M. Dennstedt (*Ber.*, **16**, 64—66).—The potassium-derivative of pyrroline was suspended in absolute ether, through which a current of cyanogen chloride was passed until the liquid smelt strongly of chlorine, the mixture being kept cool with water. After filtration from the potassium chloride, the ether was evaporated on a water-bath and the residue fractioned. No constant boiling point could be obtained, the temperature rising gradually from 130° to 210°, whilst the small residue left behind solidified on cooling to a crystalline mass. The different fractions yielded crystalline precipitates with silver nitrate, which, however, are so readily decomposed by light, that no trustworthy analysis could be made. After long standing, the different fractions became crystalline, and the crystals from each fraction were found to be identical. After crystallisation from boiling alcohol, long white needles were obtained, melting at 210°. The analytical results correspond with the formula $C_4H_4N.CN$, but the properties of the substance indicate that it is a polymeride, probably $3C_5H_4N_2$. It is insoluble in water, almost insoluble in cold alcohol, and sparingly in hot alcohol. It volatilises above 300° with decomposition. Hydrochloric and dilute nitric acids do not decompose it, concentrated sulphuric acid producing a reddish-brown coloration, which becomes black on warming. Aqueous potash has no action, whilst alcoholic potash decomposes it into pyrroline, and probably cyanuric acid. Heated with solid potash, pyrroline, carbonic anhydride, and ammonia are formed. It seems probable that the first product of the action of cyanogen chloride on the potassium-derivative of pyrroline is really $C_5H_4N_2$, which gradually becomes converted into the polymeric variety.

A. K. M.

Action of Chloroform and Iodoform on Quinoline. By O. RHOUSSOPOULOS (*Ber.*, **16**, 202—203).—*Methane-triquinoil hydriodide*, $CH(C_9H_7NI)_3$, is deposited in the form of a crystalline precipitate (m. p. 65°), on mixing ethereal solutions of iodoform (1 mol.) and quinoline (3 mols.). This compound forms transparent colourless needles, which are soluble in ether, benzene, ethyl acetate, light petroleum, &c. Chloroform does not act on quinoline at the ordinary temperature. At 300° a non-crystalline chloride is formed, which yields a non-crystalline platinochloride. W. C. W.

A New Class of Colouring-matters. II. By E. BESTHORN and O. FISCHER (*Ber.*, **16**, 68—75).—Some time ago Fischer and Rudolph (Abstr., 1882, 1066) investigated "flavaniline," at the same time expressing their opinion that it is a quinoline derivative. This view is now confirmed by the following observations:—The vapour-density of *flavoline* is in accordance with the formula $C_{16}H_{13}N$ previously given; this body, when warmed, emits an odour resembling that of the quinoline bases. On nitrating flavoline, a mononitro-body is produced, which on reduction yields amidoflavoline, identical with flavaniline. This identity was confirmed by means of the hydrochlorides, and also by the conversion of amidoflavoline into flavenol. Acetylflavenol is obtained by boiling flavenol with an excess of acetic anhydride for an hour, diluting with water and neutralising with alkali. It crystallises from alcohol in long needles melting at 128°. By the oxidation of flavenol (1 part), in alkaline solution, with potassium permanganate (6 parts), an acid is obtained, melting at 182° with violent evolution of carbonic anhydride, and yielding an oily distillate which has the characteristic odour of the quinoline bases. This distillate is probably lepidine, and the acid, lepidinecarboxylic acid. If nine parts of permanganate are used instead of six, picolinetricarboxylic acid is produced. It crystallises from water in colourless shining needles, with 2 mols. H_2O. From these facts, the authors conclude that flavoline is represented by the formula $C_{10}H_8N.Ph$ (phenyllepidine), that flavenol is the hydroxy-compound $C_{10}H_8N.C_6H_4.OH$, and flavaniline the corresponding amido-derivative. They explain the formation of flavaniline from acetanilide by assuming a molecular change, by which the latter yields amidoacetophenone. It is then easy to see how flavaniline could result by abstracting 2 mols. of water from 2 mols. of orthoamidoacetophenone—



$$\begin{array}{l} C_6H_4(NH_2)CO.CH_3 \\ C_6H_4(NH_2)CO.CH_3 \end{array} = C_6H_4\left\langle\begin{array}{c} CMe:CH \\ \overline{\qquad\quad}N \end{array}\right\rangle C.C_6H_4.NH_2 + 2H_2O.$$

By interrupting the reaction of zinc chloride on acetanilide as soon as the colouring-matter begins to be formed, the authors have further succeeded in obtaining a small quantity of an oil having the odour and other properties of orthoamidoacetophenone. Flavaniline can also be obtained by the action of acetic chloride on aniline sulphate or on acetanilide in the presence of zinc chloride. Propionanilide also gives a yellow dye, whilst formanilide yields colourless derivatives.

The base $C_{14}H_{11}N$ previously mentioned as having been formed from

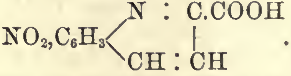
diphenylamine and glacial acetic acid, has been obtained in a pure condition, melting at 92—94°. The hydrochloride crystallises in yellow plates. Its dilute aqueous solution shows a splendid blue-green fluorescence.
A. K. M.

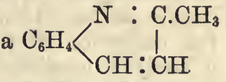
Paraxanthine, a New Constituent of Human Urine. By G. Salomon (*Ber.*, **16**, 195—200).—1·2 grams of paraxanthine were obtained from 1200 litres of human urine by the following process:—Ammonia is added to the urine, and after 24 hours the clear liquid is separated from the precipitated phosphates by decantation. The precipitate which is obtained by the addition of silver nitrate is first thoroughly washed and then decomposed by sulphuretted hydrogen. On evaporating the filtrate from the silver sulphide, a precipitate of uric acid is first deposited, and the addition of ammonia to the mother-liquor causes a further separation of uric acid in the form of ammonium urate. Nitrate of silver is added to the filtrate; the precipitate is dissolved in hot nitric acid (sp. gr. 1·1), and after 24 hours the nitrate of hypoxanthine silver is removed by filtration. The silver salt, which is thrown down on the addition of ammonia to the mother-liquor, is decomposed by sulphuretted hydrogen, ammonia is added to the solution, and, on concentrating the liquid, xanthine separates out, while paraxanthine remains in solution. Paraxanthine crystallises in colourless six-sided plates, belonging to the monoclinic system: the crystals are insoluble in alcohol and ether, but dissolve in hydrochloric and nitric acids, in ammonia, and in hot water; they do not melt at 250°, but decompose at a higher temperature. The silver salt is deposited from its solution in hot nitric acid, in silky crystals. Picric acid gives a yellow crystalline precipitate, with a hydrochloric acid solution of paraxanthine. The addition of potash or soda to a concentrated solution of paraxanthine produces a crystalline precipitate, which dissolves on the addition of warm water, but crystallises out again when the liquid cools: this reaction distinguishes paraxanthine from guanine, xanthine, and hypoxanthine. Analyses of this compound show that its composition is represented by the formula $C_{15}H_{17}N_9O_4$.
W. C. W.

Cuprea Bark. By O. Hesse (*Ber.*, **16**, 58—63).—The author has previously shown (*Ber.*, **4**, 818) that this false cinchona bark contains cinchona alkaloïds, and that it answers to the same tests as the genuine barks (*Annalen*, **166**, 218). It has several times appeared in the market, and is now found in enormous quantities in London. A microscopic examination has satisfactorily shown that it is derived from *Remijia pedunculata*, as stated by Triana. It contains quinine, quinidine, cinchonine, and amorphous bases, but no cinchonidine or paricine. By the action of permanganate in acid solution on the quinine, quinidine, and cinchonine, small quantities of the hydro-bases are produced. On boiling the amorphous bases with water, cincholine is obtained, and also diquinidine, $C_{40}H_{46}N_4O_3$; the platinochloride of this base, $C_{40}H_{46}N_4O_3,2H_2PtCl_6 + 4H_2O$, forms a dense yellow powder. Certain other barks have at different times appeared under the name of cuprea barks, as for instance *Buena magnifolia*, *Remijia purdicana*, &c. The base contained in cuprea bark, which in composition and certain properties resembles cusconine, differs from the latter in the following properties:—It melts at 144° (instead of at 110°), crystallises with 1 mol. H_2O (cusconine with $2H_2O$), dissolves with greater difficulty in cold alcohol, and turns the plane of polarised light to the right, cusconine being lævorotatory. This *concusconine* therefore bears the same relation to cusconine that quinidine does to quinine. The base previously assumed to be aricine is found to be a distinct body, and of different composition, $C_{19}H_{24}N_2O$. It melts at 184°, is dextrorotatory, and turns red litmus blue. Its solution in sulphuric acid does not fluoresce; with chlorine and ammonia, no green coloration is produced. The platinochloride, $(C_{19}H_{24}N_2O)_2,H_2PtCl_6$, forms a yellow flocculent precipitate. The normal sulphate, $(C_{19}H_{24}N_2O)_2,H_2SO_4$, crystallises in prisms, sparingly soluble in alcohol, readily in water. The body formed by oxidation with acid permanganate is probably identical with Arnaud's cinchonamine. Another base contained in cuprea bark is *concusconidine*, $C_{23}H_{26}N_2O_4$, corresponding to cusconidine. It melts at 124°, and is an amorphous yellowish-white powder. The platinochloride, $(C_{23}H_{26}N_2O_4)_2,H_2PtCl_6 + 5H_2O$, forms an amorphous flocculent precipitate. A. K. M.

Hydroconquinine and Conquinine. By O. HESSE (*Ber.*, **15**, 3008—3011).—*Hydroconquinine sulphate*, $(C_{20}H_{26}N_2O)_2H_2SO_4$, is deposited on evaporating its aqueous solution at 30—50° in slender needles containing 2 mols. H_2O. 92·3 parts of water at 16° dissolve one part of this salt. On exposing a solution saturated at 20° to a temperature of 10°, the sulphate is deposited in thick monoclinic prisms or rhombic plates containing 8 mols. H_2O. One part of this salt dissolves in 81·1 parts of water at 16°.

Conquinine may be easily separated from hydroconquinine by recrystallising the neutral hydrochloride or acid sulphate from water or alcohol. W. C. W.

Quinaldine. By O. DOEBNER and W. v. MILLER (*Ber.*, **15**, 3075—3080).—The following salts of quinaldine (*Ber.*, **14**, 2812) have been prepared. The hydrochloride, nitrate acetate and sulphate are freely soluble in water; the picrate and dichromate are sparingly soluble. The picrate, $C_{10}H_9N + C_6H_3N_3O_7$, forms yellow crystals soluble in hot alcohol; the dichromate, $(C_{10}H_9N)_2H_2Cr_2O_7$, crystallises in beautiful yellowish-red needles soluble in hot water, and resembling quinoline chromate in appearance. Quinaldine is not attacked by an aqueous solution of chromic acid, but it is completely decomposed by a solution of chromic acid in acetic acid. On oxidation with potassium permanganate, it yields acetylanthranilic acid, COOH.C_6H_4.NH.COMe, which was obtained by Bedson and King (this Journal, 1880, 752) from orthoacetotoluidide. Strong nitric acid converts quinaldine into nitroquinolinecarboxylic acid,  $NO_2,C_6H_3\left\langle\begin{array}{l}N : C.COOH\\ \qquad\ \ |\\ CH : CH\end{array}\right.$. This acid forms colourless crystals soluble in hot water. The sparingly soluble silver salt, $C_{10}H_5AgN_2O_4$, is crystalline.

The formation of these acids from quinaldine shows that this base has the formula  $C_6H_4\left\langle\begin{array}{l} N : C.CH_3 \\ \qquad\ \ | \\ CH : CH \end{array}\right.$

W. C. W.

Formation of Peptone and its Conversion into Albuminoïd Substances. By A. Poehl (*Jour. Russ. Chem. Soc.*, 1882, 353—354).—The author has established the occurrence of peptone in urine by analyses. Moreover, many animal and vegetable tissues were found to exhibit the properties of peptones, so that many physiological and pathological processes, hitherto unexplained, become clear. In order to investigate the relation of peptones to albumin, the author has studied the conversion of peptone into albumin. The conversion of albumin into peptone is, according to his view, due to the swelling up of the *colloid* of albumin. The inner constitution of peptone remains the same as that of albumin unaltered in this process of swelling up, as has been found by the study of the optical phenomena occurring during the peptonisation of albumin. B. B.

Physiological Chemistry.

Tissue-waste in the Fowl during Starvation. By F. Kuckein (*Zeits. Biol.*, **18**, 17—40).—Voit has already shown by his experiments in regard to the influence of abstention from food on tissue consumption in cats and dogs, that the destruction of albuminoïds is determined not only by the size of the organ but by the amount of fat present. The more the fat, so much less the destruction of albumin (*ibid.*, 1866, 307). Later, Rubner confirmed these conclusions in the case of herbivorous animals, such as rabbits (*ibid.*, 1881, 214); the decrease of fat was correlated to an increased consumption of albumin, which was longer delayed as the animal happened to be rich in fat, but in lean animals was manifest in a few days, albumin alone being ultimately destroyed. On *à priori* grounds, therefore, the author of this paper expected that the same law would hold good for other animals, and, in the case of birds, was likely to be well marked by reason of their more active tissue expenditure and consumption of oxygen. At the same time, Schimanski's researches (*Zeitschr. f. Physiol. Chem.*, 1879, 396) in this direction, showing the existence of very small quantities of nitrogen in the excretions, and the fact that the domestic fowl commonly receives an inconsiderable amount of nitrogenous as compared with unnitrogenous constituents in its food, were apparently opposed to this view. The author briefly reviews the work of previous experimenters, Chossat, Boussingault, Regnault, and others, by none of whom, however, had the simultaneous determination of excreted nitrogen and carbon, essential to the insight into the true nature of the tissue-changes going on within the body, been made.

Kuckein's experiments were carried out upon two fowls, the bird in each instance being confined in a cage so arranged that the head and tail projected, allowing thereby the collection of the whole of the voided excretions. The method of analysis consisted in the estimation of nitrogen by Will and Varrentrapp's method, in the excrement previously dried at 100°, after addition of tartaric or oxalic acid, whilst the carbonic acid exhaled was determined by Voit's modification of Pettenkofer's method which allowed of the introduction of bird and cage into the apparatus.

In both instances the birds were provided with water, the author remarking that small quantities have no perceptible influence over the tissue destruction.

In the first experiment, Fowl No. 1 described as lean and wanting in fat, died on the ninth day after deprivation of food. On section, no fat was visible in the subcutaneous cellular tissue nor in the peritoneal cavity, and the body weight had suffered a reduction from 1884·6 grams to 1240·3 grams, or 34·19 per cent.

In the following table are given the results of the progressive destruction of albumin and fat in the organism, the nitrogen being reckoned as albumin (with 15·5 per cent. of nitrogen) or as tissue (with 3·4 per cent. nitrogen), and the carbon in the breath and excrement after deduction of that belonging to the albumin or tissue (12·52 per cent.) as fat (with 76·5 per cent. of carbon):—

Day.	Mean body weight.	Albumin used up.	Tissue used up.	Fat used up.	In 1 kilogram of body weight.			
					Albumin.	Tissue.	Fat.	CO_2 in breath.
2	1753	20·35	92·78	—	11·61	52·93	—	—
3	1686	19·61	89·41	3·23	11·63	53·04	1·91	21·73
4	1605	19·61	89·41	—	12·22	55·71	—	—
5	1509	17·33	78·99	2·86	11·84	52·35	1·88	21·47
6	1410	17·33	78·99	—	12·29	56·04	—	—
7	1335	17·71	80·72	1·32	13·27	60·47	0·99	21·43
8	1290	17·71	80·72	—	13·72	61·01	—	—
*9	1257	12·19	55·59	—	9·70	44·23	—	—

Fowl No. 2, of average fatness, died on the 12th day of starvation. The body weight had diminished from 997 grams to 607·5 grams, or 39 per cent. On section it was found that the fat had entirely disappeared, save in the axillary region, where patches of adipose tissue could still be seen.

The results are here tabulated as in the first instance.

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* Including only 12 hours of the ninth day.

					Of body weight per kilogram.			
Day.	Mean body weight.	Albumin used up.	Tissue used up.	Fat used up.	Albumin.	Tissue.	Fat.	CO_2 in breath.
1	984	2·01	9·17	—	2·04	9·32	—	—
2	958	2·01	9·17	8·58	2·10	9·57	8·96	28·23
3	931	—	—	—	—	—	—	—
4	900	3·09	14·06	8·78	3·43	15·62	9·76	32·17
5	868	4·13	18·81	—	4·75	21·67	—	—
6	836	5·19	23·67	8·26	6·21	28·31	9·88	36·43
7	804	6·58	29·99	—	8·18	37·30	—	—
8	770	6·58	29·99	7·18	8·54	38·96	9·32	38·17
9	734	7·59	34·61	—	10·34	47·15	—	—
10	698	9·05	41·28	4·49	12·97	59·14	6·43	36·27
11	682	10·27	46·81	—	15·05	68·63	—	—
12*	626	6·89	31·43	1·99	11·01	50·20	3·18	24·42

As regards the unequal lengths of time for which fowls thus deprived of food survive, Kuckein concludes from the above data and those of other experimenters, that the fat present in the system is the determining factor. The same has been observed in the case of cats by Voit, of dogs by F. Hofmann, and of rabbits by Rubner. The varying excretion of nitrogen noticed in all these cases is similarly accounted for.

In fowls which survive longest, the nitrogenous excretion at first diminishes slowly, then remains for some time unchanged, rising again at the end, and usually in excess of that at the outset. In the case of those fowls surviving for shorter periods, a marked increase takes place within a few days, ultimately amounting to perhaps even five times the early excretion. Hence it is impossible to arrive at any average estimate of the amount of decomposed albumin for any kind of animal, unless the state of the system, especially in relation to the fat constituents, is taken into account.

The author cites one of Schimanski's experiments, in which a fat fowl survived until the 32nd day. The increase of nitrogenous excretion was nevertheless very small, owing, the author explains, to the abundance of fat present as found upon post-mortem examination, death resulting not from want of fat, but from exhaustion of the albuminous principles essential for the phenomena of vitality.

In contrast with this result were those of experiments in which fowls were of average fatness. At first the disintegration of albuminoïds was exactly as in the former case, but in 6—11 days an increase occurred to the extent of from 5—8 times this amount.

Thirdly and lastly, in the case of lean fowls, the albumin decomposed amounted already on the second day of starvation to the same, viz., 5—8 times the quantity decomposed in the others at the same period, and equal to that of the later period of starvation.

* Less three hours.

The influence of the fat he assumes to be exerted in restraining the solution and circulation of albuminoïds and the consequent smaller chance for their disintegration, this being chiefly effected by the fat present in the juices and in the organs where albumin disintegration occurs, and not by the fat stored up in the subcutaneous cellular tissue, peritoneal sac, &c. Regarding the common assumption of a more active tissue change in the case of birds than of other animals, Kuckein, from a comparison of his results and those of Rubner and others upon mammals of equal weight, shows that there is no essential difference between them when the influence of the fat is eliminated, as in the last stage of the process of starvation. Apparent discrepancies are thus accounted for. In birds, it is probable that there is, under equal conditions as to fat, more of the latter in circulation than in other animals.

The carbonic anhydride eliminated gives no insight into the individual changes going on, or measure of the extent of tissue consumption, for whilst CO_2 in 24 hours varied in five experiments from 25·3 to 30·4 grams only, and the fat consumed to a corresponding degree, the disintegration of albumin increased to fourfold or even fivefold its original amount. In conclusion, Kuckein agrees with Voit, that the domestic fowl affords the best subject for experiments of this kind. D. P.

Decrease in Weight of Individual Organs in Children Dying from Atrophy. By W. Ohlmüller (*Zeits. Biol.*, **16**, 78—103).—The author refers to earlier experiments upon animals by Chossat, Schuchardt, Bidder, and Schmidt and others, and gives a *résumé* of their results.

His own were undertaken to verify the conjecture of H. Ranke, that in children dying from wasting diarrhœa, atrophy of the various organs will be found to have occurred just as in animals dead from starvation.

The bodies of four infants were the subjects of his observations, but complete investigation was attainable in two only; these were both infants of 56 days old; one dying from diarrhœa of 2½ weeks' duration, the other of capillary bronchitis after only four days' illness, and so taken as representing as nearly as possible the normal weight of health.

I. *Alterations in Weight of Organs in Proportion to Body Weight.*—The several organs do not decrease in weight in equal ratios, but some more than others. The most striking differences are exhibited in the instance of the bones, the brain, and the skin. The two former lose much less weight than the other organs, and consequently form a larger proportion of the total body weight in the atrophic than in the normal infant. The skin, on the other hand, decreases considerably in relative weight, owing to the complete disappearance of the adipose tissue.

	Normal infant. Organic percentage of body weight.	Atrophic infant. Organic percentage of body weight.
Brain and Spinal cord	12·75	20·20
Liver	3·41	4·38
Heart	0·66	0·98
Muscles	25·82	23·61
Bone	16·99	25·53
Skin	31·16	12·21
Kidneys	0·78	1·05
Spleen	0·49	0·28
Lungs	2·56	3·57

II. *Alterations in the Percentage of Water and Fat in the several Organs.*—The percentage of water in the organs of the normal and of the atrophic infant does not greatly vary, decreasing proportionately with decrease of the solid constituents, save in the case of the skin when an increase, due to the extraordinary loss of fat, takes place.

In the atrophic infant, there is a decrease of fat in the several organs save in the brain and heart, apparently dependent in the latter on fatty degeneration of the muscular tissue, and in the brain either on more active nutrition or on decrease of the grey and relative increase of white substance.

III. *Absolute Decrease of Organs in Solid Constituents and Fat in Atrophy.*—The normal infant contains 40 per cent. of solid constituents and 60 per cent. of water; the atrophic 74 per cent. of water and only 24 per cent. of solids: the relative increase of water being due to the less amount of fat constituents, which are only 3 per cent. in comparison with 21 per cent. in the normal infant. The skin loses 97 per cent., the liver 70 per cent., the bones 66 per cent., and the muscles 64 per cent. of original fat. The loss in albuminous and gelatinous constituents amounts to 49 per cent. in the case of the skin, the intestines and muscles, but only to 23 per cent. for the heart, 18 per cent. for the brain, 16 per cent. for the liver, and 9 per cent. for the bones. To the total loss of fat the skin contributes 91 per cent., the muscles 5 per cent., and the bones 2 per cent.; the remaining organs contributing altogether only 2 per cent. To the total loss in albuminous and gelatin-yielding constituents, the muscles contribute 49 per cent., the skin 31 per cent., the intestines 17 per cent., and the remaining organs only 13 per cent.

In the atrophic child the loss in solid constituents (minus fat) of the heart, brain, liver, and bones, is much less, therefore, than that of the skin, intestines, or muscles. The former may possibly, up to a certain point, continue to receive nutrition at the expense of the organic albuminoïds which, becoming fluid, enter the circulation and for the most part are consumed.

In conclusion, the author draws attention to the probability that the active organs of the body upon which the maintenance of life depends, are protected from decrease by nutrition in this way at the expense, so to speak, of the less active organs. Only when this supply becomes insufficient do they begin to suffer loss of substance, and from this condition a long period of recovery is then needful. Especially is this the case when the loss is brought about, not by simple inanition, but by long-continued fever. D. P.

Coagulation of the Blood. By K. Hasebrock (*Zeits. Biol.*, **18**, 41—59).—Vierordt's method (*Archiv. f. Heilkunde*, **19**, 193) was employed; it has the advantage of requiring a minimum quantity of blood, and may shortly be described. A drop of blood from a prick with a needle of the finger pulp or other part of the body is taken up in a capillary tube, into which a horsehair deprived of fatty matter is then slowly inserted from the empty end. As soon as a coagulum has formed the hair is withdrawn, and this procedure repeated so long as coagula can be brought away. The number of seconds elapsing between the withdrawal of the blood from the body and the formation of the first and last coagula respectively gives approximately the times of the beginning, end, and duration of the coagulation.

In the author's experiments, blood obtained by pricking the tip of the finger in his own person, was withdrawn in a pipette of 12·9 cm. capacity, mixed in a watch-glass with measured amounts of the reagents experimented with, and then taken up in capillary tubes as explained.

The end reaction was found to be more definite than the beginning of coagulation.

I. *Influence of Water.*—Additions of water up to one-half the volume of the blood hastened coagulation; larger quantities hindered it.

A maximum of rapidity was reached when the added water was equal to four-tenths of the volume of the blood.

II. *Influence of Sodium Chloride.*—Solutions of different densities were prepared, so that equal volumes might be employed.

When added to the blood in proportion of one-half its volume, coagulation was delayed in proportion to the concentration of the salt solution; when this amounted to one-half, a trifling coagulum formed, and when saturated, coagulation ceased to take place. Weak solutions of $\frac{1}{384}$ to $\frac{1}{256}$ acted similarly to equal volumes of water, but with this difference, that while the termination of the process is hastened and the outset correspondingly delayed by the salt solution, in the case of water both beginning and end of the reaction are hastened.

III. *Influence of Holding the Breath.*—The results showed that for shorter periods coagulation was hastened, but delayed at a later stage. Hasebrock refers to this difference as accounting for discrepancies of statements by authors as to the influence of carbonic anhydride on coagulation of the blood, by the explanation that while small amounts of the latter promote coagulation large amounts delay it.

IV. *Influence of Increased Frequency of Respiration.*—In these experiments coagulation was hindered.

V. *The Influence of Temporary Arrest of Circulation.*—Vierordt's experiments in his own case, by applying a ligature to the finger for some minutes, and upon the paralysed limbs of a hemiplegic patient, showed that the blood coagulated sooner than that taken from the unligatured and sound members. The author obtained similar results, showing, according to his view, that want of oxygen hastens, whilst richness in oxygen delays coagulation, and explaining thereby the rapid coagulation witnessed after venesection, when the loss of oxygen is absolutely as well as relatively decreased.

The slower coagulation of venous than of arterial blood is dependent not on want of oxygen, but on richness in carbonic anhydride; for on continued ligature of the finger, when all oxygen was permanently given off by the hæmoglobin, delay in coagulation likewise was noted.

In conclusion Hasebrock alludes to his observations during the course of the series of experiments on the collateral influence of temperature on blood coagulation, which is the more rapid accordingly as the temperature is high; but further experiments are wanting upon this point. D. P.

Occurrence of Crystals of Ammonium-Magnesium Phosphate in Urine. By H. WEISKE (*Ber.*, **16**, 63—64).—Schwanert (Abstr., 1882, 637) has mentioned the occurrence of large crystals of ammonium magnesium phosphate in human urine supposed to be 100 years old. The urine examined by the author was fresh, had a strong acid reaction, dark yellow colour, and rapidly deposited a considerable quantity of ammonium urate. On standing in a beaker, a fungoid growth appeared on the surface, the liquid becoming strongly alkaline, whilst crystals of ammonium magnesium phosphate were formed, the largest of which measured 9 mm. A. K. M.

Chemistry of Vegetable Physiology and Agriculture.

Reduction of Nitrates to Nitrites. By U. GAYON and G. DUPETIT.—In a former paper, the authors described a microbe having the property of decomposing alkaline nitrates with evolution of nitrogen. They now find that a great many microbes have the power of reducing nitrates to nitrites. Some of these are very hardy, even living in chicken broth saturated with potassium nitrate, and reducing considerable quantities of nitrate. Four species of such microbes specially examined reduced respectively 9·6, 2·8, 6·8, and 5·6 grams of potassium nitrate into nitrite per day. On the other hand, experiments with the microbe of chicken cholera, the carbuncle bacteria, and the *Vibrio septica*, obtained in a state of purity by Pasteur, showed that these latter reduce nitrates but very slowly. The authors consider that the presence of these microbes explains in great measure the presence of nitrites in soils. L. T. T.

Butyric Ferment in Arable Soils. By P. P. DÉHÉRAIN and L. MAQUENNE (*Bull. Soc. Chim.* [2], **39**, 49—52).—Arable soil rich in organic matter contains a ferment which acts as a powerful reducing agent, and decomposes the nitrates in the soil with evolution of nitrogen. If such a soil, charged with nitrates, is sealed up in a tube with exclusion of oxygen, the nitrates will completely disappear in a few weeks, or sooner if the temperature is kept at about 35°. In presence of chloroform, or if the soil has been heated for at least an hour at 120—125°, the reduction does not take place. On adding a small quantity of fresh soil to the heated soil reduction again begins. The reduction is always accompanied by a rapid absorption of oxygen and evolution of carbonic anhydride, and is due to the action of the butyric ferment which is contained in the soil. If some of the soil is added to an aqueous solution of sugar, previously sterilised by prolonged boiling, and kept at a suitable temperature, butyric acid is rapidly formed. Solutions of sugar mixed with potassium nitrate are reduced by the ferment, butyric acid being formed and nitrogen and nitrous oxide evolved, but no hydrogen is given off. Reduction also takes place in presence of ferric hydroxide, which is converted into ferrous butyrate. Nitrogen and nitrous oxide are apparently the sole products of the reduction of nitrates by the butyric ferment.

The ferment appears to exist in the soil in a very pure state and the fermentation of sugar by means of such soil may be employed for the preparation of butyric acid. After fermentation, the liquid, which still contains a considerable quantity of unaltered sugar, is evaporated to dryness, and distilled several times with small quantities of water and an excess of boric acid. In a paraffin-bath at 160° almost the whole of the butyric acid is rapidly obtained in the distillate, which is exactly neutralised with sodium bicarbonate, evaporated to dryness, and the sodium butyrate recrystallised from alcohol.

The importance of the destruction of nitrates in soils caused by this butyric ferment is obvious. It is found, however, that the fermentation does not take place in presence of lime, even in small quantities.

C. H. B.

Reduction of Sulphates by "Sulfuraires," and Formation of Natural Mineral Sulphides. By PLAUCHUD (*Compt. rend.*, **95**, 1363—1365).—In a former paper (this Journal, **31**, 704) the author proved the hydrogen sulphide present in water containing vegetable matter to be due to the action of some species of *Confervæ* (*i.e.*, *beggiotoa*, *oscillaria*, *ulothrix*, &c.). These algæ, which are vaguely designated "sulfuraires," have the power of reducing sulphates. The author's present results confirm those of Étard and Olivier (*Compt. rend.*, **95**, 846). Small quantities of chloroform or phenol arrest the activity of these algæ; phenol in larger quantities kills them. Lifeless organisms have no reducing influence on sulphates. The granules of sulphur often deposited in the cells of "sulfuraires" are sulphur. Some "sulfuraires" hermetically sealed between plates of gypsum and left for some months, gave in one instance a few granules of sulphur. The author believes the formation of natural mineral sulphides to be due to the reducing action of this class of algæ.

L. T. T.

Influence of Chemical Agents on the Assimilative Capacity of Green Plants. By T. WEYL (*Bied. Centr.*, 1883, 65).—*Elodea canadensis* was employed in this research. A 1 per cent. solution of phenol suppresses the expiration of gas, and in 20 minutes turns the plant brown, whilst 0·5 and 0·25 per cent. solutions only reduce the quantity. Saturated solutions of salicylic acid and thymol act more rapidly and effectively than phenol. Strychnine nitrate turns the plant yellow, and hinders the expiration of oxygen, but dilute solutions of morphine hydrochloride and veratrine have no effect. Strong solutions of sodium chloride, even if sodium phosphate is present, and dilute sodium hydroxide solutions are harmful. On the other hand, in a one per cent. solution of acid sodium carbonate, more oxygen is evolved than in plain water. E. W. P.

Assimilation by Hæmatococcus. By T. W. ENGELMANN (*Bied. Centr.*, 1883, 36).—Rostafinski has stated that hæmatococcus was able to decompose carbonic anhydride without the assistance of chlorophyll. This the author shows to be incorrect, and that the red hæmatococcus, although apparently unaccompanied by chlorophyll, is not so, but that the latter is present, although to a small extent. E. W. P.

Presence of Formic and Acetic Acid in Plants. By E. BORGMANN (*Bied. Centr.*, 1883, 65).—In a great number of plants, and in various parts of those plants, whether chlorophyll is present or absent, formic and acetic acids have been detected. In chlorophyll-bearing plants, the percentage of acids rises when assimilation is repressed by removal of light, so that it would appear as if the substances were the product of regressive metamorphosis. Below the minimum temperature of growth, the acids are not formed, and since there is no respiration, acetic and formic acids are evidently dependent on respiration for their formation. E. W. P

Occurrence of Coniferin in the Woody Structures of the Beetroot. By E. O. v. LIPPMANN (*Ber.*, **16**, 44—48).—It has been previously shown by the author (Abstr., 1880, 646) as well as by Scheibler (Abstr., 1880, 467) that vanillin is present in certain kinds of raw beetroot sugar, but its origin has not been explained. The author shows that it comes from the decomposition of coniferin, but from the difficulty with which the latter is extracted by water, the coniferin cannot exist in the free state in the beetroot, but is probably in combination with the lignin. A. K. M.

Poisonous Principle of Edible Mushrooms. By G. DUPETIT (*Compt. rend.*, **95**, 1367—1369).—The author finds that all mushrooms contain a poisonous substance when uncooked. The fresh sap of the *Boletus edulis* administered to rabbits, guinea-pigs, and rats, by subcutaneous injection caused their death. The sap of *Amanita cæsarea*, *Amanita vaginata*, *Amanita rubescens*, *Agaricus campestris*, &c., has a similar action. The sap of *Amanita rubescens* is poisonous to frogs, whilst that of the others is not. The poisonous action is due to something in solution, and not to extraneous microbes, as sterilisation by means of a Pasteur's filter does not render the liquids innocuous. The active principle is insoluble in ether, chloroform, alcohol, &c., and is precipitated from the sap by the addition of alcohol, tannin, &c. It thus resembles the soluble ferments and not the known alkaloïds. A temperature of 100° renders all these mushrooms innocuous. The author has also obtained two alkaloïds, apparently nevrin and ptomaïne. L. T. T.

Diseases of Plants and their Prevention. By C. NIESSING and others (*Bied. Centr.*, 1883, 51—54).—Barberry plants growing in hedges should be removed, as they harbour the germs of "rust" (*Puccinia graminis*), which germs are developed most readily during damp summer evenings at a temperature of 12·5—15°. Plants of *Mahonia aquifolium* bear *Aecidium berberidis*, the first generation of Puccinia, they should therefore also be removed from the neighbourhood of fields of grain. This also applies to the blackberry and buckthorn. According to Kühn "smut" (*Ustilago carbo*) on barley and oats may be avoided by pickling the seed for 12 hours in dilute sulphuric acid (1·5 : 100). Copper sulphate is active against "smut" as against wheat bunt (*Tilletia caries* and *T. lævis*), but it may injure the germinating power of the seed. Prilleux describes the mode of action of *Peronospora Schachtii*, which, although well known in Germany, has but just commenced its attacks on the beets in France. Drechsler recommends treating beet seeds and the beets themselves with crude phenol dissolved in 100 parts water, to preserve them from the attacks of insects—*Julus guttulatus* and *Atomaria linearis*. This treatment has no deteriorating effect on the seeds or root.

E. W. P.

Poisoning of Plants. By C. KRAUCH (*Bied. Centr.*, 1883, 46—49).—It is well known that certain solid and gaseous substances act destructively on plants; in this article we have additions to the literature of the subject. Ammonium thiocyanate (0·25 gram and upwards per litre) is a powerful poison to germinating as well as to developed plants. Solution of zinc sulphate (0·1 gram per litre) kills barley and grasses, previously causing brown spots to appear on the leaves, but what the action is remains unknown. Sodium chloride, in small quantities, acts as a manure, but when its concentrated solutions are applied to grasses, they die, and their ash contains an abnormal percentage of this compound. In practice, manuring with salt may produce undesirable results if the weather be dry, for then its solutions became concentrated, and, moreover, chlorides of calcium, magnesium, and potassium are formed, and washed away as well as phosphates, which are rendered soluble by sodium chloride. E. W. P.

Cultivation of Cereals. By STREBEL and others (*Bied. Centr.*, 1883, 41—44).—Reports from Hohenheim and elsewhere on the yield of varieties of wheat, barley, &c. E. W. P.

Cultivation and Feeding Value of some Varieties of Vetches. By W. DÖHN and F. NOBBE (*Bied. Centr.*, 1883, 30—32).—The kind of vetch grown by Döhn is not clearly stated, but it appears to have been either a variety of the ordinary field pea or *Vicia sativa dura*, but the yield was good, and the straw was nourishing and palatable. Nobbe reports on the cultivation of tufted vetch (*V. cracca*), bush vetch (*V. sepium*), and meadow vetching (*Lathyrus pratensis*) on a sterile soil which was useless for the growth of clover. The composition of red clover is compared with that of tufted vetch, and we find that the latter is much richer in proteïn, poorer in fat and fibre than the former. The yield also was double that of clover. The seeds of wild vetches frequently fail to germinate, even after long steeping in water; this is due to the very hard outer coating; to remedy this, it is recommended to shake the seeds in a sack with sand, which process, although damaging some of the seeds, raises the percentage of germination. E. W. P.

Comparative Feeding Value of Symphytum Asperrimum. By H. WEISKE and others (*Bied. Centr.*, 1883, 33—35).—The composition of this fodder-plant was: albuminoïds, 19·88; fat, 2·69; fibre, 13·19; extractive, 42·39; ash, 21·85 per cent.; and of this a Southdown merino, when fed with it and an equal weight of hay, digested—

Dry matter.	Org. matter.	Albumin.	Fat.	Fibre.	Extract.	Ash.
5·21	69·27	58·3	71·1	18·05	84·64	4·9

Or, making allowances for admixture of sand, the comfrey contains of digestible albuminoïds 11·59 per cent.; fat, 1·9; fibre, 2·38; extract, 35·88. Stutzer finds only 0·66 per cent. of the fresh leaves to consist of digestible albuminoïds, whose nitrogen is present in the following forms:—25·79 per cent. of digestible albuminoïds, 26·76 as amides, 47·35 as indigestible nucleïn, so that this fodder is less valuable than good hay. The editor adds a note, in which it is shown that if Stutzer's percentages are referred to total dry matter, comfrey appears to be much richer in proteïn than meadow-grass, and to contain more digestible proteïn, as well as wholly digestible amides. E. W. P.

Cultivation of Gombo. By T. GRÉGOIRE (*Bied. Centr.*, 1883, 44). —This plant (*Hibiscus esculentus*), known in Marseilles as "gombo," is recommended for cultivation on account of its nourishing properties. No analysis is given. E. W. P.

Removal of the Leaves of Roots. By P. GEIBEL and others (*Bied. Centr.*, 1883, 39).—The leaves of turnips are frequently used as green fodder; but their removal acts prejudicially on the weight of the crop. Experiments on sugar-beet show that not only is the quantity reduced, but the quality likewise, the sugar being reduced by 3·7 per cent. The leaves are also less nourishing than young grass. E. W. P.

Biological Researches on the Beetroot. By B. CORENWINDER (*Compt. rend.*, **95**, 1361—1363).—The author has cultivated beet under three different conditions: *a*, in pure sand, watered with chemical manure free from carbonates and organic matter; *b*, in a field prepared in the ordinary way; *c*, in highly manured mould. After about three months, the percentage of sugar in samples taken from each section was: $a = 5\cdot45$; $b = 2\cdot85$; $c = 4\cdot10$. After 6—7 months, $a = 12\cdot26$; $b = 9\cdot0$; $c = 10\cdot60$. The weight of the beet prepared under condition c was, however, more than double that of the others, and therefore the total quantity of sugar produced was much larger. From these experiments, the author concludes that in soil deprived of organic matter the beet obtains all its carbon through its leaves from the carbonic acid of the air; in soil of average fertility the greater part of the carbon is still assimilated through the leaves; in soil of great fertility, a great deal is also derived from the organic matter of the soil. L. T. T.

Employment of Dried Potatoes. By Köhne and others (*Bied. Centr.*, 1883, 69).—Potatoes are to be sliced by a machine and then dried in a chicory kiln, whereby 64—65 per cent. of their weight is lost. A mash made from such dried potatoes ferments normally; it is expected that this process might be employed with advantage, should there be any great outbreak of potato disease. E. W. P.

Comparative Meteorological Observations in Forests. By Fankhäuser (*Bied. Centr.*, 1883, 6—9).—The observations, carried out in the Canton of Berne during 13 years, take cognizance of the temperature of the soil and air inside and outside the forests, also of the temperature of trees, moisture of air, &c. The yearly mean temperature of the same parts of the upper soil is generally the same, it is lower in the forest than in the open, a difference also is noticed between by soils overshadowed by evergreen or deciduous trees; the greatest difference of temperature occurs in the summer. The mean temperature of the air is lowest in the forest, the greatest difference occurring in summer. The highest parts of the trees are the warmer, and the interior is colder than the surrounding air. In spring and summer the trees are warmer, in autumn and winter colder than the soil. The air of the forest is moister than that of the plain. In the whole year, the soil of the forest receives 15·9 per cent. less rain than the open country. These results agree with those obtained and published by Ebermayer. E. W. P.

Influence of Climate and Weather on the Amount of Carbonic Anhydride in Terrestrial Air. By E. Wollny (*Bied. Centr.*, 1883, 9—12).—The amount of carbonic anhydride which is so necessary to vegetable life, depends on the quantity produced in the soil, and on the amount which passes off into the atmosphere; the factors which affect the production are temperature, moisture, and aeration, and these factors do not all act in the same direction, but in varied and complicated combinations when the air-pressure, direction, and force of wind remain the same. The evolution is dependent on the resistance presented by the particles of the soil, for when the soil is dense, consisting of fine particles, and the interstices are filled with water, then the resistance is increased.

In consequence of all these conditions, the percentage of gas in the superior layers is very variable, and in such a climate as that of Munich, where the rainfall is fairly constant, but the temperature very varying, the amount of carbonic anhydride found in the soil alters very considerably. When the air of the soil is warmer than the external air, then atmospheric air enters, and the carbonic anhydride is diluted. A horizontal wind current also lowers the percentage, thus in a mixture of peat and sand the percentage was reduced from 1·92 to 1·69, in humous chalky sand from 3·42 to 3·08, and in a compost from 2·94 to 2·39. When a soil is covered with vegetation, then the rainfall has great effect in regulating the percentage present, whilst in bare soils it is the temperature that exerts most influence.

E. W. P.

Rise of Temperature induced in Soils by the Condensation of Liquid and Gaseous Water and of Gases. By A. Stellwaag (*Bied. Centr.*, 1883, 12—14).—Different soils were submitted to the action of water in properly constructed apparatus. The rise of temperature was the higher the drier the original state of the soil, the finer its condition, and the lower the outside temperature; a humous chalky sand was raised 8·33°, ferric hydroxide 6·60°, and clay 5·57°; when the water contained plant food, the rise was less. When the soil condensed water vapour, the rise was more remarkable, humus rising 12·25°, and ferric hydroxide 9·3°, kaolin 2·63°. When dry carbonic anhydride was condensed, the increase was but slight; but when this gas was moist, then the rise was more remarkable (peat 11·80°, ferric hydrate 11·80°); dry ammonia gas caused a rise in the temperature of humus of 28·3°, of ferric hydroxide of 18·05°. E. W. P.

Decomposition of Nitrogenous Animal Manures. By A. Stutzer and W. Klingenberg (*Bied. Centr.*, 1883, 14—17).—Morgen and Petermann have investigated the solubility, decomposition, &c., of the nitrogenous matter of animal manures. But the authors have investigated the actual power to produce effects by determining the amount of soluble and insoluble (nucleïn) albuminoïd matter by means of hydrochloric acid solutions of pepsin; this solvent acts in an analogous, although not identical, manner to the ferments present in the soil. All animal and vegetable matter contains nucleïn, even peat and coal. A table is appended which gives the percentage of soluble and insoluble nitrogen in various waste products: blood meal contains 89·7 per cent. of its total nitrogen, soluble leather meal, on the other hand, only 39 per cent.; nearly all the nitrogen of wool waste is insoluble, and part of that in bones is rendered insoluble by steaming. E. W. P.

Evaporation of Water from the Soil. By F. Masure (*Bied. Centr.*, 1883, 1—6).—The soils submitted to experiment were Loire sand, chalky soil consisting of sand 1·6 per cent., chalk 96 per cent., clay 2·3 per cent.; clay soil, consisting of sand, 4 per cent., clay 95·6 per cent.; garden soil, consisting of sand 61 per cent., chalk 12·6 per cent., clay 20 per cent., stable manure 5·3 per cent. The following table shows the effect of the character of the soil on the amount of moisture retained, &c.:—

	Garden soil.	Sand.	Chalk.	Clay.	Manure.
(1.) Coefficient of saturation	weak	weak	strong	very strong	strong
For rain water referred to (1 volume)	0·39	0·30	0·44	0·68	0·56
For rain water referred to (1 weight)	0·37	0·20	0·42	0·84	1·03
(2.) Drying after saturation	quick	quick	slow	slow	quick
Rapidity of evaporation (mm. per day)	4·20	3·70	3·50	4·30	4·50
Duration of drying (days)	3	3	5	7	3
(3.) Permeability estimated in the morning from the evaporation	high	low	very low	low	very high
Ratio between the days on which evaporation predominated and the remaining period	0·57	0·24	0·14	0·29	0·81
(4.) Density. Mechanical resistance opposed to evaporation, which hinders drying	high	high	medium	medium	low
Relative amounts of water retained	0·89	1·17	0·76	0·81	0·56
(5.) Hygroscopic power	feeble	very feeble	feeble	strong	very strong
For 200 grams soil, grams of water absorbed	5·60	2·10	3·60	7·00	41·00
(6.) Capacity of condensing moisture from the air	high	high	very low	high	very high
Comparative length of column of water absorbed at night (mm.)	0·13	0·13	0·05	0·19	0·30
(7.) Comparative excess of the temperature of the soil exposed to the sun, over the temperature of the air	14·20°	10·70°	9·00°	11·50°	14·70°
(8.) Lowering of the temperature at night compared with surrounding air	−1·6°	−1·7°	−1·8°	−1·8°	−0·8°
(9.) Permeability for air (Schübler)	high	very low	high	high	very high
Weight of oxygen which 100 grams absorbed	14—18	1·6	10·10	15·3	20·3

The deductions to be made from examination of this table are of considerable importance; sand retains but little water and soon dries, on account of its porosity and density; a small supply of water is retained in the lower layers, and its hygroscopic power causes a sufficient condensation of water to take place on its surface. Farmyard manure must be added plentifully to render cultivation satisfactory. Chalky land is less dense, absorbs less water, becomes less hot when exposed to the sun, and is more easily aerated; such a soil must be cultivated like a sandy soil, but is more productive. Clay soils hold much water and dry slowly, and their high hygroscopic power prevents them from becoming too dry, and as they are easily heated by the sun, manure rapidly decomposes, also the amount of oxygen which they are capable of absorbing, greatly aids plant growth. Farmyard manure retains the greatest amount of water, yet by reason of its porosity it soon loses the excess of water, but from its hygroscopic power still retains sufficient moisture; when on the surface it readily absorbs dew, carbonic anhydride, ammonia, and nitrates.

E. W. P.

Manuring Experiments in Holland. By G. Reinders (*Bied. Centr.*, 1883, 17—27).—These experiments, commenced in 1870 on different farms, were conducted on the principles recommended by Ville, in which artificial manures containing all the ingredients necessary for plants are to be used. On one plot, therefore, a complete mixture was used, whilst to the others the same mixture, less one or other of the ingredients, was added. With oats and wheat, the omission of nitrogen resulted in a reduction of straw, and the omission of phosphates, a reduction in the yield of grain. Compared with the artificial manure, farmyard manure produced much lower yields. The absence of phosphoric acid in all cases was most detrimental to the crop, then next the absence of nitrogen (Chili saltpetre), and finally potash; superphosphate mixed with Chili saltpetre produced the highest results. When the crop was rape, the absence of phosphates and nitrogen was equally harmful. The advantage of phosphates to red clover and vetches was undoubted, whilst potash at one time seemed to influence the grain, at another the straw, although it seems to exert the greatest effect on those plants, as beans and wheat, whose ash is rich in potash. The highest net value of the crops was obtained from those plots which had received no magnesia, as this element was given in a pure and expensive form. In one case when ammonium sulphate was used, the value of the increase in the crop did not cover the expense of the manure; but when Chili saltpetre was employed, a profit was made, and this last result was obtained at more than one of the stations. There was only one case in which a crop manured with Chili saltpetre was unsatisfactory, namely, clover sown together with rye, but this was most probably due to the choking of the one crop by the other. E. W. P.

Manuring of Forest Trees. By M. E. Muel (*Bied. Centr.*, 1883, 27—30).—Young oaks, beeches, firs, and pines were manured with a complete mixture, also with a mixture containing no nitrogen, and with ammonium sulphate. The results do not seem to be very satisfactory; the complete manure did not produce effects sufficient to compensate for the expenses incurred, and nitrogen was harmful.

On the other hand, the incomplete manure (containing no nitrogen) was more advantageous to the growth of the young seedlings than to that of the other plants. E. W. P.

Analytical Chemistry.

Vapour-density Determination. By V. Meyer (*Ber.*, **15**, 2775—2778).—The author offers some remarks on his system of vapour-density determination now so generally adopted by chemists, but draws attention to the fact that when first introduced, it was recommended as applicable to the determination of the vapour-densities of bodies whose boiling point is higher than 440°, which attack mercury or Wood's metal; for other substances, various suitable methods were already known, and the method which most sharply and accurately gives the results in each case is the most suitable for use with that particular substance. If the air displacement method gives generally satisfactory results, and is in some cases the only method that can be employed, the author does not himself think that at lower temperatures it possesses the almost absolute freedom from error of the methods of Dumas, Gay-Lussac, and Hofmann, or of the author's previously described system of displacement by mercury or Wood's metal.

In the vapour determinations of new substances during last year, those made by the air displacement method did not differ from the theoretical numbers more than those made according to other methods, but too much importance should not be attached to this, as those new substances may contain impurities, the quantity at the disposal of the operator may be insufficient, &c. For the purpose of comparison of methods, only known and quite pure substances should be used, as in the author's published determinations of naphthalene vapour: by the mercury method he obtained the figures 4·41, by the air displacement, 4·52, theory demanding 4·43, the former agreeing well with theory, the latter being 0·09 too high, and the author thinks that under ordinary circumstances this method yields results slightly too high. Pettersson and Ekstrand assert the contrary, and say the results are too low, but they work under different conditions. These variations, however slight, should be avoided, and the older and more exact methods employed when practicable, the air method being reserved for cases such as it was originally intended to meet. Thus restricted, there is a large field for its employment in new determinations, such as the dissociation of iodine, &c.

For bodies which boil about 260°, and bear to be heated 30° over their boiling point, he advises his own mercury process as being simple and exact, provided the substance does not attack mercury. It requires but about 35 cm. mercury, and is rapid.

For substances which do not vaporise unaltered at atmospheric pressure, or do not bear heating beyond their boiling point, if they do not boil higher than 310°, and are neutral to mercury, Hofmann's method is recommended.

For bodies which volatilise with difficulty, do not attack metals, and boil between 260° and 420°, the author's method with the use of Wood's alloy is suitable.

For substances with a higher boiling point, and which attack metals, the air displacement system is suitable.

In rare cases, when a body vaporises with difficulty under diminished pressure, Dumas's method modified by Habermann is recommended.

J. F.

Manufacture and Correction of Burettes. By W. Ostwald (*J. pr. Chem.*, **25** [2], 452—458).—The author calls attention to the almost invariable inaccuracy of the graduation of burettes as obtained from the instrument makers, and to the necessity of a careful calibration of each instrument. He has frequently found the error due to the graduation to be many times that of the analytical process.

A. J. G.

Storage of Oxygen in Zinc Gasholders. By J. Loewe (*Ann. Phys. Chem.* [2], **18**, 176).—In order to store oxygen in zinc gasholders with safety, and to guard against explosions such as that experienced by Pfaundler (*vide* p. 524), the author has adopted the plan of hanging a linen bag filled with slaked lime in the water near the tube through which the water flows into the gasholder. The limewater thus formed absorbs all the carbonic anhydride and acid vapour. The lime does not require renewal even after several years' use.

V. H. V.

Estimation of Phosphoric Acid in Arable Soils. By P. de Gasparin (*Compt. rend.*, **96**, 314—315).—Twenty grams of the soil, finely powdered and passed through a hair sieve, are treated in a porcelain capsule with dilute hydrochloric acid (1 : 4) until effervescence ceases, 80 c.c. of aqua regia added, the mixture evaporated on the water-bath to a syrupy consistence, diluted with cold water, filtered, and the residue washed with hot water. The filtrate is mixed with ammonia in excess, and the precipitate which forms is collected, dried, calcined in a platinum capsule at a cherry-red heat, and powdered. It is then digested in the cold with dilute nitric acid (1 in 40), and the liquid filtered. The filtrate contains the whole of the phosphoric acid, free from lime, iron, and silica. It is concentrated on the water-bath, precipitated with ammonium molybdate, the precipitate washed once, dissolved in ammonia, and the phosphoric acid precipitated with magnesia mixture.

This method gives higher results than the old method, which entailed loss. After the concentration of the dilute nitric acid solution, the phosphorus is present entirely as tribasic phosphoric acid, having probably been brought into this condition by ignition with the ferric oxide, &c. C. H. B.

Estimation of Phosphoric Acid in Manures. (*Dingl. polyt. J.*, **247**, 85—93, and 125—130).—Wagner has made a series of experiments as to the extraction of superphosphates by water, and concludes that in the case of double superphosphates and Lahn-phosphorite superphosphates it is necessary to digest for 24 hours, whilst for other superphosphates it suffices to digest for two hours. It is further stated that ammonium citrate extracts larger quantities of phosphoric acid from normal phosphates than "citrate" solution containing free ammonia or ammonium carbonate does, and that addition of ammonia to the alkaline citrate solution does not materially alter the results obtained.

At a meeting held at Halle to consider the methods for estimating different forms of phosphoric acid, the following conclusions were arrived at. For the estimation of soluble phosphoric acid, 20 grams of superphosphate are mixed with water in a mortar, and transferred to a litre flask. The mixture is made up with water to the mark, and allowed to digest for two hours, the flask being shaken from time to time. The volume of the undissolved residue is disregarded in the subsequent calculation. For the separation of iron and aluminium phosphates in superphosphates containing about 20 per cent. phosphoric acid, 200 c.c. of the filtrate are treated with 50 c.c. ammonium acetate (100 grams pure ammonium acetate and 100 c.c. concentrated acetic acid per litre). The precipitate is filtered off, washed three times with hot water, ignited, weighed, and one half calculated as phosphoric acid. For superphosphates containing more than 20 per cent. of phosphoric acid, 100 c.c. of the above filtrate are diluted with 100 c.c. of distilled water and treated as above described. The volumetric estimation of phosphoric acid is applicable to all superphosphates which do not contain more than 1 per cent. phosphoric acid in combination with ferric oxide or alumina. A solution of uranium nitrate is used, its normal strength (1 c.c. uranium = 0·005 phosphoric acid) being obtained by dissolving 1000 grams pure uranium nitrate in 28·2 litres water, and neutralising any free nitric acid which may be present by adding 100 grams ammonium acetate. The solution is standardised with a solution of superphosphate as above prepared, or with tricalcium phosphate dissolved in the theoretical quantity of sulphuric acid, the phosphoric acid in these solutions having been previously determined by the molybdate method. For the titration, 50 c.c. of the superphosphate filtrate are taken, the end reaction being determined by potassium ferrocyanide.

The gravimetric determination of phosphoric acid is effected by the known methods, and it is also recommended to use the condensed method proposed by Wagner. For this purpose, 25 c.c. of phosphate solution free from silicic acid and containing 0·1 to 0·2 gram phosphoric acid are treated with ammonium nitrate and molybdate solution, so that the total liquid contains 15 per cent. ammonium nitrate, and for 0·1 gram phosphoric acid, 50 c.c. molybdate solution. After heating it to 80—90°, and allowing it to settle for an hour, the solution is filtered and washed with weak ammonium nitrate. The precipitate is dissolved in ammonia (of 2·5 per cent.), so that the total quantity of liquid amounts to 75 c.c. To this solution 10 c.c. magnesia mixture of the usual strength is added for 0·1 gram phosphoric acid. The precipitate is allowed to stand for two hours and filtered off. Referring to the phosphoric acid soluble in citrate solution, it is recommended by Petermann to mix 5 grams superphosphate with 100 c.c. citrate solution; the mixture is transferred to a 250 c.c. flask, agitated for an hour at 40°, and filled with water to the mark. The phosphoric acid is then determined in the filtrate. In estimating bone black, ignition, especially of fermented bone black, is objected to, and in its place wet oxidation by means of potassium chlorate is recommended. Fish guano, animal excreta, and similar raw materials, are treated in a like manner. D. B.

Estimation of Sulphurous Acid in Wine. By V. WARTHA (*Ber.*, **16**, 200—201).—A continuation of the discussion between the author and Liebermann on this subject.

Mechanical and Chemical Analysis of Soils. By A. ORTH (*Ber.*, **15**, 3025—3034).—By means of sieves, the soil is separated into particles of 5, 2, 1, 0·5 and 0·2 mm. diameter. A further division of the more finely divided portion is effected by taking advantage of the time required by the different sized particles to be deposited from a stream of running water. The author points out the necessity of making a separate analysis of that portion of the soil which is present in particles of less than 0·01 mm. diameter, in order to form a correct opinion of the true value of the soil. W. C. W.

Separation of Nickel from Cobalt. By G. VORTMANN (*Monatsh. Chem.*, **4**, 1—9).—The author, after pointing out the defects of all the ordinary methods of separating these metals, suggests the following process, depending on the oxidation of cobalt salts in ammoniacal solution by sodium hypochlorite. When such a cobalt solution mixed with sal-ammoniac is treated with this reagent, complete oxidation takes place, even at ordinary temperature, the liquid assuming a red colour. The reaction is accelerated by boiling, the solution in a few minutes assuming a deep reddish-yellow colour, and then containing the cobalt chiefly in the form of a luteo-cobaltic salt. On diluting with water after cooling, and adding a small quantity of potash-solution, the liquid, if it contain nothing but cobalt, will remain clear even after standing for several hours, but nickel if also present will be deposited in a short time as hydroxide. In this manner, mere traces of nickel may be detected in a cobalt solution, and likewise a very small quantity of cobalt in presence of nickel. A blue ammoniacal solution of nickel containing a very small quantity of cobalt usually exhibits, after treatment in the cold with sodium hypochlorite, a distinct red-violet colour; but even if the quantity of cobalt present is too small to produce this effect, the liquid, after dilution with water, addition of potash-lye, and filtration from precipitated nickel hydroxide, will exhibit a faint yellow colour; and if the quantity of cobalt be too small to produce even this faint coloration, its presence may be detected by the black precipitate formed on addition of ammonium sulphide. If the quantity of cobalt present is sufficient to give the solution a strong red colour, the cobalt-ammonium compound contained in it will be decomposed on boiling, with separation of brown cobaltic hydroxide. As nickel hydroxide is dissolved in small quantity by ammonia, even in presence of potash or soda, care must be taken in the first stage of the process not to add too large an excess of ammonia, as it would then become necessary, in precipitating with potash, to dilute the liquid to a considerable extent, which would interfere with the subsequent operations.

The author gives the details of a number of experiments made by this method, showing that in many cases it gives results more exact than those which are obtained by the use of potassium nitrite or potassium cyanide. H. W.

Analyses of some Moscow Waters. By P. Grigoreff (*Jour. Russ. Chem. Soc.*, 1882, 328—340).—Moscow is at present very badly supplied with water. Good water comes chiefly from the sources of Mitischtschi and Sokolniki, and from the Cholodinsk wells, but in such small quantities that only a few gallons per diem are available per head of the population. About 15 times as much *bad* water is drawn from the old wells and from the rivers Iaousa and Moscow. In order to find new sources of good water, and to compare the quality with that of the water used at present, the author has analysed eight different kinds of water, and for this purpose he used chiefly methods recommended by Kubel and Tiemann. The results of the analyses of the following samples are given in the tables below. (I) and (II) water from Mitischtschi wells, (III) from Sokolniki, (IV) from the source of the River Iaousa, (V) from the junction of the same river with the River Moscow, (VI) from the well of Chodynsk, (VII) from an artesian well, (VIII) from an artificial well. The first table gives the direct results of analysis; in the second table the quantities of salts were calculated from the data obtained in the first table. The quantities given in both tables refer to 100,000 parts of water.

Table I.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Suspended matter	0·18	0·21	0·22	0·15	1·24	0·074	0·24	5·45
Residue dried at 180°	14·70	14·20	8·63	10·56	30·60	31·60	82·08	178·60
Residue after calcination	12·65	11·10	6·47	8·44	26·10	27·24	75·55	154·20
SiO_2	1·20	1·23	2·05	0·85	0·94	1·40	0·76	1·13
SO_3	0·54	0·53	0·44	0·07	2·58	2·36	37·56	31·90
P_2O_5	0·21	0·32	—	—	traces	0·11	—	—
N_2O_5	0·128	0·182	0·39	0·175	0·149	1·496	0·087	21·17
Cl	0·12	0·22	0·91	0·11	2·08	1·35	1·14	24·51
CaO	5·44	5 27	2·05	3·14	9·20	11·70	12·34	45·52
MgO	1·09	1·02	0·41	0·65	2·04	1·95	8·26	10·67
K_2O	0·19	0·28	0·31	0·31	1·87	0·37	2·58	16·09
Na_2O	0·52	0·60	0·50	0·34	1·48	1·35	11·90	8·60
$Fe_2O_3 + Al_2O_3$	0·10	traces	traces	0·10	traces	—	0·20	—
NH_3	0·0076	0·0038	—	—	0·68	0·0114	0·038	traces
CO_2 (trace and half combined)	6·10	6·60	3·74	0·40	14·36	9·90	8·25	0·614
H_2S	—	—	—	—	—	—	traces	traces
MnO_4K used for oxidation or	0·73	0·89	2·29	6·49	6·56	0·85	0·40	6·62
O, for the same purpose	0·18	0·23	0·57	1·64	1·66	0·22	0·10	1·67
Hardness, German degrees	6·96	6·69	2·61	4·00	12·04	14·43	23·90	60·46
„ French degrees	12·43	11·95	4·66	7·14	21·50	25·77	42·68	107·96

TABLE II.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
KCl	0·25	0·46	0·50	0·22	2·95	0·58	2·39	25·52
$NaCl$	—	—	0·94	—	1·11	1·76	—	16·23
$MgCl_2$	—	—	0·13	—	—	—	—	3·34
K_2SO_4	0·05	—	—	—	—	—	1·98	—
Na_2SO_4	0·92	0·94	—	0·13	2·05	0·96	27·25	—
$MgSO_4$	—	—	0·66	—	0·96	2·73	24·78	27·79
$CaSO_4$	—	—	—	—	—	—	8·04	22·72
K_2CO_3	—	—	—	0·26	—	—	—	—
Na_2CO_3	0·20	0·32	—	0·48	—	—	—	—
$MgCO_3$	2·28	2·14	0·29	1·36	3·61	2·18	—	—
$CaCO_3$	9·18	8·58	3·30	5·45	16·42	19·30	16·11	44·98
$Ca_3(PO_4)_3$	0·46	0·70	—	—	..	0·24	—	—
$Ca(NO_3)_2$	0·15	0·25	0·59	0·27	..	2·22	—	32·15
NH_4NO_3	0·03	0·02	—	—	1·33*	0·05	0·12	—
$Fe_2O_3 + Al_2O_3$ ..	0·10	—	—	0·10	—	—	0·20	—
SiO_2	1·20	1·23	2·05	0·85	0·94	1·40	0·76	1·13
Total	14·82	14·64	8·46	9·12	29·37	31·42	81·63	173·86

B. B.

Examination of Molasses for Dextrin Syrup. By C. H. WOLFF (*Dingl. polyt. J.*, **247**, 228).—The author dissolved blackish-brown cane-sugar molasses in water, agitated the solution with lead acetate, then with a solution of alum and animal charcoal, and filtered the mixture. The colourless 10 per cent. solution was placed in a 200 mm. tube, and produced a rotation of +7°, hence its specific rotatory power amounted to +35°. A 10 per cent. solution of pure dextrin syrup rotated 25·6°; its specific rotatory power therefore equalled +128°. Two samples of light brown molasses showed a specific rotatory power of +97° and +88°: hence they contained 66·6 and 57 per cent. dextrin syrup respectively. D. B.

Estimation of Starch in Grain. By G. FRANCKE (*Bied. Centr.*, 1883, 37—39).—The method of conversion of starch by a glycerol malt extract at 140° is inaccurate; the result is always low. Analytical figures are quoted to prove that modifications of this process do not yield very satisfactory results; neither could good determinations of starch in rye, maize, and dari by means of hydrochloric or sulphuric acid be made, and the author states his opinion that for the present the method of conversion by water or lactic acid at high temperatures must be retained. E. W. P.

Genesis of Ptomaïnes. By F. COPPOLA (*Gazzetta*, **13**, 11—14).—The author, in continuing his experiments on this subject, already noticed (this vol., p. 522), arrives at the following conclusions:—1. Arterial blood in its normal state does not contain any substance of alkaloïdal nature. 2. In the decompositions which albuminoïds

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* *i.e.*, 0·20 NH_4NO_3, and 1·13 $(NH_4)_2SO_4$.

undergo during the process of extraction by the methods of Dragendorff and of Stas-Otto, toxic principles are formed which exhibit the reactions of alkaloïds.—These conclusions throw great doubt on all experiments hitherto made on the genesis of ptomaïnes, since the extraction of these bodies either from cadaveric substances or putrefaction products, or from liquids pathological or physiological, is always effected by one or other of these processes, or by some method chemically equivalent thereto. Moreover it is impossible to say how far the formation of such products is influenced by putrefaction, cadaveric or ordinary; and indeed, notwithstanding the conclusions of Gautier and Étard (this vol., p. 100), it may even be regarded as doubtful whether putrefaction alone is capable of giving rise to the production of ptomaïnes. H. W.

Examination of Wine coloured by Aromatic Sulphonic Derivatives. By C. THOMAS (*Bied. Centr.*, 1883, 68).—100 c.c. of the wine mixed with excess of baryta-water is boiled, filtered, and the excess of barium precipitated by ammonium carbonate. The filtrate is afterwards evaporated down in a platinum basin, and the residue ignited. The ash is to be dissolved in acidulated water, and from this solution sulphuric acid may be tested for in the usual manner. E. W. P.

Technical Chemistry.

Photo-electric Battery. By BORGMANN (*Dingl. polyt. J.*, **247**, 46).—The author places a number of **U**-tubes in a black box having removable sides, and fills the tubes with a 2 per cent. solution of sulphuric acid, the light being excluded. Silver plates, iodised on the surface by electrolytic means, are immersed in the acid. On exposure to light, an electric current is set up. D. B.

Practical Application of Thermo-electricity. By F. FISCHER (*Dingl. polyt. J.*, **246**, 324—328).—In 1823, Seebeck made the observation that on heating the points of junction of two metals so that the temperature of one of the points is different from that of the other, an electric current is excited; but although Nobili used this reaction for determining slight differences of temperature, apparatus for producing powerful thermo-electric currents have not been devised until recently. The author briefly refers to the thermo-electric batteries of Mure and Clamond and Noë, which are said to have been superseded by a new form of battery constructed by Koch, and resembling Clamond's battery. It consists of 144 elements, which with a consumption of 220 litres of coal-gas per hour produce 660 c.c. oxyhydrogen gas from a small water-decomposing apparatus. With two copper electrodes having a surface of 30 sq. cm., and being placed in a solution of cupric sulphate 5 mm. apart, 1·691 gram of copper was precipitated per hour, but after the introduction of two of the above decomposing cells the quantity was increased to 2·278 grams. The combustion-products escaping at a temperature of 480° contained 6·8 per cent. carbonic anhydride and 6·5 oxygen. The author points out that this apparatus is capable of being improved, and recommends its construction of larger dimensions in order to utilise the heat of the combustion-products more completely. As the strength of the current for low heats increases in proportion to the difference of temperature of the points of junction, whereas for higher heats the electromotive power increases at a slower rate than the difference of temperature, it seems more advisable to cool the temperature of the outer points of junction than to heat the inner ones. The author concludes by stating that the application of thermo-electricity cannot be carried out successfully on a large scale until it is possible to convert a larger percentage of heat used into electricity.

D. B.

Fuel to Produce Electricity. By BRARD (*Dingl. polyt. J.*, **247**, 94).—The electric current is formed by the combustion of coal at a high temperature and in the presence of potassium or sodium nitrate. The fuel is shaped into bricks, which are 150 mm. long, 35 mm. wide, and 25 mm. deep. The outside is covered with asbestos paper, whilst the interior consists of a coal and saltpetre prism separated by a thin sheet of asbestos. The bricks contain a large number of holes, which serve to facilitate the combustion and increase the number of points of contact with the saltpetre. A copper or brass wire is introduced into the coal and saltpetre prisms, the ends of which form the poles of the element. One brick is capable of working an electric bell.

D. B.

Flameless Combustion. By F. FISCHER (*Dingl. polyt. J.*, **247**, 32—35).—The author has repeated Fletcher's experiments on flameless combustion (*ibid.*, **246**, 293) with the view of investigating the combustion-products. For this purpose iron wire was wound round the end of a thin clay pipe, so that a ball 6 to 8 cm. thick was produced. This was heated as suggested by Fletcher, and whilst the ball was at its most intense heat, a sample of gas was withdrawn from the interior, the gas being drawn through the clay pipe and examined over mercury. The experiments corresponding to the samples of gas I, II, were made with the ordinary gas pressure, in experiment III the pressure was increased, whilst the pressure in experiment IV was still greater. The ball in experiment II was made of very thin wire, in experiments I and III the wire was 1 mm. in thickness, and in experiment IV the ball consisted of a mixture of both wires :—

	CO_2.	CO.	CH_4.	H.	O.	N.
I.	5·11	—	—	—	6·26	88·63
II.	5·03	—	—	—	3·34	91·63
III.	6·60	—	—	—	4·98	88·42
IV.	7·72	1·08	traces	0·32	traces	90·88

The composition of the gas corresponds with that of the gaseous mixture at the point of the flame of a blowpipe or Bunsen burner; the smaller proportion of oxygen, however, shows that part of it is retained by the iron; moreover, it was found that when thin wire was used, one half of the fused mass consisted of ferrosoferric oxide. Referring to the practical application of flameless combustion, the author considers that it is not available for solid fuels. D. B.

Manufacture of Sodium Sulphide. By W. WELDON (*Pharm. J. Trans.* [3], 483—484).—Some years ago the author observed that when "alkali-waste" is digested with water under a pressure of about 5 atmospheres, the following change takes place:—$2CaS + 2H_2O = 2CaH_2O_2 + CaH_2S_2$, and that the hydrogen calcium sulphide thus produced can be converted into a sodium salt by means of the action of sodium sulphate, thus:—$CaH_2S_2 + Na_2SO_4 = CaSO_4 + 2NaHS$; the subsequent conversion of this hydrogen sodium sulphide into sulphide could of course be effected by treatment with caustic soda, but this is out of the question as a manufacturing operation: Helbig has lately overcome this last difficulty by making use of what he calls "a passing formation" of caustic soda. This chemist heats, by means of steam injection, a mixture of black ash, alkali-waste, and water, in iron digesters furnished with mechanical agitators kept in motion during the operation; when this digestion is complete, the resulting solution of sodium sulphide is filtered, concentrated to 32° B., any salts separating out during evaporation are fished out, and, finally, the concentrated liquid is allowed to cool, when it yields crystals of the hydrate $Na_2S,9H_2O$. The chemistry of the process is explained in this manner: the calcium hydroxide and calcium hydrogen sulphide being formed as above described, the sodium carbonate of the black ash then reacts with the calcium hydrogen sulphide and with calcium hydroxide, producing the corresponding sodium salts, which in their turn react on one another in this manner: $NaHO + NaHS = Na_2S + H_2O$. Contrary to the statement of the text-books, anhydrous sodium sulphide does not fuse in closed vessels made of material upon which it has no action, and the hydrated sodium sulphide crystals prepared by the above process absorb oxygen from the air only very slowly; this Helbig attributes to the fact that they are quite free from caustic soda. D. A. L.

Analysis of Clay from Löthain. By H. SEGER (*Dingl. polyt. J.*, **247**, 185).—The colour of the clay is light brownish-grey. Its composition and that of the clay substance is as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	H_2O and org. matter.
Clay	54·51	31·41	0·68	0·04	0·43	0·55	12·37
Clay substance	45·53	37·68	0·82	0·05	0·51	0·52	14·89

corresponding with the formula $Al_2Si_2O_7H_2O$. Owing to its white colour, refractoriness, and great cohesive power, this clay may be used with advantage as a substitute for blue clay in the manufacture of stoneware. D. B.

Analysis of Puzzuolanas and Estimation of their Comparative Values. By E. LANDRIN (*Compt. rend.*, **96**, 491—494).— In order to obtain some insight into the constitution of puzzuolanas, the author proposes to treat them with hydrochloric acid, at a temperature of the water-bath, for two hours, in order to effect a separation into a soluble and insoluble portion. The following are his results of analyses of four samples of puzzuolana, two of which came from Réunion, one from Italy, and one an artificial specimen from Paris:—

Portion Soluble in Hydrochloric Acid.

	Réunion.		Italy.	Paris.
	I.	II.	III.	IV.
Silica	1·9	1·15	0·45	0·25
Alumina and ferric oxide	23·80	31·90	25·85	4·53
Lime	2·6	1·5	5·6	2·25
Magnesia	1·4	0·83	2·5	0·6
Alkalis, loss, &c.	0·75	0·12	0·75	0·12

Portion Insoluble in Hydrochloric Acid.

	I.	II.	III.	IV.
Silica	41·7	37·8	44·7	74·8
Alumina and ferric oxide	10·6	7·56	2·25	13·8
Lime	6·05	3·2	4·05	1·8
Magnesia	1·29	3·05	1·36	0·06
Alkalis, loss, &c.	1·16	0·49	0·74	0·44

From these analyses, it is shown that by far the greater part of the silica present is in the insoluble portion. But a determination of this proportion of silica cannot be considered as a final indication of the value of the puzzuolana as a hydraulic cement, without recourse to the method of Girard and Vical, which consists in agitating the sample with standard lime-water, and ascertaining the quantity of lime absorbed.

The following results were obtained by this process, 3 grams of the sample being used for each determination:—

	Lime absorbed after 24 hours.
Puzzuolana from Réunion (I)	0·0017
Insoluble portion from ditto	0·0224
Puzzuolana from Réunion (II)	0·0051
Insoluble portion from ditto	0·0396
Puzzuolana from Italy	0·0017
Insoluble portion from Italy	0·0404
Puzzuolana from Paris	0·0017
Insoluble portion from Paris	0·0025

These two methods, that is, treatment with hydrochloric acid, and estimation of lime absorbed are, in the author's opinion, sufficient to fix the value of a sample of puzzuolana. V. H. V.

Crystals in Cementation Steel. By L. Stoltler (*Compt. rend.*, **96**, 490).—The bars of steel obtained by the cementation process in the works at Unieux frequently contained, in those portions exposed to the hottest portion of the furnace, blebs surmounted by crystals. Des Cloiseaux has examined these crystals, and finds that they belong to the cubic system; he considers it probable that they are regular octohedra, like those of cast and wrought iron. V. H. V.

Presence of Gold in German Standard Silver Coins. (*Dingl. polyt. J.*, **247**, 186).—Dannenberg, in preparing silver nitrate from 12 marks in 50 pfennig pieces, obtained 5 to 6 mgrm. gold. His statement that when the mark coinage was introduced into Germany, the gold contained in the silver was not removed, is erroneous, as after the introduction of the wet process in 1825, the Hamburg parting works refined more than half the silver coins collected, whilst the others were worked up at Frankfort-on-the-Main, Munich, Karlsruhe, and Stutgart. D. B.

Examination of Illuminating Gas. By C. v. Than (*Ber.*, **15**, 2790—2802).—It is well known that when illuminating gas is mixed, in a closed space, with air, it becomes dangerously explosive; the author's experiments were made to discover the proportions in which the mixture is most liable to explosion. The apparatus employed was a graduated glass tube, 50 cm. long and 3 cm. in diameter, closed at one end. Fifteen experiments were made with percentages of gas to air, varying from 4 to 40 per cent.: when the amount of gas was under 5 per cent., the mixture was not inflammable; from 5 to 20 per cent. the explosions became more violent in proportion to the gas present; from 25 to 30 per cent. they gradually decreased, and between 30 to 40 per cent. the mixture burned at the mouth of the tube quietly and without explosion.

The chemical composition of the gas has an undoubted influence on the explosiveness of the mixture.

The rapid discovery of leakages in gas fittings is a matter of great importance, and the author criticises Ansell's indicator, which is supposed to give an alarm when dangerous leakages occur; he considers it untrustworthy, and describes an invention of his own, which he calls a diffusometer. It consists of a porous earthen cell, such as is employed in galvanic batteries, inverted, closed with a perforated india-rubber plug, through which it is connected with a manometer, the lower limb of which is bent, and contains a little water coloured with litmus; the cell stands on a small table capable of holding a bell-glass cover—this bell-glass is filled with air to be examined and placed in position, the mixture of gas and air diffuses into the interior of the cell, and causes an alteration of level in the coloured fluid. The author graduated the instrument with measured volumes, and found that its indications were very trustworthy; attention must be paid to differences of temperature; if the instrument is brought into a room where there is an escape of gas, it will very closely point out whether the escape is within the dangerous limits or not. Various applications of the instrument are given, such as drawing samples of air from the higher parts of theatres, public buildings, &c., for the purposes of examination. The precise locality of leakage is often difficult to find, the ordinary plan of using a light being dangerous. The author has constructed another little apparatus for the purpose, which he calls *diffusioscope*, which may be described as a very flat glass funnel, closed about half way from the edge with a very thin, circular, porous earthen plate. The stem of the funnel is provided with a tap to admit air to equalise the pressure on a miniature manometer, which is connected with the stem of the instrument. The portion containing the porous plate is placed over the suspected spot and the tap closed, when, if there is leakage, the rise of the column in the manometer is instantaneous. The apparatus is so sensitive, that when an argand burner is gradually turned down until it will no longer ignite, and the instrument held over it, the manometer rises 7 cm. in four or five seconds, held over an ordinary burner, letting so much gas out as will just kindle, the fluid rises very rapidly, and is almost ejected from the tube. If the manometer be graduated to millimeters, one half per cent. of gas can be detected in a room. An instance is given of a case of sickness, which in the opinion of the physician was due to gas poisoning, but could not be traced, as there was not a service of gas in the house. The instrument was used, when it was found that a pipe, distant 3 meters from the house, had burst underground.

A somewhat similar instrument is described by Weyde (*Dingl. polyt. J.*, **196**, 513). J. F.

Manufacture of Spirit from Wheat. (*Dingl. polyt. J.*, **247**, 228.)—According to Maciejewsky, it pays better to manufacture overgrown wheat into spirit than to use it for bread-making. The best results are obtained from unbruised wheat. The value of 100 kilos. sprouted wheat to the distiller is estimated at 16·20 marks, a price which sprouted wheat ordinarily does not attain. D. B.

Simultaneous Employment of Potatoes and Grain in Spirit Factories. (*Bied. Centr.*, 1883, 69.)—A mixture of two-third potatoes and one-third maize may be satisfactorily mashed in steamers under pressure. E. W. P.

Purification of Alcohol prepared from Molasses or Beetroot. By L. Salzer (*Bied. Centr.*, 1883, 70).—According to this patent, 70—80 grams pure potassium hydroxide are to be added to every hectolitre of 90 per cent. alcohol in tinned iron vessels. During the first 24 hours, the mixture is to be stirred with glass or highly-polished iron rods, then left to itself for 12 hours; after which 10 per cent. water is to be added, and the stirring repeated. After filtration, 200 grams tartaric acid per 100 grams potash are to be added, and after 12 hours, 10 litres water for every hectolitre alcohol, and the whole filtered and distilled. E. W. P.

Analyses of Markgräfler of different Districts and Vintages. By H. Wachter (*Bied. Centr.*, 1883, 59).—The results of 64 analyses of Markgräfler made in the years 1868—1881 show that sugar was present in quantities less than 0·1 per cent. In three specimens, glycerol occurred to the amount of 1·6—0·86 per cent.; in three old wines SO_3 to the extent of 0·0724, 0·069, 0·0583 per cent.

E. W. P.

A New Alcohol in Wine. By Henninger (*Bied. Centr.*, 1883, 69).—Ethylene glycol (b. p. 197°) occurs in wines, and up to the present time has always been estimated with the glycerol present.

E. W. P.

Influence of Foreign Matter on the Conversion of Starch by Diastase. By W. Detmer (*Bied. Centr.*, 1883, 71).—Carbonic anhydride hastens the conversion, so do small quantities of citric acid; in large quantities however, the latter destroys the action of the diastase. The same may be said of phosphoric and hydrochloric acids; whilst fairly large quantities of phenol have only a very slight retarding action. Addition of an alkali, even in very small amount, prevents the change of starch from taking place. E. W. P.

On Malt. (*Dingl. polyt. J.*, **247**, 82—85; 168—173, and 214—218.)—With a view of ascertaining the influence of different kinds of waters in steeping, Michel and Jaeckel-Handwerk have made a series of experiments, using Bohemian barley of sp. gr. 1·1994, containing 15·01 per cent. water, 2·55 ash, and 63·75 extract. In Experiment I, 50 grams of barley was steeped in 60 c.c. distilled water; in II 60 c.c. water containing 1 per cent. common salt was used; and in Experiment III 60 c.c. well water (1 litre = 425 mgrms. residue on evaporation, of which 120 mgrms. was organic matter), was taken. After 25 hours, the first steeping water was replaced in all three trials by 60 c.c. of the original water used, and this operation repeated after 20, and again after 29 hours' steeping. The following table illustrates the results obtained, calculated on 100 grams barley:—

Sample.	First soaking. Time: 25 hours.			Second soaking. Time: 20 hours.		
	Water absorbed.	Extracted matter.		Water absorbed.	Extracted matter.	
		inorg.	org.		inorg.	org.
	c.c.	g.	g.	c.c.	g.	g.
I	42	0·129	0·109	13·6	0·070	0·064
II	38	0·087	0·130	12·8	0·650	0·109
III	42	0·131	0·121	8·0	0·067	0·077

Sample.	Third soaking. Time: 29 hours.			Total— 74 hours.		
	Water absorbed.	Extracted matter.		Water absorbed.	Extracted matter.	
		inorg.	org.		inorg.	org.
	c.c.	g.	g.	c.c.	g.	g.
I..............	8	0·053	0·048	63·6	0·252	0·221
II..............	6	0·324	0·040	56·8	1·061	0·279
III..............	10	0·043	0·043	60·0	0·241	0·231

It was found that the addition of salt to the water retards the germinating process. Barley tinges the water in which it has been steeped of an orange-yellow colour, and imparts to it a slightly acid reaction. The water used for steeping contains two albuminoïds, one precipitable by metaphosphoric acid in the cold, the other on heating. The former may be retained in the grain by the addition of gypsum to the water. The repute which the Burton water has is confined to the presence of nitrates, which promote the germinating process. In order to prevent the loss of extract in steeping barley, it is recommended to treat the latter with 0·1 per cent. gypsum, and add a small quantity of calcium nitrate to the mixture. For determining the value of barley for brewing purposes, it is proposed to allow about 1 litre of the grain to germinate and make it into malt. The following table gives the results of eight malting tests; the barley was steeped, germinated, and dried under the same conditions in each experiment:—

No.	Sample.	Per cent. of dry matter in the barley.	Average weight of air-dried barley grains.	Per cent. of husks, &c., from air-dried barley.	Time of soaking. In hours.	Time of germination. Days.	Germination began after hours.	Green malt from air-dried barley. Per cent.	Kiln-dried malt from air-dried barley. Per cent.	Per cent. dry matter in malt.	Per cent. dry malt from dry barley.
1	Hungarian	85·87	37·64	0·73	75	11·0	41	148·1	83·2	5·79	91·27
2	Slavonian...............	87·03	38·02	0·44	92	9·4	34	153·1	84·4	6·55	90·62
3	Ratisbon	84·65	41·17	1·28	79	8·9	47	157·3	81·0	4·80	91·09
4	Bohemian	86·31	44·50	0·82	74	8·9	38	151·9	83·3	5·40	91·30
5	Franconian	82·35	47·40	1·40	95	10·25	57	146·4	78·5	4·72	90·82
6	Saalgerste	86·56	43·60	0·56	73	9·33	48	153·7	83·3	5·42	91·01
7	Moravian	86·70	38·65	1·34	94	9·25	46	158·2	80·8	5·07	89·17
8	Swedish	81·69	39·93	1·14	92	11·05	92	152·9	79·6	4·85	92·86

The amount of nitrogen contained in the barley and malt obtained therefrom, and the percentage composition of the ash of the barley and malt, is illustrated by the following table:—

	Barley.							
	1.	2.	3.	4.	5.	6.	7.	8.
Nitrogen......	1·809	1·629	1·877	1·809	1·859	1·696	1·750	1·605
Ash..........	2·690	2·640	2·850	2·570	2·810	2·860	2·650	2·630
Silicic acid	0·599	0·671	0·656	0·651	0·826	0·579	0·645	0·711
Phosphoric acid	1·010	0·790	1·078	0·923	0·798	0·817	0·804	0·767
Sulphuric acid.	—	—	—	0·082	0·147	—	—	0·107
Lime.........	0·056	0·059	0·065	0·062	0·059	0·037	0·640	0·067
Magnesia......	—	—	—	0·231	0·229	0·216	—	0·224
Ferric oxide ...	0·009	0·013	0·016	0·015	0·007	0·013	0·009	0·003
Potash........	—	—	—	0·315	0·608	0·528	—	0·592

	Malt.							
	1.	2.	3.	4.	5.	6.	7.	8.
Nitrogen......	1·625	1·600	1·857	1·798	1·729	1·568	1·733	1·413
Ash..........	2·480	2·390	2·440	2·300	2·420	2·350	2·320	2·310
Silicic acid	0·598	0·711	0·677	0·644	0·725	0·556	0·770	0·651
Phosphoric acid	0·929	0·868	0·904	0·708	0·779	0·784	0·830	0·693
Sulphuric acid.	0·029	0·054	0·012	0·029	0·012	0·019	0·031	0·058
Lime.........	0·091	0·072	0·087	0·077	0·084	0·096	0·085	0·082
Magnesia	0·253	0·266	0·236	0·219	0·239	0·239	0·219	0·212
Ferric oxide ...	0·022	0·018	0·019	0·014	0·017	0·011	0·015	0·015
Potash........	0·468	0·363	0·470	0·367	0·385	0·417	—	0·407

In the remaining portion of the paper, various processes of kiln-drying are described. D. B.

Manufacture of Sorgho- and Imphy-sugar in the United States. By F. Böckmann (*Ann. Agron.*, 1882, 146—155; from *Deutsche Industriezeit.*, 1881, 12 and 43).—True sorgho from Chinese seed was imported into the United States in 1855; imphy, the variety from African seed, in 1857. The cultivation of sorgho for sugar making has not hitherto taken root in Europe, but in the States of Ohio, Iowa, Illinois, Missouri, &c., considerable progress has been made, the production of sorgho sugar in America reaching 640,000 lbs. in 1875. For the same year the total production of sugar-cane sugar is estimated at 63,000,000 lbs., and of beet-sugar 20,000,000 lbs. There are certain difficulties attending the growth of sorgho, but it presents the advantage of flourishing in a climate too cold for the sugar-cane and too warm for the sugar-beet. The quantity of cane-sugar contained in the plant is at its maximum when the seed begins to ripen; the colour of the plant then changes from apple-green touched with red to citron-yellow. When this point is reached, the plants are deprived of their leaves, the stems cut off a few inches above the ground, and immediately crushed between large vertical or horizontal rollers. If this operation is delayed, a portion of the cane-sugar reverts to glucose; *e.g.*, a sample of sorgho containing 15·47 per cent. cane-sugar and 1·71 per cent. glucose the day it was cut, contained 45 days later 6·32 per cent. cane-sugar and 15·73 per cent. glucose. The proportions of the two varieties of sugar contained in the plant at different stages of growth were, in the crops of 1863, 1865, and 1866, as follows:—

	Cane-sugar.	Glucose.
1. When the ear was half out of the sheath......	0·23— 4·91	3·32—6·37
2. Just before the fall of the stamens............	2·89— 6·54	3·26—5·26
3. When the ears commenced to turn colour.....	7·84—11·78	2·16—6·04
4. Completely ripe	9·24—13·57	1·19—4·05

An analysis of sorgho juice gave—water, 80 per cent.; cane-sugar, 15—17 per cent.; glucose, 1 per cent.; starch, gum, pectic acid, albumin, red colouring-matter, ash, &c., undetermined. The most primitive method of defecating the juice consists in heating it to 70—80° and adding lime; at this temperature, the starch swells and diffuses throughout the liquid, and subsequently prevents the evaporation being carried to the point necessary for the crystallisation of the cane-sugar. A better method is to carefully filter the juice through a series of filters to remove impurities which promote fermentation, hinder evaporation, and impart a colour to the product. After filtration the juice is mixed with lime, and allowed to stand at the ordinary temperature for a certain time; the clear liquid is then evaporated. A still more complex method proposed is to mix the juice from the mill with lime, magnesia, and its own volume of alcohol of 84 per cent.; to decant the clear liquor after settling, and to press the residue into cakes for feeding, or for the production of alcohol; to distil the alcohol off from the purified solution, and continue the evaporation of the latter to the crystallising point. F. L. Stewart's process of defecation proceeds by heating the juice to 82° with lime in copper vessels, *filtering*, and evaporating with the addition of an acid liquid, the composition of which is not published. The evaporation of the defecated liquid is conducted in a very primitive fashion in the States. Four kettles of diminishing size are used, each being divided into several compartments to moderate the ebullition; the syrup is transferred from one kettle to another by a long-handled bowl, skimmed from time to time, and when sufficiently concentrated filtered through canvas.

The refining is conducted in a simple cylindrical vessel packed with animal charcoal and sand or gravel. The only analysis of sorgho sugar known to the author gave—water, 1·72; cane-sugar, 93·05; glucose, 0·41; ash, 0·68; organic matter, 4·14. J. M. H. M.

Changes occurring in Preserved Milk. By O. LOEW and others (*Bied. Centr.*, 1883, 57).—A specimen of milk, sealed up after heating to 101° by Nägeli in 1872, was found to have become brown and slightly acid when opened in 1880; the taste was bitter, and the milk-sugar was converted into lactose and dextrose, the albuminoïds being all converted into peptone, leucin, tyrosin, and ammonia. Other specimens of preserved milk had all changed. It is evident that heating to 120° under a pressure of 2—4 atmospheres is insufficient to destroy organisms. Scherff's process only preserves for about a year.

E. W. P.

Oiling and the Operations connected therewith in Turkey-red Dyeing. By F. SCHATZ (*Dingl. polyt. J.*, **247**, 38—43).—By soaking cloth in oil and dyeing in an alizarin bath without previously mordanting with a metal (aluminium, iron, &c.), no colour is produced. The oil does not take the part of a mordant, but effects the precipitation of alizarin in the presence of a mordant, the fatty acids contained in the oil forming insoluble compounds with the mordant. If, therefore, the oiling is abandoned, the mordant being soluble is washed out, and the fabric is not dyed. In dyeing, the alizarin combines with the alumina of the alumina soap, the fatty acids forming as it were a cover, which protects the aluminium alizarate molecules. In this respect, the oil imparts fastness to the colour. In the remaining portion of the paper the author discusses the changes occurring in Turkey-red dyeing, more especially with regard to the influence of steaming on cloth, after oiling, mordanting, and dyeing. D. B.

Process for Preparing Crocin-scarlet and Crocin-yellow. (*Dingl. polyt. J.*, **246**, 348.)—For the preparation of crocin-scarlet, 50 kilos. amidoazobenzenemonosulphonic acid are diazotised by means of hydrochloric acid and sodium nitrite. The diazobenzenesulphonic acid is introduced into a solution of 75 kilos. β-naphthol-α-sulphonic acid in 500 litres water and 150 kilos. ammonia (10 per cent.).

$$SO_3H.C_6H_4.N_2.C_6H_4.N_2.Cl + ONa.C_{10}H_6.SO_3Na + 2NH_3.$$
$$SO_3NH_4.C_6H_4.N_2.C_6H_4.N_2.(ONa)C_{10}H_6.SO_3Na + NH_4Cl.$$

When free amidoazobenzene is used, the dye-stuff has a yellowish tinge. The homologues of amidoazobenzene form bluish-red colouring-matters, diazobenzene and its homologues give reddish-yellow dyes, α-diazonaphthalene forms a bluish-red colour, and β-diazonaphthalene a brick-red dye-stuff. With nitric acid (50 per cent.) at 40—50°, the new β-naphtholsulphonic acid gives nitro-products, whose alkaline salts are readily soluble in water, and form yellow colouring-matters. D. B.

Alizarin-blue. (*Dingl. polyt. J.*, **246**, 92—95.)—In the *Bulletin de Rouen* (1882, 13 and 243) Mattauch, Schmidt, Blondel, and Balanche make observations as to the unstable character of soluble alizarin-blue brought into commerce by the Badische Anilin und Soda Fabrik. This colouring-matter is prepared by mixing alizarin-blue (in 10—12 per cent. paste) with sodium bisulphite of 25—30° B., allowing the mixture to stand for 8—14 days, and filtering from unconverted alizarin-blue. The new dye-stuff is obtained from the filtrate either by evaporation or by precipitation with salt. Its solution is decomposed by sulphuric or hydrochloric acid with precipitation of ordinary insoluble alizarin-blue; it forms lakes with aluminium, iron, and chromium, and yields shades which resist the action of light, soap, and chlorine as well as indigo. The best shades are produced with chromium lakes, a neutral or acid chromate being the most advantageous, as it is reduced by sodium bisulphite. The colour is developed by steaming, no mordant being required. To overcome the difficulties raised by Balanche and others as to the instability of this compound, the Baden works recommends to dissolve the colouring-matter in cold distilled water, and to avoid contact with acid fumes and iron vessels. D. B.

New Coal-tar Colours. (*Dingl. polyt. J.*, **247**, 130—136 and 173—178.)—A process for preparing yellow, red, and violet colouring matters by the action of diazo-compounds of amidobenzene and its homologues, as also of the sulphonic acids of these bodies, on phenols, naphthols, and dioxynaphthalene, and their sulphonic acids, has been patented by Krügener. In order to produce a red dye-stuff equal in shade to cochineal, 50 kilos. amidazobenzenesulphonate or 47 kilos. of the hydrochloride are gradually introduced into 230 kilos. fuming sulphuric acid (14 per cent. anhydride), cooling the vessel during the operation. The mixture is then heated slowly on a water-bath at 60° to 70° until it is perfectly soluble in water, amidobenzenedisulphonic acid being produced. From its sodium salt, diazo-azobenzenedisulphonic acid is prepared by treatment with sodium nitrite in a hydrochloric acid solution. 29 kilos. of β-naphthol are then dissolved with 16 kilos. sodium hydroxide in sufficient water so that all the naphthol remains in solution on cooling. The mixture is cooled and the diazo-azobenzenedisulphonic acid poured gradually into the same. The colouring matter is immediately formed. It is treated with salt, filtered, pressed, and purified by dissolving it in water. The homologues of amidazobenzene give similar dye-stuffs. Instead of β-naphthol—α-naphthol, phenol and dihydroxynaphthalene may be used. Amidazonaphthalene treated in like manner also gives a red colouring matter. The phenols may be replaced by their mono- and di-sulphonic acids. Again, mixtures of amidoazo-compounds may be used; *e.g.*, aniline is converted into diazobenzene chloride by treatment with an equivalent quantity of sodium nitrite and hydrochloric acid, and an equivalent quantity of xylidine is added; in this way diazobenzamidoxylol is formed, which is converted into the isomeric amidoazo-compound by the action of xylidine hydrochloride. The preparation of the sulphonic acids of the mixed amidazo-compounds is analogous to the preparation of the disulphonic acids of amidazobenzene. The mono- and di-sulphonic acids of the mixed amidazo-compounds yield, when diazotised with sodium nitrite and hydrochloric acid, diazo-azo bodies forming with naphthols, dihydroxynaphthalenes, and phenol, yellow, red, and violet dye-stuffs. From Graessler's amidazobenzenemonosulphonic acid (*ibid.*, **234**, 422) and its homologues red and violet colours are obtained by diazotising and acting on α- and β-naphthol, phenol, and dihydroxynaphthalene.

Graessler has improved the above patent by diazotising his amidazobenzenesulphonic acid and acting on resorinol or orcinol with diazoazobenzenesulphonic acid. He has also patented dye-stuffs obtained by the action of diazoazobenzene hydrochloride on naphthols, resorcinol, orcinol, dihydroxynaphthalene, and their corresponding sulphonic acids.

For preparing paranitro-compounds from the colouring matters obtained by oxidising the condensation-products of benzaldehyde with primary, secondary, and tertiary aromatic monamines, Bindschedler and Busch effect the nitration by introducing the nitrate into concentrated sulphuric acid, or dissolving the colour base in sulphuric acid and adding a nitrate, or allowing a mixture of nitric and sulphuric acid to flow into the sulphuric acid solution. For preparing paranitro-compounds from the leuco-bases obtained by the condensation of benzaldehyde with aromatic monamines, Bindschedler and Busch introduce the nitrate of the leuco-base into concentrated sulphuric acid, or dissolve the base in sulphuric acid and treat with nitric acid or a nitrate. By reducing and oxidising the nitro-bodies obtained, rosaniline colouring matters are produced.

For the preparation of dye-stuffs from the rosaniline group, Greiff proposes to allow nitrobenzoyl chloride to act on aniline, or toluidine, or their salts, in presence of oxidising agents such as iron, its oxides or salts.

For the manufacture of colouring matters by the action of nitroso-compounds or chloroquinonimides on aromatic monamines, Witt adds to 1 mol. of an aromatic monamine—especially a secondary or tertiary base—in a hot acetic acid solution 1 mol. of nitrosodimethylaniline nitrate. The colouring matter which is contained in the solution as acetate is transformed into the hydrochloride by the addition of hydrochloric acid. Dimethylaniline and similar bases give violet, diphenylamine and its homologues blue and green, naphthylamine and its homologues, as well as the naphthylphenylamines, give red and violet colouring matters.

For the preparation of dye-stuffs obtained by the action of nitrosodimethylaniline hydrochloride on tannin, tannic acid, or gallic acid, Koechlin dissolves 2 parts of tannin and 1 part of nitrosodimethylaniline hydrochloride in 10 parts of water, and heats the mixture. It is then poured into a large quantity of water, and the solution precipitated with salt. Other tannic acids, gallic acid, and other aromatic hydroxy-acids yield similar dye-stuffs. They dissolve in alkalis with reddish to bluish-violet colour. With alumina or tin mordants, violet shades are produced.

Jacobsen has patented a method for the preparation of red and violet colouring matters, by the action of benzotrichloride on pyridine and quinoline bases. The product of the continued heating at 130° of equal volumes of quinoline and benzotrichloride is treated with cold water to dissolve that part of the base which has not been converted, and the residue is extracted with boiling water; the deep red-coloured base is then precipitated from this solution by an alkali. It is insoluble in ether, and sparingly soluble in water, but dissolves readily in alcohol. The solution of the base, like that of its salts, is of a purple colour, and exhibits a strong reddish-yellow fluorescence, which is also imparted to wool and silk dyed with the colouring matter. For quinoline, its homologues can be substituted, as well as pyridine and its homologues.

Geigy prepares dye-stuffs by the action of 1 mol. of an amidazo-compound on 4 mols. of a phenol or quinone at a temperature of 130—200°. The colours formed are mostly soluble in alcohol, and are purified by washing with acidulated water and subsequent treatment with dilute alkali. By the employment of amidazo-compounds with more than one amido group, colouring matters are obtained, soluble in water, from the sulpho- or nitro-derivatives of the amidoazo-compounds, or from the polybasic phenols bodies are obtained soluble in alkalis. Amidazobenzene yields a blue with phenol, with naphthol a grey, with paranitrophenol a violet, and with salicylic acid a pearl-grey colouring matter, and so on.

According to Casella and Co., the colouring matters described as indophenols are formed also by the direct action of nitroso-compounds or chloroquinonimides on phenols. These colouring matters are obtained also by the oxidation of mixtures of paramido-phenols and monamines.

According to the Farbwerke, formerly Meister Lucius and Brüning, in melting the anthraquinonesulphonic acids with alkali, lime, or the lime salt of the sulphonic acids, is used. Thus, the calcium compound of alizarin is produced, from which the alkaline liquor is removed by filtration, and the caustic alkali recovered. The alizarin lakes are decomposed with acids, or treated with alkalis to remove impurities, and subsequently precipitated with acids. According to the Farbwerke, the salts of paraleucaniline and its homologues are converted into colouring matters of the rosaniline-group by heating them with the hydroxides of iron, manganese, and copper. The acetyl-compounds of primary or secondary aromatic bases form colouring matters *per se* or when mixed with a salt of an aromatic base by heating them with dehydrating agents. A yellow dye is obtained by heating acetanilide with zinc chloride at 230—250°. The methyl, &c., derivatives of these dye-stuffs and the sulphonic acids are prepared in a similar manner.

For the preparation of azo-colouring matters, Oehler combines metadiazosulphobenzene with diphenylamine; for the formation of the former, metamidobenzenesulphonic acid is diazotised with sodium nitrite in a weak acid solution. The diazo-compound is then treated with an equivalent quantity of diphenylamine in an alcoholic solution at as low a temperature as possible. The acid formed is filtered off, treated with alkali, and the salt dried down or precipitated with sodium chloride.

For the preparation of colouring matters from paranitrobenzaldehyde, Fischer allows 2 mols. of aniline to act on 3 mols. of nitrobenzaldehyde; an intermediate product is thus obtained which, after long continued boiling with strong acids, is converted into nitrodiamidotriphenylmethane. Aniline salts of easily volatile acids behave in a similar manner. If, however, salts of the primary aniline bases with heavy or non-volatile acids be used, then 2 mols. of aniline act on 1 mol. of nitrobenzaldehyde, and form at once the nitroleuco-base. By the condensation of paranitrobenzaldehyde with secondary and tertiary aromatic amines, nitroleuco-bases are formed, which are converted into derivatives of leucaniline by reduction of the nitro-group. These derivatives form colours by direct oxidation. Methyl, ethyl, benzyl, or phenyl may be substituted either before or after oxidation. Leuco-bases as well as the colours may be transformed into sulphonic acids. Paranitrobenzaldehyde and diphenylamine, for instance, yield a nitroleuco-base, from which diphenylparaleucaniline is obtained by reduction according to the following equations:—

$$C_6H_4(NO_2).COH + 2NHPhC_6H_5 = NO_2.C_6H_4.CH(C_6H_4.NHPh)_2 + H_2O;$$

$$NO_2.C_6H_4.CH(C_6H_4.NHPh)_2 + 6H = 2H_2O + NH_2.C_6H_4.CH(C_6H_4.NHPh)_2;$$

oxidation of the latter produces diphenylrosaniline, $C_{31}H_{27}N_3O$. A mixture of 5 parts paranitrobenzaldehyde, 12 parts diphenylamine, and 12 parts zinc chloride is heated at 100° until the aldehyde has disappeared; on boiling the product with dilute hydrochloric acid, the zinc chloride is removed and a greenish-yellow substance left. The nitro-group is then reduced with a solution of stannous chloride, the whole precipitated by water, and the amido-base purified. By oxidation, diphenylparaleucaniline yields a violet colour. According to Kalle and Company, rosaniline forms very unstable acid sulphates, which at a higher temperature are transformed into the disulphonic acid. For the preparation of the sulphonic acids of rosaniline, alizarin, &c., by the combined action of sulphuric and metaphosphoric acid, Kalle and Company use a mixture of 1 part of vitreous metaphosphoric acid and 2 parts of common sulphuric acid. This is said to act quite as strongly but more evenly in the formation of the sulphonic acids than sulphuric acid containing from 25 to 30 per cent. of anhydride.

Espenschied prepares a blue colouring matter from tetramethylparadiamidoazoxybenzene by treating the cold solution of the latter in hydrochloric acid with sulphuretted hydrogen, or such sulphides as evolve this gas when brought into contact with an acid, and then oxidising with ferric chloride.

According to the Farbwerke, formerly Meister Lucius and Brüning, artificial indigo is prepared by nitrating monobenzylidenacetone. From the alcoholic solution of the nitro-bodies the para-compound is separated, whilst from the mother-liquor the orthonitro-compound is obtained. This, on treatment with alcoholic soda-ley, forms a substance which is acidified and extracted with ether. By heating the aqueous solution of the extract, or treating it with alkali, indigo is produced. D. B.

Manufacture of Thiocyanates. By J. TCHERNIAC and LAUBER and HAUSMANN (*Dingl. polyt. J.*, **246**, 533—536).—Referring to Lauber and Haussman's process (this vol., p. 256) for preparing aluminium thiocyanate by means of calcium thiocyanate liquor, Tcherniac mentions that the method of converting sulphuretted ammonium thiocyanate liquors into calcium thiocyanate by decomposition with a definite quantity of lime, worked in suitable vessels, was patented by him in conjunction with Günzberg (*ibid.*, **245**, 214). The paper mainly discusses questions of priority between Tcherniac and Lauber and Haussman. D. B.

Dressing for Driving-bands. (*Chem. Centr.*, 1882, 768.) A half kilo. of india-rubber is melted with a half kilo. of turpentine, in an iron pot, 400 grams of rosin are now mixed in, and then 400 grams of yellow wax, stirring well all the time. This mixture, whilst still warm, is mixed with a solution of half a kilo. of tallow in $1\frac{1}{2}$ kilo. of fish oil. When used, it is put on with a brush, in a warm place. India-rubber refuse can be used; it must, however, be boiled with soda-lime, and instead of 500 grams 625 must be taken. D. A. L.

Ergot. By C. S. Hallberg (*Pharm. J. Trans.* [3], **13**, 628—629). —In order that ergot may be obtained in a condition so that it may be kept without becoming worm-eaten, &c., so that its most valuable medical constituent may be retained, whilst the useless substances are removed, and, finally, so that it may be worked up into pills, &c., with facility, the author recommends the following treatment:—Light petroleum (sp. gr. 0·716) which has been purified by shaking with sulphuric acid, washing, and distillation, is allowed to percolate through coarsely powdered ergot; this removes the fixed oils; it is then extracted with strong alcohol, which displaces the petroleum and takes up 2 to 3 per cent. of resinous matter and the poisonous alkaloïd ergotine. During this process, the ergot loses 25 to 30 per cent. in weight, and the prepared ergot is therefore stronger than the crude drug. This coarse powder, when pulverised, may be administered as such. Oil of ergot, constituting 25 to 30 per cent. of the ergot, is very heavy, dark brown, and almost odourless; pearly stellate tufts (*cholesterin ?*) sometimes separate from it. The oil yields an orange-yellow soap, which has been recommended in skin diseases; the oil is an excellent lubricator for machinery. Tested for alkaloïds by treatment with dilute sulphuric acid, caustic soda, and, finally, citric acid, the oil yielded a crystalline substance, not an alkaloïd, but probably *sclerocrystallin.* An attempt to extract the alkaloïd from the alcoholic extract, proved fruitless. The remainder of the paper relates to various pharmaceutical preparations, such as fluid ergot, made by extracting the prepared ergot with water by maceration, &c.: alcohol is subsequently added; the author is of opinion that not more than 25 per cent. of alcohol ought to be added, this quantity being quite sufficient to precipitate the gummy matter, whilst a larger quantity would remove some valuable constituents. For pills, powders, &c., the fluid ergot extract is evaporated down and mixed with milk-sugar.

D. A. L.

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1 h

General and Physical Chemistry.

Origin of the Hydrocarbon Flame Spectrum. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **34**, 418—429).—In former researches, the authors traced characteristic spectra to carbon associated with nitrogen, magnesium with hydrogen and water, of which the two former, according to the simplest interpretations of the results, emanate from cyanogen and a compound magnesium hydrogen molecule (Abstr., 1882, 252). In the course of their examination of the spectrum of carbon, they were led to assign a peculiar flame spectrum to acetylene, a view which receives support from the fact that carbonic oxide forms a distinct spectrum of a character similar to that of the flame spectrum. In order to exhaust this question, a study was made of the ultra-violet spectrum of carbon (this vol., 261), by which it was shown that seven marked spark lines of carbon occur in the spectrum of the arc discharge, and that the strongest ultra-violet line of carbon occurs in the flame of cyanogen fed with oxygen. As it seems probable from these observations that the same kind of carbon molecule exists in the arc and in flame, further experiments were made regarding the origin of the flame spectrum. By a method similar to that adopted by Wesendonck, the authors have succeeded in perfectly drying vacuous tubes, and the gases introduced into them, and thus eliminating the inevitable traces of hydrogen. The general results of the observations for such tubes prove that the channelled spectrum of the flame of hydrocarbon, is not necessarily connected with the presence of hydrogen. A tube filled with hydrogen containing a small percentage of cyanogen, and then exhausted, gave only a trace of the brightest green line of the spectrum of the hydrocarbon flame; tubes filled with carbonic oxide exhibit the hydrocarbon flame spectrum when the exhaustion is commencing, but as the exhaustion proceeds the carbonic oxide spectrum appears, and finally supersedes the hydrocarbon spectrum. These results were confirmed by other modifications of the above experiments. In the spark taken between poles of graphite in hydrogen, the spectrum of the hydrocarbon flame is seen, but if carbonic oxide be substituted for hydrogen under ordinary atmospheric pressure, the spectra of carbonic oxide and of the hydrocarbons appear; if the pressure is increased, the former grows fainter, the latter brighter, and the line spectrum of carbon is also visible.

The authors prepared with great care specimens of liquid cyanogen free from traces of moisture; this, when burnt in oxygen, gave all the hydrocarbon flame sets; but with air only the single green line appeared faintly. Thus the hydrocarbon flame spectrum requires a higher temperature for its production in the combustion of cyanogen, than that which is sufficient to produce the special cyanogen molecule spectrum. Now, cyanogen and acetylene, of all carbon compounds, give the highest temperature on combustion, and the authors infer that these flames may reach a temperature of 6000—7000°. A further evidence of the high temperature of the flame of cyanogen is afforded by the occurrence in the spectrum of the flame, when burnt in oxygen, of a series of flutings in the ultra-violet, commencing approximately at λ2718, λ2588, λ2479, and λ2373, which are in all probability due to nitrogen.

The authors have further noticed some slight differences in their observations of the electric discharge between carbon poles in different gases, when graphite is substituted for ordinary carbon poles (comp. this vol., 261). In carbonic anhydride, channellings are seen through the whole length of the spectrum, the triple set of cyanogen flame spectrum remained strong, when all the cyanogen groups in the violet had disappeared. On displacing the carbonic anhydride by hydrogen, the hydrocarbon and hydrogen lines and one of the strongest lines of carbon appear in the same field of view. The arc in carbonic oxide shows the triplet and the usual sets of the hydrocarbon flame spectrum, without any traces of the carbonic oxide spectrum. V. H. V.

Sulphuric Monochloride. By J. OGIER (*Compt. rend.*, **96**, 646—648).—Sulphuric monochloride, $SO_2(OH)Cl$, is easily obtained by the action of hydrochloric acid gas on solid sulphuric anhydride. Its specific heat between 15° and 80° is 0·282; the heat of vaporisation is 12·8 cal.; heat of solution in water 40·3 cal. It follows therefore that—

SO_3 sol. + HCl gas = SO_3HCl, liquid, develops + 14·4 cal.
SO_3 gas + HCl gas = SO_3HCl, gas „ + 13·4 „

This value is of the same order as the heat of formation of analogous compounds, such as the compounds of hydrocarbons with hydracids.

From the above data, it would follow that pyrosulphuric chloride can be converted into sulphuric monochloride by the action of water, for—

$$S_2O_5Cl_2 + H_2O = 2SO_3(OH)Cl \text{ would develop } + 54 \text{ cal.}$$

This change takes place slowly when pyrosulphuric chloride is exposed to an atmosphere containing a limited quantity of moisture. Inversely sulphuric monochloride can be converted into pyrosulphuric chloride by the action of a powerful dehydrating agent, such as phosphoric anhydride.

The vapour-density of sulphuric monochloride at 180° and 216° is 2·40; the calculated value is 4·03. It is evident that the compound dissociates at this temperature, although possibly at a temperature nearer its boiling point its vapour-density would approach more closely to the calculated value. C. H. B.

Heat of Formation of Chromic Acid. By BERTHELOT (*Compt. rend.*, **96**, 536—542).—*Chromic Sulphate.*—The heat of formation of this compound was determined by decomposing chrome-alum with an equivalent quantity of potassium hydroxide—

$$Cr_2O_3, \text{ pptd. } + 3H_2SO_4, \text{ dilute, at } 8° \text{ develops } + 47·0 \text{ cal.,}$$

or + 15·6 cal. for each mol. H_2SO_4, dilute. The actual heat of formation will depend on the molecular condition of the chromic oxide, the difference from this cause amounting in some cases to 4·6 × 3 = 13·8 cal. If the chrome-alum is decomposed by an excess of potassium hydroxide, instead of by an equivalent quantity, the heat of formation of the chromic sulphate becomes + 41·40 cal., the difference, 5·6 cal., being due to the different molecular condition of the chromic oxide. With an excess of potassium hydroxide, the precipitate is darker in colour, and apparently denser than when an equivalent quantity is employed. With anhydrous chromic oxide, and especially with the varieties produced by ignition, the differences would doubtless be greater, but no method of dissolving ignited chromic oxide in the cold is yet known.

Chromic Chloride.—The heat of formation was determined by decomposing chrome-alum by means of barium chloride—

Cr_2O_3, pptd. + 6HCl, dilute, at 8·4° develops + 37·0 cal.,

or 6·2 cal. for each mol. HCl. In this case also, the heat of formation will depend on the condition of the chromic oxide.

The addition of sulphuric acid to chrome-alum develops a sensible quantity of heat, and in this respect chromic sulphate differs from the alkaline sulphates, but resembles ferric sulphate. Chromic oxide, in fact, belongs to that group of weak bases, the salts of which are partially decomposed by water, but are brought back to their original condition by addition of an excess of acid. Thermochemical measurements show that dilute hydrochloric acid and stannous and stannic chlorides have no action on chromic chloride, any thermal disturbance being simply due to the dilution of the solutions.

Chromic Anhydride.—The heat of formation of this compound was determined by the action of hydriodic acid and stannous chloride respectively, on potassium chromate and potassium dichromate. When stannous chloride is the reducing agent, the presence of a considerable excess of hydrochloric acid is essential. The mean value of several concordant determinations, is—

Cr_2O_3 pptd. + O_3 + water = $2CrO_3$ dilute, develops + 10·2 cal.

From this result the following numbers can be calculated:—

		Develops.
Chromic anhydride	Cr_2O_3 pptd. + O_3 = $2CrO_3$, crystallised ..	+ 6·2 cal.
Potassium chromate	Cr_2O_3 pptd. + O_3 + $2K_2O$, dil., = $2K_2CrO_4$, dil. at 8°	+ 61·4 ,,
	Cr_2O_3 pptd. + O_3 + $2K_2O$, dil., = $2K_2CrO_4$, solid	+ 71·8 ,,
	Cr_2O_3 pptd. + O_3 + $2K_2O$, sol., = $2K_2CrO_4$, solid	+101·8 ,,
Potassium dichromate	Cr_2O_3 pptd. + O_3 + K_2O, dil., = $K_2Cr_2O_7$, dil. at 8°	+ 37·8 ,,
	Cr_2O_3 pptd. + O_3 + K_2O, dil., = $K_2Cr_2O_7$, solid	+ 54·8 ,,
	Cr_2O_3 pptd. + O_3 + K_2O, sol., = $K_2Cr_2O_7$, solid	+113·0 ,,

		Develops.
Ammonium dichromate	Cr_2O_3 pptd. + O_3 + $2NH_3$, dil., + H_2O, liq., = $(NH_4)_2Cr_2O_7$ dil. at 12°	+ 34·6 cal.
	Cr_2O_3 pptd. + O_3 + $2NH_3$, dil., + H_2O, liq., = $(NH_4)_2Cr_2O_7$ cryst.	+ 47·0 „

These values ought to be increased by Q, the heat developed by the conversion of precipitated chromic oxide into the ignited variety.

The decomposition of ammonium dichromate—

$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$, gas, will develop + 78 cal. + Q,

and, from the known specific heats of the products. it follows that the heat thus developed would raise their temperature to about $1150° + \frac{Q}{34}$, a fact which explains the explosive nature of the decomposition and the incandescence of the chromic oxide formed.

C. H. B.

Heat of Formation of Solid Glycollates. By DE FORCRAND (*Compt. rend.*, **96**, 649—652).—*Potassium glycollate*, $2C_2H_3O_3K + H_2O$, crystallises in slender needles which become anhydrous at 120°. Heat of solution of hydrated salt − 4·66 cal., of anhydrous salt −1·64 cal. Heat of formation from $C_2H_4O_3 + KHO = + 26·52$ cal.*

Sodium glycollate crystallises from hot solutions in anhydrous rhombic prisms; from cold solutions in brilliant plates of the composition $2C_2H_3O_3Na + H_2O$. Heat of solution of hydrated salt − 3·52 cal. of anhydrous salt −2·56 cals. Heat of formation from $C_2H_4O_3 + NaHO = + 24·64$ cal.

Acid sodium glycollate, $C_2H_3O_3Na + C_2H_4O_3$, obtained in silky needles by evaporating a solution of the normal glycollate mixed with an equivalent of acid. Heat of solution − 8·02 cal.; heat of formation from $2C_2H_4O_3 + NaHO = + 27·52$ cal.

Ammonium Glycollate.—An acid salt, $C_2H_3O_3.NH_4 + C_2H_4O_3$, is obtained by evaporating a solution of glycollic acid neutralised exactly with ammonia. Heat of solution − 9·66 cal.; heat of formation from $2C_2H_4O_3 + NH_3$ gas = + 25·39 cal. The normal salt is obtained in crystals by passing a current of ammonia gas into a cold concentrated solution of glycollic acid. Heat of solution − 3·23 cal.; heat of formation from $C_2H_4O_3 + NH_3$ gas = + 21·51 cal.

Barium glycollate forms anhydrous monoclinic prisms. Heat of solution − 5·08 cal.; heat of formation from $2C_2H_4O_3 + BaH_2O_2 =$ + 40·44 cal.

Strontium glycollate, an anhydrous salt. Heat of solution − 1·20 cal.; heat of formation from $2C_2H_4O_3 + SrH_2O_2 = + 36·16$ cal.

Calcium glycollate crystallises from cold solutions with $5H_2O$. If precipitated from an aqueous solution by adding an equal volume of alcohol of 90°, the crystals contain $3H_2O$; both hydrates lose their water at 110°. Heat of solution of $(C_3H_3O_3)_2Ca + 5H_2O$ − 7·8 cal.;

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* In every case, with exception of the ammonium salts, the value given is the heat of formation of the solid anhydrous salt from the solid acid and solid base. The heats of solution were determined between 8° and 10°.

of $(C_2H_3O_3)_2Ca + 3H_2O$, − 7·06 cal.; of $(C_2H_3O_3)_2Ca$, − 1·62 cal. Heat of formation of anhydrous salt from $2C_2H_4O_3 + CaH_2O_2 =$ + 26·98 cal.

Magnesium glycollate crystallises with $2H_2O$. Heat of solution of hydrated salt, − 1·52 cal., of anhydrous salt, + 4·4 cal. Heat of formation from $2C_2H_4O_3 + MgO =$ + 18·92 cal.

Zinc glycollate also crystallises with $2H_2O$. Heat of solution of hydrated salt, − 4·06 cal.; of anhydrous salt, + 0·66 cal. Heat of formation from $2C_2H_4O_3 + ZnO =$ + 15·98 cal.

Copper glycollate, anhydrous salt. Heat of solution, − 1·62 cal.; heat of formation from $2C_2H_4O_3 + CuO =$ + 12·74 cal.

Lead glycollate, anhydrous salt. Heat of solution, − 5·80 cal.; heat of formation from $2C_2H_4O_3 + PbO =$ + 16·82 cal.

In every case, the heat of formation of the glycollate, both solid and in solution, is intermediate between the heats of formation of the corresponding acetate and oxalate, the heat of formation increasing as the quantity of oxygen in the acid increases. C. H. B.

Vapour of Carbamide. By F. ISAMBERT (*Compt. rend.*, **96**, 340—341).—The vapour of carbamide at 61—62° behaves under changes of pressure exactly like a mixture of carbonic anhydride and ammonia gas. Moreover, the condensation of the vapour is accompanied by a development of heat = 39·8 cal., a number identical with the heat of formation of carbamide. It is evident, therefore, that the volatilisation of carbamide is a case of dissociation, and the limiting tension at a given temperature is the sum of the pressures of ammonia gas and carbonic anhydride (in the proportion of 2 vols. to 1 vol.) which limit the dissociation at that temperature. Solid carbamide may be regarded as formed by the simple addition of carbonic anhydride to ammonia. C. H. B.

Supersaturation. By S. U. PICKERING (*Chem. News*, **47**, 85).—The author has observed a case of supersaturation in the presence of some of the solid substance. On cooling a filtered boiling saturated solution of copper sulphate, a considerable crop of crystals was formed on the sides of the beaker, and on a glass rod; as soon as the latter was disturbed, a sudden and copious separation of small crystals of copper sulphate took place. D. A. L.

Inorganic Chemistry.

Oxyacids of Chlorine. By C. W. BLOMSTRAND (*Ber.*, **16**, 183—189).—The author does not consider that his views on the constitution of the oxyacids of chlorine are rendered untenable by the results of Spring's experiments (*Bull. Acad. Belg.*, **39**, 882) on the action of phosphorus pentachloride on chlorates and perchlorates.

W. C. W.

Hydroxylamine Hydrochloride. By V. MEYER (*Ber.*, **15**, 2789—2790).—Small quantities of chemically pure hydroxylamine are easily produced by Dumreicher's method, but the case is different when large quantities are required. If some few hundred grams of it are to be made, a large weight of tin must be precipitated with sulphuretted hydrogen. An unmanageable quantity of tin sulphide has to be filtered and washed, and perhaps a hundred litres of hydrochloric acid filtrate to be evaporated; the method besides being troublesome and tedious on the large scale, does not yield a pure product, and the impure salt is difficult to keep, whilst if chemically pure it may be preserved unaltered for a long time. As a small quantity of ammonium chloride left in the salt is not so injurious as ferric chloride or free hydrochloric acid, the author gives a method by which a very white and stable substance can be prepared tolerably free from ammonium chloride. The acid liquid obtained in the Dumreicher process, which contains chlorides of iron and sometimes of other heavy metals, calcium chloride, &c., &c., is strongly concentrated, and when well cooled supersaturated with soda; all the heavy metals, together with calcium, are precipitated and removed by filtration; the filtrate is then carefully acidified with hydrochloric acid and evaporated. The residue consists of sodium and ammonium chlorides, and the hydroxylamine chloride, which is extracted by hot alcohol and crystallises out on cooling in shining white crystals containing about 90 per cent. of the pure substance in a very durable form, and available for most purposes. It is only when a chemically pure substance is required that the removal of the remaining ammonium chloride is necessary, which may be effected by platinum chloride. J. F.

Dissociation of Phosphine Hydrobromide. By F. ISAMBERT (*Compt. rend.*, **96**, 643—646).—The vapour of phosphine hydrobromide is a mixture of equal volumes of hydrogen phosphide and hydrobromic acid, and the compound obeys the same law of dissociation as ammonium bisulphide (*Compt. rend.*, **95**, 1355). It splits up into hydrogen phosphide and hydrobromic acid until the tension of these gases reaches a certain limit, which is constant for the same temperature, but increases at first slowly, and afterwards more rapidly, with the temperature. C. H. B.

Pyrosulphuric Chloride. By J. OGIER (*Compt. rend.*, **96**, 648—649).—The author has redetermined the vapour-density of this compound, using a specimen distilled twice over phosphoric anhydride in order to remove all traces of sulphuric monochloride, $SO_2(OH)Cl$. The pure product boils at 140·5° (corr.). Its vapour-density at 185° was 3·53 and 3·65; at 215° 3·59 and 3·81, mean = 3·72. (See also this vol., 423.) C. H. B.

Potassium Sesquicarbonate. By C. RAMMELSBERG (*Ber.*, **16**, 273—275).—According to Bauer, potassium sesquicarbonate is formed by the evaporation and crystallisation of large quantities of the bicarbonate: it neither deliquesces nor effloresces. Analyses made by Bauer and by the author are in accordance with the formula $2K_2CO_3,H_2CO_3 + 3H_2O$. A. K. M.

Constitution of "Liquor Sodæ Chloratæ." By W. R. Dunstan and F. Ransom (*Pharm. J. Trans.* [3], **13**, 667—668).—*Liquor sodæ chloratæ* of the British Pharmacopœia is prepared by passing chlorine through a solution of sodium carbonate, and is generally supposed to contain sodium hypochlorite and chloride, and sodium hydrogen carbonate, but from observations of Williamson and some experiments of their own, the authors concluded that this preparation contained free hypochlorous acid and not sodium hypochlorite; this conclusion is now confirmed by the results of the experiments described in this paper. After several experiments with various reagents ether was found to be an excellent solvent for hypochlorous acid, therefore some *liquor sodæ chloratæ*, B.P., was prepared and extracted with ether. The ethereal extract had the strong odour of hypochlorous acid, and readily bleached litmus; when neutralised with soda, however, and mixed with nickelous chloride, it gave a precipitate of green nickelous hydrate only as long as the ether was present, but as soon as this was driven off a precipitate of black nickel hydrate was obtained. This anomaly is explained by the fact that ether readily reduces black nickel hydrate to the green nickelous hydrate. Cobalt hydrate is also reduced, but not nearly so readily as nickel; in fact, this reaction can be used as a distinguishing test for these metals. The residual liquid from *liquor sodæ chloratæ*, after extraction with ether, contains sodium chloride and sodium hydrogen carbonate; on keeping it, sodium chlorate is formed. Some samples of commercial *liquor sodæ chloratæ* were alkaline to test-paper, contained sodium hypochlorite, but no free hypochlorous acid and traces of calcium. It is evident that they were prepared by decomposing bleaching powder with sodium carbonate. D. A. L.

Action of Chlorine on Solutions of Sodium Carbonate. By W. R. Dunstan and F. Ransom (*Pharm. J. Trans.* [3], **13**, 668—669). —The chlorine employed in these experiments was purified by passing it through copper sulphate solution: when the chlorination was complete, excess of chlorine was driven out by a current of air before testing for hypochlorous acid with ether, &c. (preceding Abstract).

In the first series of experiments, a 25 per cent. sodium carbonate solution was employed, and several quantities of 50 c.c. of this solution were treated with varying quantities of chlorine. If the chlorine is not in excess and the solution is still alkaline, it contains no free hypochlorous acid, but sodium hypochlorite in quantities varying directly with the chlorine; the gas evolved consists of chlorine and carbonic anhydride. When chlorine is passed until the solution is only faintly alkaline, it bleaches powerfully, and contains both sodium hypochlorite and free hypochlorous acid. The small quantity of gas evolved in this stage of the reaction consists of carbonic acid. On continuing to pass chlorine, a further small quantity of carbonic acid is evolved, the solution has the physical properties of *liquor sodæ chloratæ*, and contains sodium hydrogen carbonate, sodium chloride, and free hypochlorous acid, but no sodium hypochlorite. Beyond this point, carbonic anhydride is given off with effervescence, and if the treatment with chlorine is continued until this ceases, the solution contains hypochlorous acid, sodium chloride. and some sodium chlorate. Exactly similar changes occur in a saturated solution of sodium carbonate; at first, however, more carbonic anhydride is given off than in the case of the more dilute solution. In the next stage, sodium hydrogen carbonate is precipitated, and when this precipitation ceases, the solution contains hypochlorous acid, sodium chloride, and some chlorate; effervescence then sets in, and the precipitate disappears, leaving the solution as in the previous experiment. When the reaction is conducted at 0°, the changes are the same; at 100° the products are sodium chloride and chlorate. The action of chlorine on sodium hypochlorite gives rise to the production of hypochlorous acid, sodium chloride, and chlorate. With a mixture of equal parts of hypochlorite and sodium hydrogen carbonate, chlorine causes no effervescence at first, and just before it commences the solution is like the *liquor sodæ chloratæ* of the B.P.; finally, all the carbonate disappears in the manner already described. From these results the authors represent the changes thus:—$Cl_2 + Na_2CO_3 = NaClO + NaCl + CO_2$; $CO_2 + OH_2 + Na_2CO_3 = 2NaHCO_3$; $NaClO + Cl_2 + H_2O = NaCl + 2HClO$; $Cl_2 + NaHCO_3 = NaCl + HClO + CO_2$, and the formation of chlorate by the equation $NaCl + 6HClO = NaClO_3 + 3Cl_2 + 3H_2O$, whilst they explain the reaction in boiling solutions in the following manner, $3Na_2CO_3 + 3Cl_2 = 5NaCl + NaClO_3 + 3CO_2$. They are studying the action of chlorine on certain metallic oxides and carbonates, and have already obtained some interesting results.

D. A. L.

Production of Brom-apatite and Bromo-wagnerites. By A. Ditte (*Compt. rend.*, **96**, 575—577).—When a mixture of calcium phosphate with sodium bromide is heated from one to two hours at a temperature a little above the melting point of the latter salt, the calcium phosphate is converted into brom-apatite, $CaBr_2,3Ca_3P_2O_8$, which forms regular transparent hexagonal prisms often terminated by hexagonal pyramids. The products of the reaction are brom-apatite and sodium phosphate. The proportion of the latter increases with the amount of calcium phosphate employed, and when it reaches a certain amount a condition of equilibrium is established between the reaction of the sodium bromide on the calcium phosphate and that of the sodium phosphate on the brom-apatite. If the quantity of calcium phosphate used is small, it is completely converted into brom-apatite, but if large the conversion is incomplete, for the sodium phosphate formed acts on and decomposes the apatite. Indeed apatite heated with sodium bromide and sodium phosphate in certain proportions is converted into a double phosphate of calcium and sodium.

The corresponding wagnerite, $CaBr_2,Ca_3P_2O_8$, cannot be obtained under these conditions, since it is at once decomposed by fused sodium bromide with removal of calcium bromide and formation of apatite. This decomposition ceases, however, when the fused mass contains a very large proportion of calcium bromide, and if a small quantity of calcium phosphate is heated with pure calcium bromide it is converted into long slender needles, sometimes terminated by elongated pyramids. These crystals have the composition $CaBr_2,Ca_3P_2O_8$. With a larger amount of calcium phosphate, a mixture of wagnerite and apatite is obtained, whilst if the amount of phosphate is very large, apatite is the sole product.

Similar compounds are obtained and similar phenomena are observed with calcium arsenate and calcium vanadates. In the latter case, a portion of the vanadic acid is sometimes reduced to dark-coloured lower oxides which remain mixed with the crystals of chlor-vanadate, &c.

In all cases it is necessary to keep the fused mixtures as much as possible out of contact with the air. It is evident that the bromapatites and bromo-wagnerites are formed and decomposed under the same conditions as the corresponding chlorine compounds (*Compt. rend.*, **94**, 1592). C. H. B.

Basic Halogen Salts of Barium. By E. BECKMANN (*J. pr. Chem.* [2], **27**, 126—147).—A continuation of the author's paper (Abstr., 1882, 141). These basic barium salts were obtained by crystallisation of mixed concentrated solutions of barium hydroxide and the halogen salt; a varying excess of barium hydroxide beyond that required by the formulæ given by the author was always observed. *Basic barium chloride*, $BaCl(OH),2H_2O$, crystallises in plates of fatty lustre; it readily loses four-fifths of its water at 120°, the remaining one-fifth is not given off below the fusing point of the salt, and requires several hours' heating to redness in a stream of hydrogen for its complete removal. Basic barium bromide, $BaBr(OH),2H_2O$, resembles the chloride in appearance and behaviour on heating. On adding alcohol to mixed solutions of barium bromide and hydroxide, the basic salt, $BaBr(OH),3H_2O$, was obtained. Basic barium iodide, $BaI(OH),4H_2O$, crystallises in short thick needles.

Crystallised barium hydroxide, $Ba(OH)_2,8H_2O$, loses 8 mols. H_2O on long heating at 75°, or on heating for two hours at 100° (not 7 mols. only as generally stated); and the combined water is expelled on heating to redness in a current of hydrogen. Crystallised barium chloride loses more than 1 mol. H_2O when dried over sulphuric acid, and is rendered anhydrous by heating for some hours at 75°. Crystallised barium bromide, $BaBr_2.2H_2O$, loses 1 mol. H_2O at 75°, the second at 120°. Barium iodide, $BaI_2,7H_2O$, loses 6 mols. H_2O at 125°, the remainder is not expelled until above 150°. A. J. G.

Barium Aluminates. By E. BECKMANN (*J. pr. Chem.* [2], **26**, 474—503).—On adding aluminium chloride to barium hydroxide solution until a permanent precipitate of alumina is produced, filtering and boiling, the compound $Al_2O_3,BaO,3BaCl_2 + 6H_2O$ separates in the crystalline state. The same compound is formed from mono- or di-barium aluminate (Abstr., 1882, 141) and barium chloride. It crystallises in hard rhombic tablets, is but little soluble in cold, readily in hot water.

The author also describes the compound $Al_2O_3,BaO,BaCl_2 + 11H_2O$, obtained from the mono- or di-barium aluminate or the previous salt, and analogous bromides and iodides. O. H.

Specific Heat and Valency of Thorium. By L. F. NILSON (*Ber.*, **16**, 153—163).—The specimens of metallic thorium used in these experiments contained 2·4 per cent. of oxygen and 0·84 of iron. The sp. gr. of the metal varies from 10·968 to 11·230. The specific heat of thorium is 0·02787, the atomic weight 232·4, and the atomic heat 6·41. Thorium also resembles the tetravalent elements, Zr, Ce, La, and Di, in its atomic volume = 20·94, and silicon in its crystalline form. Thoria is isomorphous with the dioxides of tin, zirconium, and titanium, and the molecular volume of thoria agrees with the molecular volume of CeO_2 and UrO_2. The molecular heat of thoria is the same as the molecular heats of the dioxides of zirconium, cerium, titanium, manganese, and tin. The thorium double fluorides correspond to the double fluorides of zirconium. The platinochloride corresponds to the platinochlorides of tin and zirconium. Thorium attacks platinum, forming a fusible alloy. The close resemblance between thorium and the tetravalent elements as exhibited by the above facts shows that thorium is tetravalent, and that its only known oxide is a di-oxide, ThO_2. W. C. W.

Formation of Arsenides by Pressure. By W. SPRING (*Ber.*, **16**, 324—326).—When a mixture of zinc and arsenic in the proportions to form Zn_3As_2, is subjected to a pressure of 6500 atmospheres, the resulting block powdered, and the operation repeated, a homogeneous mass is obtained showing crystalline structure. It dissolves in dilute sulphuric acid with evolution of arseniuretted hydrogen, leaving but a small black insoluble residue. In a similar manner, *lead arsenide*, Pb_3As_2, *tin arsenide*, Sn_3As_2, *cadmium arsenide*, Cd_3As_2, *copper arsenides*, Cu_3As_2, Cu_6As_2, and $Cu_{12}As_2$, and *silver arsenides*, Ag_3As and Ag_6As, can with more or less difficulty be obtained. When *amorphous* arsenic (sp. gr. 4·71) is subjected to a pressure of 6500 atmospheres, it assumes a metallic lustre, whilst its sp. gr. becomes raised to 4·91; as the sp. gr. of crystalline arsenic is 5·71, it is assumed that one quarter is converted by pressure into the *crystalline* variety. (For previous investigations see Abstr., 1882, 921.) A. K. M.

Tungsten Compounds. By G. v. KNORRE (*J. pr. Chem.* [2], **27**, 49—98).—*Tungsten Bronzes.*—Only a single *potassium tungsten bronze* can be obtained by the reduction of the acid potassium tungstates by heating in hydrogen, by fusion with tin, or by electrolysis. It has the formula $K_2W_4O_{12}$, and crystallises in prisms of reddish-violet colour; when finely powdered it assumes a fine blue colour; the powder when suspended in water gives a liquid, blue by transmitted, greenish by reflected light. Its sp. gr. is 7·09 when prepared by heating in hydrogen, and 7·135 when prepared by electrolysis. The author could not obtain the bronze $K_2W_5O_{12}$ described by Zetnow (*Pogg. Ann.*, **130**, 262).

By fusing a mixture of equal mols. of $5K_2O,12WO_3,11H_2O$, and $5Na_2O,12WO_3,28H_2O$, and then heating to low redness in a stream of hydrogen, the sodium potassium bronze, $5K_2W_4O_{12},2Na_4W_5O_{15}$, is obtained crystallising in dark purple-red quadratic (?) prisms. Its sp. gr. is 7·117. The powder is blue. The same mixture of acid tungstates gave on another occasion a bronze of darker red colour than the preceding, and of the formula $3K_2W_4O_{12},2Na_2W_3O_9$.

No bronzes could be obtained by the reduction of the acid lithium tungstates, tungsten dioxide being formed. By the action for a short time of tin on fused $5Li_2O,12WO_3$, a body of the approximate formula $Li_2W_5O_{15}$ was obtained. (The sodium bronzes have been described by Phillip, Abstr., 1882, 930.)

Tungstates.—The acid sodium salt, $5Na_2O,12WO_3,28H_2O$, is decomposed on fusion according to the equation $3(5Na_2O,12WO_3) = 7Na_2W_4O_{12} + 8Na_2WO_4$. Contrary to Scheibler's statement (*J. pr. Chem.*, **83**, 291) the salt, $Na_2W_4O_{13}$, dissolves on continued treatment with cold water; but, in agreement with Scheibler, the author finds that the *unignited* salt dissolves in water at 135°, the solution giving the reactions of sodium metatungstate.

Sodium ditungstate, $Na_2W_2O_7$, is obtained by fusion of the mixture $Na_2O + 2WO_3$, and separates on cooling in long needle-shaped crystals. It dissolves completely on heating it for some hours with water at 130—150°; the alkaline solution does not recrystallise, and contains tungstate and metatungstate.

Sodium pentatungstate, $Na_2W_5O_{16}$, is obtained by fusion of the mixture $Na_2WO_4 + 2WO_3$, or by heating sodium paratungstate to incipient fusion. On extracting the fused mass with cold water, it is left in very brilliant plates or scales. When heated for three hours with water at 150°, but little dissolves, the faintly acid liquid containing tungstate and metatungstate, the latter in by far the larger quantity.

Sodium octotungstate, $Na_2W_8O_{25}$, is obtained by fusing sodium metatungstate, or $Na_2W_4O_{13}$, and after extraction of the fused mass with water, is left crystallised in brilliant scales or plates. It is attacked with difficulty by acids or alkalis.

The author has endeavoured to prepare the ditungstate, $Na_2W_2O_7,6H_2O$, described by Lefort, but, although exactly following the method of the latter, finds the product to be the ordinary acid salt, $5Na_2O,12WO_3,28H_2O$. With the potassium salt, an exactly similar result was obtained. A. J. G.

A Phosphide of Nickel. By E. JANNETAZ (*Jahrb. f. Min.*, 1883, **1**, Ref., 198).—This compound, N_5P, was obtained by melting together calcium phosphate, powdered charcoal, and metallic nickel (or, better, nickel oxide). On cooling slowly, cavities lined with acicular crystals were formed in the mass. The crystals are long rectangular prisms belonging to the tetragonal system. They are of a pale-yellow colour, have a hardness of 5·5, and a sp. gr. of 7·283. B. H. B.

Organic Chemistry.

Normal Paraffins. By C. SCHORLEMMER and T. E. THORPE (*Annalen*, **217**, 149—152).—In a previous communication, the authors stated their intention of investigating the heptane of *Pinus sabiniana*, the subject of the present paper. When treated with chlorine, this heptane yields a mixture of monochlorides (b. p. 143—157·5°), from which are obtained alcohols (b. p. 156—168° and 165—170°) yielding on oxidation *methyl pentyl ketone* and *œnanthylic* or *heptoic acid*. The ketone when further oxidised—with chromic acid solution in sealed tubes at 100°—gives *valeric* and *acetic acids*. By treatment with alcoholic potash, the mixture of chlorides yields *heptylene* and a mixture of *ethyl heptyl* ethers. When left in contact with fuming hydrochloric acid for six weeks in a dark place, only 10 per cent. of the pine heptylene (b. p. 98·5°) is chlorinated, whilst under similar circumstances hexylene from mannitol is entirely converted into secondary hexyl chloride, and heptylene from petroleum is half converted into heptyl chloride. On allowing the unattacked portion of the olefines to remain in contact with the acid for several months, the pine heptylene combines almost completely with the hydrochloric acid, whereas only a small additional quantity of the petroleum heptylene enters into combination. From these results it is evident that treatment with hydrochloric acid in the cold is not an efficient means for the separation of isomeric olefines. By oxidation with chromic acid mixture, this heptylene breaks up into valeric and acetic acids; it can therefore be represented by the formula $C_4H_9.CH\colon CHMe$, and is *butylmethylethylene*. From these and previous results, the authors conclude that by chlorinating normal paraffins, not several but only two chlorides are produced, viz., the primary and one secondary, containing the group $-CHClMe$. Bromine acts in a similar manner (*Annalen*, **188**, 249, and *Ber.*, **13**, 1649) with petroleum paraffin.

D. A. L.

Hydrocarbons from Peat. By E. Durin (*Compt. rend.*, **96**, 652—653).—The author has previously found that the solid products obtained by distilling peat in a current of superheated steam in a vacuum consist largely of fatty acids (*Compt. rend.*, 1881). He now finds that a waxy substance, giving the same reactions as the fatty acids from peat, is obtained by applying the same treatment to fresh moss resembling that from which the peat has been formed. It would appear, therefore, that these fatty acids are not formed during the decomposition of the vegetable matter, but exist in the fresh moss. Analyses of the fatty acids from peat lead to the empirical formula $C_{47}H_{47}O_2$, but in all probability the acids were not perfectly purified.

C. H. B.

Maltose and Isomeric Gluconic Acids. By A. Herzfeld (*Bied. Centr.*, 1883, 127—129).—Maltose prepared from potato-starch has a rotatory coefficient of $[\alpha]_D = 140·6°$, and combines with calcium, barium, and strontium with 1 mol. water; neither alkaline compounds nor a compound with borax have been obtained, but an acetyl derivative, $C_{12}H_{14}O_{12}\overline{A}c_8$, having a rotatory coefficient $[\alpha]_D = 81·18°$ has been prepared. It is well known that maltose reduces Fehling's solution to the extent of two-thirds of the copper suboxide, but if this suboxide be filtered off and the filtrate acidified with hydrochloric acid, it will when warmed reduce a further quantity of Fehling equal to about half of the original quantity, the total quantity being equal to that reduced by an equivalent of grape-sugar. Lactose behaves in a like manner. Dextrinic, maltoic, and gluconic acids, prepared by the action of bromine and water on dextrin, maltose, and grape-sugar, are shown to be identical, and not capable of reducing Fehling's solution. E. W. P.

Action of Zinc-ethyl on Amines and Phosphines. By H. GAL (*Compt. rend.*, **96**, 578—580).—Frankland obtained the compound $N_2Ph_2H_2Zn$ by the action of zinc-ethyl on aniline, and Drechsel and Finkelstein obtained the analogous compound $(PH_2)_2Zn$ by passing hydrogen phosphide through an ethereal solution of zinc-ethyl. The author finds that similar compounds are obtained by the action of zinc-ethyl on dry ammonia, $(NH_2)_2Zn$, ethylamine, $(NHEt)_2Zn$, and toluidine, $(NHC_7H_7)_2Zn$. It would appear, therefore, that when zinc-ethyl acts on an ammoniacal derivative in which all the hydrogen has not been replaced, a metallic derivative is formed and ethane is given off in accordance with the following equation, where Am represents any primary or secondary amine :—

$$2Am + ZnEt_2 = (2Am - H_2 + Zn) + 2C_2H_6.$$

A similar reaction takes place with the phosphines. As a rule, these reactions are very violent, and it is better to use an ethereal solution of zinc-ethyl.

Tertiary amines and tertiary phosphines, such as triethylamine, dimethylaniline, methyldiphenylamine, and triethylphosphine, do not react with zinc-ethyl under ordinary conditions. The reaction described above consequently furnishes a ready means of distinguishing between a primary or secondary amine or phosphine on the one hand, and a tertiary amine or phosphine on the other.

Zinc-ethyl has no action either on nicotine or on quinoline. These compounds appear, therefore, to contain no hydrogen replaceable by zinc.

The majority of the alkaloïds containing oxygen are, however, readily attacked by zinc-ethyl with formation of metallic derivatives which alter slowly when exposed to air, and are rapidly decomposed by water with reproduction of the alkaloïd and formation of zinc oxide. C. H. B.

Cyanmethine. By E. v. MEYER (*J. pr. Chem.* [27], 152—156).—Cyanmethine is best prepared by treating sodium (1 part) with dry methyl cyanide (6 parts) under a pressure of about 10 cm. of mercury; the gas evolved during the reaction is pure methane, not ethane as stated by Bayer (*Ber.*, **2**, 319). Cyanmethine dissolves in 5·25 parts alcohol at 18°, and in 0·64 part of water at 18°, thus differing widely from cyanethine, which requires 1370 parts of water at 17° for solution. Mixed in aqueous solution with solution of silver nitrate, a voluminous white precipitate of the compound

$$(C_6H_9N_3)_2,AgNO_3,$$

is obtained; this crystallises from hot water in colourless rhombohedrons. An aqueous solution of cyanmethine also gives amorphous voluminous precipitates with lead acetate, mercury, and barium chlorides, &c. Treated in glacial acetic acid solution with nitrous acid, it exchanges the amido- for the hydroxy-group, being converted into the corresponding hydroxy-base, whose nitrate, $C_6H_8N_2O,NO_3H$, separates on cooling as a crystalline mass, readily soluble in water, sparingly in cold alcohol, more readily in hot, from which it recrystallises in tufts of long brilliant needles.

The free base, $C_6H_7N_2(OH)$, obtained by the action of soda on the nitrate, crystallises in white needles melting at 194°. On adding silver nitrate and ammonia to the nitrate, a flocculent voluminous precipitate of the silver derivative, $C_6H_7AgN_2O$, is obtained: this crystallises from ammonia in thin plates. Bromine acts more readily on cyanmethine than on cyanethine, yielding bromocyanmethine; but, contrary to expectation, succinic acid could not be obtained from the products of the reaction (comp. cyanethine, this vol., 352, and also Abstr., 1881, 54). From bromocyanmethine the bromhydroxy base, $C_6H_7BrN_2O$, and its silver derivative, $C_6H_6BrAgN_2O$, have been prepared, and are being submitted to further examination.

A. J. G.

Thiocyanacetone. By J. Tcherniac and R. Hellon (*Compt. rend.*, **96**, 587—589; and *Ber.*, **16**, 348—359).—Barium thiocyanate is the only thiocyanate which yields thiocyanacetone in satisfactory quantity (compare this vol., p. 568). This salt is very soluble in alcohol; at 20° the saturated solution contains 30 per cent. of the anhydrous salt, and boiling alcohol dissolves 32·8 per cent.

To prepare thiocyanacetone, 175 grams crystallised barium thiocyanate are dissolved in 525 grams alcohol and mixed with 100 grams monochloracetone; barium chloride is precipitated, and after some days, when precipitation of this salt is complete, the liquid is filtered and the filtrate evaporated on the water-bath. The syrupy residue is boiled with 10 times its weight of water, the solution allowed to stand 24 hours, the clear liquid decanted from the layer of tarry substances which separate out, filtered, and evaporated on the water-bath until the volume of the oil which is gradually deposited is equal to the volume of the aqueous solution. The oil is then separated from the aqueous liquid, washed with a small quantity of distilled water, and dried in a vacuum over sulphuric acid.

Thiocyanacetone, $SCN.CH_2.CO.Me$, is an odourless liquid almost colourless when pure, but becoming deep red by long exposure to air. Its sp. gr. at 0° is 1·209; at 20°, 1·195. It is slightly soluble in alcohol, ether, &c. It cannot be distilled without decomposition, even in a vacuum, and it is not sensibly volatile in a current of steam. If dry, it does not lose weight when exposed over sulphuric acid in a vacuum, a fact which would indicate that it is a polymeric modification. It dissolves rapidly with development of heat in a concentrated solution of an alkaline bisulphite, and can be separated from this solution by the ordinary reagents, though only in an impure condition. When heated on the water-bath for some hours with an equivalent quantity of ammonium thiocyanate, thiocyanacetone yields a considerable quantity of *thiocyanopropimine thiocyanate* identical with that obtained by the action of ammonium thiocyanate on monochloracetone.

This fact confirms the general view of the constitution of thiocyanopropimine. C. H. B.

Decomposition of α-Fluoboracetone by Water. By F. Landolf (*Compt. rend.*, **96**, 580—582).—α-Fluoboracetone is a liquid which boils at 120°, and does not solidify at − 15°. It is immediately decomposed by water with separation of boric acid and formation of gaseous and liquid products, all of which dissolve in water and have an agreeable ethereal odour.

Acetone monohydrofluoride, C_3H_6O,HF, a liquid which boils at 55°, has an agreeable odour, is very soluble in water, and burns with an almost invisible bluish flame.

Acetone dihydrofluoride, $C_3H_6O,2HF$, is a gas which has a strong ethereal odour, burns with an almost invisible bluish flame, and is very soluble in water, from which it is expelled by a slight rise of temperature. It can be liquefied by means of a mixture of ice and salt, and the liquid boils at from − 15° to − 12°. The vapour-density of the compound, 1·72, is somewhat more than half the calculated value, 3·18. The author regards this compound as not merely an addition-product, but as a true chemical compound, in which carbon is hexatomic. He considers that it will be possible by means of these fluoboro-compounds, to obtain what may be called *supersaturated compounds.* The compounds of boron fluoride, with organic substances, furnish a simple and certain method of obtaining any required fluorine derivative.

The vapours of these compounds when inhaled, produce strong nervous irritation, with somewhat high fever. Salivation increases considerably, and the skin of the gums of the lower maxillary is strongly attacked and partly corroded. These effects last for some time. C. H. B.

New Method for Preparing Carbonic Oxide. By H. Jahn (*Ber.*, **16**, 308).—A reply to Noack (this volume, p. 574).

Insoluble Residue from the Distillation of Castor-oil. By A. R. Leeds (*Ber.*, **16**, 290—293).—The residue obtained in the preparation of œnanthaldehyde from castor-oil was examined by Stanck (*J. pr. Chem.* **63**, 138), but its nature has not been determined. The author distilled castor-oil under diminished pressure (100 mm.), and obtained a residue which when cold had the consistence of caoutchouc. On washing it with alcohol and afterwards with ether, it lost its stickiness and its elasticity almost entirely disappeared, the colour changing from brownish-red to yellowish-grey. Its composition, $C_{42}H_{68}O_5$, agrees with that given by Stanck. When the caoutchouc-like residue is saponified with potash, the solution filtered hot and hydrochloric acid added, an oil is obtained lighter than water, and of a brownish-red colour. It is very readily soluble in alcohol and ether, but insoluble in water. Its composition agrees with Stanck's formula, $C_{36}H_{68}O_7$. It decomposes when heated, yielding a distillate boiling between 110° and 250°, the different fractions of which yield no salts with the alkalis. By exposure to light and air, they absorb oxygen, and darken in colour. No nitrogen could be detected in any of the oils. The author does not agree with Stanck as to the constitution of the body, $C_{42}H_{68}O_5$, as he is unable to obtain acraldehyde from it; neither does he think that the compound, $C_{36}H_{68}O_7$, can be regarded as $C_{36}H_{58}O_2$ plus water of crystallisation, its formula being more probably $C_{36}H_{62}O_4$. A. K. M.

Addition of Bromine to Ethyl Acetoacetate. By C. DUISBERG (*Ber.*, **16**, 295—297).—A reply to Lippmann and Conrad. The author doubts the existence of Lippmann's ethyl acetoacetate dibromide (Abstr., 1882, 177). A. K. M.

Allylsuccinic and Carbocaprolactonic Acids. By E. HJELT (*Ber.*, **16**, 333—335).—By the action of sodium ethylate and ethyl chloracetate on ethyl malonate, ethyl ethenyltricarboxylate is obtained, and by the introduction of an allyl-group into the latter, ethyl allylethenyltricarboxylate (b. p. 282—283°). The free allylethenyltricarboxylic acid dissolves readily in the ordinary solvents, but forms insoluble calcium, barium, and silver salts. With hydrobromic acid, it forms a crystalline body melting at 159°. The acid melts at 151° with evolution of carbonic anhydride and formation of allylsuccinic acid, $COOH.CH(C_3H_5).CH_2.COOH$, the latter crystallising in plates, which melt at 93—94°. It is isomeric with teraconic acid, to which it bears much resemblance. It forms an anhydride when heated, and in its reactions it resembles propylsuccinic acid (*Annalen*, **214**, 58). It dissolves in fuming hydrobromic acid, but not easily, and on adding water to the solution, boiling, and finally extracting with ether, an oily acid is obtained which crystallises in a vacuum. After recrystallisation from alcohol, *carbocaprolactonic acid*, $C_7H_{10}O_4$, melts at 68—69°. It decomposes but slightly on heating, and distils at about 260°. It is isomeric with terebic acid. A. K. M.

Meconic Acid and some of its Derivatives. By E. MENNEL (*J. pr. Chem.* [2], **26**, 449—473).—Meconic acid, as Liebig has shown, yields three different silver compounds, and has therefore been considered to be a trihydric acid. All attempts to prepare the three corresponding ethyl salts have, however, proved abortive, only mono- and di-ethylic ethers being known. The author, suspecting that the acid was only dibasic, the third replaceable hydrogen-atom not belonging to a carboxyl-group, undertook the study of the methyl and ethyl salts of the acid, which have also been examined by How (*Ann.*, **83**, 350).

If a current of dry hydrochloric acid gas is passed into absolute alcohol containing in suspension half its weight of meconic acid (dried at 120°), the meconic acid dissolves, and crystals soon begin to form. The current of hydrochloric acid is then stopped, and the crystals are washed with absolute alcohol, crystallised from the same solvent, and lastly from boiling water.

Monethyl meconate, $C_5HO_2(OH)(COOH).COOEt$, is thus obtained in large colourless needles, melting at 179°. Sometimes from the alcoholic mother-liquors *monethyl comenate* (m. p. 126·5°) separates in well-formed crystals, meconic acid readily losing carbon dioxide with formation of comenic acid. If the current of hydrochloric acid gas is continued until the crystals formed at first have again passed into solution, and the syrupy liquor is then poured into water, *diethyl meconate*, $C_5HO_2(OH)(COOEt)_2$, at once separates in anhydrous laminar crystals, melting at 111·5°. From a more dilute solution the compound crystallises with $\frac{1}{2}$ mol. H_2O.

When argentic diethylmeconate, prepared by precipitating a hot solution of diethylmeconic acid with silver nitrate, and carefully neutralising the fluid with ammonia, is heated for 4 hours with ethyl iodide, it yields *triethyl meconate*, melting at 67°, and crystallising readily from alcohol. It is but very sparingly soluble in water, readily so in alcohol, ether, or chloroform. It does not give a red coloration with ferric chloride (as do the two other ethylic compounds), and does not therefore include any hydroxyl-group.

The author considers the formation of this ether as a conclusive proof of the dibasic nature of meconic acid, to which he assigns the formula $C_5HO_2(COOH)_2.OH$. That this conclusion is correct is further demonstrated by the fact that two isomeric monethylic compounds exist, *ethylmeconic acid*, $C_5HO_2(COOH)_2.EtO + H_2O$, being obtained on boiling the triethylic compound for several days with water in a flask with reflux condenser. The acid separates from the solution in small white prisms, melting at 200°, with copious evolution of carbonic anhydride. The aqueous solution is strongly acid, and does not colour ferric chloride. It does not precipitate any metallic solutions, even after neutralisation, with the exception of those of copper and lead. *Lead ethylmeconate* crystallises with $1\frac{1}{2}$ mols. H_2O. As stated above, the acid loses carbonic anhydride at 200°, leaving *ethylcomenic acid*, $C_5H_2O_2(COOH).EtO$; this crystallises readily from hot water or alcohol, and melts at 239—240°. *Silver ethylcomenate* crystallises with $2\frac{1}{2}$ mols. H_2O.

On adding ammonia in excess to a solution of monethyl meconate in hot water, and allowing it to cool, a voluminous yellow precipitate separates, consisting of *diammonic meconaminate*,

$$C_5HO_2(CONH_2)(COONH_4).ONH_4,$$

from which *monomeconamic acid*, $C_5HO_2(CONH_2)(COOH).OH$, is readily obtained. On evaporating a solution of meconaminate, it loses ammonia, and yields meconate.

On adding bromine to solutions of meconic acid, carbonic anhydride is given off, even at very low temperatures, and bromocomenic acid is formed, and this when treated with another molecular weight of bromine gives rise to *bromoxybromocomenic acid*,

$$C_5HBrO_2(COOH).OBr + 3H_2O,$$

in which the hydrogen of the hydroxyl-group is also replaced by bromine. It is readily soluble in water and alcohol, less so in chloroform, ether, or benzene. Its aqueous solution gives a characteristic reaction with barium chloride, as follows: barium chloride alone produces no effect, but on the addition of ammonia a yellow precipitate is formed, which with excess of ammonia becomes voluminous, and of an orange colour.

By treating monethyl meconate with bromine, the *ethylic salt* of bromoxybromocomenic acid is obtained. O. H.

Dry Distillation of Tartaric and Citric Acids with Excess of Lime. By FREYDL (*Monatsh. Chem.*, **4**, 149—152).—Dried Rochelle salt, when distilled with an equal weight of quicklime, yields much gas, consisting almost entirely of hydrogen, together with a distillate separating into an oily and an aqueous layer. In the aqueous solution only acetone could be found, whilst in the oily layer benzene occurs in small quantity.

The aqueous layer of the distillate from the distillation of sodium citrate contains acetone. This was tested for isopropyl alcohol by Linnemann's method, with negative result. A. J. G.

Biuret Dicyanamide. By F. RESINSKI (*J. pr. Chem.* [2], **27**, 157—159).—Baumann having shown (this Journal, 1874, 793; 1875, 446) that dicyanodiamidine is formed on fusing carbamide with guanidine carbonate, the author endeavoured to ascertain if substituted ureas behaved in a similar manner. Acetyl-carbamide was mixed with two and a half times its weight of guanidine carbonate, and the mixture slowly heated at 140—150°, until the fused mass resolidified. The product was boiled with water, and on cooling, the filtrate deposited an amorphous white precipitate of biuret dicyanamide. This is soluble in alkalis and mineral acids, being reprecipitated from its solutions in the latter by addition of ammonia. It has only weak basic properties, its salts being readily decomposed by water. The nitrate, $C_4H_7N_9O_2,HNO_3$, crystallises in anhydrous rhombic needles.

A. J. G.

Glutamine. By E. SCHULZE and E. BOSSHARD (*Ber.*, **16**, 312—315).—The existence of an amide of glutamic acid in the sap of the beetroot and pumpkin-shoots has been previously shown (*Ber.*, **10**, 85 and 199); the authors have succeeded in isolating this body (*glutamine*), and show that it is a homologue of asparagine. Fresh beetroot sap is precipitated with acetate of lead, and then a neutral solution of mercuric nitrate is added to the filtrate. The white flocculent precipitate thus obtained is decomposed with hydrogen sulphide, and the filtrate neutralised with ammonia and evaporated. Glutamine then separates in slender white anhydrous needles, readily soluble in boiling water, insoluble in strong alcohol. With cupric hydroxide, it forms a crystalline compound very similar in appearance to the corresponding asparagine compound. When glutamine is heated with alkalis or with baryta-water, half the nitrogen is given off as ammonia, whilst a salt of glutamic acid is formed. From the analogy which glutamine bears to asparagine, the authors assign to it a similar constitution, $COOH.C_3H_5(NH_2).CONH_2$. From 1 litre of beetroot sap 0·7—0·9 gram glutainine was obtained.

Similar results have been obtained with pumpkin-shoots, but in this case the isolation of the glutamine is more difficult, apparently from the presence of other substances which interfere with its crystallisation. A. K. M.

Action of Chlorine on Sulpho-derivatives and Organic Oxysulphides. By W. Spring and C. Winssinger (*Ber.*, **16**, 326—330).—In continuation of previous experiments (Abstr., 1882, 938), the authors find that pure propylsulphonic acid (like ethylsulphonic acid) completely resists the action of chlorine, showing that the sulpho-group exerts an influence over the entire molecule. By the action of iodine trichloride (2 mols.) on the sulpho-acid (3 mols.) at 150—160° in sealed tubes, the following reaction is supposed to take place:— $22ICl_3 + 33C_3H_7SO_3H = 6[C_3H_6ClSO_3H + 3(C_3H_7.SO_3H)] + 9C_3H_5Cl_3 + 9SO_2(OH)Cl + 24HCl + 11I_2$. The chloro-sulphonic acid first formed becomes further chlorinated with displacement of the sulpho-group, sulphonic acids in which more than one hydrogen-atom is replaced by chlorine being incapable of existing in the presence of iodine trichloride. If propylsulphonic acid (1 mol.) is heated for three days with iodine trichloride (6 mols.), the chlorination goes much further, C_3Cl_8 being probably first formed, but finally converted into C_2Cl_6 and CCl_4. If the heating is carried on only half as long, the chief product is an acid, the barium salt of which has the formula $(C_3H_7.SO_3.Ba.SO_3.C_3H_6Cl)_2,H_2O$. By the action of chlorine on propyloxysulphide in aqueous solution, dipropylsulphone, chloropropylsulphonic acid, and trichloro- and tetrachloro-propane are produced. Since neither $C_3H_7SO_3H$, $(C_3H_7)_2SO_2$ nor $C_3H_7SO_2Cl$ is acted on by chlorine, the authors assume that monochlorodipropyloxysulphide, $C_3H_6Cl.SO.C_3H_7$, is first formed, and then the chloride $C_3H_6Cl.SO_2Cl$. Since ethyloxysulphide does not yield similar results, it seems probable that in the latter compound the SO-group exerts an influence over the whole molecule, preventing substitution. A. K. M.

Amylbenzene. By F. W. Dafert (*Monatsh. Chem.*, **4**, 153—155).—By the action of zinc-ethyl on benzotrichloride, the author has obtained, not as he expected, a heptyl-benzene of the formula $Ph.CEt_3$, but ethylene and Lippmann and Louguinine's amylbenzene, $Ph.CHEt_2$. A. J. G.

Œnanthal-aniline, Œnanthal-xylidine, and Œnanthal-naphthylamine. By A. R. Leeds (*Ber.*, **16**, 287—288).—To prepare these compounds, œnanthaldehyde is gradually mixed with the amine in molecular proportions, and the whole heated for six hours with reflux condenser: the product is purified by dissolving it in glacial acetic acid, heating the solution for some hours on a water-bath, and largely diluting with water; the precipitate is finally washed with water until free from acid. Œnanthal-aniline,

$$C_6H_7N,C_7H_{14}O,$$

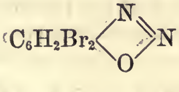
and œnanthal-xylidine, $C_8H_{11}N,C_7H_{14}O$, are perfectly similar mobile liquids of agreeable ethereal odour. Œnanthal-naphthylamine,

$$C_{10}H_9N,C_7H_{14}O,$$

is similar to the above, but has a more decided odour, resembling that of the pine-apple. These bodies are stable, and can be sublimed with partial decomposition. A. K. M.

Diazo-derivatives of "Symmetrical" Tribromaniline. By H. Silberstein (*J. pr. Chem.* [2], **27**, 98—125).—When tribromaniline [1 : 2 : 4 : 6], half dissolved, half suspended in alcohol, and well cooled, is treated with a rapid stream of the gas obtained by heating a mixture of arsenic trioxide and nitric acid, the main product is a yellow body, tribromodiazobenzene nitrate, a pale coloured compound, hexbromodiazoamidobenzene being obtained at the same time. If a slow stream of the gas, obtained without heating from a mixture of arsenic trioxide and nitric acid be employed, the latter compound is obtained with only a very small admixture of the yellow body.

Tribromodiazobenzene Nitrate, $C_6H_2Br_3.N_2.NO_3$, crystallises in yellow rhombic tables, readily soluble in water and hydrochloric acid, sparingly in glacial acetic acid, more sparingly in alcohol. It is moderately stable in the dry state, but soon decomposes in presence of moisture. It explodes sharply when rubbed strongly, or when heated to 85°. It is decomposed with evolution of nitrogen by treatment with solution of caustic soda, ammonia, or potassium cyanide. Heated with alcohol, it yields tribromobenzene (m. p. 119°), nitrogen, nitric acid, and aldehyde. No nitrogen is evolved on boiling it with water. A cold aqueous solution of tribromodiazobenzene nitrate decomposes after a time with formation of tri- and tetra-bromobenzene, together with other products not yet identified. On heating it with glacial acetic acid, a violent reaction takes place, nitrogen and oxidation products are evolved, and tribromobenzene (m. p. 119°) is formed. On heating tribromobenzene nitrate at 50° with benzene, nitrogen and reddish-brown vapours are evolved, and an amorphous body separates. This latter, on treatment with alcohol or water, is decomposed into nitric acid and *dibromodiazophenol*,

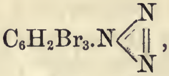


$$C_6H_2Br_2\left\langle\begin{matrix}N\\ \\ O\end{matrix}\right\rangle N \quad [Br : Br : N_2 : O = 2 : 6 : 1 : 4].$$

It crystallises in yellow oblique prisms, is insoluble in cold, but little soluble in boiling water, readily soluble in hot ethyl or amyl alcohols; it explodes when heated to 142°. It possesses weak basic properties, and forms very unstable salts on gentle heating with concentrated acids. When heated more strongly with acids, it decomposes, *e.g.*, with hydrobromic acid, it yields nitrogen and tribromophenol. By oxidation with chromic acid it yields dibromoquinone in small quantity; on reduction with tin and hydrochloric acid, it is converted into ammonia and dibromoparamidophenol. Free dibromodiazophenol is also formed to some extent in the reaction between benzene and tribromodiazobenzene nitrate, together with tetrabromobenzene (m. p. 98°) and nitro-benzene.

Tribromodiazobenzene sulphate, $C_6H_2Br_3.N_2.HSO_4$, is best prepared by adding nitrous acid to a mixture of sulphuric acid and alcoholic solution of tribromaniline. It forms nearly colourless prisms, moderately soluble in water, sparingly soluble in alcohol and glacial acetic acid, insoluble in ether and benzene. On heating it with alcohol, it is decomposed into tribromobenzene, nitrogen, and sulphuric acid. Boiled with acidulated water, it does not yield tribromobenzene; with glacial acetic acid and also with benzaldehyde, it gives a large yield of tribromobenzene. Boiling benzene does not attack the sulphate.

Tribromodiazobenzene chloride was obtained in solution only, but the corresponding *perbromide*, $C_6H_2Br_3.N_2.Cl,Br_2$, is obtained by heating a solution of tribromodiazobenzene nitrate in concentrated hydrochloric acid; it separates in clear yellow brilliant prisms, explodes on heating to 100°, yielding tribromochlorobenzene, nitrogen, and bromine. It is nearly insoluble in most solvents. Heated with glacial acetic acid, it gives *tribromochlorobenzene*, $C_6H_2Br_3Cl$, crystallising in long silky colourless needles (m. p. 80°), readily soluble in ether, benzene, chloroform, and hot alcohol, and in glacial acetic acid, sparingly soluble in cold alcohol or acetic acid.



Tribromodiazobenzeneimide, $C_6H_2Br_3.N<\begin{matrix}N\\ \Vert\\ N\end{matrix}$, is obtained by the action of dilute aqueous ammonia on the perbromide. It crystallises in colourless needles melting at 59°. It can be distilled with water vapour; is insoluble in water, readily soluble in alcohol, ether, and chloroform, and is not reduced by zinc and sulphuric acid.

Tribromodiazobenzene bromide, $C_6H_2Br_3.N_2Br$, obtained by the action of hydrobromic acid on the nitrate, crystallises in brilliant golden-yellow rhombic tables. It explodes nearly as violently as the nitrate on heating. It is sparingly soluble in water, insoluble in alcohol and ether. The corresponding perbromide, $C_6H_2Br_3.N_2.Br_3$, crystallising in orange-yellow prismatic needles, is obtained by the action of bromine and hydrobromic acid on the nitrate. Both the bromide and perbromide yield unsymmetrical tetrabromobenzene (m. p. 98·5°) when heated with glacial acetic acid.

Hydriodic acid reacts violently with an aqueous solution of the nitrate, yielding *tribromiodobenzene*, $C_6H_2Br_3I$. This crystallises in colourless needles melting at 103·5°, sublimes readily, is insoluble in water, sparingly soluble in cold alcohol, ether, chloroform, and benzene.

Hexabromodiazoamidobenzene, $C_6H_2Br_3.N_2.NH.C_6H_2Br_3$, is obtained as previously mentioned by the action of nitrous anhydride on tribromobenzene. It crystallises in small colourless needles (m. p. 158°), which are insoluble in water and alcohol, very sparingly soluble in ether, more readily in chloroform, and readily in benzene.

Tribromodiazoamidobenzene, $C_6H_2Br_3.N_2.NHPh$, is obtained on adding solid tribromodiazobenzene nitrate (1 mol.) in small quantities to an alcoholic solution of aniline (2 mols.), the resulting yellow precipitate being recrystallised from alcohol. It forms brilliant yellow triclinic prisms, melts at 104°, is insoluble in water, readily soluble in benzene, ether, and hot alcohol. Heated with glacial acetic acid, it yields tribromaniline.

Dimethylamidoazotribromobenzene, $C_6H_2Br_3.N_2.C_6H_4.NMe_2$, prepared by the action of dimethylaniline on tribromazobenzene nitrate, crystallises in red plates, melting at 161°; it is insoluble in water, sparingly soluble in hot alcohol, readily soluble in glacial acetic acid. It gives crystalline salts with acids; the chloride crystallises in golden-yellow plates.

Methylphenylamidoazotribromobenzene, $C_6H_2Br_3.N_2.C_6H_4.NMePh$, is prepared by means of methyldiphenylamine in a manner similar to the above, which it resembles in solubilities. It crystallises in red-brown plates (m. p. 138°), and has no basic properties. A. J. G.

Substitution-products of Ethereal Derivatives of Phenols. By W. Staedel (*Annalen*, **217**, 24—40).—This paper is mainly a catalogue of work done by various authors on the substitution-products of various phenols, and serves as an introduction to the author's publications, which are statements of experimental facts, intended to support future theoretical considerations. D. A. L.

Nitrocresols. By W. Staedel (*Annalen*, **217**, 49—54).—*Nitro-orthocresol* is prepared by Hofmann and v. Miller's method (*Ber.*, **14**, 567), and from it the ethyl derivative, $C_6H_3Me(NO_2).OEt$ [1 : 2 : 3] is made, which is a liquid. The residue from the preparation of nitro-orthocresol contained dinitro-paracresol. When metacresol dissolved in glacial acetic acid is acted on by nitric acid likewise diluted with acetic acid, two products are obtained, one of which is volatile in steam, and crystallises from benzene in compact yellow crystals (m. p. 56°), readily soluble in ether, alcohol, and benzene, but only slightly in water. The *potassium derivative* is a very soluble stable red crystalline substance. The *ammonium derivative* forms soluble needles, which on evaporation lose ammonia and nitrocresol. The *silver derivative* is red. This nitrocresol is probably $C_6H_3(OH)(NO_2)Me$ [1 : 2 : 3]. The second product is not volatile, crystallises from water in slender white, or in long thick brownish needles. It melts at 129°, and is soluble in ether, alcohol, and benzene, from which solutions it cannot be crystallised. It dissolves in potassium carbonate solution with evolution of carbonic anhydride. The *potassium derivative* forms yellow leaflets, the *ammonium derivative* yellow needles, and the *silver derivative* a yellow precipitate. This nitrocresol is probably $C_6H_3(OH)(NO_2)Me$ [1 : 4 : 3]. When paracresol is treated with nitric acid by Hofmann's and v. Miller's method, a mixture of meta- and dinitro-paracresol is obtained The author washes this mixture with water, dissolves in potash and filters hot, whilst potassium dinitroparacresolate soon separates out, and when the mother-liquor is evaporated it deposits the mononitroparacresolate, from which the nitrocresol is easily obtained. *Ethyl nitroparacresolate* is a pale yellow liquid, boiling at 275—285°, with partial decomposition. It has an aromatic odour.

D. A. L.

Bromonitro- and Bromamido-anisoïls and -phenetoïls. By W. Staedel (*Annalen*, **217**, 55—74).—*Monobromorthonitronitranisoïl*, $C_6H_3Br(NO_2).OMe$, is the product of the action of methyl iodide on silver (or potassium) monobromonitrophenate; it crystallises in long needles melting at 88°, easily soluble in ether and hot alcohol, sparingly in cold alcohol, and insoluble in water. *Monobromorthonitrophenetoïl*, $C_6H_3Br(NO_2).OEt$, obtained by the action of methyl iodide and alcohol on potassium monobromorthonitrophenate, is crystalline (m. p. 43°), and soluble in alcohol and ether. *Dibromorthonitrophenetoïl*,

$$C_6H_2Br_2(NO_2).OEt,$$

is produced when ethyl iodide and alcohol act on silver dibromorthonitrophenate. It melts at 46°, is insoluble in water, soluble in alcohol, benzene, and ether. By similar reactions, the paranitro-derivatives have been obtained. *Monobromoparanitroanisoïl* crystallises in white needles melting at 106°, easily soluble in hot alcohol and ether, moderately so in hot water, and insoluble in cold water. *Monobromoparanitrophenetoïl* forms large pale yellow needles melting at 98°, soluble in alcohol and ether. *Dibromoparanitrophenetoïl* crystallises in needles melting at 108°; when the solution contains ethyl iodide, the crystals are long quadratic prisms. The respective amido-derivatives are obtained from these nitro-products by reduction with tin and hydrochloric acid. *Monobromorthoanisidine*, $C_6H_3Br(NH_2).OMe$, crystallises in white leaflets melting at 97—98°, soluble in benzene, ether, and hot alcohol. The *hydrochloride* forms white needles, soluble without decomposition in alcohol, but resolved into monobromanisidine and hydrochloric acid by water; if the water is acidulated, this decomposition is prevented. The *sulphate* forms silvery needles, soluble in hot alcohol without, and in hot water with decomposition. The *oxalate* forms flat white needles, similar in properties to the other salts, and when heated decomposes with evolution of gas. *Monobromorthophenetidine*, $C_6H_3Br(NH_2).OEt$, is obtained in flat needles with oblique ends melting at 57°, soluble in benzene, ether, and alcohol. The *hydrochloride*, the *sulphate*, and the *oxalate* crystallise in small white needles, are all soluble in alcohol, and are decomposed by water. *Dibromorthanisidine*,

$$C_6H_2Br_2(NH_2).OMe,$$

is a brownish oil, soluble in alcohol, ether, and dilute acids, insoluble in cold, and only sparingly soluble in boiling water. The *hydrochloride* and *sulphate* crystallise in silvery white needles, and behave in a similar manner to the salts described above. The sulphate melts at 177°, with partial decomposition. The *oxalate* forms white needles or leaflets, which are decomposed by water, and when heated at 147—148° melt, giving off gas with the formation of a crystalline sublimate. *Dibromorthophenetidine*, $C_6H_2Br_2(NH_2).OEt$, crystallises in brilliant quadratic crystals melting at 92°, soluble in alcohol and ether. The *hydrochloride*, *sulphate*, and *oxalate* crystallise in small brilliant needles, and have the abovementioned properties. *Monobromoparanisidine* is a red-brown oil, soluble in alcohol, ether, and benzene, and soon becomes tarry. Its three salts form white leaflets, with usual properties; the oxalate decomposes at 170°. *Monobromoparaphenetidine* is also an oil; *dibromoparanisidine* is crystalline (same as that of Körner), and *dibromoparaphenetidine* crystallises in needles melting at 67°; their salts are crystalline, and have usual properties. Dibromoparanisidine oxalate browns at 190°, then becomes black, and melts at 195°, when it decomposes.

D. A. L.

Hydroxybenzoic Acid. By A. KLEPL (*J. pr. Chem.* [2], **27**, 159—160).—On heating 2 mols. of metahydroxybenzoic acid with 3 mols. of barium hydroxide at 350°, no phenol is formed, the hydroxybenzoic acid remaining unchanged, but on increasing the amount of baryta to 7 mols. decomposition occurs, and the product of the reaction when treated with hydrochloric acid and distilled with steam yields nearly the theoretical quantity of chemically pure phenol. A. J. G.

Products of the Distillation of Calcium Parahydroxybenzoate. By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **4**, 127—130).—In a former communication on this subject in conjunction with Herzig (Abstr., 1882, 617), mention was made of a substance insoluble in alkalis, smelling like diphenylene oxide, crystallising from alcohol in white needles, melting at 99°, but obtained in quantity too small for complete examination. These crystals have now been prepared in larger quantity, and found to be a mixture of diphenylene oxide and carbonyldiphenyl oxide. A. J. G.

Products of the Distillation of the Salicylic Anhydrides. By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **4**, 121—126).—Märcker states (*Annalen*, **124**, 249) that salicylic anhydride on dry distillation yields phenol and a body C_6H_4O, crystallising in silky needles melting at 103°, whilst Limpricht, who had previously investigated the subject, describes C_6H_4O as crystallising in small white needles melting at 156°. Frequent reference to the body C_6H_4O is also made by Kraut, Schröder, and Prinzhorn (*Annalen*, **150**, 1), but no melting point is given. The author has made numerous experiments, but failed to obtain a compound of the formula C_6H_4O. He has distilled trisalicylosalicylic acid, Schiff's tetrasalicylide, and the anhydride obtained by the action of phosphorus oxychloride on sodium salicylate, and in each case the only definite products were phenol, salicylic acid, and Merz and Weith's carbonyldiphenyl oxide (diphenyl oxide ketone) (Abstr., 1881, 264). A. J. G.

Acroleïnureide and Condensed Ureides. By A. R. LEEDS (*Ber.*, **16**, 293—295).—A reply to Schiff (Abstr., 1882, 1195).

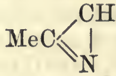
Oxidation of the Bases obtained by the Action of Halogen Compounds on Thiocarbamide. By R. ANDREASCH (*Monatsh. Chem.*, **4**, 131—148).—By the oxidation of thiohydantoïn, the author obtained an acid, which, from its reaction with nitrous acid, he regarded as carbamidoacetosulphonic acid (Abstr., 1880, 877; 1881, 257); he now confirms that view by showing that on boiling the potassium salt with baryta-water, carbamide and barium sulphonacetate are formed.

By oxidation of diphenylhydrothiohydantoïn with potassium chlorate and hydrochloric acid, phenyltaurine and diphenyltaurocarbamic anhydride are obtained.

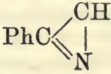
Diphenyltaurocarbamic anhydride, $C_{15}H_{14}N_2SO_3$, crystallises in brilliant thin plates, or in tufts of very brilliant colourless needles; it melts with decomposition at 186—187°. It is insoluble in water, ether, and chloroform, moderately soluble in boiling alcohol, readily in glacial acetic acid, even in the cold. When boiled with baryta-water, it is converted into barium carbonate, aniline, and *barium phenylamidoisethionate.* The latter crystallises in groups of plates, is readily soluble in water, moderately soluble in dilute, but insoluble in strong alcohol. It does not give precipitates with solutions of the ordinary metallic salts, but reduces silver nitrate. The *potassium salt* crystallises in thin brilliant plates very readily soluble in water. *Phenylamidoisethionic acid* or *phenyltaurine*, $SO_3H.CH_2.CH_2.NHPh$, crystallises in colourless plates of strong silvery lustre, which melt at about 260°; it is soluble in water, the solution having a strongly acid reaction, but is insoluble in alcohol and ether. It is distinguished from taurine by its pronounced acid properties, decomposing carbonates and forming salts.

In the expectation of obtaining hydrothiohydantoïn, the author investigated the action of ethylene bromide on thiocarbamide, but finds the product of the reaction to be *ethyleneimidothiocarbamate hydrobromide*, $C_2H_4[S.C(\colon NH).NH_3Br]_2$; this crystallises in broad white prisms resembling thiocarbamide in appearance, or in stellate groups of thin needles. It is soluble in cold, more readily in hot water, less soluble in alcohol. It gives a precipitate of silver bromide on treatment with silver nitrate; with sodium hydroxide it gives a white flocculent precipitate, probably the free base; on digestion with excess of silver chloride, it is converted into the hydrochloride, $C_4H_{12}N_4S_2Cl_2$, which crystallises in groups of slender needles, and is much more soluble in water than the hydrobromide. On oxidation with potassium chlorate and hydrochloric acid, ethylene disulphonic acid and carbamide are formed. A. J. G.

Molecular Weight of Isoindole. By F. P. Treadwell and V. Meyer (*Ber.*, **16**, 342—344).—The fact that ketine, $C_6H_8N_2$, is produced by the reduction of isonitrosoacetone and not amidoacetone or its anhydro-derivative,



, seems to point to the instability of such bodies, and it led the authors to doubt the correctness of the formula



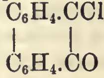
for isoindole, as produced by the action of ammonia on bromacetone. The fact that isoindole is odourless, sparingly soluble in the ordinary solvents, and far less volatile than indole, also indicates a higher molecular weight for the former compound. Vapour-density determinations made in sulphur vapour, the air in the apparatus being replaced by nitrogen, are perfectly in accordance with this view, and show that isoindole is related rather to the ketines than to indole, its formula being $C_{16}H_{14}N_2$. In Städel's determinations, the air was not replaced by nitrogen, and the partial decomposition of the isoindole under these circumstances would account for his abnormal results. A. K. M.

α-β-Hydroxynaphthobenzoic Acid. By H. WALDER (*Ber.*, **16**, 299—307).—In a previous communication (*Ber.*, **15**, 2177), the author announced the formation of an acid of the formula $C_{18}H_{12}O_4$ by the action of alkaline permanganate on β-dinaphthol. The β-dinaphthol is dissolved in dilute soda solution, and the calculated quantity of permanganate gradually added, the whole being gently heated on a water-bath; the solution is then filtered, hydrochloric acid added, and the precipitate collected. It can be purified by means of animal charcoal and repeated crystallisation, when it is obtained in prisms melting at 256°. It dissolves readily in the alkalis and alkaline carbonates, also in alcohol, ether, benzene, acetone, and glacial acetic acid, but is almost insoluble in water. With concentrated sulphuric acid, it forms a fluorescent solution, from which it is reprecipitated on the addition of water. The *sodium salt*, $C_{18}H_{11}O_4Na$, forms a white crystalline powder readily soluble in hot water, the *barium salt*, $(C_{18}H_{11}O_4)_2Ba + 2H_2O$, a white gelatinous precipitate nearly insoluble in water, and the *silver salt*, $C_{18}H_{11}O_4Ag$, an insoluble white gelatinous precipitate. The *methyl-derivative*, $C_{18}H_{11}O_4Me$, is best obtained by boiling the silver salt with methyl iodide, distilling off the excess of the latter, and extracting the residue with warm benzene. It crystallises in prisms melting at 199°. The *ethyl-derivative*, $C_{18}H_{11}O_4Et$, forms white silky needles melting at 206°. It dissolves readily in hot alcohol and benzene, sparingly in ether and wood-spirit. The *acetyl-derivative*, $C_{18}H_{11}O_4\overline{Ac}$, forms small shining prisms melting at 170°. When heated with melted potash, the acid, $C_{18}H_{12}O_4$, splits up into phthalic acid and β-naphthol, showing that it must be a *hydroxynaphthobenzoic acid*, thus:—

$$COOK.C_6H_4.CO.C_{10}H_6.OK + KOH = C_6H_4(COOK)_2 + C_{10}H_7.OK.$$

On heating it with red phosphorus and fuming hydriodic acid at 190—200°, *hydroxynaphthotoluic acid*, $C_{18}H_{14}O_3$, is formed, crystallising in prisms. It melts at 261°, is almost insoluble in water, sparingly soluble in alcohol and in ether, but readily in hot glacial acetic acid. Its *silver salt*, $C_{18}H_{13}O_3Ag$, is obtained as a flocculent precipitate. By the action of zinc chloride (4 parts) on β-hydroxynaphthobenzoic acid (1 part) at 210—230°, a dark red mass is produced, from which a crystalline body, $O(C_{10}H_6.CO.C_6H_4.COOH)_2$, can be obtained, melting at 146°. It is readily soluble in boiling alcohol, in chloroform, in the alkalis and alkaline carbonates. When hydroxynaphthobenzoic acid is distilled, carbonic oxide is evolved, and a body of the formula $C_{16}H_{12}O$ (m. p. 108°) is formed, crystallising in yellowish plates which are almost insoluble in sodium carbonate, but dissolve readily in sodium hydroxide solution. If the heating is effected in sealed tubes at 270—300°, a compound is produced melting at 114°, and crystallising in plates. Its probable formula is $C_{17}H_{12}O_2$. From β-hydroxynaphthobenzoic acid and resorcinol a compound can be formed crystallising in small prisms with metallic lustre. It dissolves in alkalis to a splendid cherry-red solution, from which it is reprecipitated by acids.

A. K. M.

Action of the Chlorides of Phosphorus on Phenanthraquinone. By B. LACHOWICZ (*Ber.*, **16**, 330—333).—By the action of phosphorus pentachloride on phenanthraquinone at 150°, Schultz (*Annalen*, **196**, 10) obtained a red resinous substance which he was unable to crystallise. The author finds that equivalent quantities of the above-mentioned substances react violently when warmed on a water-bath, or in a few minutes without warming. After the action has ceased, the product solidifies to a crystalline mass, which after crystallisation from chloroform yields characteristic bright yellow rhombic prisms. The constitution of this *phenanthradichloroketone* is probably  $\begin{array}{l} C_6H_4.CCl_2 \\ | \qquad\quad | \\ C_6H_4.CO \end{array}$. If double the quantity of pentachloride is taken, the same body is produced, but at the same time a larger quantity of a red resinous substance. Phenanthradichloroketone melts at 165°, is readily soluble in chloroform and in benzene, less so in ether, and sparingly in cold alcohol. Alcoholic potash dissolves it, and on shaking the solution in contact with air, a phosphorescent light is emitted, dependent on the oxidation of phenanthraquinone to diphenic acid.

A crystalline body is also obtained by the action of phosphorus trichloride on phenanthraquinone, but its study is incomplete.

A. K. M.

Chloronitrocamphor. By P. Cazeneuve (*Compt. rend.*, **96**, 589—592).—Monochlorocamphor is dissolved in four times its weight of fuming nitric acid, heated gently, and the temperature gradually raised to about 115°. As soon as the weight of the liquid is equal to the weight of the chlorocamphor employed, the heating is stopped, the product treated several times with cold water to remove excess of nitric acid, and the yellowish pasty precipitate agitated with a large excess of concentrated ammonia, which acquires a red colour, and leaves chloronitrocamphor in the form of a pulverulent white mass. The chloronitrocamphor is then dissolved in boiling alcohol, from which it separates in large prismatic needles on cooling.

Chloronitrocamphor, $C_{10}H_{14}Cl(NO_2)O$, is insoluble in water, soluble in chloroform, carbon bisulphide, and ether, moderately soluble in cold alcohol, very soluble in hot alcohol. It is remarkably white, has an odour more feeble than that of chlorocamphor, and a slightly sharp taste. It melts at 95°, and if heated above 100° decomposes completely, with evolution of acid vapours and formation of carbonaceous products. Chloronitrocamphor has a lævorotatory power for $[\alpha]_j = -6{\cdot}2$, whereas monochlorocamphor has a dextrorotatory power for $[\alpha]_j = +90$.

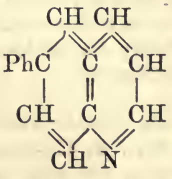
This chloronitrocamphor is analogous to the bromonitrocamphor obtained by R. Schiff (*Ber.*, 1880, 1402), and is formed under similar conditions. Like the bromo-derivative, it is reduced to nitrocamphor by nascent hydrogen, and in all probability the chloro- and bromo-derivatives have a strictly analogous constitution. C. H. B.

Action of Phthalic Anhydride on Quinoline. By M. C. Traub (*Ber.*, **16**, 297—299).—Fischer (*Ber.*, **9**, 1753) showed that a phthaleïn-derivative could be obtained from phthalic anhydride and dimethylaniline. The author has experimented with the pyridine and quinoline bases, and finds that on heating phthalic anhydride with quinoline for 3—4 hours at 150°, and then removing the excess of base by means of hydrochloric acid, a semi-solid pasty mass is formed, which can be purified by crystallisation from glacial acetic acid, and finally from benzene. It is, however, not quinoline-phthaleïn, its formula being $C_{17}H_9NO_2$ (*quinophthalone*), and the reaction corresponds with that by which anthraquinone is formed. Quinophthalone is almost insoluble in water, sparingly soluble in alcohol, ether, chloroform, and light petroleum, readily in hot benzene and glacial acetic acid. It melts at 235°, and can be sublimed with partial decomposition. Heated above 250° with potash, quinoline is given off, whilst benzoic acid is found in the residue. Fuming sulphuric acid converts it into a sulphonic acid. A. K. M.

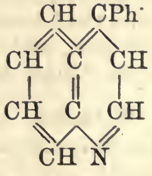
Phenolquinoline. By E. Grimaux (*Compt. rend.*, **96**, 584—585).—In Skraup's method of preparing substituted quinolines, the glycerol employed is first converted into acraldehyde. It appeared probable, therefore, that substituted quinolines would be obtained by replacing the glycerol by phenylacraldehyde (cinnamaldehyde).

A mixture of aniline, nitrobenzene, sulphuric acid, and oil of cinnamon is heated at 170—180°; the black mass thus obtained is extracted with water, and the solution filtered. On adding potassium hydroxide, the filtrate gives a black resinous precipitate, which is partially redissolved by ether. The ethereal solution on evaporation leaves a soft black confusedly crystalline mass, which is distilled in a current of air, when a yellow liquid passes over and solidifies to a crystalline mass on cooling. This product is purified by washing with a very small quantity of ether, and recrystallising twice from three or four times its weight of boiling alcohol. The *phenolquinoline*, $C_9H_6Ph.N$, thus obtained forms white slender needles, which melt at 84°. It is very soluble in ether, slightly soluble in cold alcohol, soluble in three or four times its weight of boiling alcohol, slightly soluble in boiling light petroleum. The hydrochloride, sulphate, and platinochloride are crystalline salts; the first two are partially decomposed by a large excess of water.

From its mode of formation, this base is a phenolquinoline containing the phenyl-group on the pyridic side of the quinoline, and in the para-position with respect to the nitrogen. It is isomeric with the phenolquinoline obtained by La Coste (*Ber.*, 1882, 55) by the action of glycerol and sulphuric acid on paramidodiphenyl. In this compound, the phenyl-group is on the benzene side of the quinoline, as shown by the following formulæ:—



La Coste's phenolquinoline.



Grimaux's phenolquinoline.

C. H. B.

Cryptidine. By A. R. LEEDS (*Ber.*, **16**, 289—290).—When dry powdered acralxylidine is carefully distilled, ammonia is evolved, and an oil and water pass over, leaving a porous carbonaceous mass in the retort. The crude oil has an unpleasant odour and very bitter taste. It forms crystalline compounds with sulphuric, hydrochloric, and other acids, and is best purified by means of the hydrochloride, which can be crystallised from water, and finally decomposed by potash. The purified oil has a reddish colour and a disagreeable odour, and boils at 270°. In composition it corresponds with cryptidine, $C_{11}H_{11}N$. The hydrochloride forms slender colourless tabular crystals, which can be sublimed with partial decomposition. The platinochloride forms slender yellow crystals, soluble in water and in alcohol. A. K. M.

Creatine-compounds of the Aromatic Group. By P. GRIESS (*Ber.*, **16**, 336—339).—A new method for preparing these compounds consists in the action of cyanocarbimidamidobenzoic acid on the aromatic amines and diamines. *Phenylbenzoglycocyamine*, $NHPh.C(NH).NH.C_6H_4.COOH + H_2O$, is obtained on adding cyanocarbimidamidobenzoic acid to 3—4 parts of boiling aniline, and heating until hydrocyanic acid ceases to be evolved. On mixing the product with alcohol, the above compound is precipitated. It is purified by washing thoroughly with alcohol and crystallisation from boiling water, in which it is sparingly soluble. It crystallises in indistinct needles or plates, is almost insoluble in ether, but dissolves readily in dilute mineral acids and in potash solution. Its taste is at first slightly bitter, then sweet. The *hydrochloride*,

$$C_{14}H_{13}N_3O_2,HCl,H_2O,$$

is very readily soluble in water, from which it crystallises in nodules. The author thinks it possible that Traube's phenylbenzocreatine (this vol., p. 193) is identical with phenylbenzoglycocyamine. *β-Naphthylbenzoglycocyamine*, $C_{10}H_7.NH.C(NH).NH.C_6H_4.COOH$, is prepared in a manner analogous to the above compound, using a large excess of naphthylamine. It forms small white crystalline nodules, very slightly soluble in hot water or in alcohol, insoluble in ether and chloroform. When dry, it is almost tasteless, whilst its aqueous solution tastes slightly bitter at first, then faintly sweet. The *hydrochloride*, $C_{18}H_{15}N_3O_2,HCl$, is very sparingly soluble in water, from which it crystallises in thin six-sided plates. *Amidophenylbenzoglycocyamine*, $NH_2.C_6H_4.NH.C(NH).NH.C_6H_4.COOH$, is obtained from cyanocarbimidamidobenzoic acid and paradiamidobenzene. It crystallises in small grey-coloured pointed prisms. In solubility it resembles phenylbenzoglycocyamine. The *hydrochloride*, $C_{14}H_{14}N_3O_2,2HCl$, forms small nodular crystals, readily soluble in cold water. Amidophenylbenzoglycocyamine yields a diazo-compound which combines with amines and phenols to form azo-compounds. A. K. M.

Strychnine Derivatives. By HANRIOT (*Compt. rend.*, **96**, 585—587).—Dinitrostrychnine, differing from that obtained by Claus and Glassner (Abstr., 1881, 748), is obtained by dissolving 60 grams of strychnine in 300 grams fuming nitric acid, cooled to −10°, and pouring the solution into 2 litres of water. The crystals of dinitrostrychnine nitrate, which separate out, are drained, redissolved in water, and the solution precipitated with ammonia. *Dinitrostrychnine*, $C_{22}H_{20}N_2O_2(NO_2)_2$, crystallises with some difficulty, but can be obtained in long transparent amber-yellow prisms by dissolving it in chloroform, adding twice the volume of alcohol, and allowing the liquid to evaporate spontaneously. It is soluble in alcohol and in boiling water, slightly soluble in cold water, very soluble in chloroform. It does not melt, but decomposes at about 202°. It readily undergoes alteration under the influence of heat, especially in presence of excess of ammonia.

The salts of dinitrostrychnine are slightly soluble in water, but dissolve in strong acids, and are reprecipitated from these solutions on adding water, especially if the liquid is agitated. This fact may be utilised for the detection of strychnine in presence of colouring matters which interfere with the ordinary tests. A drop of fuming nitric acid is placed in a watch-glass, mixed with a small quantity of the substance to be tested, and, when solution is complete, one or two drops of water are added and the liquid agitated, when the characteristic crystalline precipitate is thrown down.

Dinitrostrychnine nitrate crystallises in thin plates from its solution in boiling water. The hydrochloride forms a curdy mass on agitating a solution of dinitrostrychnine in boiling water with hydrochloric acid. This curdy mass melts at about 40°, and on cooling deposits needles of the anhydrous chloride.

Diamidostrychnine is obtained by dissolving dinitrostrychnine in dilute hydrochloric acid, adding a large excess of tin, and heating the liquid at 50° for 24 hours, after which time it is filtered, more tin added if the reduction is incomplete, and the tin removed from the solution by treatment with hydrogen sulphide, the filtrate boiled, precipitated by ammonia, and the precipitate purified by repeated crystallisation from chloroform. By slowly cooling the chloroform solution, the diamidostrychnine is obtained in prisms, which become opaque when dried. From aqueous solutions, ammonia throws down a very bulky precipitate. Diamidostrychnine is slightly soluble in water, soluble in alcohol, and very soluble in chloroform; almost insoluble in ether. It does not melt, but begins to decompose at about 225°. With a neutral solution of the hydrochloride, sodium hypochlorite throws down a greenish precipitate, which forms a green, then blue, then violet solution, with increasing quantities of hydrochloric acid. Sulphuric acid and potassium dichromate do not give the characteristic violet colour given with strychnine, but this colour is produced on adding a small quantity of water. Ferric chloride gives a red coloration on boiling. C. H. B.

Constitution of Atropine. By A. LADENBURG (*Annalen*, **217**, 74—149).—In this paper, the author has collected together the various facts on this subject, mostly already published and abstracted, and thus gives an historical sketch of this interesting research. When tropine had been recognised as a tertiary base, the author proceeded to synthesise atropine from its products of decomposition, tropine and tropic acid, which he succeeded in doing by the action of dilute hydrochloric acid on tropine tropate (Abstr., 1879, 733). This being accomplished, he next prepared various other alkaloïds, called by him tropeïnes, by a similar method; thus, from tropine mandelate he obtained *homatropin* or *phenylglycolic tropeïne* (Abstr., 1880, 410, 715, and 815, and 1881, 420), and measurements of the crystals and the following additional observations are now given: the *hydrochloride* crystallises from concentrated neutral solutions after some time; it is very soluble in water; the *sulphate* can be crystallised from water, and forms needles with silky lustre; solutions of the hydrochloride give a white curdy precipitate with potassium mercuric iodide, a white oil with mercuric iodide, and a crystalline *platinochloride* with platinic chloride. From tropine atrolactate, *atrolactic tropeïne* is obtained (Abstr., 1882, 984). Additional remarks; this substance crystallises in needles (m. p. 119—120°), very sparingly soluble in cold, but more readily in hot water, and easily in alcohol. It is isomeric with atropine, and its mydriatic action is equally remarkable. The hydrochloride, hydriodide, hydrobromide and sulphate, have not been obtained in crystals. The *platinochloride* forms reddish-yellow crystals, very soluble in water and alcohol. The *aurochloride*, $C_{17}H_{23}NO_3,AuCl_4H$, crystallises in yellow needles, which melt under water, but when dry, melt at 112—114°, sparingly soluble in cold water. *Salicylic tropeïne*, $C_{15}H_{19}NO_3$, is obtained from tropine salicylate (Abstr., 1880, 410 and 714); it does not act on the pupils of the eye; the platinochloride has the composition $(C_{15}H_{19}NO_3,HCl)_2,PtCl_4$, the *aurochloride*, $C_{15}H_{19}NO_3.HCl,AuCl_3$. *Hydroxybenzotropeïne* (Abstr., 1880, 714) can be partially distilled without decomposing, whilst the remainder is carbonised. It has a slightly alkaline reaction, and is soluble both in acids and in soda. It crystallises without water of crystallisation. It does not act on the eye as energetically as atropine. The *nitrate* is moderately soluble, and is coloured yellow when boiled with excess of nitric acid. Iodine gives rise to a crystalline mixture of tri- and pent-iodide. The *mercuro-* and *stanno- chlorides* have been obtained, the former in colourless leaflets, the latter in tufts of white needles. Other precipitates are formed with tannic acid, potassium mercuric iodide, potassium ferri- and ferro-cyanide, and phosphomolybdic acid. The simple salts of *parahydroxybenzotropeïne*, $C_{15}H_{19}NO_3$ (*ibid.*), are mostly soluble, the *nitrate* crystallising in prisms only sparingly soluble; this salt is turned yellow by boiling with nitric acid. It gives precipitates with all the various reagents mentioned above; the *mercurochloride*, $HgCl_2,C_{15}H_{19}NO_3,HCl,H_2O$, crystallises in needles.

Benzotropeïne, $C_{15}H_{19}NO_2$ (Abstr., 1880, 714). Additional remarks; it distils without leaving a residue. The nitrate is sparingly soluble, and is turned yellow by boiling with nitric acid. The aurochloride forms microscopic needles, slightly soluble in water, easily in alcohol. It gives precipitate with the usual reagents. *Phenylacetotropeïne*, $C_{16}H_{21}NO_2$ (Abstr., 1882, 784), sulphate forms colourless needles. *Cinnamyl tropeïne*, $C_{17}H_{21}NO_2$ (Abstr., 1880, 714), can be prepared either from cinnamic acid, tropine, and hydrochloric acid, or by treating phenylacetic acid in a similar manner. It has scarcely any mydriatic action, but is a powerful poison. *Atropyltropeïne* and *phthalyltropeïne* (*ibid.*), are the last of the series of the compounds described in this paper. The author then passes on to his work on the constitution and synthesis of tropic acid (Abstr., 1880, 472; 1881, 171), from the results of which he arrives at the constitution $CH_2(OH).CHPh.COOH$ for that acid. With regard to the constitution of tropine, the author finds that when it is heated with soda-lime, *methylamine* and a *hydrocarbon* like tropilidene, C_7H_8, stand prominent amongst the products, so that the principal reaction may be represented by the equation $C_8H_{15}NO = NH_2.CH_3 + C_7H_8 + H_2O$. When tropine is decomposed with acids, it gives rise to *tropidine* (Abstr., 1879, 733; 1880, 675); the best method for the preparation of this base is to heat a mixture of tropine (2 parts), glacial acetic (12 parts), and concentrated sulphuric acid (46 parts). In addition to the properties, &c., already given (*loc. cit.*), the vapour-density has been determined, and found to be 118. Tropidine is soluble in acids, in ether, and alcohol, scarcely soluble in soda; its aqueous solution has a strongly alkaline reaction. *Tropidine hydrochloride* forms hygroscopic crystals, soluble in water. The *hydrobromide* is similar, but not quite so hygroscopic. The *picrate* crystallises in yellow needles, very sparingly soluble in cold, somewhat more so in hot water. The *periodide* forms brown prisms (m. p. 92—93°), soluble in alcohol. With methyl or ethyl iodide, tropidine yields a mono-methyl or ethyl-derivative, which is crystalline and forms well-defined crystalline platino- and auro-chlorides. The action of hydriodic acid and phosphorus on tropine results in the formation of *hydrotropine iodide* (m. p. 115°) (Abstr., 1881, 263); if, however, during the reaction, the tube be heated to 150° or above, tropidine and its periodide are the products, owing to a secondary dehydrating reaction resulting in the conversion of tropine into tropidine. The formation of *metatropine* from hydrotropine iodide is then discussed (Abstr., 1881, 263; 1882, 984), and the conclusion arrived at is that tropine is a nitrogenous alcohol of which the tropeïnes are the ethereal derivatives. This view is supported by the author's work on alkines (Abstr., 1882, 165 and 1193), which are a class of bodies quite analogous to the tropeïnes. Then follow detailed accounts of the following experiments:—Decomposition of dimethyltropine by heat (Abstr., 1882, 216); the production of tropïlene from methyltropidine iodide and tropiledene from dimethyltropine iodide (*ibid.*); the decomposition of methyltropine, methyltropine chloride and iodide by potash, the principal products being large quantities of *di-* and small of *tri-methylamine;* the oxidation of tropilene into adipic acid (Abstr., 1882, 983), and finally the decomposition of tropidine by bromine (Abstr., 1882, 984 and 1206), by which *ethylene dibromide* and *dibromomethylpyridine* are obtained. The inferences there deduced (*ibid.*) are enlarged upon, and the formula $C_5H_7(C_2H_4O.CO.CHPh.CH_2.OH)NMe$, proposed for atropine. D. A. L.

Colchicine and Colchiceïne. By S. Zeisel (*Monatsh. Chem.*, 4, 162—164).—By the action of hydrochloric or sulphuric acid on a very dilute solution of colchicine, it is known that in addition to colchiceïne, another base is formed in small quantity. By heating colchiceïne with strong hydrochloric acid at 110—120°, it is completely converted into the new base (termed *apocolchiceïne* by the author) and methyl chloride. Apocolchiceïne is obtained as an amorphous flocculent yellow precipitate on adding sodium carbonate to its solution in acids; it is sparingly soluble in cold, more readily in hot water; the hot aqueous or dilute alcoholic solutions solidify on cooling to a gelatinous mass. It is readily soluble in caustic alkalis or acids, the solutions in the latter being of an intense yellow colour, and leaving yellow varnishes on evaporation; contrary to the statement of Hertel, the hydrochloride does not lose hydrochloric acid by repeated evaporation to dryness. On addition of powdered potassium nitrate to a solution of apocolchiceïne in concentrated sulphuric acid, the yellow colour changes to indigo, then to violet, finally to reddish-yellow, addition of alkali causing a fine red coloration. Apocolchiceïne hydrochloride gives amorphous precipitates with picric acid, potassium iodide, bromine-water, potassium bismuth iodide, phosphotungstic acid, and phosphomolybdic acid; with ferric chloride, it gives a brownish-green precipitate dissolving in hydrochloric acid to a green solution. A. J. G.

Behaviour of the Bile Acids with Albumin and Peptones, Antiseptic Action of the Bile Acids. By R. MALY and F. EMICH (*Monatsh. Chem.*, **4**, 89—120).—On mixing solutions of peptone, or of propeptone and taurocholic acid, a white milk-like precipitate is obtained in such a fine state of division as to readily pass through filter-paper and to require some days to settle to the bottom of the precipitating vessel, where it then forms a resin-like layer. It is readily soluble in alkaline liquids, even in sodium hydrogen bicarbonate solution saturated with carbonic anhydride, or in blood serum; addition of hydrochloric or acetic acid to these solutions reprecipitates it. It is insoluble in common salt solution. It dissolves in alcohol, and the solution gives merely a faint red coloration with potash and copper sulphate, showing that the precipitate can contain but little peptone; the precipitate appears to consist essentially of taurocholic acid which is precipitated by the peptones in a manner similar to its precipitation by sodium chloride. Glycocholic acid is not precipitated by the peptones.

On mixing solutions of albumin and taurocholic acid, a white flocculent precipitate is obtained consisting of albumin and a small quantity of taurocholic acid, the latter being in all probability merely held mechanically by the albumin; the precipitation of the albumin is so complete that no reaction is given in the filtrate with tannic acid or phosphotungstic acid, although the latter reagent, according to Hofmeister, can detect 1 part of albumin in 100,000 parts of water. From these results taurocholic acid is regarded by the author as a reagent of great importance, precipitating albumin and syntonin, but not peptone and propeptone, whilst all the other delicate reagents for albumin also precipitate the peptones. Glycocholic acid precipitates albumin but very partially.

The antiseptic properties of bile have been long known, although no researches have been made as to which constituent the antiseptic action was due; the authors show that taurocholic and glycocholic acids, and especially the former, are powerful antiseptics, that the addition of 0·2 per cent. solution of either acid will prevent the putrefaction of flesh (with pancreas a 0·5 per cent. solution of taurocholic acid or a 1 per cent. solution [suspension] of glycocholic acid was required to prevent putrefaction). The fermentation of sugar by yeast was prevented by the addition of 0·5 per cent. of taurocholic acid, but the addition of glycocholic acid, on the contrary, appears to accelerate the fermentation. The lactic fermentation is prevented by addition of 0·25 per cent. of taurocholic acid; glycocholic acid although not stopping the fermentation makes it proceed very slowly. The digestive action of pepsine is prevented by 0·2 per cent. of taurocholic acid, 1 per cent. of glycocholic acid has, on the contrary, no action. The conversion of starch into sugar by trypsin is prevented by the addition of 0·1 per cent. of either acid, by ptyalin by the presence of 0·2 per cent. of taurocholic acid or of 1 per cent. of glycocholic acid. The decomposition of amygdalin by emulsion is prevented by 0·5 per cent. of taurocholic acid; 1 per cent. of glycocholic acid is without influence on the reaction. A. J. G.

Oxidation of Kynurine and Kynurenic Acid. By M. Kretschy (*Monatsh. Chem.*, **4**, 156—161).—Both kynurine and kynurenic acid when oxidised with an alkaline solution of potassium permanganate yield kynuric acid; the yield being 95 per cent. from the former and 65 per cent. from the latter substance.

Kynuric acid, $C_9H_7NO_5,H_2O$, isomeric with carbostyrilic acid, crystallises in very brilliant slender needles; it loses its water of crystallisation at 100°, and, on further heating in an open capillary tube, it gives a white sublimate at 183—185°; at 188—189° it intumesces without being in clear fusion, and, after the intumescence ceases, the walls of the tube are covered with a microcrystalline deposit which does not again fuse on heating up to 250°. The acid has a strongly acid reaction and a faintly bitter taste. It is sparingly soluble in cold water, moderately soluble in hot water, soluble in alcohol and ether. A dilute solution gives a pale crimson coloration with ferric chloride; in concentrated solution, it is precipitated. Its compounds with the heavy metals are almost insoluble in water. The silver salt, $C_9H_5NO_5Ag_2$, is obtained as a gelatinous precipitate on adding silver nitrate to the ammonium salt; when dry, it forms microscopic prismatic crystals. The acid is readily precipitated by addition of mineral acids to its soluble salts, more slowly by acetic acid. It does not give any odour of pyridine when heated with excess of lime.

A. J. G.

Action of Potash on Albumin. By G. S. Johnson (*Chem. News*, **47**, 87).—The author is of opinion that potassium tetrathionate, and not sulphide, is formed when albumin is boiled with potash. He has observed that lead sulphide is always formed when white of egg, filtered or otherwise, or pure albumin is boiled with lead hydrate dissolved in dilute potash; also when fresh white of egg is boiled for a short time, cooled, and tested with lead acetate, a red colour is produced which might be mistaken for sulphide. When, however, white of egg filtered through charcoal, or pure albumin, is boiled with potash solution (sp. gr. 1·08) alone, no indication of sulphide is obtained with lead acetate, and, if the boiling has been prolonged, no sulphide is formed, even on boiling in the presence of lead. The author objects to this result being attributed to the oxidation of sulphide formed in the first instance; firstly, because the same result (the non-appearance of sulphide after prolonged boiling of albumin with dilute potash) was obtained in an experiment conducted in an atmosphere of pure hydrogen; secondly, because a solution of albumin after being boiled with potash until it gave no indication of sulphide, and then mixed with concentrated potash (sp. gr. 1·3) and again boiled, yielded an abundance of sulphide. These phenomena are accounted for by the author's hypothesis of the formation of tetrathionate. This salt yields no sulphide when boiled with dilute potash, but yields large quantities with concentrated potash. D. A. L.

Legumin. By H. RITTHAUSEN (*J. pr. Chem.* [2], **26**, 504—512).—By treating legumin prepared from peas, vetches, broad beans, and other leguminous seeds with solution of chloride of sodium, a considerable fraction passes into solution. This portion has essentially the same composition as that dissolved by very dilute alkali.

O. H.

Physiological Chemistry.

Exhalation of Nitrogen-gas during the Respiration of Animals. By J. REISET (*Compt. rend.*, **96**, 549—553).—A historical and critical summary. C. H. B.

Feeding Calves with Skim-milk. By G. A. PAUL (*Bied. Centr.*, 1883, 108).—A statement of the loss and gain experienced by feeding three calves with skim-milk, to which was added malt-combs and earth-nut cake. In the case of the first calf, 80 kilos. live weight were produced at the cost of 63 marks, whilst the milk produced by the cow was 187 marks, of which the calf only received 56 marks' worth; 42·5 kilos. live weight of second calf cost 38 marks, the cow's milk was valued at 79 marks, of which the calf received 36 marks' worth; to obtain 34·5 kilos. increase in live weight in the second calf, 52 marks were spent, cow's milk valued at 119 marks, of which the calf received 47 marks' worth, so that there was a saving of about 67 marks. E. W. P.

Distribution of Peptone in the Animal Body. By F. HOFMEISTER (*Zeitschr. Physiol. Chem.*, **6**, 51—68).—Nothing has as yet been accurately determined in regard to the way in which nitrogenous nutritive principles absorbed from the alimentary tract are disposed of in the system.

Peptone has always been looked upon with special interest amongst the products of the digestion of albumin, and Schmidt and Mülheim (*Du Bois Reymond's Archiv. für Physiol.*, 1879, 39) have established by their observations the fact of the transformation in chief part of albumin into this body. It has generally been believed that peptone, being relatively of easy diffusibility, passes through the alimentary mucous membrane into the blood-vessels, and is then carried to the place of its assimilation. Support to this view was given by the observations of Drosdoff and Plósz and Gyergyai, who found peptone in the blood of the portal vein. The quantity was, however, very small. Two different modes of explanation of these facts present themselves: either very little unchanged peptone reaches the blood through the intestinal mucous layer, or the peptone undergoes transformation immediately after its passage, losing its own characteristic properties, and so ceasing to be recognisable. This latter view has, hitherto, been chiefly adopted, some observers ascribing the place of change to the muscular tissue, and especially to the liver and other cellular organs, while others have deemed it to occur in the blood itself.

The author does not agree with either of these views, owing to the circumstances that when peptone is introduced into the circulation in some other way than by absorption from the intestine, by direct injection for instance, the greatest part escapes unchanged in the urine. This would point to the intestinal mucous membrane itself as the place of actual transformation.

In the first place, it was necessary to ascertain the normal distribution of peptone in the body at successive stages of the process of digestion, so as to exclude the possible influence of other organs besides the intestine and the blood, on the destiny of peptone.

The experiments were made upon dogs fed upon flesh, which was killed at different periods of the digestive process by means of blood letting. The amount of peptone was then determined in the various organs. The blood, heart, lungs, stomach, large and small intestines, liver, pancreas, spleen, mesenteric glands, mesentery, kidneys, and brain were severally examined. The method followed by the author is given in the present and also in a previous memoir (**4**, 264), to which the reader is referred for details.

The results of these experimental observations showed that only in one locality was peptone to be constantly found, in the intestinal mucous membrane. The proportions varied in different parts of the alimentary tract.

In the stomach the amount of peptone did not appear to have any ratio to the progress of digestion, save that in the case of long deprivation of food it sank to the limits of recognition. In the small intestines, on the contrary, a regular increase in the amount of peptone up to the eleventh hour after food was given was observed, followed by a diminution; the formation of peptone in the small intestine was *pari passu* with its absorption by the mucous layer. These observations agree with those of Schmidt-Mülheim, and likewise with those of Panum and Falck, in which the excretion of urea in flesh-fed dogs attained its maximum at the same period. This analogy between the formation of peptone and excretion of urea would favour the acceptance of the view that much of the absorbed peptone is at once broken up into its final products.

The total amount of peptone in the alimentary walls, including stomach and intestines, is more than double that present in the blood as a whole. The proportion of peptone found in the walls of the small intestine was 14 times greater than that in the walls of the stomach. On the other hand, the proportion of peptone in the gastric cavity was 15 times that present in the gastric mucous membrane. Either the stomach plays a much less part in the absorption of peptone than the intestine, or the absorbed peptone disappears more quickly from its mucous membrane.

Next to the intestinal tract, the blood exhibits a pretty regular proportion. Schmidt-Mülheim had already shown that in the case of dogs 24 hours after being fed, the blood contains no peptone.

Although in the majority of cases the blood is found containing peptone, yet on three occasions out of eleven, negative results were yielded from four to six hours after food. It would appear that the circulation of unchanged peptone is not indispensably necessary to nutrition. The peptone present in the blood is never of significant amount, ranging from 0·029 to 0·055 per cent. with a well marked maximum seven hours after food. Experiments tend to establish the fact that the peptone in the blood is not dissolved in the serum, but is associated with the red corpuscles.

When peptone was absent from the blood it was never present in the spleen. Contrary to the results of Plzós and Gyergyai, peptone could not be detected in the liver or mesenteric glands.

From the above observations it is inferred that the transformation of peptone takes place either in the mucous membrane itself or immediately after reception by the blood. D. P.

The Proportion of Peptone in the Gastric Mucous Membrane. By F. Hofmeister (*Zeitschr. Physiol. Chem.*, 69—73).—During the act of digestion, the stomach of the dog is opened along the smaller curvature, spread out and then divided by a suture carried from the pylorus to the cardiac end into two halves as nearly as possible symmetrical. It might be anticipated that when the viscus was carefully freed from adhering contents, both portions would yield equal proportions of peptone. This however, is true only when both are simultaneously immersed in boiling water. Should one be left undisturbed for a time, its peptone will be found to diminish in a remarkable manner, and even wholly disappear.

This disappearance of peptone is a vital act, taking place according to the stage of digestion with unequal rapidity, and arrested by heating for a few minutes to 60° C. If the stomach, previously extracted and wiped dry, be placed in the moist chamber for one or two hours at 40°, the mucous membrane is further observed to secrete a fresh layer of mucus, and the muscular contraction to restore the stomach to its original condition.

Since the transformation of peptone also takes place in the stomach of bled animals, it follows that the blood has no share in the result. The cause is to be sought for in chemical changes which have their seat in the gastric mucous membrane. An explanation is thus afforded of Salvioli's experiments (*Archiv. f. Physiol., von Du Bois Reymond*, 1880, Supplement Band 112), in which it was observed that peptone introduced into the intestine disappeared in a few hours without being detected in the efferent venous blood, whilst no such disappearance took place when blood injected with peptone circulated through the intestinal vessels. It also proves that the property of assimilating peptone belongs not merely to the stomach, but is a common characteristic of the intestinal mucous membrane.

Whether this assimilation is accompanied by a re-formation of albumin or by a complete disintegration, or in what part of the mucous layer it takes place, whether in the epithelial cells of the glandular portion, or the lymph cells of the adenoid tissue, has not yet been determined. But to this the author hopes shortly to proceed.

D. P.

On the Oxygen Pressure under which at a Temperature of 35° the Oxyhæmoglobin of the Dog begins to give up its Oxygen. By G. Hüfner (*Zeitschr. Physiol. Chem.*, **6**, 94—111).—From the experiments of J. Worm Müller, it appeared probable that the highest limit of oxygen pressure at which a solution of oxyhæmoglobin yields its loosely combined oxygen did not exceed much more than 20 mm. of mercurial pressure.

To decide this question, further experiments were undertaken in which the method adopted differed from that of Worm Müller so far that equal quantities of freshly prepared, and as nearly as possible equally concentrated, solutions of hæmoglobin were employed. These were thoroughly saturated with oxygen, and then under similar conditions of time and temperature shaken with double the volume of a mixture of nitrogen and oxygen, in which the proportions of the latter gas ranged systematically from 0·0 per cent. to 4 per cent.

It was to be expected that the amount of oxygen given off during agitation under otherwise equal conditions, would decrease in proportion to the amount of oxygen present in the mixture of gases, so that it appeared possible by varying this latter amount to find the value of the pressure beyond which a solution of oxyhæmoglobin of certain concentration ceases to yield its oxygen.

For a figure and description of the apparatus used, as also of the process, the reader is referred to the paper itself. It is highly probable that when oxyhæmoglobin and free absorbed oxygen are simultaneously present in a solution, it is only the latter which is used up in oxidation, and not directly the molecule combined with the hæmoglobin. Hence, in a concentrated solution of oxyhæmoglobin, the hæmoglobin may be in combination with oxygen, while the aqueous medium itself is no longer saturated with the latter. When such a solution is shaken with a mixture of gases, the oxygen pressure of which exceeds a certain limit, a diminution of this pressure takes place.

The substances which may consume the absorbed oxygen in such a solution of oxyhæmoglobin are not far to seek. Well purified colouring matter of blood may contain nevertheless traces of fat or lecithin, even particles of albumin, and it is possible that ultimately the oxyhæmoglobin may as an albuminate itself, be seized upon by the free oxygen. In the author's experiments such oxidation actually did take place, as the production of small quantities of carbonic anhydride (0·2 to 0·4 per cent.) showed.

The results proved that at a definite temperature of say 35°, only a small fraction of the amount of oxyhæmoglobin mixture present undergoes dissociation.

According to the theory of probabilities, assuming that other conditions remain unchanged, this fraction should be always the same, however the total amount of colouring matter present might change. Consequently the amount of oxygen yielded should increase with increasing concentration of the solution, and therefore likewise the limit of pressure at which dissociation ceases. Why does the latter not exceed a maximum? In the author's experiments the limit of pressure was as high and even higher in the case of a 6 per cent. solution as in one of 10 per cent. Solutions of greater concentration cannot be prepared on account of the slight solubility of the colouring matter and its instability in concentrated solution.

A diagram is given, in conclusion, showing the several proportions of oxygen which are retained at 35° by 100 cm. of the blood of the dog under different increments of pressure of the absorption of oxygen employed. It illustrates at a glance the vanishing proportion which the simply absorbed oxygen bears to the loosely chemically united oxygen of the blood. D. P.

Chemistry of Vegetable Physiology and Agriculture.

A Denitrifying Ferment in Soils. By GAYON and others (*Bied. Centr.*, 1883, 82—84).—A ferment exists in the soil which deoxidises all nitrates in the presence of organic matter: at a temperature of 35—40°, this action being most energetic; it differs from the nitrifying ferment in that it only acts when air is absent. From sewage-water, nitrogen, ammonia, amido-compounds, and from soils, nitrous and nitric oxides and nitrates were produced. Schlösing and Müntz find that the reducing action ceases at 100° and under the influence of chloroform vapour, and that sterilised soil recovers its power on the addition to it of fresh soil. According to Rodionoff "blooming" of black Russian earth is due to an organism which forms fine threads in the soil; in such a condition, the soil is light, fertile, and retains moisture well. E. W. P.

Reduction of Sulphates by Algæ. By A. Étard and others (*Bied. Centr.*, 1883, 84—86).—The reduction of sulphates by the cells of *beggiatoa* has already been noticed. The same observations have been made with *Oscilleria* and *Ulothrix*, and there is little doubt but that these three algæ possess the power of reducing sulphates and forming free sulphur and sulphuretted hydrogen. This will account for the formation of sulphur waters by another theory than that formerly held to be the true one, viz., the reduction of sulphates by dead organic matter. Plauchud states that this property of reduction is hindered by chloroform, and destroyed by phenol; he also accounts for the presence of sulphur in soils (the subsoil of Paris) by this theory. E. W. P.

Cristalline or Glaciale ("Mesembrianthemum cristallinum." By E. Heckel (*Compt. rend.*, **96**, 592—594).—The annual variety of *Cristallinum* growing in Provence has the composition: sodium chloride 7, organic salt of potassium 9, organic matter 5, water 80 = 100. According to Mangon (*Compt. rend.*, **96**), plants of the same species growing in Normandy contain water 96·8, salts 1·39, organic matter 2·0 = 100. The differences in composition are explained by the fact that the climate of Provence is very dry, whilst that of Normandy is very humid. The author finds that the calyx, corolla, and ovary of *Cristallinum* contain a somewhat large proportion of sodium. This plant therefore forms an exception to Contejean's statement that sodium is never found in the flowers or fruits of marine plants. C. H. B.

Phylloxera and Means for its Destruction. By E. A. Carrières and others (*Bied. Centr.*, 1883, 116—117).—Carrières refers to a method proposed by Mandon for the destruction of phylloxera, by introducing a 1 per cent. solution of phenol between the bark and wood of the vine whereby the insect is killed, whilst the grape is in no way harmed. Balbiani recommends for the destruction of the egg, a mixture of 9 parts coal-tar with 1 part heavy coal-tar oil. E. W. P.

Cultivation of Potatoes. By F. Schulze and others (*Bied. Centr.*, 1883, 111—115).—Schulze finds of the early potatoes that Cattel's Advancer is the highest in starch, but Rotterdamer Dünen gives the highest yield; of medium potatoes, Aurora is highest in starch, Richter's Schnee Rose the largest cropper; whilst of late potatoes, Richter's Imperator is best as regards starch and yield. Tobisch finds Imperator produces the largest amount of dry matter, but is most disposed to disease. Several other authors report on the cropping quality of many varieties. E. W. P.

Feeding Value of Fresh and Dried Diffusion Residue. By A. Morgen (*Bied. Centr.*, 1883, 105—107).—By experiment it is shown that the residue suffers no harm by being dried according to Blossfield's method. E. W. P.

Influence of the Percentage of Moisture in Peaty Soils on Vegetation. By R. HEINRICH (*Bied. Centr.*, 1883, 109).—Peaty soils were employed, and the moisture present varied from 10—100 per cent. of the total amount which could be absorbed; it was found that when grass seeds were sown, the largest number germinated in those soils in which 60 per cent. of the total water was present, whilst with only 10 per cent. none germinated. These results coincide with those obtained by Hellriegel on barley, when the maximum yield was obtained with 40—60 per cent. of water. E. W. P.

Retentive Capacity for Plant Food Possessed by Soils. By L. DUMAS (*Bied. Centr.*, 1883, 136).—A certain quantity of nutritive material is retained, which cannot be removed by plants. Well cultivated soils retain more manured matters than those which are badly cultivated. There is a limit to the retentive capacity. It is unnecessary to add more manure than is requisite to replace the material removed. E. W. P.

Manuring with Sulphuric Acid. By M. MÄRCKER (*Bied. Centr.*, 1883, 137).—Märcker points out the danger of manuring with sulphuric acid, as has been recommended by Zeroch. The object of such manuring was to render phosphates soluble, but in soils poor in phosphates, carbonates, zeolites, and humates are attacked.

E. W. P.

Action of Manures on the Quantity and Quality of a Wheat Crop. By W. H. JORDAN (*Bied. Centr.*, 1883, 96—99).—The experiments were made in Pennsylvania on one-eighth acre plots which had been cropped with potatoes in the preceding season; the manures were farmyard manure and artificials, so arranged as to present one or more constituent to the plant. It was found that fine charcoal superphosphate increased the yield the most; addition of potash, or potash and nitrogen to superphosphate, raised the yield of grain and also of straw. Heavy manuring with nitrogen, in conjunction with phosphoric acid and potash, produced no better effects than when nitrogen was absent; a full supply of artificials was better than farmyard manure; lime and gypsum were of no value. The weight per hectolitre of grain was highest in those plots manured with phosphates. Nitrogen in the manure did not increase that in the grain.

E. W. P.

Researches as to the Behaviour of Insoluble Phosphates in Peaty Soils and in Dilute Solvents. By A. KÖNIG, R. KISSLING, and M. FLEISCHER (*Bied. Centr.*, 1883, 87—96).—A short account of these experiments has already been published (*ibid.*, 1882, 422), and in this communication we find more exact details of the work done, as well as analysis of the various moorland soils employed. The general outcome of the experiment is that it is more advantageous to apply insoluble phosphates rather than superphosphate on humous soils, as they are capable of bringing insoluble into a soluble condition; this applies, however, only to peaty soils, as the presence of lime hinders this action. E. W. P.

Analytical Chemistry.

Glycerylphosphoric Acid. By H. FLEMING (*Dingl. polyt. J.*, **247**, 95).—By dissolving vitreous phosphoric acid in anhydrous glycerol, a strongly hygroscopic, syrupy substance is obtained, which absorbs a larger amount of water in a definite time than sulphuric acid. (4·4 per cent. against 3·7 per cent.) It is thought that this solution may be of some use for analytical or other purposes.

D. B.

Litmus, Methyl-orange, Phenacetolin, and Phenol-phthaleïn, as Indicators. By R. T. THOMSON (*Chem. News*, **47**, 123—127).—In this paper, the results of experiments are described, which have been carried out with a view to testing the efficiency of these various indicators, used in the estimation of alkalis, &c., in the presence of various impurities. The tests were made in such a way that the solution measured about 100 c.c. at the termination of the reaction. The strength of the indicator solutions (0·5 c.c. was used for every experiment) was so arranged that the intensity of the colour was about the same in each case at the completion of the experiment.

I. *The delicacy of indicators in absence of interfering agents* is tested by adding 0·5 c.c. of the indicator solution to 100 c.c. of distilled water, and trying how much decinormal acid or alkali is required to change the colour. In the following table the results of the experiments are summarised:—

Name of indicator.	Grams of solid matter per litre of indicator solution.	Amount of decinormal acid or alkali required to change colour of indicator.
Litmus	20·0	0·5 c.c. sulphuric acid.
Methyl-orange	0·15	0·5 „ „
Phenacetolin	2·0	0·1 „ sodium carbonate.
Phenol-phthaleïn	0·5	0·1 „ sodium hydroxide.

II. *Application of the Indicators to the Determination of Soda existing as Hydrate in the presence of a small proportion of Carbonate.*—For this purpose 50 c.c. of a normal solution of caustic soda was employed for each experiment containing 1·55 gram of available soda, of which 0·024 gram was as carbonate estimated by precipitation with barium chloride. The experiment with *litmus* was conducted as usual; when almost finished a single drop only was required to effect the end reaction. With *methyl-orange* the end reaction is not very certain, for it requires from 0·15 c.c. to 0·25 c.c. of normal acid, according to strength of soda and methyl-orange solutions, to fully develop the changed colour. The author shows subsequently that this uncertainty is due to the salts formed; the point he adopts for the end reaction is that at which the first decided change in colour is apparent. The amount of indicator solution used must vary according to the volume and colour (if any) of the solution under examination. *Phenacetolin* is used for the determination of both sodium as hydroxide and as carbonate in the same solution. For the hydroxide, acid is added until a permanent rose colour is produced; for the determination of carbonate the addition of acid is continued until the rose colour, which at first becomes more intense, turns to golden-yellow; the end reaction is rendered sharper by boiling off the carbonic anhydride when estimating the carbonate. Phenacetolin does not answer when there are small quantities of hydroxide in the presence of large quantities of carbonate. *Phenol-phthaleïn* is also used for determining both hydroxide and carbonate. In using this indicator, care must be taken not to allow carbonic anhydride to escape before the colour is discharged, which happens when the hydrate is neutralised, and when the carbonate has been converted into the hydrogen carbonate, then the number noted at this point shows all the sodium as hydroxide, and half that as carbonate. The titration is continued, boiling thoroughly after each addition of acid to decompose the sodium hydrogen carbonate, and thus bring back the red colour. It is best to add excess of normal acid, and to titrate back with normal caustic soda. The more carbonate there is present the less delicate is the end reaction. This method is not trustworthy for the determination of small quantities of sodium hydroxide in presence of large quantities of carbonate. The results of this series of tests are as follows:—

Soda employed = 1·55 grams, consisting of 1·526 grams as hydrate + 0·024 as carbonate.

Indicator.	Grams of total soda found.	Grams of soda as hydrate found.	Grams of soda as carbonates found.
Litmus..........	1·55—1·55	—	—
Methyl-orange ..	1·55—1·55	—	—
Phenacetolin	1·55—1·55	1·523—1·526	0·027—0·024
Phenol-phthaleïn .	1·55—1·55	1·526—1·526	0·024—0·024

III. *The estimation of potash in caustic potash* can be conducted in the same way and with as great accuracy as in the case of soda.

IV. *For the estimation of ammonia*, 50 c.c. of a solution containing 0·547 gram of ammonia was employed for each experiment. When *litmus*, *methyl-orange*, or *phenacetolin* were used, 0·55 c.c. of ammonia was found; the end reaction being in all these cases as delicate as with caustic soda. Phenacetolin produces the dark pink colour characteristic of its reaction with sodium or potassium carbonate, and not the yellow, as with the hydroxide of those metals, it therefore cannot be used as indicator for the determination of the proportions of ammonia free and as carbonate. *Phenol-phthaleïn* gives results much too low, on account of the colour being affected by the ammonium salts produced in the reaction. The results are tabulated below:—

Ammonia, NH_3, employed for each test, 0·547 gram.

Indicator.	c.c. of normal acid consumed.	Gram of NH_3 obtained.
Litmus	32·4	0·550
Methyl-orange	32·4	0·550
Phenacetolin......	32·4	0·550
Phenol-phthaleïn ..	31·5—31·4	0·535—0·533

Richter's process for the estimation of alkalis by dichromate (*Chem. News*, **47**, 19) is fully described. The author obtained good results for soda and potash, with ammonia, however, the results were much below the truth. In the appended table, results by Richter's dichromate and the ordinary acid methods are compared, phenolphthaleïn being the indicator.

0·1550 gram soda, 0·2355 gram potash, and 0·0850 gram ammonia, were respectively used for each test:—

Alkali.	c.c. $\frac{N}{10}$ dichromate consumed.	Gram alkali obtained.	c.c. $\frac{N}{10}$ acid consumed.	Gram alkali obtained.
Soda (Na_2O)	50·1	0·1553	50·1	0·1553
„	50·0	0·1550	50·1	0·1553
Potash (K_2O)	50·1	0·2359	50·1	0·2359
„	50·2	0·2363	50·0	0·2355
Ammonia (NH_3)..	46·0	0·0782	47·1	0·0800
„	45·7	0·0777	46·9	0·0797

V. *Determination of Alkali as Carbonate and Bicarbonate.*—The use of *litmus* for this purpose is well known. Soda and potash in these forms may be determined directly, whilst for the determination of ammonia carbonate or bicarbonate, excess of acid is used, the carbonic acid expelled by boiling, and then titrated back with alkali. *Phenacetolin* is used in a similar manner. *Methyl-orange* can be used for alkaline carbonates, but does not yield good results with ammonium carbonate. *Phenol-phthaleïn* is not recommended in this case.

VI. *Behaviour of the Indicators with the Neutral Salts of the Alkalis.*—In the presence of sulphates, nitrates and chlorides of potassium, sodium and ammonium, the delicacy of the *litmus* and *phenacetolin* are unaffected, the end reaction with *methyl-orange* is affected to the extent above mentioned, whilst the *phenolphthaleïn* is unaffected by the metallic salts; the ammonium salts, however, retard development of the colour considerably, they must therefore be excluded *on all occasions* when this indicator is used.

VII. *Sodium thiosulphate* is neutral to all four indicators.

VIII. *Effect of Alkaline Sulphites.*—These salts act alkaline to *litmus*, *phenacetolin*, and *methyl-orange*. With the first two the end reaction is not very distinct, with the last it is very sharp and decided. The sulphites are practically neutral to *phenolphthaleïn* in the cold, and even after boiling, provided the solution has not a great excess of acid. Results are as follows:—3·15 grams of Na_2SO_3 (1·55 grams of Na_2O) are used for each test.

Indicator.		c c. normal acid consumed.	Gram Na_2O found.
Litmus		24·9	0·772
Methyl-orange		25·1	0·778
Phenacetolin		25·1	0·778
Phenol-phthaleïn	cold ..	0·2	0·006
	boiled.	4·0	0·124

IX. *Normal Alkaline Sulphides.*—With these salts *litmus*, *phenace-*

tolin, and *methyl-orange*, give excellent results; it is advisable to boil off the hydrogen sulphide when using the first two; this precaution is not necessary with the methyl-orange. With *phenol-phthaleïn* in the cold only about half the soda is indicated; on boiling, however, the whole of the soda is obtained, this is evidently due to the sodium hydrogen sulphide formed during the reaction being neutral to this indicator. Results obtained are as follows:—0·284 gram Na_2S used.

Indicator.		c.c. normal acid consumed.	Gram Na_2S found.
Litmus		7·2	0·280
Methyl-orange		7·2	0·280
Phenacetolin		7·2	0·280
Phenol-phthaleïn	cold	3·55	0·138
	boiled	7·15	0·278

X. *Effect of Alkaline Phosphates.*—With *litmus*, the change of colour is very gradual, and therefore difficult to ascertain; with *methyl-orange*, the end reaction is as delicate as with sodium hydroxide. With *phenacetolin* and normal phosphates, the yellow colour is at first produced, and then the pink, the mono-acid phosphates give the pink at once; normal phosphates, in fact, act with this indicator as a mixture of a hydroxide and a mono-acid phosphate. *Phenol-phthaleïn* acts in quite another way, the metallic hydrogen phosphates being neutral to it. The results obtained are as follows:—2·050 gram of sodium phosphate, Na_2PO_4 (1·162 Na_2O), used for each test. 1·775 sodium hydrogen phosphate, Na_2HPO_4 (0·0775 Na_2O), was used for each test.

		Na_3PO_4.		Na_2HPO_4.	
Indicator.		c.c. normal acid consumed.	Gram Na_2O found.	c.c. normal acid used.	Gram Na_2O found.
Litmus		24·9	0·772	12·4	0·384
Methyl-orange		25·05	0·776	12·6	0·390
Phenacetolin	1st change	11·0	0·341	—	—
	2nd change	24·9	0·772	12·4	0·384
Phenol-phthaleïn	cold	12·65	0·392	0·25	0·008
	boiled	13·7	0·425	1·4	0·043

By the term alkaline salts, those of sodium, potassium, and ammonium are meant; salts of the last-mentioned must always be excluded with phenolphthaleïn. All the substances used for these test experiments were carefully analysed. D. A. L.

Determination of Nitrogen in Mixtures containing Nitrogenous Organic Matter, Ammoniacal Salts, and Nitrates. By H. H. B. Shepherd (*Chem. News*, **47**, 75—78).—The author reviews some of the processes that have been proposed to replace Dumas's method for the determination of nitrogen. Grosjean's process (*Chem. News*, **25**, 205) is noticed, but more attention is given to the following methods. With regard to the ordinary soda-lime method, the author proves experimentally its uncertainty and inefficiency when organic matter and nitrates are present; even the addition of starch or sugar to the substance previous to burning, or the use of a copper roll in front of the tube, does not make the method trustworthy. The author states that "the chief cause of failure is the disengagement of nitric acid from the nitrate, which affects the result by distilling over and increasing the quantity of acid originally placed in the nitrogen bulb." Ruffle's method (this Journal, Trans., **39**, 87) is next discussed. The author points out the importance of making a blank nitrogen determination with the several materials used in this process, previous to using them for an actual experiment, otherwise there may be an error amounting to 0·2 per cent. when 1 gram of substance is taken for analysis. In some test experiments with pure potassium and sodium nitrates, and manurial mixtures, good but rather low results were obtained. For the Crum method, the author describes a nitrometer, which consists of a graduated cylinder, fitted at the top with the usual cup and stopcock, but bent round and upwards at the lower end, and connected by means of flexible tubing with a mercury reservoir hung on a cord working over pulleys; this arrangement is for levelling the mercury before reading the volume of gas in the graduated cylinder, the mercury in the reservoir is arranged 1° higher than that in the nitrometer for every 8° occupied by the acid, in order to compensate for the weight of the latter. He also describes an indigo method for manures. D. A. L.

Note.—With regard to the indigo method, the author retains two erroneous ideas (compare Warington, *Chem. News*, **25**, 45 and 47; and this Journal, Trans., **35**, 578), viz.: 1, he uses a volume of acid which does not bear a constant proportion to that of the combined volumes of the solution to be tried and the indigo used; and 2, he uses one standard of indigo for all strengths of nitrate solutions. The agreement of his quoted experiments is probably due to the errors balancing one another.—D. A. L.

Volumetric Estimation of Chromic Acid in Chromates and Dichromates. By J. W. C. HARVEY (*Chem. News*, **47**, 86).—This, like some methods already proposed by the author (this vol., 513), is based on the reducing action of stannous chloride. The dichromate solution in this case consists of 15 grams of the salt to the litre, and 1 c.c. = 0·017 gram iron = 0·01014 gram chromic acid. The stannous chloride solution contains 330 grams to 1 litre. The ferric chloride solution should not be too dilute, about 32 grams of iron to 1 litre. The process is conducted as usual (*loc. cit.*). To 1 gram of substance, 10 c.c. of the stannous chloride solution and some hydrochloric acid are added, the whole heated until complete reduction of the chromic acid is effected, excess of ferric chloride is then added, again heated, and the ferrous chloride formed by the residual stannous chloride is titrated with the dichromate, noting the number of c.c. required. 10 c.c. of the stannous chloride solution are now mixed with excess of ferric chloride, heated, and the ferrous chloride titrated, noting number of c.c. required. From the difference between the two readings the amount of chromic acid is readily calculated. Test experiments with potassium, lead, and barium chromates give satisfactory results. With

1 gram of lead or barium chromate, 5 c.c. of stannous chloride are sufficient. The stannous chloride should be tested before each series of experiments. A determination lasts ten minutes or so.

D. A. L.

Methods of Detecting Lead, Silver, and Mercury in the Body in Cases of Poisoning. By V. LEHMANN (*Zeits. Physiol. Chem.*, **6**, 1—42).—After fully discussing the literature of the subject, the author describes a series of quantitative experiments, in which the delicacy of various processes which have been employed for the detection of those metals is put to the test.

As regards lead, the sensitiveness of certain reagents were in the first place determined.

Hydrogen sulphide proved the most sensitive, giving a precipitate with lead nitrate in 10,000,000 of water in neutral or alkaline solution, and with 1 in 200,000 in acid solution.

Sulphuric acid with the addition of alcohol detected 1 in 50,000 of water, as also did potassium chromate, while potassium iodide sufficed only to indicate 1 part in 12,500 of water. Hydrogen sulphide in alkaline solutions is therefore the most delicate reagent for the detection of lead.

In the examination of the organs of the body and of organic fluids such as urine, it is necessary first to destroy all organic matters by hydrochloric acid and potassium chlorate, otherwise the separation of lead takes place incompletely, or even not at all.

In the separation of lead in this way, electrolysis yielded results as favourable as those obtained with hydrogen sulphide. The method employed was to place the solutions freed from organic matter and acidulated with hydrochloric acid in a bell-jar, closed below by means of parchment paper, and placed in very dilute sulphuric acid. The positive electrode from a battery of three small copper-zinc couples dipped into the solution lying on the parchment diaphragm, on the other side of which lies the negative electrode. Both electrodes were of platinum foil. After 24 hours, the lead deposited upon the positive electrode was dissolved by boiling with dilute nitric acid, the solution evaporated to dryness, and the residue redissolved in water, with addition of caustic soda. It was then tested by hydrogen sulphide in the usual way. Other methods, which it is needless to specify, Mayençon and Bergeret's and Reinsch's, gave incomplete results.

For the quantitative determination of lead under these circumstances, Lehmann adopts the colorimetric method of G. Bischoff (*Zeits. Anal. Chem.*, 1879), using hydrogen sulphide in presence of alkali.

After the administration of salts of lead, the metal may be detected in the urine and all organs of the body; in the case of rabbits to which lead had been given in doses of 3—4 mgrms. daily, traces of it were found in the urine after the first day. The greater portion of the lead is deposited in the tissues, and after four or five days, while mere traces are discernible in the blood, large quantities are found in the heart, lungs, kidneys, brain, and bones.

For silver, hydrochloric acid is the most sensitive test. The reaction with hydrogen sulphide is precipitated in solutions containing 1 part of silver nitrate in 200,000 of water, and with potassium chromate only when 1 in 10,000. Hydrochloric acid, on the other hand, still gives a visible turbidity, with 1 part in 400,000.

The separation of silver by hydrochloric acid from solutions containing salts and organic matters is not complete, as for instance from the urine which holds alkaline chlorides in solution, these latter dissolving in part silver chloride. In such cases and in the organs of the body, organic matters must first be destroyed, not by means of potassium chlorate and hydrochloric acid, but by fusion with potassium nitrate and sodium hydrate. From the residue left after extracting the alts by water, the reduced silver is dissolved in nitric acid, filtered, evaporated, redissolved in water, and precipitated by hydrochloric acid.

Other methods of determining silver, such as separation on copper foil, zinc-dust, and electrolysis, give unsatisfactory results. By the above method silver was detected in 60 cm. of the urine of a rabbit, under the skin of which 18 mgrm. silver nitrate had been injected. Similarly, after subcutaneous injection, in eight dogs of 48 mgrm., silver was discovered in the urine and liver.

Mercury is found in cases of poisoning in all the tissues and secretions of the body. The author considers the methods of Schneider (*Sitzungsberichte der Kaiserlich. Akad. der Wissenschaft., Mathemat.-Naturwissensch. Classe*, **40**, Nr. 8, Wien, 1860), and of A. Mayer (*Wiener Med. Jahrbücher*, 1 Heft, 1877) as alone yielding accurate results. In Schneider's method, the substance under examination is freed from organic matters by means of potassium chlorate and hydrochloric acid, and the filtrate subjected to electrolysis, the mercury being best deposited on a gold electrode, which Lehmann found to give more sensitive results than copper.

The deposited mercury is converted into iodide, for which purpose the electrode is introduced into a glass tube, drawn out in a capillary bore at one end, and sealed at the other. The latter part being heated, the resulting sublimate is driven into the capillary portion, which, with a bulb-shaped part of the wide tube, is then cut off before the blowpipe. This latter part is opened, and some iodine being introduced is again closed. The iodine vapour penetrates the capillary end, and changes the mercurial sublimate into iodide. According to Lehmann, the sensitiveness of the test is heightened if this reaction takes place in a slow current of air, while the gold electrode is cautiously heated, and the mercury volatilised in presence of the iodine. In this way 0·1 mgrm. $HgCl_2$ may be detected in 100 c.c. of urine. Mayer's method, by which the mercury is distilled in presence of steam, is even more sensitive. Urine, or the finely divided organ, diluted with water, is mixed with slaked lime, and solution of potash in a flask having a capacity of about thrice the volume introduced. A **U**-tube filled with glass wool moistened with silver nitrate is connected with the flask, and both are heated in a calcium chloride bath to 130—140°. The glass wool is afterwards inserted in a tube and converted into iodide as already described. A 2 per cent. solution of sodium chloride may advantageously replace the water used in this method, frothing being avoided, and the mercury more rapidly volatilised.

By this method 0·1 mgrm. $HgCl_2$ may be detected in 1 litre of urine. For details of both processes, the reader is referred to the original memoir.

After subcutaneous injection of mercuric chloride to the amount of 3—4 mgrms. daily for five days in a rabbit, mercury was found in greatest amount in the heart, lungs, liver, and muscles, least in the brain, bones, and urine. D. P.

Ready Method of Estimating the Alkalinity of Limed Beet Syrup. By P. Desprax (*Bied. Centr.*, 1883, 141).—Filter-paper is soaked in solutions of tartaric acid of various strengths, and a small quantity of rosolic acid is also added. The immersion of several of such strips of paper into an alkaline solution gives a rough estimate of the alkalinity. E. W. P.

Assay of Nux Vomica. By W. R. Dunstan and F. W. Short (*Pharm. J. Trans.* [3], **13**, 665—667).—This subject being of great importance on account of the strychnine and brucine in nux vomica, the authors have investigated the matter in order to find an accurate and simple method, Dragendorff's method being too long and intricate. Experiments were tried in which the nux vomica was made into a paste with various alkaline solutions, dried, and the dried mass extracted with chloroform; in all cases the marc (the mass after extraction) was bitter, showing that the alkaloïds were not wholly extracted, and therefore that chloroform alone is not an efficient medium for the purpose: a mixture of alcohol and chloroform (1 : 3), however, completely extracts the alkaloïds from nux vomica. Experiment showed that it was not necessary to mix the nux vomica with alkali, but that the powdered seeds could be at once extracted with chloroform containing alcohol as follows:—5 grams of the finely powdered nux vomica seeds are extracted for about two hours in an extraction apparatus, with 40 c.c. of chloroform, containing 25 per cent. of alcohol: this takes from one to two hours. The extract is well agitated with 25 c.c. of 10 per cent. dilute sulphuric acid, the chloroform separated, and again agitated with 15 c.c. of acid. The mixed acid solutions should be quite free from chloroform, filtered if necessary, then made alkaline with ammonia, and shaken with 25 c.c. of chloroform. The chloroform extract is run off, evaporated on a water-bath, and the residue, consisting of the alkaloïds, weighed. It is sometimes necessary to filter the chloroform after separation from the alkaline liquid. By this process samples of commercial nux vomica were found to contain the following percentages of alkaloïds:—2·92, 3·57, 3·32, 3·38, and 2·56.

The authors have successfully employed the mixture of chloroform and alcohol for the extraction of other alkaloïds. D. A. L.

Tests for Resorcinol Dyes. By R. Benedikt (*Chem. News*, **47**, 109).—In the tests recommended, a few drops of the solution of the colour are treated with ammonia and zinc-dust, by which treatment all eosines are completely decolorised; the colour comes back slowly on exposure to the air, but quickly on boiling. The colourless liquid

Remarks on original dye.	Remarks on original solution.	Same after ammonia and zinc-dust.	Same after boiling and adding hydrochloric acid and ammonia.	Same with potash.	Name of dye.
When boiled with potash, becomes more fluorescent; then olive-green without fluorescence.	Green fluorescence.	Becomes quickly crimson, without fluorescence.	—	—	Eosine B.N., bromo-nitro-fluorescein sodium.
—	Yellow, with yellowish-green fluorescence.	Becomes coloured slowly.	Colour same as original.	No change.	Chrysoline, benzyl-fluorescein sodium.
Soluble in water.	Crimson, without fluorescence.	Becomes coloured slowly.	Reddish-yellow, with yellowish-green fluorescence.	Slight turbidity. On boiling, becomes first purple; then blue, with green fluorescence, finally brown. When diluted, only slight colour, strong fluorescence.	Eosine B., tetriodofluorescein sodium.
Soluble in water, and is not stripped from fibre by alcohol.	If sufficiently* dilute, crimson, with orange, or yellow or yellowish-green fluorescence.	Becomes slowly coloured.	If sufficiently dilute*, crimson, with yellowish-green fluorescence.	No precipitate. When heated, turns violet, and before boiling is blue, with green fluorescence. On dilution, is blue, with green fluorescence.	Eosine G, tetrabromofluorescein potassium.
Scarcely soluble in cold water, readily in alcohol, with yellow fluorescence. Water strips dyed cloth slightly; alcohol abundantly.				Most of the colour precipitated, liquid opaque, with strong orange fluorescence. On boiling, same changes ensue, as with eosine G, but far more slowly.	Erythrine, monethyl-tetrabromofluorescein potassium.
Soluble in water, and is stripped from fibre by water, but not by alcohol.				Purple-red turbidity. On heating first, violet, with yellowish-green fluorescence; on boiling, blue, without fluorescence. Same on dilution.	Phloxine, a derivative of dichlorofluorescein.
Soluble in alcohol, with strong orange-yellow fluorescence.				Colour almost completely precipitated; liquid is less fluorescent than in the case of ethyl-eosine. On boiling, liquid becomes violet-blue and dull; when diluted, violet, with yellow fluorescence, which is intensified by adding alcohol, the liquid at the same time becoming red.	Cyanosine, a dichlorofluorescein derivative.
—	—	—	—	Slight turbidity. On boiling, blue, without fluorescence (on dilution, purple-violet); on further boiling, dirty violet (on dilution, purple, with slight fluorescence).	Rose Bengale, a dichlorofluorescein derivative.

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* These appearances are characteristic of any bromeosines.

is boiled until a copious precipitate of zinc hydroxide forms, hydrochloric acid is now added to dissolve this precipitate, the solution is next supersaturated with ammonia, and finally tested with potash (sp. gr. 1·30). The colour on fabrics is tested by stripping the dye from the cloth either with water to which a few drops of potash or ammonia have been added, or with alcohol; the liquid which comes off the cloth is tested in the same manner as the solution of a dye. The author's observations are tabulated on p. 690. D. A. L.

Technical Chemistry.

Purification of Contaminated Waters. By J. König (*Bied. Centr.*, 1883, 75—79).—The method employed consists in causing the water to flow on to wire-netting placed at such an angle that the water flows over the meshes, thus exposing a large surface to the air. Thus the water becomes thoroughly saturated with oxygen, and sulphuretted hydrogen, &c., is completely oxidised. For every 6 to 7 litres water which passes per minute, 50 cm. of netting is requisite.

E. W. P.

Bronze Implements used by the Miners of Peru. By Boussingault (*Compt. rend.*, **96**, 545—546).—The author found a bronze chisel weighing 198 grams lying amongst the *débris* of trachyte in an ancient quarry in the neighbourhood of Quito. The sp. gr. of the metal was 8·83, and it had the composition—

Cu.	Sn.	Pb.	Fe.	Ag.
95·0	4·5	0·2	0·3	traces = 100.

The hardness of the chisel was not appreciably greater than that of copper, and it could not have been used for working trachyte if this rock did not offer less resistance when freshly exposed and still saturated with water than when it has become dry by exposure to air.

A chisel found by Humboldt in a silver mine opened by the Incas at a little distance from Cusco, the other extremity of the ancient kingdom of Peru, had the composition Cu 94, Sn 6 = 100.

C. H. B.

Roasting of Gold Tellurides. By Küstel (*Chem. Centr.*, 1882, 783).—Roasting gold or silver tellurides is sometimes attended with loss of gold which the author attributes to volatilisation. As an example of the irregular behaviour of this class of compounds, a sample of petzite containing 24·80 per cent. gold, 40·60 per cent. of silver was heated on charcoal to 323° (m. p. of lead), the bluish-grey mineral suddenly became yellow without altering its outward form.

Examination under the microscope showed that innumerable small globules of gold on the surface were the cause of this appearance. Gold requires a temperature of 1200° to effect its fusion; in this case it melts at 323°. If salt is used during the roasting of telluriferous ores, large quantities of tellurium chloride pass off, and perhaps give rise to the volatilisation of the gold. In an experiment the author, having added salt during the roasting of one of these ores, lost 8 per cent. of gold before the ore was actually red hot. It is therefore indispensable to have the furnace connected with a condensation chamber when tellurium gold ores are roasted in it.

D. A. L.

Preparation of Pressed Yeast. By J. WEHMER (*Bied. Centr.*, 1883, 143).—According to this patent raw instead of steamed potatoes are used; they are to be pulped and heated with water at 50°, then mixed with green malt and rye husks, heated and allowed to saccharify, cooled, and allowed to ferment at 25°. E. W. P.

Influence of Chlorides of the Alkalis and Alkaline Earths on the Precipitation of Lime Saccharate from Warm Solutions. By P. DEGENER (*Bied. Centr.*, 1883, 127).—The precipitation of the lime as well as sugar is greatly dependent on the proportion in which these two substances are present in the solution. The tribasic saccharate is only precipitated when the solution is saturated with lime. The presence of chlorides of sodium, potassium, barium, strontium, or calcium does not hinder precipitation, and may even aid it if they are present only in small quantities, but when in excess they are distinctly detrimental. E. W. P.

New Process for the Extraction of Fish Oil. (*Pharm. J. Trans.* [3], **13**, 669—670.)—The fish is sprinkled with 5 per cent. of its own weight of ferric chloride or sulphate solution (45° B.), and can then be kept three or four days without undergoing alteration. It is then crushed, made into a paste, and pressed, when a large quantity of water and oil is forced out. The cake from the press dries readily, becomes friable, and is easily pulverised. A further quantity of fatty matter may be obtained from it, either by pressing between heated metal plates, or by extraction with benzene or carbon bisulphide. The residue forms an excellent fertiliser. D. A. L.

Uranium Oleate. By W. GIBBONS (*Pharm. J. Trans.* [3], **13**, 737).—This oleate, $(C_{18}H_{33}O_2)_2UO_2$, can be prepared by adding excess of uranic oxide to pure oleic acid. The mixture is allowed to solidify in an atmosphere of hydrogen, and the oleate extracted with ether, crystallised from alcohol, and dried in a vacuum. It is very unstable in air, and must therefore be kept in hydrogen; it softens at 85°, and on raising the temperature becomes viscid and finally decomposes. For medicinal purposes, it is advisable to mix it with vaseline or ozokerine to prevent oxidation. D. A. L.

Composition and Ripening of Emmenthal Cheese. By M. WEIDMANN (*Bied. Centr.*, 1883, 118—124).—The following table shows the composition of the dry matter of samples of cheese made at various dates extending over a period of six months:—

	Fat per cent.	Albumin precipitated by acetic acid.	Amide nitrogen per cent.	Ammonia per cent.
I....	45·13	42·45	0·05	0·01
II....	44·96	39·77	0·30	0·09
III....	44·46	38·84	0·53	—
IV....	44·84	34·20	0·88	—
V	45·05	—	—	—
V*a*....	45·64	32·96	1·08	0·16
V*b*....	44·66	—	—	—

	Nitrogen in extract free from albumin and peptones per cent.	Total nitrogen per cent.	Ash per cent.	P_2O_5 per cent.
I....	0·06	—	5·16	2·49
II....	—	—	5·19	2·47
III....	1·05	—	—	2·48
IV....	—	—	—	2·39
V	—	7·53	5·44	2·33
V*a* ..	1·53	—	—	2·31
V*b*....	—	—	—	2·35

Cholesterin was found in the ethereal extracts to the amount of 0·24—0·32 per cent., and also small quantities of free acid. The residue after removal of the fat was soluble in ammonia or potassium hydroxide, and was nearly all precipitated by addition of acetic acid, and in the filtrate were found tyrosine and leucine; in the residue there were ammonia and peptones. A substance soluble in hot alcohol, and which seems to be identical with Ritthausen's glutin, fibrin, and mucedin was found; this compound has been called caseo-glutin. The amount of water decreases as ripening proceeds, falling from 43·99 per cent. to 32·1 per cent.; but the percentage of fat is not perceptibly altered, nor the total nitrogen, although the albuminoïds become gradually soluble, being converted into caseo-glutin: hence we may conclude that although ripe cheese is more digestible, it has lost some of its nutritious matter. In the same manner Roquefort cheese, as ripening proceeds, becomes less and less nutritious. E. W. P.

Liquid Extract of Cinchona. By B. H. Caul (*Pharm. J. Trans*, [3], **13**, 737—739).—The author shows by quantitative experiments that the method of extraction and preparation of liquid extract of cinchona recommended by the British Pharmacopœia is inefficient, only a very small percentage of the alkaloïds and other medicinal principles of the bark being removed by treatment with water. Moreover, he points out that the infusion, and even more so the decoction, are pharmaceutically better preparations than the liquid extract of cinchona. The special defect is that this extract does not represent the medicinal properties of the bark.

D. A. L.

Technical Aspects of Lignification. By C. F. Cross (a paper read before the Society of Arts, January 25th).—The object of this paper is to indicate the theoretical lines of the present development of cellulose technology, more particularly with regard to the application of lignified structures to textile and other purposes. These substances were formerly employed solely for the manufacture of inferior goods, but improved processes of treatment—both for the isolation of cellulose (paper-pulp) and for merely bleaching (textiles), have brought them into more direct competition with the various forms of cellulose (cotton, linen, &c.). The standard processes for scouring and bleaching cellulose fabrics, as also for preparing cellulose from complex plant structures, all involve the employment of alkaline solutions under conditions of more or less drastic oxidation. The application of these processes to the treatment of lignified cellulose has given more or less imperfect results, and the investigation of the causes underlying these results has served to throw light on the chemistry of lignification. The main feature of the chemical constitution of lignose (bastose) in regard to its preparation by chemical processes for the purposes of the arts, is the presence of aldehydic substances of the furfural type, and from these are formed, as secondary products, acid bodies and brown colouring matters. This explains the disintegration and discoloration produced in the treatment of jute fabrics by the standard processes, and the protective action of the alkaline sulphites dried into the fabrics from solution. The author then discusses, as the principal subject of the paper, the theory of the various processes of resolving wood by the action of solutions of the acid sulphites which are at present occupying the attention of paper makers. Experiment has clearly shown that the sulphites fulfil the twofold function, first, of keeping up a condition of reduction or anti-oxidation, and, secondly, in virtue of their well-known relation to the aldehydes, of forming stable and freely soluble addition-compounds with the products of resolution of the woods, and are therefore peculiarly adapted to the work of promoting the action of the hydrolytic agents. The author discusses the work of Fry, Ekman, Tilghmann, Mitscherlich, and Francke, in developing these processes. While withholding an opinion as to the value of the pulps produced by the various processes of sulphite boiling, he indicates the existence of important differences in the specific action of the several sulphites. The following suggestions are offered in regard to the criteria of a wood pulp:—To detect residual lignose the aniline sulphate test (yellow coloration) has hitherto been considered sufficient, but as the "reduced" pulp often fails to give the reaction, although containing a large proportion of residual lignose, the author recommends the chlorine test, followed by immersion of the chlorinated pulp in a solution of a neutral sulphite: the development of a magenta coloration, affords an unfailing proof of the presence of lignose; and the depth of colour is a rough measure of the quantity. A quantitative estimation of cellulose by any of the standard methods is of course essential, as is also a determination of the loss of weight on boiling in dilute potash solution under standard conditions, the latter revealing the presence of hydrated and gelatinous modifications of cellulose, which render paper hard and brittle.

In conclusion the author briefly discusses the subject of "retting" in regard to the question of replacing this process by that of boiling the plants with solutions of the sulphites, and thus obtaining uniform and certain results in the isolation of their fibrous constituents.

C. F. C.

Indophenol. By H. KOECHLIN (*Chem. News*, **47**, 40).—This substance is obtained by the oxidation of a mixture of amidodimethylaniline and sodium naphtholate. It is insoluble in water, soluble in alcohol with a blue colour, and in glacial acetic acid. Sulphuric acid dissolves it with a red colour, but decomposes it. Alkalis are without action on indophenol prepared from α-naphthol, but decompose that prepared from β-naphthol; on the other hand, mineral acids decompose α-naphthol indophenol, but do not act on that made from β-naphthol. Indophenol is easily reduced by sulphides, stannous chloride, &c.; the product of the reduction is very soluble in acetic acid and in alkalis. Indophenol, as the name implies, is an indigo-blue dye, for fixing it on cotton, the fabric is printed with a mixture of indophenol and tin acetate, duly thickened, aged, and washed, or steamed and chromed; or tin nitromuriate, ammonia, and stannous oxide may be incorporated in the mixture. Directions are given in the paper for dyeing wool and silk. C. Mayer has obtained a violet indophenol from resorcinol; it is of great solidity but wanting in brightness, and is difficult to apply on account of its sparing solubility. The indophenol from phenol dissolves in sulphuric acid with a blue colour.

D. A. L.

New Process for Preparing Press-cake from Maize, &c. By F. BÜROW (*Bied. Centr.*, 1883, 142).—According to this patent, the materials for fermentation are previously mashed for two days at 60° in sufficient water to yield a wort containing about 15 per cent. sugar. After conversion into sugar, the whole is allowed to become acid until 2—2·2 per cent. of acid is present, then cooled, and on the third day before use 2·5 kilos. yeast free from starch is added, and 100 c.c. sulphuric acid. When half the sugar has fermented, then 25 litres of mash of 24—25° are added, and a quarter of an hour later another 200 c.c. acid. The mash is prepared from 300 kilos. potatoes with 100 kilos. maize boiled with 600 litres water; with this, 70 kilos. green malt, 100 kilos. rye, and 30 kilos. buckwheat may be mashed. The percentage of sugar must reach 11·5—12·5 per cent. and that of the acid 0·4—0·5.

E. W. P.

Preservation of Diffusion Residues from Beet-sugar Manufacture. (*Dingl. polyt. J.*, **247**, 123—125.)—Märker (*Journ. f. Landw.*, 1882, 413) having shown that diffusion residues when kept lose considerably in weight, several sugar refiners have undertaken experiments with a view of obviating this loss. The loss of solid constituents on keeping these residues from three to thirteen months, amounted to 13·8—54·6 per cent. The cause of this loss is due partly to fermentation of the carbohydrates contained in the residues, partly to oxidation, the organic matter being converted into carbonic anhydride and volatilised. To prevent this loss, it is recommended to utilise as large a quantity of fresh residues as possible for feeding purposes, and dry the remainder, after which they do not suffer so much loss. D. B.

Cause of the Acid Reaction Exhibited by some Kinds of Paper. By FLEICHTINGER (*Dingl. polyt. J.*, **247**, 218).—In a former communication (Abstr., 1882, 1339) the author stated that all paper sized with resin exhibits an acid reaction due to the presence of free sulphuric acid. Härlin, who confirmed this, states that the acidity is not due to free acid, but depends on the aluminium sulphate used for fixing the size. The author has again studied this question, and concludes, from a number of experiments, that free sulphuric acid is present in paper treated with size made from resin. The acid reaction is due also to the presence of aluminium sulphate, but whether the latter is contained in the paper as normal or basic salt cannot be decided without further investigation. D. B.

General and Physical Chemistry.

Chlorophyll and the Distribution of Energy in the Solar Spectrum. By C. TIMIRIAZEFF (*Compt. rend.*, **96**, 375—376).—In a previous communication (*Compt. rend.*, May 28, 1877), the author showed the intimate relation existing between the absorption of light by chlorophyll and the intensity of the chemical action produced, and expressed the opinion that this action is dependent on the energy, as measured by its thermal effect, of the rays absorbed. He now calls attention to the fact that Langley's measurements with the bolometer justify this opinion, and prove that the point of maximum energy in the solar spectrum corresponds with the characteristic chlorophyll band between B and C. The author is now engaged on researches on the quantitative relation between solar energy absorbed by the chlorophyll of leaves and that stored up in the chemical work performed. He finds that, under the most favourable conditions, a plant utilises 40 per cent. of the energy absorbed. L. T. T.

Luminosity of Flame. By W. HITTORF (*Ann. Phys. Chem.* [2], **19**, 73—77).—In this paper, the author claims priority over W. Siemens as regards the non-luminosity of gases at the temperature of molten steel (this vol., p. 539); for he observed in the year 1879 that a layer of air surrounding electrodes of platinum, made white-hot by the passage of a current from 1600 cells, appeared perfectly dark to the eye. The author has repeated the experiment, substituting iridium for platinum, and using a battery of 2400 elements, divided into series of 400, 600, and 800; the result arrived at was the same, and though the white-hot iridium anode was melted, yet the gas media, whether of nitrogen, hydrogen, or oxygen, remained perfectly dark.

Experiments showed that all gases at this elevated temperature become good conductors of electricity, even at the lowest difference of potential, and on passage of the current no longer emit the spectra of the first order. The temperature at which the non-metallic elements give the spectra of the second order (or line spectra) is considerably higher, and is attained by the momentary discharge of the condenser. Further, it can easily be demonstrated that the luminous gases in Geissler's tubes are at a low temperature, and that their luminosity is due to a phosphorescence, for the absorptive power of these gases differs from their emissive power, and they behave differently from metallic vapours, which become luminous in the flame. Although the author claims priority over W. Siemens, he yet points out that Melloni deduced the same conclusions from the researches of Draper, and even as early as 1792 Wedgwood noticed that air at the temperature of a furnace is non-luminous. V. H. V.

Electric Researches. By C. FROMME (*Ann. Phys. Chem.* [2], **18**, 552—578, and **19**, 86—106).—A continuation of the author's experiments (Abstr., 1880, 490). These papers contain an account of the behaviour of platinum, palladium, gold, aluminium, and gas-carbon, in chromic and nitric acids.

Part I.—I. *Platinum in Chromic Acid (Bunsen's) Solution.*—Poggendorff and Buff observed that if nitric acid be replaced by chromic acid in the Grove's cell, the E.M.F. is diminished in the ratio 100 : 62, whilst the constancy of current is materially affected, for the intensity increases in a most marked way. But if, on the other hand, the same change is made in the Bunsen's cell, the E.M.F. is increased, whilst the constancy of the current is not altered. This phenomenon was variously explained by the above physicists; Buff considered it to be due to the greater surface exposed by the gas-carbon, and in support of this view he demonstrated that carbon, soaked in wax, behaved as platinum; Poggendorff concluded that the position of metals in a difference-of-potential series was altered by the nature of the liquid in which they were immersed. The author accepts the latter explanation, but experience gained in the course of his research showed that by Ohm's method, as used by Poggendorff, results could only be obtained in the case of a cell presupposed to be constant. For under certain conditions, with the combination Pt | HNO_3, an increase of intensity occurs similar to that observed in the combination Pt | H_2CrO_4. The form of the cell used has been described in a former paper; the electrometer was of Kirchhoff's construction, the sulphuric acid was greatly diluted, the chromic acid solution prepared according to Bunsen's recipe, and the nitric acid of sp. gr. 1·4. In former experiments, an increase of intensity was observed in the combinations Pt | HNO_3 and PtH_2 | CrO_4, a decrease in the combinations C | HNO_3 and C | H_2CrO_4; Cu | H_2CrO_4 gave a feeble but perfectly constant current. If the E.M.F. of a Grove's or Bunsen's element, containing nitric acid, be taken as 100, the E.M.F's. of these elements, when containing chromic acid, are 70 and 104 respectively; while the Cu | H_2CrO_4 combination is 62. But in later experiments with the Grove's elements, an increase of E.M.F. was observed, and the author considers that his former results were possibly vitiated by impurities on the surface of the platinum. In the present paper, the results of experiments on the Pt | H_2CrO_4 combination are given, and the variations of the E.M.F., under different physical conditions, is investigated.

As a general rule, it is shown that when a lower intensity is followed by a higher intensity, the E.M.F. increases until a maximum point is reached, when it decreases, and conversely when a higher succeeds a lower intensity, the E.M.F. gradually decreases until it reaches a minimum, and then again increases without however attaining again its former maximum value. If the circuit is open, then shaking the platinum plate has no effect. Again, neither change of temperature of the platinum or chromic acid, nor movement or renovation of the platinum surface, produces any result. Hydrogen occluded in the platinum raises the maximum and minimum of the E.M.F., in proportion to the quantity of gas contained in the metal; occluded oxygen is without effect.

If pure chromic acid solution be substituted for Bunsen's chromic acid, the E.M.F. of the open element is lowered by about 2 per cent.; on closing the element, the E.M.F. decreases to its minimum point, the more rapidly the smaller the exterior resistance. If sulphuric acid be added to the solution, the E.M.F. follows the same curve of change as that observed in the experiments above.

II. *Palladium in Chromic Acid.*—The substitution of palladium for platinum in the (Bunsen's) chromic acid element decreases the E.M.F. of the open element by about 3·5 per cent., but in the pure chromic acid element by 5·8 per cent. The E.M.F. of a closed Pd | H_2CrO_4 element is, the conditions being the same, less than a Pt | H_2CrO_4 element, the diminution in value being proportional to the intensity of the current.

III. *Gold in Chromic Acid.*—The E.M.F. of an open Au | H_2CrO_4 element is equal to that of the Pt | H_2CrO_4 element; if the circuit be closed, the E.M.F. remains constant, and does not follow the same variation observed in Pt | H_2CrO_4 element.

IV. *Gas-carbon in Chromic Acid.*—The E.M.F. of this element remains perfectly constant, if the intensity be low, but with high intensity it decreases until it reaches a minimum, at which it remains constant. If the element, after being closed with a high resistance, is closed without resistance, which is gradually introduced, then there is an increase of E.M.F. until it reaches a value greater than the maximum value under normal conditions.

V. *Aluminium in Chromic Acid.*—Aluminium behaves generally as platinum.

Part II.—The interesting results obtained in the experiments above, led the author to an examination of the behaviour of the same substances with nitric acid.

Platinum in Nitric Acid.—In the case of the Pt | HNO_3 combination, experiments led to the result, viz., that on the passage from a lower to a higher intensity, the E.M.F. decreases to a minimum point and then increases, and conversely if the intensity becomes greater, the E.M.F. increases to a maximum, and then decreases. With increase of temperature of the nitric acid and platinum, the maximum and minimum values are arrived at in a shorter time; at 48° the E.M.F. is constant from the beginning. In the year 1835 Schönbein observed that if platinum foil is made the negative pole of a Volta's pile, in which nitric acid is used, an evolution of gas is observed from time to time, especially if the nitric acid be concentrated. The author has extended Schönbein's observation, and shows (i) that when platinum in nitric acid is the negative electrode, there is always a temporary evolution of gas at the moment of closing the circuit, which, after a certain time, spontaneously ceases or continues; (ii), that the time of duration is the shorter the more concentrated the acid and the greater the intensity at the surface of the platinum, and Schönbein considered the evolution of gas to be the ordinary condition of the platinum, whilst the stoppage of the gas he considered to be abnormal. The author's observations show that one of three conditions may obtain: (i) no gas is liberated from the surface of the platinum; (ii), the gas rises from the surface of the platinum; (iii), the platinum is covered with gas without rising from the surface. The second of these conditions may be prevented either by making contact with the positive pole before introducing it into the acid; (ii), by heating the negative pole; (iii), by introducing a third platinum foil into the acid, and binding it with that portion of the circuit intermediate between the negative plate and the pole of the pile.

Palladium, Gold, and Aluminium in Nitric Acid.—The E.M.F. of an open Grove's element is decreased in the ratio 1 : 0·95—0·98, when palladium is substituted for platinum. If the circuit be closed, the E.M.F. gradually decreases until it reaches a point equal to that of the open element. Generally speaking, palladium, gold, and aluminium, behave as platinum. The E.M.F. of the combination

$$Zn \mid H_2SO_4 \mid HNO_3 \mid C,$$

with low intensity, is constant, but it decreases with higher intensity.

The author proposes in a future communication to give a summary and comparison of the results obtained in these various experiments, and to refer them to some simple explanation. V. H. V.

Modification of the Bichromate Battery. By Trouvé (*Compt. rend.*, **96**, 787—789).—150 grams of potassium dichromate are placed in 1 litre of water, the solution agitated, and 450 grams (one-fourth the volume) of sulphuric acid added drop by drop. The liquid gradually becomes hot, the dichromate successively dissolves, and in this way a solution can be obtained containing 250 grams of dichromate per litre of water. The solution remains clear and yields no crystalline deposit, and chrome-alum does not crystallise out even when the battery has been in action for several months. Batteries prepared with this supersaturated solution remain constant for a long time, and can be used with advantage to work incandescent lamps. The mean electromotive force of the battery is 2 volts with fresh solutions, and the intensity of the current at the moment of immersion of the plates is 118 ampères in short circuit, with a resistance of 0·07 ohm.

C. H. B.

Observation on Trouvé's Paper on a Modified Bichromate Battery. By E. Reynier (*Compt. rend.*, **96**, 838).—The first table in Trouvé's paper shows an expenditure of 456 grams of zinc in 12 couples in five hours, or an expenditure of 7·6 grams per couple per hour, the intensity of the current being 12·6 ampères at first, and gradually descending to 6·3 ampères, or a mean intensity of 9·45 ampères. A current of this intensity however requires the expenditure of 11·34 grams of zinc per couple per hour.

C. H. B.

Electric Discharges. By H. Herz (*Ann. Phys. Chem.* [2], **19**, 78—86).—The author describes a series of phenomena accompanying the electric spark discharge in air and other gases at a moderately low pressure. A large inductorium was used capable of giving sparks of 4—5 cm. in length; this was connected with a Leyden jar of 2 square feet area. The sparks were taken in a drawn-out glass tube, in which was introduced the positive electrode, the negative electrode being placed a short distance from the mouth of the tube. When this apparatus was introduced under the receiver of an exhausting pump and the pressure reduced to 30—50 mm., there appeared on the surface of the kathode a blue glimmering light, and between it and the anode a broad dark space, crossed by a red streak of 1—2 mm. diameter. On increasing or decreasing the pressure of the air, this streak disappears. The streak is not affected by a magnet. It evolves a considerable amount of heat, as shown by the rise of 10 degrees of a thermometer and by the melting of wax introduced into it; and it exerts a remarkable mechanical action in setting into oscillation elastic mica plates and radiometers. The author shows that the formation of the streak is no momentary flashing phenomenon; for by means of a Becquerel's phosphoroscope its time of duration was found to be about $\frac{1}{20}$ second. But all parts of the streak are not illuminated at the same time; the under part shines out before the upper, which in its turn is visible after the lower part is extinguished. A similar phenomenon occurs in other gases. In oxygen and nitrous oxide, the streak is golden-yellow; in nitrogen, dark red; in hydrogen, indigo-blue; and in vapours of turpentine, ether, and coal-gas, greenish-white. The same streak can also be observed in gases at ordinary atmospheric pressure; but under these conditions it is only a few millimeters long and very faint. It appears that the streak arises from an illuminated mass of gas arising from the tube, and experiments were made to ascertain whether it was caused by the expansion of the gas owing to the rise of temperature in the experimental tube. These, however, led to a negative result. V. H. V.

Influence of Temper on the Electrical Resistance of Glass. By G. Foussereau (*Compt. rend.*, **96**, 785—787).—Temper diminishes considerably the electrical resistance of different kinds of glass. The resistance of tempered lime-glass was increased by 2·3 times by reheating and annealing. The resistance of tempered crystal-glass was increased to 11 times its original amount by similar treatment. Moderate reheating, sufficient only to partially destroy the temper, causes an intermediate increase in the electrical resistance. The electrical resistance of glass which has recently been reheated, slowly increases during some time, as if the glass gradually acquired a condition of stable equilibrium. The resistance of tempered or untempered glass which has not been heated for some time remains constant.

C. H. B.

Electric Resistance of Psilomelane. By H. Meyer (*Ann. Phys. Chem.* [2], **19**, 70—71).—The author has been engaged for some time past in the examination of exceptions to Ohm's law first observed by Braun in the case of conducting minerals. The substance selected was psilomelane, which was cut into thin plates. The author's observations agree with those of Braun in so far as demonstrating that such plates exhibit a remarkable unipolar conductivity; but the relation of the resistance in the one direction to that in the second direction is shown to be *dependent* on the intensity of the electric current; for on changing the latter the position of unipolar conductivity can be reversed. In no case was a change of resistance observed when the electric current was constant; but the remarkable changes displayed when continuous and alternating electric discharges followed in the same direction are perfectly explained by the unipolar conductivity of the mineral. But as the difference between Braun's observations and those of the author may receive some explanation by supposing a difference of the material examined, the author cut plates from another specimen of psilomelane from the same source, and found that the resistance was *independent* of the direction, continuance, and intensity of the electric current. As to the nature of the difference in the two specimens examined, no explanation is offered.

The author's observations are in opposition to those of Braun, but in agreement with those of Dupel as regards the normal behaviour of pyrites and galena to the electric current. V. H. V.

Radiation of Rock-salt at Various Temperatures. By C. BAUR (*Ann. Phys. Chem.* [2], **19**, 17—20).—The radiation of rock-salt at various temperatures has previously been studied by Melloni and Magnus. The former arrived at the result that the heat radiated from rock-salt is not to any extent absorbed by polished plates of the same material, whilst the latter considered rock-salt to be monothermic, and believed that the heat radiated from rock-salt is perfectly absorbed by another plate. In Magnus' experiments, the rock-salt plate was heated to 180°, and an absorbing plate of greater thickness was placed before the thermoelectric pile. The experiments of the author do not confirm either the results of Melloni or of Magnus.

The apparatus used consisted of a radiometer, a radiating rock-salt plate of dimensions 90 mm. × 50 mm. × 8 mm. in a copper frame, which could be brought to the temperature required by a gas flame, and whose temperature could be determined by a thermopile of copper and nickel. A zinc screen was introduced to prevent radiation from the copper and the gas flame. The heat radiated from the plate was absorbed by three rock-salt plates, mean thickness 3·4, 5·1, and 13·8 mm.

The author's results demonstrate that rock-salt is the greatest absorbent of heat radiated from the same material; that the absorption increases with decrease of difference of temperature between the radiating and absorbing plates; and that the absorption is probably perfect when the radiating and absorbing plates are at the same temperature. V. H. V.

Evolution of Heat in the Absorption of Gases by Solids and Liquids. By P. CHAPPUIS (*Ann. Phys. Chem.* [2], **19**, 21—38).—A few years ago Favre made a series of observations on the heat evolved in the absorption of gases by charcoal, a phenomenon observed by Saussaure and other physicists. Favre found that the heat of absorption is greater than the latent heat of vaporisation, and in the case of carbonic acid, it exceeds the sum of heat of vaporisation and solidification. Pouillet observed that on moistening pulverulent or porous compounds with a liquid, a considerable amount of heat is liberated, which he considered to be a physical phenomenon, and not due to the formation of a chemical compound (*vide* Abstracts). In order to extend this line of research, the author considers that more accurate determinations are required—(i) for the heat of absorption of various gases by solids; (ii) the heat of evaporation of the gases used; (iii) heat developed in moistening porous substances. In the present communication, the author restricts himself to the first of these problems.

The apparatus used consists of a Bunsen's ice calorimeter, a manometer, and a mercury exhausting pump. The absorbing substance is first heated, weighed in a vacuum, and introduced into the tube of the calorimeter, which is connected up with the manometer. The whole apparatus is then exhausted, and then there is gradually introduced a quantity of gas whose volume, pressure, and temperature are accurately known. The mercury level of the calorimeter is observed from time to time, and the heat evolved calculated from these observations.

With this apparatus the author has examined the behaviour of the following gases :—Carbonic anhydride, air, sulphurous anhydride, ammonia, and methyl chloride, using for the absorbing material wood-charcoal, meerschaum, platinum black, and asbestos.

From the experiments, the details of which are given in the paper, the author shows that a greater quantity of heat is evolved for the first than for the last portion of the gas absorbed, and that the increase of pressure corresponding to the absorption of equal quantities of gas increases at first slowly, then more rapidly; also that the heat of absorption is separable into two portions, one corresponding with the heat of vaporisation of the gas in question, and the other to the heat evolved by the further compression of the liquefied gas. The latter can be observed separately from the former by liquefying the gas before it comes into contact with the absorbing material; but as the apparatus used did not permit of the condensation of the gas within the calorimeter, the author conducted some experiments on the heat evolved by moistening solids with liquids of low vapour-tension. The cases examined were charcoal with water and carbon bisulphide, and powdered clay with water. The following results were obtained: —On moistening 1 gram of charcoal with water, 7425 cal. were developed; with carbon bisulphide, 24,364 cal.; and 1 gram of clay with water, 275 cal. As in all these experiments the porous substance came in contact with a far larger quantity of liquid than that required for its complete moistening, only a very small portion of the liquid contributed to the thermal action. Finally, the author made a series of determinations of the heat evolved in the absorption of sulphurous anhydride and ammonia by water, and of sulphurous anhydride and methyl chloride by black caoutchouc which functions as a liquid. Generally, the values obtained decrease in proportion to the quantity of gas absorbed, by a more regular gradation than those obtained in the absorption of gases by solids; the heat evolved is considerably less in the former than in the latter case, but is in excess over the heat of vaporisation of the gases. If the gas be condensed before it is brought into contact with the absorbing liquid, then by the mixture of both liquids an amount of heat is set free equal to this excess. Then the phenomenon of the solution of gases by liquids is merely a particular case of the mixture of two liquids.

V. H. V.

Thermochemical Researches. By E. WIEDEMANN (*Ann. Phys. Chim.* [2], 18, 608—612).—It is possible to estimate the molecular heat of solids for their solution in water and other liquids. For if a molecule of salt of molecular weight M be dissolved in n molecules of a solvent of molecular weight m, and c be the specific heat of the solution, then $c(M + nm)$ is the molecular heat of the solution. If γ be the specific heat of the solvent, $mn\gamma$ denotes the molecular heat of the substance in the solution in question. As the specific heat of a solution is less than unity, then $c = 1 - x$ where $x < 1$. If the solvent be water ($m = 18$), the molecular heat of the solution is $(1 - x)(M + 18n)$. Observations have frequently been made to determine whether this value is greater or less than that of the water $18n$ contained therein, *i.e.*, whether in the equation $(1 - x)(M + 18n) = 18n + \alpha$, the value $\alpha = M - x(M + 18n)$, that is to say, the difference of both molecular heats is greater or equal to *nil*.

The author has examined the values of $c(M + n18)$, α, x, and $x(M + n18)$ for solutions of sodium chloride, sulphate, and nitrate, and of ammonium sulphate in water. In all cases examined, α decreases with decrease of concentration; this follows as a necessary deduction from the equation above, for if $n = 0$, then $\alpha = M - xM$, and the specific heat $1 - x$ is a positive value, and this is the case for very small values of n, *i.e.*, for very concentrated solutions. If x decreases as n increases, so α must become negative, and the value $18nx$ must increase in proportion. This is the case for all dilute salt solutions, as the specific heat is an asymptote to the specific heat of water, as x is asymptotic to *nil*. With solutions of greater concentration, α is positive, and with increase of dilution approximates *nil*, α then becomes negative. Then the molecular heat is for solutions of greater concentration greater than for those of lower concentration, less than for those of mean concentration equal to that of the water contained therein.

If $\alpha = 0$ then $M = x(M + 18n)$, or in other words, if the molecular heat of a solution be equal to that of the water contained therein, then the difference x of the specific heat of the solution from unity, multiplied by the molecular weight $(M + 18n)$ of the solution, will be equal to the molecular weight of the salt. Thus in experiment the values of $x(M + 18n)$ varied from 57·3 to 62·84 ($M = 58·5$), for ammonium sulphate from 120—133·1 ($M = 132$), for sodium sulphate $x(M + 18n) = 141·7$ ($M = 142$), and for sodium nitrate from 81·57—94·32 ($M = 85$).

V. H. V.

Alkaline Sulphites. By BERTHELOT (*Compt. rend.*, 96, 142—146).—Besides the two classes of acid and neutral sulphites of the formulæ $RHSO_3$ and R_2SO_3 respectively, the salts $K_2S_2O_5$ and $Na_2S_2O_5$ have been obtained, and have received the name of anhydrosulphites. From the results of his thermochemical researches, and also from the chemical behaviour of these two salts, the author considers that they should be looked upon as *metasulphites*, and as standing in the same relation to the normal sulphites as the metaphosphates do to the normal phosphates. The following are the thermal results obtained by the author.

Heat of solution of sulphurous anhydride in water at 12°; SO_2 = 8·34 cal.

Heat of neutralisation of sulphurous acid by a solution of potassium hydrate:—

SO_2 in solution + KHO in solution at 13° = 16·6 cal.
SO_2 ,, + 2KHO ,, ,, = 31·8 ,,
$KHSO_3$,, + KHO ,, ,, = 15·2 ,,

A slight additional disengagement of heat takes place with an excess of potash.

K_2SO_3 in solution + 2KOH in solution at 12° = 0·33 cal.

Freshly prepared acid, and acid which had been kept several years, gave like results, although the latter reduced silver salts as noticed by Stas.

Neutral Sodium Sulphite.—The hydrated salt, K_2SO_3,H_2O, which loses its water below 120°, was obtained. The heat liberated was less than that due to the solidification of the water of crystallisation, or the heat of combination was a minus quantity, − 1·1. The heat of formation of potassium sulphite, K_2SO_3, from its elements is 272·6.

Double Decomposition.—When a solution of potassium sulphite is treated with hydrochloric acid, partial decomposition takes place, with the following thermal results:—

K_2SO_3 in solution + 2HCl in solution at 13° = −1·8 cal.
K_2SO_3 ,, + 9HCl ,, ,, = −2·4 ,,

This shows a division of the base between the two acids, as the equation $K_2SO_3 + HCl = KHSO_3 + KCl$ would require − 1·7 cal., whereas the total replacement of the sulphur radical by Cl would require − 4·0. But if only a small quantity of hydrochloric acid ($\frac{1}{2}$ HCl to 1 K_2SO_3) be added, a slight evolution of heat (+ 0·6) is observable, seeming to point to the immediate formation of the metasulphite. Sulphurous acid added to a solution of potassium chloride, also gives thermal results, proving a division of the base between the two acids.

Decomposition by Heat.—Raised to a dull red heat in an atmosphere of nitrogen, potassium sulphite decomposes exactly according to the equation $4K_2SO_3 = 3K_2SO_4 + K_2S$. Contrary to Muspratt's statement, no evolution of sulphurous anhydride takes place. At 450° no action has commenced. L. T. T.

Pyrosulphites.* By BERTHELOT (*Compt. rend.*, **96**, 208—213).—*Potassium pyrosulphite* (*potassium anhydrosulphite*), $K_2S_2O_5$, crystallises out on supersaturating a solution of potassium carbonate with sulphurous anhydride, and may then be dried at 120°. This salt differs from the normal hydrogen potassium sulphite, $KHSO_3$, in

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* Called by the author "Metasulphites."

greater stability, heat of formation, power of forming hydrates, and the way in which it decomposes when heated.

In the formation of hydrogen potassium sulphite, SO_2 in solution + KHO in sol. at 13° liberate 16·6 cal., and the immediate addition of another mol. KHO to form K_2SO_3 liberates a further 15·2 cal. If, however, the solution of the bisulphite be boiled or allowed to stand for a long time, a further addition of 1 mol. KHO only gives 12·5 cal. That this is due to the conversion of the bisulphite into the pyrosulphite is shown by the fact that a solution of the crystallised metasulphite converted into the neutral sulphite also liberates 12·5 cal. In the conversion of the bisulphite into the pyrosulphite therefore 2·6 cal. are liberated, which tallies with the greater stability of the latter over the former. With potassium anhydrosulphate (pyrosulphate) $K_2S_2O_7$, and hydrogen potassium sulphate, the reverse is the case, an absorption of heat taking place during the conversion of the latter into the former, and the hydrogen potassium sulphate being the more stable salt of the two. The heat of formation of the pyrosulphite from sulphurous anhydride and potash is therefore 19·2 cal. These results have been verified by thermometric observations of the action of hydrochloric acid on (i) solutions of potassium pyrosulphite, (ii) the anhydrous salt, (iii) solutions of hydrogen potassium sulphite, (iv) neutral potassium sulphite.

Hydrates of Potassium Pyrosulphite.—On saturating, in the cold, a concentrated solution of potassium carbonate with sulphurous acid, crystals are formed either spontaneously or on the addition of alcohol. These have hitherto been considered to be normal hydrogen potassium sulphite, $KHSO_3$. The author, however, finds on analysis, that the crystals formed spontaneously correspond with the formula

$$K_2S_2O_5,\tfrac{1}{3}H_2O,$$

those produced by the addition of alcohol to that of $K_2S_2O_5,\frac{1}{2}H_2O$. The author considers them to be without doubt pyrosulphites and not acid bisulphites. At 120° they give off no sulphurous anhydride as would be the case with bisulphites, but merely lose water and become anhydrous. The heat of solution of the hydrated and anhydrous salts is also identical (5·6), pointing to mechanical and not chemical union. From the above data it may be calculated that the heat of formation of potassium pyrosulphite is as follows:—

$$\begin{aligned} S_2 + O_5 + K_2 &= 379{\cdot}4 \text{ cal.} \\ 2SO_2\,(\text{gas}) + K_2O\,(\text{anhydrous}) &= 66{\cdot}9 \text{ ,,} \\ SO_2\,(\text{gas}) + K_2SO_3\,(\text{solid}) &= 13{\cdot}8 \text{ ,,} \end{aligned}$$

Decomposition by Heat.—The decomposition takes place at a dull red heat, exactly according to the equation $2K_2S_2O_5 = 2K_2SO_4 + SO_2 + S$, no formation of neutral potassium sulphite taking place even as an intermediate stage.

The following is a list of some of the potassium salts containing sulphur, with their heats of formation from their elements:—

Bisulphide, K_2S_2..................	+ 106·0 cal.
Thiosulphate, $K_2S_2O_3$..............	+ 267·4 ,,

Pyrosulphite, $K_2S_2O_5$	+ 369·2 cal.
Dithionate or Hyposulphate, $K_2S_2O_6$	+ 411·4 ,,
Bisulphate (pyrosulphate), $K_2S_2O_7$ ..	+ 473·2 ,,
Sulphide, K_2S	+ 102·2 ,,
Sulphite, K_2SO_3	+ 272·6 ,,
Sulphate, K_2SO_4	+ 342·2 ,,

Or conformably to the observations of Dumas, with the oxides of tin:—

$O_3 + K_2S_2 = K_2S_2O_3$ liberates 3 × 53 6 cal.
$O_2 + K_2S_2O_3 = K_2S_2O_5$,, 2 × 51·0 ,,
$O_2 + K_2S_2O_5 = K_2S_2O_7$,, 2 × 52·0 ,,
$O + K_2S_2O_5 = K_2S_2O_6$,, 42·6 ,,
$O_3 + K_2S = K_2SO_3$,, 3 × 56·8 ,,

L. T. T.

Alkaline Thiosulphates. By BERTHELOT (*Compt. rend.*, **96**, 146—147).—It has been proved that the potassium thiosulphate found amongst the products of explosion of powder is not produced during the combustion, but during the analytical manipulation by the action of cupric oxide on the polysulphides which it is used to eliminate. The author now finds that zinc oxide has the same effect on potassium polysulphides, producing, besides zinc sulphide, thiosulphate, sulphate and dithionate. The author believes that although it has hitherto escaped notice the latter body is also produced when cupric oxide is used. Zinc acetate also produces traces of dithionate under similar circumstances.

The author has determined carefully the point at which dried potassium and sodium thiosulphates are decomposed when heated in nitrogen. The sodium salt begins to decompose at 400°, the potassium salt at 430°, and in both cases decomposition is complete at 470°. The heat of solution of these salts is as follows:—

			Cal.
$K_2S_2O_3$,	dried in a vacuum	(1 pt. in 90 pts. H_2O at 10°)..	−4·98
$Na_2S_2O_3$	,, at 200°	(1 ,, 50 ,, ,, 13·5°)	+1·72
,,	,, ,, 150°	(1 ,, 50 ,, ,, 7·5°)	+1·24
,,	,, ,, 358°	(1 ,, 50 ,, ,, 7·5°)	+1·48

L. T. T.

Nitrogen Selenide. By BERTHELOT and VIEILLE (*Compt. rend.*, **96**, 213—214).—The heat disengaged by the explosion of this substance was determined, and gave for NSe + 42·6 cal., or corrected to constant pressure 42·3. Nitrogen selenide is therefore formed with the absorption of heat (− 42·3) similarly to nitrogen sulphide, &c. L. T. T.

Chromates. By BERTHELOT (*Compt. rend.*, **96**, 399—405).—From a careful collation of the thermometric determinations of the solution and neutralisation of chromates, and of their reactions with acids, together with careful thermometric determinations made by himself, where these were previously wanting, the author is enabled to draw the following conclusions. In solutions of neutral potassium chromate strong acids cause the total, weak acids the partial displacement of one of the two potassium-atoms, potassium dichromate being at the same time formed. This displacement is due not so much to the smaller heat of formation of the chromates compared with other acids capable of displacing chromic acid, as to the fact that the heat of formation of the dichromate is much greater than that of the neutral chromate, and that hence there is always a great tendency to the formation of the dichromate. This tendency renders the one potassium-atom in the neutral chromate easily replaceable, and enables much feebler acids to displace a part of the alkali than would otherwise be the case. The author has already shown that a similar cause produces a tendency towards the formation of bisulphates, and enables hydrochloric and nitric acids to cause partial displacement in the solutions of neutral sulphates. L. T. T.

Heat of Formation of Glycollates. By D. TOMMASI (*Compt. rend.*, **96**, 789—790).—The heats of formation of glycollates recently determined by Forcrand (this vol., 644) agree perfectly with the numbers calculated by means of the author's law (Abstr., 1882, 1257; this vol., 144). Only in the case of zinc glycollate is there any considerable difference between the observed and calculated values, and a redetermination of the heat of formation of this salt will probably show that the first determination is inexact. The author has calculated the heats of formation of several glycollates which have not yet been made the subject of direct determinations. C. H. B.

Heats of Formation of Glycollates. By DE FORCRAND (*Compt. rend.*, **96**, 838—839).—A reply to Tommasi (see preceding Abstract).

Mutual Displacement of Bases of Neutral Salts in Homogeneous Systems. By N. MENSCHUTKIN (*Compt. rend.*, **96**, 256—259, and 381—383).—The author has taken advantage of the fact that aniline, although a base, does not react alkaline, to investigate the above subject with respect to aniline hydrochloride, nitrate, and acetate on the one hand, and potassium, sodium, and barium hydroxides, ammonia and triethylamine on the other. A weighed quantity of the aniline salt was dissolved in water, and, after the addition of phenolphthaleïn or rosolic acid as an indicator, titrated with a decinormal solution of the alkali. It is clear that alkaline reaction sets in at the moment when the alkali added can no longer displace aniline from its salt, but remains unneutralised. Each experiment was tried with a saturated solution and also a decinormal solution of the aniline salt, and the liquid in all cases remained homogeneous, no precipitation of aniline taking place. In each case the author found that no alkaline reaction became visible until sufficient alkali had been added to neutralise the *whole* of the acid contained in the aniline salt. As these results are in antagonism to Berthollet's theory of the partition of the acid amongst the bases, the experiments were repeated with the variation that a large excess of free aniline was used. The proportions taken were 4 and 8 mols. respectively of aniline to 1 of acid: but even then as much alkali was neutralised as was theoretically equivalent to the acid present. To be quite sure that the water in which the aniline salts were dissolved had no influence on the results, the author also experimented with alcoholic solutions, but in all cases with the same effect. The whole of the aniline is therefore displaced by the stronger bases mentioned above. This does not accord with Berthollet's theory, but is in harmony with Berthelot's principle of maximum work, as the heat of combination of these bases with hydrochloric acid are:—

KHO.	$NaHO$.	$\frac{1}{2}Ba(HO)_2$.	NH_3.	$N(CH_3)_3$.	$C_6H_5.NH_2$.
13·7	13·7	13·8	12·3	8·7	7·4

In the second communication, the author gives the results of his experiments with ammonia. In a solution containing free ammonia, phenolphthaleïn produces a purplish-violet coloration; but this colour is at once discharged by the addition to the liquid of about three times its volume of 95 per cent. alcohol: the colour is, however, reproduced by a single drop of a solution of a fixed alkali or barium hydroxide. Making use of this reaction, and using ammonium bromide, nitrate, and acetate, the author finds that in alcoholic solution or in solutions where the proportion of alcohol preponderates over that of water, ammonia is entirely replaced by potassium or sodium hydroxide, but that in aqueous solution the replacement is only partial. Using barium ethoxide, prepared by acting on barium oxide with absolute alcohol, the following results were obtained:—With an alcoholic solution of ammonium bromide, the displacement is complete. With a solution of ammonium nitrate in absolute alcohol, the first drop of barium ethoxide produces a coloration (*i.e.*, no displacement takes place), but in a few seconds barium nitrate is precipitated, and the solution becomes again colourless, and this action is repeated until all the ammonia has been replaced by barium. With a solution of the nitrate in 95 per cent. alcohol, no displacement takes place: in a solution in 80 per cent. alcohol, total displacement results, whilst with alcohol of 66 per cent. strength, only 96·8 per cent. of the ammonium is replaced by barium. This case is of special interest as showing the great influence of physical conditions on mutual displacement.

Sodium hydroxide in alcoholic solution displaces methylamine and ethylamine from their salts, but not completely; 94·4 per cent. of the former and 90·4 per cent. of the latter being replaced. L. T. T.

A Correction. By M. Traube (*Ber.*, **16**, 463).—The author divides oxidisable bodies into two classes, viz., those which are oxidised by ordinary oxygen, *e.g.*, lead, zinc; and those which can only be oxidised by nascent oxygen, *e.g.*, ammonia, alcohol, carbon monoxide. The former are termed "*autoxydabel*," and the latter "*dysoxydabel*," but as this word is apt to be mistaken for desoxydabel, the author proposes to substitute the term "*bradoxydabel*" for the second class of bodies. W. C. W.

Inorganic Chemistry.

Density of Chlorine at High Temperatures. By J. M. Crafts (*Ber.*, **16**, 457—461).—To determine the density of chlorine at high temperatures (*circa* 1300°), the author uses porcelain cylinders which are enamelled in and outside. Through the neck of the cylinder, which is only 6 mm. diameter, a capillary tube of enamelled porcelain passes which reaches nearly to the bottom of the cylinder. By measuring the volume of chlorine displaced by a known volume of air, the author finds that the density of chlorine is normal at temperatures below 1200°. W. C. W.

Phosphorescence of Sulphur. By O. Jacobsen (*Ber.*, **16**, 478).—The peculiar odour which is perceived when sulphur phosphoresces, indicates the probable existence of a lower oxide of sulphur than SO_2. Attempts to isolate such a compound were unsuccessful.

W. C. W.

Action of Sulphur on Oxides. By E. Filhol and Senderens (*Compt. rend.*, **96**, 839—841).—It is well known that when sulphur is gently heated with sodium or potassium hydroxide an alkaline sulphide and thiosulphate are formed. If the substances are in the solid condition, this change is accompanied by a considerable development of heat, but if they are in solution the thermal disturbance is practically *nil.* If solid sodium or potassium hydroxide is rubbed up with an excess of sulphur in a mortar, a mixture of polysulphide and thiosulphate is obtained in a few seconds, and the same result follows if the two substances are ground up separately and then mixed. On the other hand, the action of the sulphur on the alkaline oxides is greatly diminished by diluting the solutions of the latter. A solution containing 4 grams of soda per litre has no action on sulphur in the cold, even after several months, but attacks it readily at 100°. A solution of 0·4 gram per litre has no action on sulphur, even when boiled.

C. H. B.

New Modes of Formation of Pyrosulphuric Chloride and of Chlorosulphonic Acid. By G. Billitz and K. Heumann (*Ber.*, **16**, 483—485).—Pyrosulphuric chloride is formed by heating a mixture of chlorosulphonic acid and phosphorus pentoxide in a flask provided with a reflux condenser for some time, and then distilling the crude product. The portion boiling between 135—150° is poured into water in order to decompose the unaltered chlorosulphonic acid.

Pyrosulphuric chloride absorbs moisture from the air, and is converted into chlorosulphonic acid. This fact explains the discordant results obtained by different observers in the determination of the vapour-density of pyrosulphuric chloride. W. C. W.

Pyrosulphuric Chloride. By K. Heumann and P. Köchlin (*Ber.*, **16**, 479—483).—Ogier's statement (*Compt. rend.*, **94**, 217) that the vapour-density of pyrosulphuric chloride is half the value required by the formula $S_2O_5Cl_2$, is incorrect. The density, between 160° and 442°, varies with the temperature. Near the boiling point, the density corresponds with the theoretical value, but at 442° the observed density is only half the theoretical. W. C. W.

Crystallised Phosphates. By HAUTEFEUILLE and MARGOTTET (*Compt. rend.*, **96**, 849—852).—The sesquioxides of aluminium, chromium, iron, and uranium, or, better, the amorphous phosphates obtained by adding sodium phosphate to solutions of salts of these metals, are fused with four times their weight of metaphosphoric acid. They are thus rapidly converted into crystallised metaphosphates of the general formula $M_2O_3,3P_2O_5$, or $M'''(PO_3)_3$, which can be isolated by treating the cooled mass with boiling water. *Ferric metaphosphate* forms transparent pale greenish-yellow rhombic prisms, terminated by pyramids. *Chromic metaphosphate* forms rhombic prisms, which are generally macled, and have a yellowish-green colour by transmitted light. *Uranic metaphosphate* forms emerald-green rectangular tables, derived from rhombic prisms. *Aluminium metaphosphate* forms colourless transparent crystals, the dominant form of which is a combination of the cube with the octohedron or triakisoctohedron, the faces being frequently curved. All these metaphosphates are insoluble in water and in acids.

The crystals of the aluminium compound have a cubical appearance, and are without action on polarised light; the other three compounds crystallise in the rhombic system. It is possible, however, to prepare aluminium metaphosphate containing different proportions of the chromium, iron, and uranium compounds; all the four metals, in fact, being able to replace one another in any proportions. The dominant form of these double phosphates is a prism modified by the hemihedral faces of a tetrahedron. If the proportion of aluminium is very large, the dominant form of the crystals is a tetrahedron, but they act on polarised light. If the proportion of aluminium is small, the hemihedral faces disappear, and the crystals exhibit the macles so frequently observed on substances which crystallise in rhombic prisms of nearly 90°. It is evident, therefore, that the presence of small quantities of uranium, iron, and chromium modifies the optical properties of aluminium phosphate, although the crystals of the latter retain their cubical appearance. These metaphosphates in fact exhibit a case of isomorphism similar to that observed between pure natural aluminium leucite and artificial leucite containing iron.

Crystallised metaphosphates of nickel, cobalt, the alkalis, and other metals have been obtained in a similar manner. The alkaline metaphosphates, like the others, are insoluble in water. C. H. B.

Barium Potassium Phosphate and Barium Sodium Phosphate. By A. DE SCHULTEN (*Compt. rend.*, **96**, 706—707).—A mixture of potassium silicate and baryta-water is heated to boiling and mixed with a solution of potassium silicate containing a certain quantity of potassium phosphate. On cooling, the liquid deposits cubical crystals, which dissolve easily in dilute hydrochloric acid, leaving a residue of silica amounting to about 1 per cent. If the silica be regarded as an impurity, the crystals have the composition $KBaPO_4 + 10H_2O$.

The corresponding sodium compound, $NaBaPO_4 + 10H_2O$, is obtained in a precisely similar manner, and crystallises in regular tetrahedrons. The formation of these crystallised phosphates is due to the slow action of the alkaline phosphates on the double silicates formed by adding baryta-water to solutions of the alkaline silicates. If alkaline hydroxides are used instead of alkaline silicates, only amorphous precipitates are obtained. C. H. B.

Action of Different Varieties of Silica on Lime-water. By E. LANDRIN (*Compt. rend.*, **96**, 841—844).—Hydraulic silica, gelatinous silica, and soluble silica absorb lime gradually from lime-water, the maximum absorption varying in all cases between 36 and 38 parts of lime for one equivalent of silica. The resulting compound has approximately the composition $3SiO_2,4CaO$. The combination is most rapid in the case of soluble silica, but even in this case the maximum absorption is not effected until after several hours. Silica from hydrofluosilicic acid absorbs lime much more slowly than any of the three previously mentioned varieties. The maximum absorption after 68 days, in the series of experiments quoted, was 24·2 parts of lime per equivalent of silica. C. H. B.

The Setting of Plaster of Paris. By H. LE CHATELIER (*Compt. rend.*, **96**, 715—718).—Marignac has observed that anhydrous calcium sulphate yields with water a supersaturated solution, which afterwards deposits crystals of the hydrated salt. With plaster of Paris heated at 140° a solution can be obtained containing 9 grams of the salt per litre, or four times the amount which exists in solution under normal conditions. The author considers that the setting of plaster of Paris is due to two distinct but simultaneous reactions. The anhydrous calcium sulphate when moistened with water dissolves and becomes hydrated, forming a supersaturated solution, and this supersaturated solution deposits crystals of hydrated calcium sulphate, which gradually increase in volume and unite one with another. This progressive crystallisation continues so long as any anhydrous salt remains undissolved. This theory is supported by the fact that in practice 140° is found to be the best temperature at which to heat the plaster of Paris, and Marignac found that the most highly supersaturated solutions are formed by calcium sulphate heated to this temperature. It is found that the addition of a small quantity of sulphuric acid or sodium chloride to the water used for moistening the plaster promotes setting. Both these compounds increase the amount of calcium sulphate which can exist in the supersaturated solution.

Similar phenomena of setting, due to deposition of crystals from a supersaturated solution, are observed on moistening coarsely powdered anhydrous very soluble salts, such as sodium sulphate and carbonate, which readily form supersaturated solutions.

This theory is applicable to the setting of all mortars, especially cements and hydraulic mortars. The solubility of lime is well known. The author has recently shown that calcium aluminate is soluble, and he hopes to prove that calcium silicate is also soluble.

C. H. B.

Preparation of Cerium Oxide. By H. Debray (*Compt. rend.*, **96**, 828—830).—The cerium, lanthanum, and didymium oxalates are prepared from cerite in the usual way, and converted into nitrates. The nitrates are then fused in a porcelain capsule with eight or ten times their weight of potassium nitrate, and kept in fusion between 300—350°; at this temperature cerium nitrate is decomposed, whilst the nitrates of didymium and lanthanum are not sensibly affected even at 350°. After some hours the evolution of nitrogen oxides ceases, the fused mass is allowed to cool, extracted with water, and the residue washed with very dilute nitric acid in order to remove any traces of basic didymium nitrate; this residue, which consists of cerium oxide with traces of didymium and lanthanum, is reconverted into nitrate, which is again fused with potassium nitrate; the last traces of didymium and lanthanum are thus removed, and the cerium oxide is obtained perfectly pure. The aqueous solution of didymium and lanthanum nitrates with excess of potassium nitrate is evaporated to dryness and again fused, the temperature being allowed to rise somewhat above 350°. The small quantity of cerium nitrate previously undecomposed is now decomposed, and on treating the fused mass with water after cooling, a solution of didymium and lanthanum nitrates is obtained free from cerium. C. H. B.

Ammoniobromides and Oxybromides of Zinc. By G. André (*Compt. rend.*, **96**, 703—706).—A 30 per cent. solution of ammonium bromide is boiled for some time with precipitated zinc oxide, the liquid filtered, and allowed to cool. The compound $3ZnBr_2,6NH_3,H_2O$ is deposited in slender white needles, which melt when heated in a closed tube, and give off water and ammonia gas. They are decomposed by boiling water, a residue of zinc oxide being left. When these crystals are heated with water in sealed tubes at 200°, they are decomposed, with formation of brilliant white scales, of the composition $ZnBr_2,3ZnO,2NH_3,5H_2O$. The ammoniacal chlorides yield similar compounds. By dissolving zinc bromide in hot ammonia, and allowing the liquid to cool, Rammelsberg obtained a compound which he described as anhydrous; the author finds, however, that the compound obtained in this way has the composition $ZnBr_2,2NH_3,H_2O$. If the zinc bromide is dissolved in cold ammonia, and the solution allowed to evaporate, the compound

$$3ZnBr_2,8NH_3,2H_2O$$

is formed. If ammonia gas is passed into a concentrated solution of zinc bromide until the precipitate is redissolved, and the solution is then evaporated, slender needles of the composition

$$3ZnBr_2,10NH_3,H_2O$$

are obtained. They are easily decomposed by water, especially if heated. By treating zinc bromide in the manner described by Divers for the preparation of $2ZnCl_2,10NH_3,2H_2O$, voluminous brilliant crystals are obtained, but they lose their brilliancy unless kept in an atmosphere of ammonia. They have the composition

$$ZnBr_2,5NH_3.$$

When heated in a closed tube, they melt and give off ammonia, but no trace of water, and if exposed to the air they give off ammonia and become covered with a white pellicle. They are easily decomposed by water.

When a concentrated solution of zinc bromide is heated with zinc oxide, filtered, and allowed to cool, nacreous lamellæ of the composition $ZnBr_2,4ZnO,13H_2O$, are deposited. When a solution of zinc bromide is precipitated with an insufficient quantity of ammonia, the compound $ZnBr_2,4ZnO,19H_2O$ is obtained. By heating 30 grams of zinc oxide with 100 grams of zinc bromide, and adding a concentrated solution of ammonium bromide until the zinc oxide is completely dissolved, a white powder is obtained which has the composition $ZnBr_2,4ZnO,10H_2O$, and which, when washed with water until all soluble bromide is removed, yields the compound

$$ZnBr_2,6ZnO,35H_2O.$$

These two last compounds retain a small quantity of ammonia. If zinc oxide is heated with a concentrated solution of zinc bromide in sealed tubes at about 200°, small brilliant crystals of the composition $ZnBr_2,5ZnO,6H_2O$ are obtained. C. H. B.

Aluminium Sulphate. By P. MARGUERITE-DELACHARLONNY (*Compt. rend.*, **96**, 844—846).—Pure hydrated aluminium sulphate crystallises in rhombic prisms, which are not hygroscopic, but, on the contrary, show a marked tendency to effloresce. Analyses of these crystals, prepared by different methods from different sources, prove that they have the composition $Al_2(SO_4)_3 + 16H_2O$. The formula $Al_2(SO_4)_3 + 18H_2O$, generally given to the hydrated salt, has been deduced from analyses of impure specimens containing ferric sulphate. The presence of a small quantity of ferric sulphate in aluminium sulphate makes the latter hygroscopic. The natural aluminium sulphate found at Rio Saldana has the composition $Al_2(SO_4)_3 + 16H_2O$. C. H. B.

Ultramarine. By G. GUCKELBERGER (*Dingl. polyt. J.*, **247**, 343—348, and 383—389).—This paper gives an account of recent investigations on ultramarine. In order to obtain the pure colouring matter, the manufactured product as it is taken from the furnace is allowed to soak in cold or lukewarm water (not hot) without being previously ground. Before it is washed thoroughly, it is treated with caustic lye until it ceases to produce a black coloration when treated with an alkaline solution of lead. It is then washed with water containing ammonium acetate.

From his analyses, the author comes to the conclusion that ultramarine-blue is a definite compound of the formula $Si_6Al_4Na_6S_4O_{20}$, agreeing with that of Silber and Hoffmann. The following are the analytical results:—

	I.	II.	III.	IV.	V.	VI.
Si	19·2	19·0	19·0	19·3	19·3	19·0
Al	12·6	12·7	13·0	12·5	12·8	13·0
Na	16·5	16·8	16·5	16·8	16·1	15·9
S........	14·2	14·0	13·8	13·9	14·0	14·0
O	37·5	37·5	37·7	37·5	37·8	38·1

I—III are samples of ultramarine-blue rich in silicon from the Hirschberg works, V and VI from the works at Marienberg.

The author's results with respect to ultramarine-green agree for the most part with those of other investigators. He concludes that ultramarine-green is a definite compound of the formula $Si_6Al_6Na_8S_2O_{24}$. He then tries to prove that the different ultramarines may be best derived from a typical formula with Si_{18} and Na_{20}. Thus, for ultramarine containing large quantities of silicon, the formula

$$Si_{18}Al_{12}Na_{20}S_{12}O_{62}$$

is given, whilst for ultramarines poor in silicon the formula $Si_{18}Al_{18}Na_{20}S_6O_{70} - O_{72}$ is assumed, so that the sulphur may vary in accordance with the proportion of Si : Al. Between $Si_{18}Al_{12}S_{12}$ and $Si_{18}Al_{18}S_6$ there are the intermediate stages $Si_{18}Al_{14}S_{10}$ and $Si_{18}Al_{16}S_8$.

In the original paper the author discusses in detail the hypotheses of other investigators. D. B.

Separation of Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, **96**, 152—154; see also Abstr., 1882, 897 and 1323, and this vol., 153, 156, 293).—*From Rhodium.*—i. In very acid hydrochloric solution, gallium is precipitated by potassium ferrocyanide, whilst the whole of the rhodium remains in solution. ii. Hydrogen sulphide acts very slowly on dilute solutions of rhodium chloride in the cold, quickly at 100°. The sulphide precipitated from the slightly acid boiling solution must be dissolved in aqua regia, the nitric acid expelled, and reprecipitated by hydrogen sulphide, as it contains traces of gallium. If great exactness is required, the mother-liquors from the first precipitation must be concentrated and re-treated with hydrogen sulphide. The precipitated rhodium sulphide often contains traces of *metallic* rhodium, insoluble in aqua regia. iii. Copper precipitates metallic rhodium from its salts. The solution should be as concentrated as possible, slightly acidulated with hydrochloric acid, and digested at about 90° for several hours, the hydrochloric acid and water lost by evaporation being renewed from time to time. The reduced rhodium contains no gallium or at most the merest trace. iv. Zinc slowly precipitates metallic rhodium from acid solutions. The rhodium contains a little gallium.

Some Reactions of the Salts of Rhodium.—The usual text-books give many incorrect or incomplete data of these salts. *Hydrogen ammonium sulphide* in excess redissolves the rhodium sulphide first produced, forming an orange-red liquid: rhodium sulphide is only reprecipitated from this solution on *very* long standing. Rhodium sulphide precipitated from a boiling solution by hydrogen sulphide is insoluble in hydrogen ammonium sulphide, but the sulphide precipitated on boiling an ammoniacal solution, dissolves readily in that reagent. The solubility of rhodium sulphide in hydrogen ammonium sulphide may be used to separate that metal from copper, iron, zinc, &c. If rhodium sulphide be precipitated from ammoniacal solution by a *very slight* excess of hydrochloric acid, it is of a light reddish-brown, partially soluble in concentrated hydrochloric acid; but in the presence of hydrogen sulphide and in acid solutions, it rapidly becomes much darker in colour and insoluble in hydrochloric acid. There are thus two modifications of rhodium sulphide, the one of a chocolate-brown colour, easily soluble in hydrogen ammonium sulphide, partially soluble in hydrochloric acid; the other dark-brown, and insoluble in those reagents. L. T. T.

Crystallised Stannates. By A. DITTE (*Compt. rend.*, **96**, 701—703).—*Calcium Stannate.*—When the gelatinous precipitate obtained by adding potassium stannate to a solution of calcium chloride is heated to 100°, it is converted into small, colourless, transparent, apparently cubical crystals of the composition $SnO_2,CaO,5H_2O$. When a mixture of stannic oxide, calcium chloride, and a small quantity of calcium oxide is heated for several hours to bright redness, the mass allowed to cool, washed with water, and then treated with very dilute hydrochloric acid, small, transparent, square lamellæ are obtained consisting of modified cubes or octohedrons. These crystals have the composition SnO_2,CaO, are not attacked by acids, and undergo but little alteration when fused with sodium carbonate. If ammonium chloride is used instead of calcium oxide, no stannate is formed, but colourless, transparent, slender needles of stannic oxide are obtained.

Strontium Stannate. — The gelatinous precipitate obtained by addition of potassium stannate to a solution of a strontium salt, gradually changes at the ordinary temperature into small, transparent, acute rhombohedrons of the composition $2SnO_2,3S_2O,10H_2O$. Similar crystals are obtained by adding a small quantity of a dilute solution of potassium stannate to a large excess of a cold saturated solution of strontium oxide, and allowing the precipitate to stand, or heating the liquid to boiling.

Barium stannate is prepared in a similar manner from saturated solutions of barium oxide or chloride. It forms small, brilliant, nacreous plates of the composition $SnO_2,2BaO,10H_2O$.

Nickel stannate is obtained by adding potassium stannate to a concentrated ammoniacal solution of a nickel salt until a slight permanent precipitate is produced. The liquid on standing deposits small, transparent, green, apparently cubical crystals, of the composition

$$SnO_2,NiO,5H_2O.$$

Cobalt stannate is obtained in a similar manner. It forms small, transparent, rose-coloured crystals of the composition $SnO_2,CoO,6H_2O$.

Zinc stannate is also obtained in the same way. It forms colourless transparent crystals of the composition $2SnO_2,3ZnO,10H_2O$.

Silver stannate is prepared by adding potassium stannate to a solution of silver nitrate, dissolving the precipitate which is formed in ammonia, and allowing the ammoniacal solution to evaporate over sulphuric acid, when small crystals of the composition SnO_2,Ag_2O separate out. They melt at bright redness to a deep brown liquid, and are decomposed by potassium hydrogen sulphate.

Copper stannate is prepared by adding potassium stannate to an ammoniacal solution of copper salt so long as the precipitate re-dissolves, and allowing the liquid to evaporate over sulphuric acid; it forms blue crystals of the composition $SnO_2,CuO,4H_2O$. If these crystals are left in the ammoniacal mother-liquor at the ordinary temperature, they gradually change into deep blue, more bulky crystals of $SnO_2.CuO,(NH_4)_2O,2H_2O$. These crystals are but slightly soluble in cold water, which, however, gradually removes their ammonia; they dissolve in acids forming a solution which gelatinises when heated.

All these hydrated stannates are insoluble in water, but dissolve in the cold in hydrochloric or nitric acid, forming limpid solutions which gelatinise on heating. When heated, the crystals change colour, lose their water, and become insoluble in acids in the cold. The anhydrous salts are attacked by nitric acid, which dissolves out the base and leaves an insoluble residue of stannic oxide. C. H. B.

Double Chlorides of Lead and Ammonium and Oxychlorides of Lead. By G. ANDRÉ (*Compt. rend.*, **96**, 435—437).—A saturated solution of ammonium chloride dissolves lead chloride, and from such solutions the author has obtained several double salts. If 90 grams of lead chloride be dissolved in a boiling solution of ammonium chloride (200 grams of salt to 200 of water), brilliant mother-of-pearl-like flakes are deposited having the formula $4PbCl_2,22NH_4Cl,7H_2O$; from the same solution a salt, $4PbCl_2,18NH_4Cl,5H_2O$, was obtained. 50 grams of litharge, dissolved in a boiling solution of 200 grams ammonium chloride in 400 of water, gave hard crystals of

$$PbCl_2,18NH_4Cl,4H_2O,$$

and on continued boiling $PbCl_2,10NH_4Cl,H_2O$. A solution of ammonium chloride saturated in the cold, heated to boiling and treated with lead chloride, gave crystals of $2PbCl_2,18NH_4Cl,3H_2O$. If a solution of litharge in ammonium chloride be poured into a large excess of cold water, a white precipitate is produced, which, dried at 100°, has the formula $PbCl_2,PbO$. L. T. T.

Chromic Selenite. By C. TAQUET (*Compt. rend.*, **96**, 707—708).—On adding potassium selenite to a boiling solution of chromic chloride containing free hydrochloric acid, a bulky pale-green precipitate is thrown down, which, after drying at about 120°, forms a greenish-grey mass of the composition $Cr_2(SeO_3)_3$. It dissolves in hot concentrated hydrochloric acid, and is almost insoluble in water, but dissolves slightly when boiled with an excess of selenious acid, probably with formation of an acid selenite. The filtrate from the first precipitate deposits a further quantity of the same compound on standing. C. H. B.

Double Sulphites of Manganese and the Alkalis. By A. Görgeu (*Compt. rend.*, **96**, 376—379).—If 3 or 4 grams of manganese sulphite are dissolved in 100 c.c. of a saturated solution of sulphurous acid containing 15 to 20 grams of potassium sulphite, and the whole placed for some time under a bell-jar together with an absorbent for sulphurous anhydride, hexagonal plates of a double sulphite of the formula $K_2SO_3,MnSO_3$ are formed. The mother-liquor, concentrated on a brine-bath, either deposits a further crop of the same salt in hexagonal prisms grouped into stars, or a second salt is formed of the formula $K_2SO_3,2MnSO_3$, and crystallising in tetragonal needles.

Both salts have a slight roseate tint and oxidise rapidly in moist air. $K_2SO_3,MnSO_3$ is very stable towards water, in which it is very slightly soluble. Heated to redness out of contact with the air, both salts give off sulphurous anhydride, and leave a mixture of sulphates and sulphides together with manganous oxide: in contact with air, the residue consists of sulphates and red manganic oxide. The salt, $(NH_4)_2SO_3,MnSO_3$, crystallising in regular hexagonal plates of mother-of-pearl-like appearance, is obtained in an analogous manner to the potassium salt. It is much less easily oxidised, and withstands a temperature of 180°, although ammonium sulphite decomposes at 60°. It is very slightly soluble in cold water. Heated out of contact with the air, it leaves manganous oxide mixed with a little sulphide; in the air, manganic oxide. Sodium manganese sulphite, $Na_2SO_3,MnSO_3 + H_2O$, is obtained by mixing a 20 per cent. solution of manganous chloride with a solution of sodium sulphite saturated in the cold, and to which a little hydrogen sodium sulphite has been added. The reaction does not take place in the cold, but does so easily if the solutions are heated to about 80°. With a weaker solution of the alkaline sulphite, a salt, $Na_2SO_3,4MnSO_3$, was formed; it is only very slightly soluble in cold water. The action of water on the salt, $Na_2SO_3,MnSO_3 + H_2O$, is peculiar; although boiling water scarcely alters the crystals, cold water at once decomposes them, crystals of $MnSO_3 + 3H_2O$ being formed. This, which is identical with the action of water on $MnSO_3 + H_2O$, already described by the author, leads him to consider the double salt as a compound of anhydrous sodium sulphite with monohydrated manganous sulphate, or $Na_2SO(MnSO_3,H_2O)$. This compound, like $MnSO_3,H_2O$, only loses its water of crystallisation above 150°.

L. T. T.

Mineralogical Chemistry.

Aluminium Borate from Siberia. By A. DAMOUR (*Compt. rend.*, **96**, 675—677).—This mineral was found in the pegmatite of the Soktoui mountains, near Adoun-Tchilon, in Eastern Siberia. It occurs in regular, transparent, almost colourless prisms, with a hardness between that of quartz and that of felspar; sp. gr. = 3·28. The crystals appear to have no cleavage, and break with a vitreous fracture. In the blowpipe flame, the mineral becomes white and opaque, and gives the green coloration characteristic of boric acid. It dissolves completely in microcosmic salt or in borax, forming a colourless bead, and it turns blue when moistened with cobalt nitrate solution and strongly heated. The mineral is not attacked by nitric or hydrochloric acid, but after being strongly heated, it dissolves slowly in strong sulphuric acid at 300°, solution being facilitated by the addition of a small quantity of hydrofluoric acid. When heated to bright redness, it loses 33 per cent. of its weight, but still contains boric acid. The mineral has the composition B_2O_3, 40·19; Al_2O_3, 55·03; Fe_2O_3, 4·08; K_2O, 0·70 = 100·00. The oxygen ratio of $Al_2O_3 : B_2O_3$ is 1 : 1, and the formula of the mineral is therefore Al_2O_3,B_2O_3. The name *Jérémérewite* is proposed for the new mineral in honour of its discoverer, M. Jéréméiew.

C. H. B.

Melilite and Melilite Basalts. By A. STELZNER (*Jahrb. f. Min.*, **2**, Beil. Bd., 369—439).—In a previous communication, the author states that a certain constituent of some basalts is not nepheline, as previously supposed, but melilite, or at least something very nearly related to it. In the present paper the details are more fully recorded.

The imbedded melilite crystals are short quadratic prisms, four- or eight-sided, with rounded prism faces, but well-formed basal planes. The crystals show not unfrequently cleavage parallel to the basal plane; they are seldom quite free from inclosures; colourless or very pale yellow, some of the darker crystalline granules are slightly dichroic. Oblique sections show, in patches, a very fine striation parallel to the basal plane.

By means of a mercuric iodide solution, the melilite was isolated from a sample of undecomposed basalt. Sp. gr. = 2·29; an analysis gave :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.
44·76	7·90	5·16	1·39	27·47	8·60	2·65	0·33	1·42 = 99·68

These numbers show that the crystalline mineral of sp. gr. 2·99, which is a principal constituent of the basalt from Hochbohl, near Owen, and which was formerly considered as nephiline, is in reality melilite. Following are remarks on the accompanying minerals, and descriptions of the localities (Swabian Alps, N.E. spurs of the Bohemian Forest), and modes of occurrence of the melilite basalts. Melilite occurs also in nephiline and leucite basalts, as in those of

Hegan, the Kaiserstuhl, the Fichtelgebirge, Erzgebirge, the Eifel, Vesuvius, &c. The author concludes:—The described rocks differ from the known members of the basalt family, since in them melilite plays the part usually taken by plagioclase, nephiline, leucite, or a glassy matrix, and in accordance with Zirkel's nomenclature of the basalts, should be called melilite basalts. The petrographic character of the melilite basalts may be described thus: olivine, melilite, and, lastly, augite, are the predominating constituents; the olivine and part of the augite are macroscopically, and part of the melilite microscopically developed, while most of the augite and melilite forms the microscopically crystalline ground-mass; in the latter are also nephiline, mica, magnetite, perowskite, chromite, and occasionally apatite and hauyn. Chemically regarded, they are extraordinarily basic, and are characterised by the action of hydrochloric acid, which decomposes 92—95 per cent. of the rock with separation of gelatinous siliça. The name nepheline-picrite is no longer needed, since it is founded on a false determination of melilite. Melilite basalts occur mostly as veins or masses in other rocks; but much more frequent are nepheline and leucite basalts containing melilite. H. B.

The Volcanic Rocks of the Cape Verde Islands. By C. Dölter (*Jahrb. f. Min.*, 1883, **1**, Mem., 396—405).—This paper gives the results of the author's geological investigations at the islands of S. Antâo, S. Vicente, S. Thiago, and Mayo. After a topographical and geological description of the islands, follows a petrographical description of the various rocks. The older eruptive rocks occurring are: fozaite, diabase, and diorite. A complete analysis of fozaite from S. Vicente is given under I. The rock consisted of orthoclase, with some plagioclase and elaeolite, together with pyroxene, hornblende, and magnetite, and occasionally analcime. Titanite and hauyn were absent. An analysis of the felspar is given under II, and of the pyroxene under III:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO_2....	55·76	67·82	41·08	39·64	50·41	49·66	56·36	47·99
Al_2O_3 ..	21·61	16·99	9·11	16·98	29·00	21·19	27·01	13·30
Fe_2O_3 ..	1·65	1·03	17·18	6·61	—	4·91	0·17	11·32
FeO	4·09	—	15·99	9·31	—	5·37	—	10·39
CaO	2·26	0·19	6·09	10·58	13·41	6·78	8·57	5·14
MgO....	0·74	—	2·29	6·65	—	2·59	—	6·16
K_2O	5·34	7·89	—	3·09	6·57	0·81	0·67	—
Na_2O ...	6·94	4·11	8·70	5·95		7·02	8·11	6·60
H_2O	3·49	1·75	—	1·32	0·61	1·32	—	—
Total ...	101·88	99·78	100·44	100·13	100·00	99·65	100·89	100·90

The *diabase* described is a dark rock, rich in augite, from S. Vicente. The complete analysis of the rock is given above (IV). The analysis of the felspar, with sp. gr. = 2·7, which forms 60 per cent. of the rock, is also given (V). The rock described by the author as *diorite* consists of 66—68 per cent. of plagioclase (analysis VII) and 11—13 per cent. of pyroxene (analysis VIII), with 7—8 per cent. of biotite and 15 per cent. magnetite. Titanite and apatite are accessory constituents. The complete analysis gave the figures under (VI).

Among the younger eruptive rocks, leucitite, phonolite, tephrite, basanite, basalt, nephelinite, nepheline basalt, limburgite, and pyroxenite, were distinguished.

The *leucite* consists principally of leucite together with hauyn. A complete analysis of the rock gave the following results (IX):—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	SO_3.	Cl.	Loss.	Total.
IX.	48·46	21·81	2·17	3·75	4·58	0·68	5·86	8·41	2·97	0·13	2·08	100·90

Phonolite occurs very frequently. The results of an analysis of the porphyritic variety from S. Thiago are given under X. The analysis of the portion soluble in HCl (XI), of the interspersed augite (XII), of the augite of the ground-mass (XIII), and of the felspar (XIV), are also given. XV is an analysis of hornblende phonolite from Mayo. The hornblende isolated from it had the composition given under XVI:—

	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.
SiO_2....	53·80	47·56	43·99	38·15	62·42	50·05	39·96
Al_2O_3...	23·59	25·17	14·01	25·96	18·99	20·98	16·91
Fe_2O_3...	3·57	2·11	2·09	11·08	trace	2·12	3·42
FeO....	1·88	—	8·84	6·17	—	4·05	8·86
CaO ...	2·26	2·96	19·42	4·53	1·52	4·12	15·94
MgO ...	0·87	0·84	10·88	1·99	trace	1·65	6·03
K_2O....	4·77	4·07	—	—	8·16	6·19	—
Na_2O ..	9·05	12·41	1·09	7·91	8·66	8·43	9·01
SO_3	trace	trace	0·30	4·97	—	—	—
Cl......	—	—	—	—	—	—	—
H_2O....	1·50	4·88	—	—	—	4·35	—
Total ..	101·29	100·00	100·62	100·76	99·75	101·94	100·13

The *tephrites* have a grey colour and a crystalline structure. Besides the augite, a separate analysis of which is given (XVII), mica, and less frequently hornblende, occur. Hauyn is frequently present as an accessory constituent; titanite very rarely. An analysis of the rock from S. Antâo is given under XVIII:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
XVII.	47·44	23·71	6·83	3·53	6·47	1·95	3·34	6·40	1·73	101·40
XVIII.	37·20	16·93	15·42	3·55	14·81	6·89	—	5·06	—	99·51

The *basanites.* The author distinguishes two groups:—basanite rich in plagioclase, and basanite rich in nepheline. A representative of the latter group from S. Thiago, gave the following analytical results (XIX):—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
XIX.	43·09	17·45	18·99	9·76	4·63	1·81	5·02	0·33	101·08

Basalt.—The analysis of a compact basalt from S. Thiago, gave the results under XX. The augite (XXI), and the plagioclase (XXII), were also separately analysed :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
XX.	42·65	15·35	6·46	8·19	11·96	7·14	1·47	5·02	1·28	99·52
XXI.	42·15	21·51	3·79	9·43	12·28	7·55	—	2·98	—	99·69
XXII.	48·88	28·92	1·52	—	11·29	1·01	0·61	6·79	—	99·02

Nephelinite.—Two varieties of this rock were analysed, a yellowish-grey nephelinite rich in hauyn (XXIII), and another with plagioclase as an accessory constituent (XXIV), both from the island of S. Antâo :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	SO_3.	Cl.	H_2O.	Total.
XXIII.	41·09	18·35	14·89	8·79	1·78	3·14	8·79	2·11	0·45	1·26	100·65
XXIV.	46·95	21·59	8·09	7·97	2·49	2·04	8·93	—	—	2·09	100·15

Nepheline Basalt.—Analyses were made of this rock from S. Antâo (XXV), and of the olivine (XXVI), and the augite (XXVII), isolated from it :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	SO_2.	CO_2.	H_2O.	Total.
XXV.	40·13	16·17	5·71	8·89	10·99	7·05	1·22	4·10	—	5·97	0·97	101·20
XXVI.	29·37	—	—	20·79	—	26·56	—	—	20·52	—	2·68	99·92
XXVII.	40·81	14·24	7·89	5·95	16·01	14·35	—	0·61	—	—	—	99·86

Limburgite. — A variety containing plagioclase was analysed (XXVIII), and separate analyses were made of the augite (XXIX), and olivine (XXX) :

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Loss.	Total.
XXVIII.	41·12	10·17	2 60	9·82	14·90	13·34	2·27	6·61	0·67	101·50
XXIX.	46·94	5·67	6·18	5·43	17·83	14·18	—	1·83	—	98·06
XXX.	39·33	1·24	—	15·63	—	43·88	—	—	—	100·08

Pyroxenite is the name the author gives to younger eruptive rocks which consist mainly of augite and magnetite in a glassy basis, but as this term is applied quite differently by Dana and Sterry Hunt, it would be desirable to adopt some other name, such as "augitite." Analyses of this rock from S. Vicente (XXXI), and of the portion (32 per cent.) soluble in hydrochloric acid (XXXII) are given:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
XXXI.	40·95	24·19	9·51	10·99	5·11	1·89	5·69	1·62	99·95
XXXII.	42·91	24·06	11·26	12·10	2·01	1·92	4·89	0·85	100·00

The *volcanic fragmental rocks* are not described at any length, the only analysis given being that of phonolite-pumice from S. Antâo, the results obtained being:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	$MgO.SO_2$.	Total.
51·61	24·72	1·10	0·49	7·89	8·35	5·62	trace	99·78

B. H. B.

The Silurian Rocks of Christiana. By W. C. Brögger (*Jahrb. f. Min.*, 1883, **1**, Mem., 388—396).—Two principal groups of the eruptive rocks, in the Silurian district, near Christiana, may be distinguished.—1. Hornblende granites, syenites, granitites, and mica syenites; 2. Augite syenites and elaeolite syenites. The felspar of the augite syenite is mostly monoclinic, but in the augite syenite from Fredericksvärn and other localities, and in the elaeolite syenite the felspar is found optically to be triclinic. The following are the analytical results obtained:—I being an analysis of the monoclinic felspar of the augite syenite from Byskoven; II, the analysis of the anorthic felspar:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.	Sp. gr.
I.	62·42	22·68	0·58	3·23	0·22	4·42	6·48	100·03	2·623
II.	61·35	22·37	trace	4·66	0·04	4·97	6·59	99·98	2·63

The eruptive rocks occurring as masses and veins, may be arranged according to age, as follows:—1. Quartz-porphyry; 2. Augite porphyry; 3. Augite syenite; 4. Elaeolite syenite; 5. Hornblende granites, granitites, syenites, &c.; 6. Felspar porphyry. This order is not absolute for the veins, as exceptions seem to occur. As the oldest eruptive rock, the quartz porphyry, is spread over the faulted silurian strata, all the above-mentioned eruptive rocks are not only younger than the silurian strata, but also younger than the act of their faulting.

B. H. B.

The Eruptive Rocks near Tryberg in the Black Forest. By G. H. Williams (*Jahrb. f. Min.*, 1883, **2**, Beil. Bd., 585—634).—The district petrographically examined forms a circle with a radius of about 6 miles round Tryberg. Rather more than half of this consists of gneiss, while the remaining (northerly) portion is composed of granitite. Both are traversed by numerous veins of a quartz-porphyry; whilst the basic eruptive rocks belong exclusively to the gneiss district.

No special attention was paid to the gneiss, as it has already been described by Vogelgesang.

The *granitite* might be termed the "Tryberg" granitite, as it attains here its most typical development. It is a crystalline mixture of felspar, quartz, and biotite. The analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	Total.
69·19	14·12	1·64	1·71	1·58	1·66	8·45	1·81	0·15	100·31

Sp. gr. = 2·39.

The eruptive rocks, traversing the gneiss and granitite, may be divided into two groups: A. The acid rocks, including (1) the vein granite, (2) the quartz-porphyry, and B. The basic rocks including (3) mica-syenite porphyry, (4) mica diorite, (5) nepheline basalt.

1. The *vein granite* occurs in all varieties of colour and grain, but the mineralogical composition remains almost constant, being a mixture of biotite and muscovite micas with felspar and quartz.

2. *Quartz-porphyry.*—Whilst the vein granite traverses the granitite in all directions, the quartz-porphyry occurs in parallel fissures coursing N.N.E.—S.S.W. It has always a compact red ground-mass in which crystals of quartz and felspar are embedded: the red colour due to iron is highly characteristic. The results obtained on analysis were:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	P_2O_5.	Total.
77·68	12·95	0·96	0·37	0·30	0·21	4·37	3·18	0·71	trace	100·73

Sp. gr. = 2·597.

This analysis is thoroughly typical for acid quartz-porphyry, and agrees very well with that made by Rosenbusch of similar rocks in the Vosges. The small amount of magnesia and iron oxide proves that mica and bi-silicates are almost entirely absent, so the rock is apparently an almost pure mixture of quartz and felspar.

3. *Mica Syenite Porphyry.*—These basic rocks occur in the gneiss in the form of veins, but are never met with in the granitite. They are of a brownish-red to bright grey colour. Under the microscope the porphyritic structure is very distinctly seen; the rocks presenting a reddish ground-mass containing numerous crystals of biotite and felspar. Zircon and apatite are common, but titanite, so common, according to Rosenbusch, in the mica-syenite-porphyry of the Vosges, is not to be found in any of the analogous rocks in the Black Forest. No conclusion can be arrived at with regard to the nature of the felspar of the ground-mass, as unfortunately the author did not make a complete analysis, and neither the sp. gr. (2·667) nor the percentage of SiO_2 (64·68 per cent.) is sufficient evidence. There can be little doubt, however, that it is a soda-potash-felspar, of which the system is not determined, and hence it is also uncertain whether the rock belongs to the syenites or diorites.

4. *Mica Diorite.*—The compact ground-mass of this rock has a violet-grey colour, and contains hexagonal plates of mica and crystals of felspar. By means of the microscope, quartz is found in considerable quantities; apatite, zircon, and iron pyrites occur as accessory constituents. The magnesia mica is especially interesting, as it con-

tains the small needles which have attracted the attention of so many observers. Sandberger has recently proved that similar needles in the mica of Bodenmais and Ontario (Abstr., 1883, 34) are composed of pure TiO_2. The author examined these needles microscopically, and arrived at the conclusion that they consist of rutile; he confirmed this view by a qualitative analysis, applying Schönn's method (*Zeits. Anal. Chem.*, **9**, 41), which gave most satisfactory results. A complete analysis of the rock gave:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
64·94	17·50	0·69	3·94	2·59	2·83	3·44	3·11	1·36	100·40

5. *Nepheline Basalt.*—This forms a small vein in the granitite. The rock consists of a compact grey mass containing crystals of olivine. Under the microscope, the compact ground-mass appears as an irregular mass of augite and olivine crystals with magnetite and a colourless cementing material, consisting principally of nepheline. Hauyn is entirely absent.

The *Porphyry Tuff.*—This is quarried at the Kesselberg and used as road metal. The colour is a reddish to yellowish-grey. The sp. gr. is 2·619. The analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3 and FeO.	CaO and MgO.	K_2O.	Na_2O.	H_2O.	Total.
82·56	11·57	0·86	trace	0·10	0·10	4·37	99·26

B. H. B.

Manganese in Sea-water and in Certain Marine Deposits.

By Dieulafait (*Compt. rend.*, **96**, 718—721).—Specimens of sea-water were collected in each degree between Marseilles and New York, and were allowed to remain in the bottles for a month, at the end of which time manganese could easily be detected in the deposit which had formed. Similar results were obtained with sea-water from the Indian Ocean, the Red Sea, and the eastern part of the Mediterranean. The manganese exists in the sea-water in the form of carbonate. At the surface, where the water is in contact with the air, the manganese carbonate is precipitated and oxidised. In shallow seas the manganese oxide becomes mixed with the suspended matter in the water; but in the deep sea, where there is no other suspended matter, the manganese oxide sinks slowly to the bottom, and it is at the greater depths that deposits, concretions, &c., rich in manganese, are found. The "Challenger" soundings showed that the bottom of the deeper parts of the Atlantic is covered with a mud closely resembling the chalk of the Paris basin, and hence it has been concluded that this chalk is a deep-sea formation. But the calcium carbonate is really precipitated in the superficial layer of the sea which is in contact with the atmosphere, and sinks to the bottom under the action of gravity, the only condition necessary for the formation of chalk with all its special characteristics being that the calcium carbonate shall be deposited in a part of the sea which remains free from other suspended matter for a very long interval of time. Now these conditions are also the most favourable for the accumulation of manganese oxide, and it might therefore be expected that deep-sea chalk would contain a notable quantity of manganese. The author was able to detect manganese easily in 0·5 gram of 50 different specimens of chalk from different parts of the Paris basin, and finds that this chalk contains more than 50 times as much manganese as the coloured marbles of the Pyrenees and of Italy. If the fact thus proved for the Paris basin is equally true for the chalk of all countries, it will no longer be necessary to ascribe the origin of the manganese oxide at the bottom of the sea to submarine volcanic exhalations, or to submarine springs. It must be regarded as separated from the sea-water itself by ordinary chemical changes. C. H. B.

Organic Chemistry.

Aldehydethyl Chloride and Behaviour of Acetals with Alcohols at a High Temperature. By A. BACHMANN (*Annalen*, **218**, 38—56).—By the action of phosphorus pentachloride on diethylacetal, a substance is obtained identical in boiling point with the aldehydethyl chloride obtained by Wurtz and Frapolli on saturating a mixture of alcohol and aldehyde with hydrochloric acid. The reaction is represented as follows: $C_2H_4(OEt)_2 + PCl_5 = C_2H_4Cl.OEt + EtCl + POCl_3$. In order to identify the aldehydethyl chloride, the author studied the action of sodium methylate on it, and obtained methylethylacetal and dimethylacetal, the latter being produced by the replacement of the ethyl-group of the former by methyl, thus: $C_2H_4(OMe).OEt + MeOH = C_2H_4(OMe)_2 + EtOH$. It was found that the aldehydethyl chloride obtained by Wurtz's process underwent the same reaction. Similarly, by the action of phosphorus pentachloride on methylethylacetal, aldehydethyl chloride is formed, according to the equation $CHMe(OEt).OMe + PCl_5 = CHMeCl.OEt + MeCl + POCl_3$, which was also converted by sodium methylate into methylethylacetal. Aldehydethyl chloride is decomposed slowly on keeping, but more rapidly on warming with evolution of ethyl chloride; the author was unable to obtain any other definite product of the decomposition.

Röse, in the course of his work on the ethereal salts of carbonic acid, demonstrated that a less complex alcoholic group is replaced by a more complex group when the ethereal salts are heated with the alcohols at the temperature of the water-bath.

In the present paper, the author, starting from the above-mentioned result obtained in the decomposition of aldehydethyl chloride by sodium methylate, has studied the action of various alcohols on various acetals, and proves that in this case the more complex is replaced by the less complex group. Thus methylethylacetal, when heated with methyl alcohol, yield a considerable quantity of dimethylacetal, whilst dimethylacetal with ethyl, propyl, isobutyl, and isoamyl alcohols, yield but traces of the mixed acetal containing two different alcoholic groups. Similarly diethylacetal with methyl alcohol is converted for the greater part into dimethylacetal, but is practically unaltered by propyl and amyl alcohols. The following table contains the various acetals identified by the author:—

Substances.	Boiling point.	Sp. gr.
Dimethylacetal, $C_2H_4(OMe)_2$	65°	0·8655
Methylethylacetal, $C_2H_4(OMe)(OEt)$	85	0·8433
Diethylacetal, $C_2H_4(OEt)_2$	104	0·8210
Methylpropylacetal, $C_2H_4(OMe)(OPr^a)$	103—105	—
Ethylpropylacetal, $C_2H_4OEt(OPr^a)$	124—126	—
Methylbutylacetal, $C_2H_4OMe(OC_4H_9)$	125—127	—
Dipropylacetal, $C_2H_4(OPr^a)_2$	142	—
Methylamylacetal, $C_2H_4(OMe)(OC_5H_{11})$	141—144	—
Diamylacetal, $C_2H_4(OC_8H_{11})_2$	194—196	0·8012

The author further studied the action of various alcohols on ethyl oxide and various ethereal salts of acetic and butyric acids, but was unable to effect the replacement of one alcoholic group by another.

V. H. V.

Vapour-tensions of Ethylamine and Diethylamine Hydrosulphides. By ISAMBERT (*Compt. rend.*, **96**, 708—710).—Diethylamine hydrosulphide was prepared by the direct union of the acid and base in barometer tubes. The white crystalline hydrosulphide is at once formed even in presence of excess of diethylamine. The maximum vapour-tension of this compound is 150 mm. at 10°, and increases with the temperature in the ordinary manner. Under the same conditions, diethylamine has a vapour-tension of 120 mm. only. In presence of excess of diethylamine, the solid hydrosulphide has a vapour-tension of 120 mm. only, and this equality persists at all temperatures between 6° and 22°, whatever the relative proportions of the solid hydrosulphide and the liquid diethylamine. It is evident, therefore, that the vapour-tension of diethylamine hydrosulphide in presence of excess of diethylamine obeys the same laws as the vapour-tension of ammonium cyanide in presence of excess of hydrocyanic acid.

With ethylamine hydrosulphide different results are obtained. The first bubbles of hydrogen sulphide are absorbed by the ethylamine without formation of any crystalline hydrosulphide and without any alteration in the vapour-tension of the ethylamine; but as the quantity of hydrogen sulphide increases, the liquid becomes viscous, the vapour-tension diminishes, and eventually, in presence of excess of hydrogen sulphide, all the ethylamine is converted into a white solid crystalline hydrosulphide, which can be volatilised in the tube and condenses in crystals resembling those of ammonium dihydrosulphide, but having a vapour-tension of only 48 mm. at 13°. An excess of hydrogen sulphide, in presence of the crystalline hydrosulphide, obeys the law which the author has proved to hold good in the cases of ammonium dihydrosulphide and phosphine hydrobromide (Abstr., 1881, 674).

It is evident that although the vapour-tension of a mixture of a solid compound with one of its liquid constituents is equal to the vapour-tension of the liquid constituent alone in the case of a solid only slightly soluble in the liquid, yet where the solid compound is very soluble in the liquid constituent, the vapour-tension of the mixture may be much lower than that of the liquid, and in fact resembles the vapours given off by liquids dissolved in one another in considerable proportions. C. H. B.

The Hydroxylamine Reaction. By E. NÄGELI (*Ber.*, **16**, 494—500).—The following compounds were prepared by adding solutions of hydroxylamine hydrochloride and soda to an alcoholic solution of the substance under investigation. If the mixture is turbid, sufficient alcohol is added to render the liquid clear. After an interval of eight days, the alcohol is removed by evaporation, the residue is diluted with water, and extracted with ether. The compound which remains on distilling off the ether, is purified by distillation or by recrystallisation:—

Mesityloxime, $C_6H_{10}\colon N.OH$, is an oily liquid, boiling with partial decomposition between 180° and 190°. It is insoluble in water, but dissolves in alkalis, mineral acids, alcohol, ether, carbon bisulphide, benzene, and light petroleum. On boiling with dilute acids, it splits up, liberating hydroxylamine.

Phoronoxime, $C_9H_{14}\colon N.OH$, crystallises in plates, which melt at 48° and boil at 218°. It is soluble in alcohol, ether, benzene, light petroleum, carbon bisulphide, and in acids and alkalis.

Allylacetoxime, $C_6H_{10}\colon N.OH$, is a mobile liquid (b. p. 187·5°) of unpleasant penetrating odour. It unites with bromine to form a dibromide, $C_6H_{11}Br_2NO$.

Suberoxime, $C_7H_{12}\colon N.OH$, is a pale yellow liquid, which boils without decomposition. It has an odour like peppermint.

Camphoroxime, $C_{10}H_{16}\colon N.OH$, crystallises in white needles, which melt at 115° and boil at 249—254°. It resembles camphor in many of its physical properties. It is not decomposed by strong hydrochloric acid at 110°.

Hydroxylamine has no action on menthol, borneol, benzyl alcohol, or benzyl ether.

A crystalline compound, $HO.N\colon CH.CCl\colon NOH$ (m. p. 151°), is obtained by the action of hydroxylamine on chloral hydrate. It is soluble in water and in alcohol. W. C. W.

Synthesis of Oxaline Bases. By B. RADZISZEWSKI (*Ber.*, **16**, 487—494).—*Glyoxalethyline* (paroxalmethyline), $C_4H_6N_2$, is best prepared by slowly adding an aqueous solution of aldehyde ammonia to a solution of glyoxal. The mixture must be well cooled. After some hours the liquid is evaporated on a water-bath and the residue distilled, the portion boiling above 160° is fractionated. The liquid which comes over between 260° and 270° solidifies on cooling, and is obtained in a pure state by recrystallisation from benzene. The aqueous solution of glyoxalethyline and of the bases derived from it, resemble the alkaloïds in their reactions with tannic, picric, and phosphomolybdic acids.

Oxalmethylethyline, $C_4H_5MeN_2$, prepared by acting on an ethereal solution of glyoxalethyline with methyl iodide and distilling the product with potash, is a liquid boiling at 205°; sp. gr. at 11° = 1·0051. It is soluble in water, alcohol, and ether. With copper sulphate, it gives a blue precipitate soluble in excess, and it also forms precipitates with mercuric chloride, silver nitrate, tannic, picric and phosphomolybdic acids, which are soluble in boiling water. With zinc chloride and hydrochloric acid, oxalmethylethyline forms transparent prisms (melting at 137°). It also yields a crystalline platinochloride, and forms a crystalline compound with methyl iodide, $C_4H_5MeN_2,MeI$.

Oxalethylethyline, $C_4H_5EtN_2$, obtained by dissolving glyoxalethyline in ethyl bromide and decomposing the solution with potash, is identical with Wallach's oxalethyline boiling at 212°.

Oxalpropylethyline, $C_4H_5PrN_2$, is a colourless liquid (b. p. 224°; sp. gr. 0·9641). It forms a crystalline platinochloride and a deliquescent crystalline compound with propyl bromide.

Glyoxalpropyline, $C_5H_8N_2$, prepared from propylaldehyde and glyoxal, crystallises in prisms soluble in alcohol, water, ether, and cold benzene. It melts at 79°, and boils at 268°, and resembles the preceding bases in its chemical properties.

Oxalmethylpropyline has not yet been obtained. When the product of the action of methyl iodide on glyoxalpropyline is treated with soda, the crystalline compound, $C_5H_7MeN_2,MeI$, is produced.

Oxalethylpropyline, $C_5H_7EtN_2$, is a colourless liquid of sp. gr. 0·9813 and boiling at 220°. It is soluble in water, alcohol, and ether, and yields crystalline double salts with platinum and zinc chlorides.

β-Oxalpropylpropyline, $C_5H_7PrN_2$, is identical with Wallach's oxalpropyline. W. C. W.

Preparation of Ethers of Trichloracetic Acid. By A. CLERMONT (*Compt. rend.*, **96**, 437).—To a mixture of molecular equivalents of the acid and the respective alcohol, a mol. of sulphuric acid is added. The mixture becomes heated and coloured. On cooling and adding water, the ether separates. *Propyl trichloracetate* boils at 187°; *amyl trichloracetate* at 217°. L. T. T.

Action of Carbonic Oxide on a Mixture of Sodium Acetate and Sodium Isopentylate. By W. POETSCH (*Annalen*, **218**, 56—84).—By the action of carbonic oxide on a mixture of sodium acetate and isopentylate on hexylmethylketone, the author obtained the sodium salts of formic, isoamylacetic, and oxyethenylamylacetic acids.

Hexylmethylketone, formed by the action of sodium acetate on sodium isoamylacetate thus, ($C_7H_{13}NaO_2 + C_2H_3NaO_2 = CO_8H_{26}O + Na_2CO_3$), is a transparent, oily liquid, having an ethereal odour (b. p. 208—210°; sp. gr. = 0·8430). Traces of another ketone, probably dihexylketone, were obtained, possibly formed from two molecules of isoamylacetic acid, $2C_7H_{13}NaO_2 = C_{14}H_{26}O + Na_2CO_3$.

Isopentylacetic acid, obtained by the decomposition of the sodium salt by sulphuric acid, is a colourless transparent liquid (b. p. 212—213°; sp. gr. = 0·926), which, as derived from fermentation amyl alcohol is probably dimethylpropylacetic acid, $CHMe_2.[CH_2]_3.COOH$. It is probably identical with Grimshaw's iso-œnanthylic acid. Its *methyl* salt is a colourless liquid of pleasant fruity odour (b. p. 166°; sp. gr. = 884), the *ethyl* salt a light mobile liquid (b. p. 182°; sp. gr. = 872); the sodium salt crystallises with 1 mol. H_2O; the calcium salt forms silky glistening crystals with 2 mols. H_2O.

Oxyethenylamylacetic acid, $C_7H_{13}\overline{Ac}O_2$, derived from isoamylacetic acid by the replacement of a hydrogen-atom by the grouping oxyethenyl, $CH_2 : COH$, was obtained as a viscid mass, having a strong acid reaction; its *methyl* salt boils about 250°, its *sodium* salt crystallises in leaflets containing 2 molecules water, its *calcium* salt is an insoluble precipitate. V. H. V.

A Non-saturated Acid Isomeric with Itaconic Acid. By R. Fittig and F. Roeder (*Ber.*, **16**, 372—373).—By the action of sodium ethylmalonate on ethylene bromide, an ethereal salt is produced, which on saponification yields a crystalline acid of the composition

$$CH_2 : C_2H_2(COOH)_2.$$

The acid unites with hydrobromic acid to form bromethylmalonic acid melting at 116°. It melts at 139°, and at a higher temperature splits up into carbonic anhydride, a volatile acid, and a neutral compound (probably isocrotonic acid, and butyrolactone).

W. C. W.

Tetric Acid. By W. Pawlow (*Ber.*, **16**, 486—487).—Pure dry ethyl monobromomethacetoacetate is converted into a crystalline mass when it is heated at 100° for six hours in a sealed tube. Ethyl bromide and carbonic acid are formed, and the crystalline product consists entirely of *tetric acid:* 15 grams of ethyl methacetate yielded 7·8 grams of tetric acid (m. p. 189°; b. p. 262°). W. C. W.

Action of Water on Lactones. By R. Fittig (*Ber.*, **16**, 373—374).—The true lactones, as well as the delta lactones, yield an oxy-acid when boiled with water. But as these oxy-acids themselves pass into the lactones on boiling with water, a state of equilibrium is soon established, and the formation of acid ceases, unless the free acid is neutralised, and in this way protected from decomposition. The quantity of acid which is formed from the lactones is very small. It is larger for lactones of simple structure containing a small number of carbon-atoms, than it is for the lactones of more complicated constitution. W. C. W.

Conversion of Unsaturated Acids into the Isomeric Lactones. By R. Fittig (*Ber.*, **16**, 373).—Unsaturated acids are converted into lactones by boiling for a short time with strong sulphuric acid diluted with an equal volume of water. On prolonged boiling, a further change takes place, acids of the same composition, but of a higher molecular weight, being formed, *e.g.*, phenylbutyrolactone is converted into a crystalline dibasic acid, $C_{20}H_{20}O_4$. W. C. W.

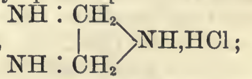
Conversion of Nitrils into Imides. Action of Hydrocyanic Acid and of Ethylene Cyanide on Hydrochloric Acid and

Alcohol. By A. Pinner (*Ber.*, **16**, 352—363).—*Ethyl formimide*, $NH : CH.OEt$, is prepared by passing dry hydrochloric acid gas into a mixture of absolute hydrocyanic acid diluted with four times its volume of ether (free from water and alcohol), and the calculated amount of ethyl alcohol. The liquid, which should be surrounded by a freezing mixture, is stirred continuously during the reaction. When fumes of hydrochloric acid begin to escape, the operation is complete. As the heat evolved during the crystallisation of the substance is sometimes sufficient to cause its decomposition, it must be thoroughly well cooled in a freezing mixture and continuously stirred during the solidification of the hydrochloride. This salt forms beautiful transparent prisms. On exposure to the air, the crystals decompose spontaneously, forming ammonium chloride and other products. They are decomposed by heat, splitting up into ethyl chloride, ethyl formate, formamidine hydrochloride, and a small quantity of ammonium chloride. Ethyl formimide hydrochloride is decomposed by alcohols thus: with ethyl alcohol it yields ammonium chloride and ethyl orthoformate, $CH(OEt)_3$, and with methyl alcohol it gives ethyl dimethyl orthoformate, $(MeO)_2CH.OEt$ (b. p. 115—120°). Amyl alcohol acts slowly on the imido-ether, forming ethyl diamylorthoformate, $(C_5H_{11}O)_2CH.OEt$ (b. p. 255°). *Formamidine hydrochloride* is produced by the action of alcoholic ammonia on ethyl formimide hydrochloride, and by substituting methylamine or aniline for ammonia dimethyl formamidine, $NMe : CH.NHMe$, diphenyl formamidine, $NPh : CH.NHPh$, are obtained. *Dimethylformamidine hydrochloride* is a deliquescent salt crystallising in plates which dissolve freely in alcohol and water.

The action of alcohol on ethyl formimide hydrochloride explains why the author and Klein (*Ber.*, **10**, 1870; **11**, 4, 764, 1475, 1825) failed in their previous experiments to isolate ethyl formimide.

When hydrochloric acid gas is passed into a well-cooled mixture of ethylene cyanide and alcohol diluted with three times its volume of absolute ether, crystals of *ethylsuccinimide hydrochloride*,

$$C_2H_4(OEt)_2(NH)_2,2HCl,$$

are deposited. This salt is sparingly soluble in alcohol and ether. It is decomposed by water into ammonium chloride and ethyl succinate, and by the action of alcoholic ammonia it is converted into succinamidine hydrochloride, $NH : CH_2(NH_2).CH_2(NH_2) : NH,2HCl$. On recrystallisation from water, this body splits up into succinimidine hydrochloride and ammonium chloride,  $\begin{array}{l} NH : CH_2 \\ \;\;\;\;\;| \\ NH : CH_2 \end{array} \Big> NH,HCl$; succinimide hydrochloride crystallises in colourless plates soluble in water. It is decomposed by heat. W. C. W.

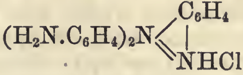
Colouring Matters of the Safranine Series. By R. Nietzki (*Ber.*, **16**, 464—478).—*Phenosafranine*, $C_{18}H_{16}N_4$, obtained by Witt by oxidising a mixture of aniline (2 mols.) and paraphenylenediamine (1 mol.) or of equal molecules of aniline and paradiamidodiphenylamine, forms beautifully crystalline salts. The hydrochloride crystallises in flat needles of a green colour which dissolve in hot water, but are insoluble in hydrochloric acid. The nitrate, which resembles the hydrochloride, is insoluble in dilute nitric acid. The sulphate crystallises in steel-blue needles. The platinochloride, $(C_{18}H_{16}N_4)_2,H_2PtCl_6$, forms golden plates. Phenosafranine is coloured green by strong sulphuric acid, and blue by hydrochloric or, rather, dilute sulphuric acid. On reduction with zinc-dust, it is converted into diamidodiphenylamine. On heating a mixture of phenosafranine hydrochloride with sodium nitrate and acetic anhydride, diacetylsafranine hydrochloride, $C_{18}H_{14}N_4\overline{Ac}_2,HCl$, is deposited in brown plates possessing a metallic lustre. This salt is insoluble in the ordinary solvents, and is decomposed by heat without melting. It dissolves in a weak alcoholic solution of soda, yielding a violet solution from which it is reprecipitated by acids. On boiling an aqueous solution of phenosafranine with hydrochloric acid and dilute sodium nitrite solution, the colour of the solution changes from red to blue, and, when gold chloride is added, a blue crystalline precipitate having the composition $C_{18}H_{14}(N\colon NCl)(N_3HCl) + 2AuCl_3$, is deposited. A green diazo-compound appears to be formed when sodium nitrite is added to a solution of phenosafranine in sulphuric acid which has been diluted with water until the blue solution changes to green.

Two *diethylsafranines*, $C_{18}H_{14}N_4Et_2$, can be obtained, viz., α, by oxidising a mixture of diethylparaphenylenediamine and aniline (2 mols.), and β, by oxidising a mixture of aniline, diethylaniline, and paraphenylenediamine. The two isomerides bear a close resemblance to each other; they are distinguished by the greater solubility of the hydrochloride of the β variety. The hydrochlorides and the platinochlorides, $(C_{18}H_{14}N_4Et_2)_2,H_2PtCl_6$, form green needles. The hydrochloride of the acetic derivative, $C_{18}H_{13}Et_2N_4\overline{Ac},HCl$, crystallises in needles of a brown colour; these are decomposed by boiling with dilute sulphuric acid, splitting up into diethylsafranine and acetic acid. The solution of the diazo-derivative of diethylsafranine has a greenish-blue colour; the platinochloride forms black needle-shaped crystals, $C_{18}H_{11}N_5Et_2,H_2PtCl_6$.

Tetrethylsafranine, $C_{18}H_{11}Pt_4N_4$, obtained by the oxidation of a mixture of equivalent proportions of diethylparaphenylamine, diethylaniline, and aniline, yields a very soluble hydrochloride and a sparingly soluble zinc chloride crystallising in large golden plates. The platinochloride has the composition $(C_{18}H_{12}Et_4N_4)_2,H_2PtCl_6$. Tetrethylsafranine colours wool and silk violet. It is not attacked either by nitrous acid or by acetic anhydride. The green colouring matter which Bindschedler (*Ber.*, **12**, 207) obtained by oxidising a mixture of dimethylaniline and dimethylparaphenylenediamine at the ordinary temperature, yields a crystalline hydriodide, $C_{16}H_{19}N_3,HI$, and a platinochloride, $C_{16}H_{19}N_3,H_2PtCl_6$. By the action of stannous chloride on the zinc chloride a crystalline zinc double chloride is obtained, which has the composition $C_{16}H_{21}N_3H_2Cl_2 + ZnCl_2$, probably

$$HCl,NMe_2,C_6H_4.NH.C_6H_4.NMe_2HCl + ZnCl_2,$$

tetramethyldiamidodiphenylamine zincochloride. When phenosafranine is heated with 4 parts of strong hydrochloric acid at 170° it splits up into ammonia and a substance which closely resembles aniline-black. Safranine is regarded by the author as a derivative of triphenylmethane,



$$(H_2N.C_6H_4)_2N{<}\begin{array}{l}C_6H_4\\ |\\ NHCl.\end{array}$$

W. C. W.

Mononitroresorcinol. By A. Fèvre (*Compt. rend.*, **96**, 790—792).—The action of 1 mol. amyl nitrite on 1 mol. monosodiumresorcinol in the cold yields the sodium derivative of mononitroresorcinol, and when this is treated with sulphuric acid, *mononitroresorcinol* is liberated. It crystallises from dilute alcohol in dull golden-yellow needles of the composition $C_6H_3(NO_2)(OH)_2 + H_2O$, which become brown at 112° and are completely carbonised without melting at 148°. Mononitroresorcinol is very soluble in alcohol and in acetone; less soluble in water, chloroform, and ether; insoluble in benzene and carbon bisulphide. It dissolves without alteration in concentrated hydrochloric and sulphuric acids in the cold. Nitric acid converts it into trinitroresorcinol. In neutral solutions, it yields an intense green coloration with ferrous salts and with iron filings. The potassium, sodium, and silver salts of mononitroresorcinol crystallise with difficulty; the salts of ammonium, calcium, and the heavy metals are amorphous powders, the colour of which varies from orange-red to black. When reduced by means of stannous chloride and hydrochloric acid, mononitroresorcinol yields an amidoresorcinol, apparently identical with the paramidoresorcinol described by Weselsky; it would appear, therefore, that in mononitroresorcinol the NO_2-group occupies the para-position. The action of nitrous anhydride on an ethereal solution of mononitroresorcinol yields *dinitroresorcinol*,

$$C_6H_2(NO_2)_2(OH)_2,$$

which forms small yellow tables melting at about 142·5°. Bromine-water converts mononitroresorcinol into dibromonitroresorcinol, $C_6HBr_2(NO_2)(OH)_2 + 2H_2O$; this crystallises in large brilliant yellow needles which decompose at about 138° without melting. It dissolves readily in alcohol and acetone, but is less soluble in ether, acetic acid, and cold water. It is not attacked by alcoholic potash. When dibromonitroresorcinol is treated with nitric acid, hydrobromic acid is liberated and dinitromonobromoresorcinol, $C_6HBr(NO_2)_2(OH)_2$, is formed. This compound, which differs from that obtained by the action of bromine on the dinitroresorcinol previously described, crystallises from boiling alcohol in large orange-yellow needles; these melt at 193° and are soluble in acetone, but almost insoluble in water, and dissolve with difficulty in boiling alcohol. With the alkalis and with baryta, it forms beautiful dichroic crystals which detonate violently when heated. The acetyl-derivative forms yellow transparent prisms which melt at 135°.

Nitroresorcinol gives colour reactions with all the phenols. With resorcinol and sulphuric acid, it yields *diazoresorufin*, which is prepared commercially at Basle by this method. It also yields coloured products with the aromatic amines. The compound formed by its action on dimethylamine is violet, and is closely analogous to the product obtained by Meldola by the action of resorcinol on nitrosodimethylaniline. The action of nitroresorcinol on aniline acetate in alcoholic solution yields a compound which has the composition $C_{18}H_{14}N_2O_2$, and is formed in accordance with the equation $2PhNH_2 + C_6H_3(NO)(OH)_2 = C_{18}H_{14}N_2O_2 + NH_3 + H_2O$. This compound crystallises from chloroform in small brilliant steel-blue needles which melt at about 238—239°. It does not dissolve in alkalis nor in dilute acids. It dissolves without alteration in nitric acid or hydrochloric acid forming a blue solution, and in sulphuric acid forming a green solution. C. H. B.

An Aromatic Tribromhydrin. By A. Colson (*Compt. rend.*, **96**, 713—715).—When boiling mesitylene is mixed with 6 atoms of bromine, a black oil is produced which is distilled under reduced pressure; the fraction which passes over between 210° and 220° under a pressure of 0·01 m. is strongly cooled for some time, the solid portion separated by filtration, and purified by recrystallisation from boiling alcohol. The crystals thus obtained are elongated birefractive needles belonging to the monoclinic or triclinic system. They melt at 94·5°, are very soluble in benzene, dissolve readily in ether, and in their own weight of boiling alcohol, but are only slightly soluble in cold alcohol. They have the composition $C_6H_3(CH_2Br)_3$, and are the tribromhydrin of an aromatic glycerol, the acid corresponding to which is the trimesic acid described by Fittig. This compound is decomposed by prolonged ebullition with 30 times its weight of water with formation of a very soluble compound, the concentrated solution of which when distilled with excess of hydrobromic acid, yields the original bromhydrin.

The action of bromine on mesitylene yields also a monobromo- and dibromo-derivative, corresponding respectively with an alcohol and a glycol. The monobromo-derivative, $C_6H_3Me_2.CH_2Br$, boils at 230° under the ordinary pressure, and forms white elongated birefractive needles, which probably belong to the rhombic system. They melt at 38·3°, dissolve readily in ether and in benzene, and are easily saponified by water. The dibromo-derivative, $C_6H_4Me(CH_2Br)_2$, has already been described by Robinet. It forms elongated birefractive prisms, probably belonging to the monoclinic system, and melting at 66·4°. When boiled with water, it yields a very soluble compound, in all probability the corresponding glycol, which is reconverted into the original bromide by hydrobromic acid of b. p. 125°.

The melting points of the three bromo-derivatives increase by 28·1° for each atom of bromine introduced.

	Melting point.	Difference.
$C_6H_4Me_2CH_2Br$	38·3	28·1
$C_6H_4Me(CH_2Br)_2$	66·4	
$C_6H_4(CH_2Br)_3$............	94·4	28·1

C. H. B.

Amido-phenols. By F. Kalckhoff (*Ber.*, **16**, 374—376).—Orthohydroxyphenylcarbamide, $NH_2.CO.NH.C_6H_4.OH$, is prepared by warming a mixture of orthamidophenol hydrochloride with potassium cyanate. The crude product is purified by adding a few drops of stannous chloride to the warm aqueous solution, and passing sulphuretted hydrogen through the liquid. On evaporating the filtrate in a vacuum, colourless prisms of orthohydroxyphenyl carbamide are deposited. The crystals melt at 154° with decomposition. The substance is freely soluble in water, alcohol, ether, alkalis, and acids. The aqueous solution rapidly decomposes.

Parahydroxyphenyl thiocarbamide is deposited from boiling absolute alcohol in lustrous red plates, which melt with decomposition at 214°. It is sparingly soluble in cold water and cold alkalis, and forms a crystalline platinochloride. Parahydroxyphenylcarbamide could not be prepared by the action of mercuric oxide on the thiocarbamide, but it is easily obtained from paramidophenol hydrochloride and potassium cyanate in needle-shaped tabular crystals melting at 165°. It is soluble in water, alcohol, alkalis, and acids.

Parahydroxythiocarbanilide, prepared by the action of sodium hydroxide on an alcoholic solution of paramidophenol hydrochloride and phenylthiocarbamide, melts at 162°. It dissolves freely in strong sulphuric acid, alkalis, and alcohol. W. C. W.

Phenyl Salts of Phosphorous Acid. By E. Noack (*Annalen*, **218**, 85—113).—The author calls attention to the two structural formulæ proposed for phosphorous acid, the one symmetrical, $P(OH)_3$, based on the formation of the acid by the action of water on phosphorus trichloride, the other unsymmetrical, $O.PH(OH)_2$, which derives support from the fact that under normal conditions only two hydrogen-atoms can be replaced by a metallic element. As certain acids, notably sulphurous, hydrocyanic, and nitrous, form isomeric ethereal salts, it is probable that phosphorous acid would form such salts, corresponding with the two above formulæ. Phosphenyl compounds derivable from the unsymmetrical formulæ have been studied by Michaelis, whilst the author in the present communication describes derivatives of the symmetrical formulæ.

By the action of phenol on phosphorus trichloride in excess of that required by the equation $PCl_3 + PhOH = PCl_2.OPh + HCl$, and separating the products by fractional distillation, *mono-* and *diphenylphosphoryl chlorides* and *triphenyl phosphite* are obtained. The former, $PCl_2.OPh$, is a colourless strongly refractive liquid, which boils at 216° with partial decomposition. It fumes in the air, and reacts with water with formation of a cloud of hydrochloric acid; sp. gr. = 1·348.

The latter, $PCl(OPh)_2$, similar in appearance to the above compound, boils at about 295° under a pressure of 731 mm.; sp. gr. = 1·221. The author was unsuccessful in his attempts to obtain by the action of water on the chloride mono- and diphenyl-phosphorous acids; only a mixture of phenyl and phosphorous acid in various proportions was formed. Under certain conditions phenol and phosphorous acid crystallised out together as a molecular compound similar in appearance and analogous in composition to the substances formed by the direct addition of sulphurous and carbonic anhydride to phenol.

Triphenyl phosphite, $P(OPh)_3$, is best prepared by the action of 1 mol. of phosphorous trichloride on rather more than 3 mols. of phenol, according to the equation $PCl_3 + 3PhOH = P(OPh)_3 + 3HCl$. It is a colourless, odourless, strongly refractive liquid, boiling above 360°, easily soluble in alcohol and benzene, insoluble in, but gradually decomposed by water into phenol and phosphorous acid; sp. gr. = 1·184. It solidifies into a glassy mass when exposed to the cold produced by a mixture of solid carbonic anhydride and ether.

Michelhaus has shown that by the action of bromine on triethyl phosphite no hydrobromic acid, but ethyl bromide and diethyl phosphoryl bromide are formed. On repeating the experiment with triphenyl phosphite, it is found that *triphenylphosphoryl dibromide* is obtained thus: $P(OPh)_3 + Br_2 = P(OPh)_3Br_2$. This substance crystallises in small right-angled tables, which gradually deliquesce into an oily mass. It is decomposed by cold water, yielding triphenyl phosphate [$Br_2P(OPh)_3 + H_2O = O\colon P(OPh)_3 + 2HBr$], identical with the product of the action of phenol on phosphorus oxychloride.

The readiness with which triphenyl phosphite combines with bromine and takes up oxygen points to its possessing a symmetrical constitution. The decomposition of the compounds obtained by the author, especially monophenylphosphorous acid into phenol and phosphorous acid, points to the combination of the oxygen to the phenyl-group, while the isomeric phosphenylic acid decomposes into benzene and metaphosphoric acid, $PhPO(OH)_2 = PhH + HPO_3$.

A short comparison of the compounds obtained by Michaelis and by the author is appended below.

Michaelis' Compounds.	*Noack's Compounds.*
Phosphenyl oxychloride, $O\colon PPhCl_2$, from $PPhCl_2 + O$; b. p. 258°, sp. gr. 1·375, slowly decomposed by water into phosphenylic acid, $PhPOCl + 2H_2O = PhPO(OH)_2 + 2HCl$.	Monophenylphosphoryl chloride, $PCl_2.OPH$, from PCl_3 and $PhOH$; b. p. 216°, sp. gr. 1·348, decomposed violently by water, $OPhPCl_3 + 2H_2O = OPhP(OH)_2 + 2HCl$.
Phenol phosphenyl chloride, $O\colon PPh(OPh)Cl$, from $PhPOCl_2 + PhOH$; b. p. over 360°; decomposed by boiling water into crystalline phenolphosphenylic acid, $PhPOCl.OPh + H_2O = O\colon PPh(OH).OPh + HCl$.	Diphenylphosphoryl chloride, $P(OPh)_2Cl$, from PCl_3 and $PhOH$; b. p. over 295°, fuming in the air, decomposed by ice thus: $(OPh)_2PCl + H_2O = (OPh)_2P(OH) + HCl$.
Phosphenylic acid, $O\colon PPh(OH)_2$, from $PhPCl_4 + H_2O$; crystalline stable compound, m. p. 158°, soluble in water, and crystallising from the solution.	Monophenylphosphorous acid, $P(OPh)(OH)_2$; very unstable, decomposing at once with water into phosphoric acid and phenol.

Michaelis' Compounds.	*Noack's Compounds.*
Phenol phenylic acid, $O:PPh(OPh).OH$, from the corresponding chloride; crystalline stable substance, m. p. 57°, sparingly soluble in water.	Diphenylphosphorous acid, $P(OPh)_2.OH$; very unstable, decomposed at once by water into phosphoric acid and phenol.
Diphenyl phosphenylate, $O:PPh(OPh)_2$, from $PhPCl_4 + 3PhOH$; crystalline, m. p. 63·5°, not decomposed by water.	Triphenyl phosphite, $P(OPh)_3$, from $PCl_3 + 3PhOH$; not crystalline, decomposed by water into phosphoric acid and phenol.

The difference of constitution of these compounds is sufficiently elucidated by their difference of behaviour. V. H. V.

β-Naphtholtrisulphonic Acid. By I. LEWINSTEIN (*Ber.*, **16**, 462—463).—The trisulphonic acid of β-naphthol is formed by the action of 4 parts of fuming sulphuric acid on 1 part of naphthol at 135°. Better results are obtained by first preparing the monosulphonic acid by the action of chamber acid (2 parts) on naphthol (1 part) at 70—80°. Two parts of sulphuric acid are again added, and the mixture is heated at 120°. Finally 2 parts of fuming acid (containing 40 per cent. of trioxide) are added, and the temperature is raised to 150°. The trisulphonic acid does not form a colouring matter with diazoxylene, although it produces beautiful dyes with analogous diazo-compounds. W. C. W.

Dinitroanthraquinone and Diorthamidoanthraquinone: a New Method of Preparing Anthrarufin. By H. ROEMER (*Ber.*, **16**, 363—374).—The author has recently shown (*Ber.*, **15**, 1786) that a mixture of orthonitranthraquinone and two other nitro-compounds is produced by the action of nitric acid on a solution of anthraquinone in strong sulphuric acid. That portion of the mixture which is least soluble in alcohol consists of [1 : 4] dinitroanthraquinone. This compound is best prepared by adding 10 g. of nitric acid (sp. gr. 1·48) to 10 g. of anthraquinone dissolved in strong sulphuric acid. The crude product is repeatedly treated with boiling alcohol, until a portion of the residue gives a pure blue colour on the addition of stannous chloride mixed with excess of potash [1 : 4]. Dinitroanthraquinone dissolves readily in boiling nitrobenzene, and is deposited from the solution on cooling in yellow needles, which melt at a temperature above 300°. It is insoluble in water, sparingly soluble in alcohol, ether, benzene, chloroform, acetic acid, and cold xylene. It dissolves in strong sulphuric acid at 100°, and is deposited from the solution on cooling. If the liquid is heated more strongly, gas is evolved, and on pouring the solution into water a purple precipitate is thrown down, which is soluble in ether. The dinitroquinone is not attacked by alkalis, but it is converted into [1 : 4] *diorthamidoanthraquinone* by treatment with a warm mixture of stannous chloride and potash. This compound does not melt at 300°; at a higher temperature it sublimes, forming red needles with metallic lustre. It is sparingly soluble in water, alcohol, ether, benzene, acetone, and chloroform, but dissolves in strong hydrochloric acid, forming a colourless liquid, which deposits a white crystalline salt. It dissolves in dilute hydrochloric acid, yielding a red solution, which deposits the free amido-compound. By the action of acetic anhydride and sodium acetate, a diacetic derivative,

$$C_{14}H_6O_2(NH\overline{Ac})_2,$$

is obtained, which is insoluble in cold hydrochloric acid, but is decomposed by boiling with hydrochloric acid. [1 : 4] Dinitroanthraquinone is also produced by treating a solution of orthomononitroanthraquinone in sulphuric acid with strong nitric acid.

Diorthamidoanthraquinone may be converted into anthrarufine by the diazo-reaction. Water is added to a solution of the diamidoanthraquinone in excess of strong sulphuric acid, until the amido-compound is reprecipitated; potassium nitrite is then poured into the cold mixture until the precipitate redissolves, and the liquid is diluted with water and boiled for an hour. The precipitate of crude anthrarufine thus obtained is treated with hot baryta-water, in order to remove erythro-oxyquinone, and on decomposing the insoluble barium compound with hydrochloric acid, anthrarufine is obtained as a crystalline precipitate. In the preparation of anthrarufine, it is not necessary to use pure dinitroanthraquinone, as the presence of a small quantity of orthonitroanthraquinone does not interfere with this reaction.

W. C. W.

Occurrence of Methyl Alcohol in the Products of the Dry Distillation of Colophony. By W. KELBE and J. LWOFF (*Ber.*, **16**, 351—352).—The aqueous liquid obtained in the destructive distillation of colophony contains in addition to acetic acid and higher acids of the acetic series, small quantities of methyl alcohol. About 50 grams of methyl alcohol were obtained from 150 kilos. of colophony. W. C. W.

Bases of the Pyridine and Quinoline Series. By O. DE CONINCK (*Ann. Chim. Phys.*, **5**, 433—532).—This long memoir is divided into three parts. In the first part the author gives a brief account, with references, of the results of previous researches on the pyridine and quinoline bases, under the heads: history; synthesis; bases having the same composition; oxidation products; hydrogenation products; physiological action; isomerism of leucoline and quinoline. The second part contains an exhaustive *résumé* of the author's researches on the fractional distillation of crude quinoline; the oxidation and hydrogenation of β-lutidine and β-collidine; hydrates of the pyridine bases; fractional distillation of oils from brucine; and the physiological action of the pyridine and quinoline bases. Most of these researches have already appeared in the *Compt. rend.* and *Bull. Soc. Chim.*, and abstracts of them are contained in this Journal, 1881 and 1882. The conclusions drawn by the author from these experiments are summarised as follows:—

1. The distillation of cinchonine with potash furnishes two series of isomeric pyridine bases, amongst which are notably two lutidines and

two collidines. The first fractions contain also methylamine and some fatty ethers, *e.g.*, amyl acetate.

2. The distillation of brucine with potash furnishes a small quantity of neutral products, and some pyridine bases, amongst others β-lutidine and β-collidine. The lower fractions contain a pyridine base insoluble in water, probably another lutidine.

3. β-Lutidine has been separated from its isomeride and obtained pure by a process generally applicable to the purification of the bases of these series.

4. β-Lutidine aurochloride undergoes modifications similar to those of the pyridine platinochloride, hitherto regarded as characteristic. By regulated oxidation, this base yields *nicotianic acid*. β-Lutidine is a violent poison, more energetic in its action than β-collidine.

5. The existence of β-collidine (b. p. 196°) in the crude quinoline from cinchonine and brucine goes to prove definitely the isomerism of the pyridine bases derived from cinchonine and brucine with those derived from coal-tar and Dippel's animal oil.

6. By partial oxidation, β-collidine furnishes *homonicotianic acid*, $C_5H_3MeN.COOH$, analogous to toluic acid. By further oxidation this acid becomes *cinchomeronic acid*, $C_5H_3N(COOH)_2$, hence β-collidine may be regarded as *methyl-ethyl-pyridine*. By oxidation in hot solutions, β-collidine furnishes *nicotianic acid*. β-Collidine is an antipyretic, a powerful poison, and has the curious property of preventing the reflex movements of the cornea.

7. The crude quinoline from cinchonine contains *tetrahydroquinoline*, the first instance of a hydroquinoleic base derived from an alkaloïd containing oxygen; its existence confirms Wischnegradsky's hypothesis that the pyridine and quinoline bases exist in the alkaloïds as hydrides.

8. Tetrahydroquinoline from cinchonine is isomeric with that formed by synthesis, and, like it, is transformed into quinoline by very feeble oxidising agents. It constitutes an intermediate term between the two series of bases formed simultaneously in the destructive distillation of cinchonine with caustic potash.

9. Quinoline from cinchonine is mixed with tarry products, from which it can be easily separated. Purified from these products and from its homologue lepidine, which it retains with much persistence, it boils at 236—237° (corrected) under a pressure of 775 mm. In certain cases of fever (hectic fever) quinoline acts more powerfully than quinine.

10. Pyridine appears to be as violent a poison as β-lutidine. The author concludes, from a careful review of the formation and properties of pyridine and quinoline and their homologues, and of their oxidation-, reduction-, and substitution-products, that all the known facts are in favour of Körner's theory that pyridine is correctly represented by Kekulé's formula for benzene, $(N)'''$ taking the place of one of the $(CH)'''$ groups, and that quinoline is similarly related to naphthalene, the higher homologues of these bases being formed, like the homologues of benzene and naphthalene, by the introduction of lateral chains of methyl, ethyl, propyl, &c., in place of hydrogen.

J. M. H. M.

Isomerism in the Pyridine Series. By O. de Coninck (*Compt. rend.*, **96**, 437—439).—The author has applied Anderson's reaction to the separation of the isomeric lutidines. The lutidines contained in crude quinoline prepared from brucine cannot be separated by fractional distillation. They were therefore converted into the platinochlorides, the precipitate boiled for an hour and a half and filtered; a yellow precipitate was at once formed, and the filtrate deposited a red salt slightly admixed with the yellow; the filtrate from this gave a homogeneous red salt. The yellow salt fuses at 204—205°, and is the *modified* salt $(C_7H_9N)_2,PtCl_4$. The red salt fused at 179—180°, and gave numbers agreeing with the platinochloride of normal lutidine, $(C_7H_9N)_2,H_2PtCl_6$. The platinochloride of β-lutidine fuses above 200°. The author has also studied the effect of boiling the platinochlorides of the quinoline series with water. They are, however, much more stable than those of the pyridine series.

The isomerides of the pyridine series also appear to be distinguishable by the varying rapidity with which they unite with the alcoholic iodides. L. T. T.

Poisonous Principles contained in certain Lupines. By C. Arnold (*Ber.*, **16**, 461—462).—A resinous compound may be obtained from diseased lupines by digesting them for two days at a temperature of 40—50° in a 2 per cent. solution of sodium hydroxide. The extract is neutralised with acetic acid and concentrated by evaporation at a temperature not exceeding 60°. After carefully precipitating the legumin with strong acetic acid, the filtrate is gently evaporated to a syrup and poured into 15 times its volume of 90 per cent. alcohol. The resinous precipitate is slowly soluble in water. A dose of 10 grams of this substance causes cattle to exhibit the usual symptoms of poisoning by diseased lupines. W. C. W.

Physiological Chemistry.

Nutrition by Fat. By A. Lebedeff (*Zeitschr. Physiol. Chem.*, **6**, 139—154).—The subject of the absorption of fat has been frequently worked at, but recently rather from a histological than a chemical point of view. In regard to the origin and disposal of fats the researches of Radziszewski, Subbotin, and Hoffmann, especially, have been accomplished. The author undertook the investigation of the chemical composition of the fats and fatty tissues of the animal body, in order if possible to arrive at conclusions as to the nature of the processes through which by oxidation fats are formed or changed from one kind into another. He succeeded in devising a new and exact method of quantitative analysis for fats, details of which are given in this article, and likewise as regards the fattening of the goose in arriving at certain facts concerning the nutrition of geese, and the composition of the fat contained in the maize employed for this purpose. Goose fat obtained from the liver as used in the manufacture of *pâté de foie gras* yielded in two analysis, per cent.—

1. 61·4	oleic acid.	31·1	palmitic and
2. 61·2		32·8	stearic acids.

Strassburg, it is well known, is the centre of this industry. The mode of feeding these birds is such as to produce a fatty infiltration and degeneration of the liver to an extraordinary extent in a very short time; the liver is presumably the fat-forming organ. The author has proved that on feeding with richly nitrogenous matters poor in fat, no fat is present in the liver. In geese which had fed upon peas for six weeks only trifling deposits of fat were found in the omentum and around the intestines, whilst the slightly developed liver yielded lecithin, but no fat. From these results, he conjectures that the fat is derived from the maize and not from the albuminates of the foods, the maize fat differing, as shown by comparative experiments, from the liver fat only in its larger proportion of olein.

Maize fat. Percentage results of two analyses:—

1. 76·5	oleic acid.	12·4	palmitic and
2. 79·9		13·9	stearic acids.

Peritoneal fat from investment of liver (commercial *foie gras*)—

1. 64·3	oleic acid.	24·6	palmitic and
2. 66·2		27·3	stearic acids.

Intestinal fat of geese fed with peas—

1. 66·4	oleic acid.	29·9	palmitic and
2. 63·7		31·3	stearic acids.

Mesenteric fat (suet) of ditto—

68·7	oleic acid.	21·2	palmitic and stearic acids.

The author gives the results of similar estimations of the constituents of fat derived from various organs and regions of the human body, and also from chronic fatty liver, lipoma or fatty tumour, and an acute fatty infiltration of the lung following upon embolism caused by a compound fracture of the ribs. These lead to the conclusion that the maximum proportion of oleic acid and glycerid is formed in rapidly occurring fatty infiltration. The subcutaneous fat is the most fluid, next the intestinal fat, and most consistent is the fat of lipoma and of chronic deposits.

An attempt was made by the author to determine the mode of disposal of fats foreign to the organism, by feeding dogs upon tributyrin, but although tributyrin was digested and absorbed by the system, it appeared to be deposited in the tissues in such insignificant proportions that the results, as in the previous experiments of Radziszewski and Subbotin, were indecisive. So far, therefore, it remains undemonstrated whether fats foreign to the animal body may be deposited therein. The phenomenon of fat deposit is much more complicated than might appear at first glance. The process is probably dependent not merely on the chemical but also on the physical properties of the fat in question. D. P.

Blue Milk. By J. Reiset (*Compt. rend.*, **96**, 682—685 and 745—750).—In the dairies in some localities, notably in the district of Caux, a blue mould not unfrequently forms on the surface of the standing milk, and the same mould has been observed on the milk of ewes and goats. This mould forms in deep blue patches at the edges of the earthern pans in which the milk is kept, and also in the centre. Sometimes these patches do not increase; sometimes they develop rapidly, and after a few hours the mould covers the entire surface of the milk, the development taking place more rapidly the higher the temperature. The blue mould can be cultivated by the usual methods, but sometimes the cultivated mould is sterile, and a white mould is developed simultaneously, and appears to crowd out or destroy the blue mould. Milk on which the mould forms has a distinctly acid reaction. The freshly formed mould is free from mycelium growth, and consists of membranous tissue composed of fatty matter and transparent spherical immobile bacteria. Scattered throughout the tissue are groups of transparent striated crystalline plates, united at a common centre. These plates undoubtedly consist of fatty acids. A white mould which often forms at the same time as, and frequently more rapidly than, the blue mould, consists mainly of *Mucor racemosus* with some *Penicillium*. The nature of the blue colouring matter has not yet been determined. It is not affected by acids, and is therefore not identical with the *pyocyanine* of Fordos or the *Bacteridum cyaneum* of Schroeter (*Micrococcus cyaneus* of Cohn).

The causes of the formation of the mould are not clearly ascertained. It is not a result of aphthous fever, for the mould did not form on the milk of several cows affected with this fever. No beneficial results were obtained by bleeding several cows which were apparently too fat, nor by the administration of drinks containing sodium sulphate or sodium bicarbonate. Marchand considers that its formation is due to one of the three following causes: want of cleanliness in the dairy and dairy utensils; overfeeding; and absence of a proper proportion of lime in the soil on which the cows are pastured. The growth of the mould is, however, more probably due to the too frequent manuring of the pasturage with animal manure, and to the presence of organisms in the water drunk by the cows; these organisms are taken into the bodies of these animals, and pass into the milk, which constitutes a favourable medium for their development.

The formation of the mould may be prevented by adding 0·5 gram of glacial acetic acid to each litre of milk at the time when it is put into the pans. This quantity of acid does not coagulate the milk, and exerts no effect on the rising of the cream. The milk pans should be immersed in *boiling* water for at least five minutes, and the use of brushes and cloths should be avoided.

As the result of a large number of experiments made with delicate red and blue litmus-paper on milk immediately after it was drawn from the cow, the author finds that normal milk distinctly reddens blue litmus-paper, and the colour remains after drying. The same milk imparts to red litmus-paper a pale blue colour which gradually disappears on drying. C. H. B.

Influence of Calomel on Fermentation and the Life of Micro-organisms. By N. P. WASSILIEFF (*Zeitschr. Physiol. Chem.*, 6, 112—134).—Calomel has always held a foremost place amongst those remedies which are confidently resorted to in certain gastric and intestinal disorders, especially of childhood, but the precise nature of its beneficial effect has heretofore been unexplained. Recent works on pharmacology pass over the question, and only Köhler refers to the favourable action of the drug in typhus, cholera, dysentery, and other diseases, as being due to its germicidal and anti-fermentative qualities. No evidence in support of this view is adduced. Voit, however, had noticed in 1857 that egg-albumin and blood, when mixed with calomel, remained for days without undergoing putrefaction. Hoppe-Seyler also mentions an aseptic influence of calomel, and ascribes to it the well-known green colour of bowel discharges after an administration of calomel.

The author undertook this investigation at the request of Hoppe-Seyler, first, in regard to the behaviour of calomel towards the so-called unorganised ferments of the digestive fluids (enzymes), and secondly, as to its action on the lower organisms associated with the processes of fermentation and putrefaction.

The first series of experiments were made in order to determine the influence of calomel on the normal process of digestion in the stomach. The results proved that its presence in no way interfered with the properties of the gastric juice, fibrin being digested in the same time, whether calomel was present or not.

In the next series, the influence of calomel on the process of pancreatic digestion was investigated. It is now known that three separate ferments exist in the pancreatic secretion by which albuminates, fats, and carbohydrates are severally transformed and fitted for assimilation in the system. The object in view was to observe the possible influence of calomel on each of these respective ferments. For the purpose of experiment a watery extract was prepared from the finely minced gland, and strained through linen. It was found that the action of the ferment, by which albuminates become digested, was in no respect hindered by the presence of the calomel, and further, that there was a conspicuous absence from the liquid mixture of all products of putrefaction. In the mixture containing calomel, large quantities of leucin and tyrosin were found, whilst indol and phenol were absent. In the mixture without the addition of calomel, the two latter bodies were both present, but only traces of leucin and tyrosin. The latter solutions had likewise a putrid smell and a dirty brown colour, whilst the former was of a dark grey colour and odourless.

In some additional experiments, wherein the process was allowed to proceed in a Bunsen gasometer, and the evolved gases examined, it was found that from the mixture containing calomel, hydrogen and hydrogen sulphide were never given off, and carbonic anhydride in very considerably less amount than from the control mixtures without calomel.

These results accord with those of Hüfner (*J. pr. Chem.*, **10** and **11**), who found in his experiments on artificial digestion with pancreatic extract, that when by means of a properly arranged apparatus entrance of micro-organisms was prevented, neither hydrogen nor hydrogen sulphide made its appearance, but only carbonic anhydride. These two first-named gases have therefore nothing to do with digestion proper, but are the result of putrefactive changes, brought about by the presence of microzymes in the alimentary canal. The action of calomel on the ferment of the pancreatic juice, to which the digestion of fat is due, was next examined. The existence of such a principle has, until now, been considered highly doubtful, Paschutin's observations on this head being all that is known of the subject (W. Paschutin, *Ueber Trennung der Verdauungsfermente. Centralbl. für die Medicin. Wissensch.*, 1882).

As in putrid solutions, fats become saponified rather quickly, the problem became an important one to determine whether the transformation of fat in the alimentary canal was owing to the action of an unorganised ferment or merely to the putrescent changes going on there. The experiments made proved beyond a doubt that the action of pancreatic juice upon fat took place in the complete absence of putrefaction, and the digestion of the fat by the pancreatic extract in presence of calomel, proceeded precisely as in the instance of the experiments in regard to the peptic ferment (trypsin) of that gland.

The action of the third and remaining ferment of the pancreas, the diastatic, upon starch, and the transformation of the latter into glucose, proceeded equally undisturbed in the presence of calomel. Hence it follows that calomel, by its presence in these experiments on artificial digestion, allows the actual process of digestion to go on without injury, whilst it effectually prevents putrefactive change. And this in the same way as proved for salicylic acid by Kühn, and in the case of arsenic by Scheffer and Böhm.

The author also found the action of calomel in the process of butyric acid fermentation, which sometimes occurs in certain pathological states of the digestive system, similar to that in common putrefaction, entirely preventing it.

A further series of experiments, which need only be referred to here, were carried out to determine the disinfectant action of calomel in fluids containing bacteria and micrococci, the bacterioscopic method of Bucholtz-Wernich being used. The results showed that calomel acted as a true antiseptic and disinfectant in preventing the development of such organisms in culture fluids, and arresting their activity when already developed therein.

The difference in the influence of calomel on the process of digestion on the one hand, and on putrefactive and fermentative changes on the other, is dependent upon a distinct difference of action on organised and unorganised ferments. Whilst it does not interfere with the activity of the latter, it destroys the vitality of the former, and with it the power of inducing subsequent septic changes.

Finally, as regards the green colour of the bowel discharges witnessed after the exhibition of calomel, this was formerly attributed to the presence of bile, expelled by virtue of the assumed action of calomel as a cholagogue; this appearance was considered by Hoppe-Seyler to be due to the presence of undecomposed bile, and the author's experiments now confirm this view. Under ordinary conditions, the bile pigments, bilirubin and biliverdin, become decomposed in the intestine under the influence of putrescent changes, forming hydrobilirubin. During the administration of calomel this decomposition does not take place, and the bile pigments are expelled unchanged.

The author concludes that the therapeutic virtues of calomel are to be ascribed to its antiseptic and disinfectant properties. D. P.

Physiological Action of Coffee. By J. A. FORT (*Compt. rend.*, **96**, 793—796).—From the results of a series of experiments made upon himself, the author concludes that coffee acts on the central cerebro-spinal nervous system. In strong doses, it produces sleeplessness by exciting the brain; and, by exciting the medullary, it also produces cramp in the muscles, pains in the stomach, and disorder of the intestines, and disturbs the action of the heart. In moderate quantities, it exerts a much milder exciting action, slightly stimulating the brain, which is less inclined to sleep and works with somewhat greater activity. It also stimulates the spinal marrow, and thus produces increased activity of the different functions. As an article of diet, coffee does not diminish the waste of nitrogenous matter, but on the other hand it does not directly increase this waste, its direct action being exerted on the central nervous system. C. H. B.

Relative Toxic Power of Metallic Salts. By J. BLAKE (*Compt. rend.*, **96**, 439—441).—Rabuteau gave as the law on this subject that "the metals are more active in proportion as their atomic weight is higher and their specific heat lower." The author denies the correctness of this law, but finds that *in the same isomorphic group the effect is greater the higher the atomic weight.* The salt was introduced into the system by subcutaneous injection, and in the annexed table the third column represents approximately the weight in grams per kilogram weight of the animal which is fatal.

Metal.	Atomic weight.	Fatal dose per kilogram.
Lithium	7	1·2
Rubidium	85	0·12
Cæsium	133	0·12
Silver	108	0·028
Gold	196	0·003
Magnesium	24	0·97
Iron (FeO)	56	0·32
Nickel	58	0·18
Cobalt	58	0·17
Copper	63	0·17
Zinc	65	0·18
Cadmium	112	0·085

Metal.	Atomic weight.	Fatal dose per kilogram.
Calcium	40	0·5
Strontium	87	0·38
Barium	137	0·08
Glucinum	14	0·023
Aluminium	27	0·007
Iron (Fe_2O_3)	56	0·004
Yttrium	90	0·004
Cerium (Ce_2O_3)	140	0·005
Cerium (CeO_2)	140	0·062
Thorium	231	0·034
Lanthanum	139	0·025
Didymium	147	0·017
Palladium	106	0·008
Platinum	197	0·027
Lead	200	0·11

L. T. T.

Chemistry of Vegetable Physiology and Agriculture.

Action of Air on Yeast. By D. Cochin (*Compt. rend.*, **96**, 852—855).—The membrane surrounding yeast cells is penetrated by glucose solution, and fermentation does not commence until some time after this endosmose has taken place. If yeast is suspended in water and aërated by repeatedly decanting the liquid from one vessel to another, the aërated yeast, when added to a solution of glucose, exerts simply a diluting effect equal to that which would be produced by the same volume of water. If, however, the yeast is deprived of air, by suspending it in recently boiled water, covering the water with a somewhat thick layer of oil, and heating the liquid at 20° for periods varying from two hours to several days, the effect which it produces in glucose solution is different. After eight days' heating, the yeast is still permeable to the sugar solution, but fermentation scarcely commences; the yeast has been asphyxiated. After two hours' heating, the absorption of sugar begins, but it is only after 24 hours' heating that the phenomena are most distinctly observed. At the end of this time, under the conditions stated, the yeast has not experienced any alteration: when the yeast, thus deprived of air, is added to a solution of glucose, the latter is absorbed by the yeast cells to such an extent before fermentation commences, that the amount in solution is diminished by one-half. If a quantity of the liquid is boiled, mixed with an equal volume of alcohol and filtered, almost the whole of the sugar is found in the filtrate, only a small proportion having been converted into alcohol. From these experiments, it is evident that the transformation of sugar takes place *in the interior* of the cells, and that deprivation of air brings the cells into the condition most favourable for absorbing the sugar.

Aërated yeast, and yeast deprived of air, also show great difference in their fermentative power. The former produces an amount of alcohol much below the normal amount, and decomposes part of the sugar without converting it into alcohol. C. H. B.

Chemistry of the Maize Plant. By H. LEPLAY (*Compt. rend.*, **96**, 159—161).—The following are the results obtained by the author: i. The total nitrogen contained in the stalk and leaves of the maize is greater before the formation of the ear than after the maturity of the grain, and the quantity in the mature grain is greater than that in the stalk, leaves, or rachis. The albumin, potassic nitrate, and vegetable acids contained in the sap probably derive their origin in a similar way to that already suggested by the author (this vol., 368) in the case of the sap of the beetroot. ii. The percentage of phosphoric acid to dried substance is greater in the grains than in the leaves and stalk, and greater in these latter than in the rachis. A migration of phosphorus therefore takes place from root to grain. The quantity of base in combination with mineral acids is less than that combined with vegetable acids in all portions of the plant except the grain.

The percentage of base combined is as follows:—

	With mineral acid.	With organic acid.
Stalk and leaves	17·00	83·00
Rachis	3·30	96·70
Grain	51·00	49·00

Of the mineral acids, phosphoric acid forms about 90 per cent., and of the bases magnesia 49 per cent., lime 6 per cent., and potash 42 per cent. iii. The nitrogenous and mineral matter, during the vegetating period of the maize, passes from the root through the various organs to the grains in a similar manner as with beetroot. The author believes these various organic and mineral substances, although often present only in the minutest traces, to be essential to the proper discharge of their functions by the various organs; and that their presence in the soil in suitable form for assimilation is necessary for the growth of the plant. (See also this volume, p. 366.)

L. T. T.

Respiration of Aquatic and Submerged Aëro-aquatic Plants. By A. BARTHÉLEMY (*Compt. rend.*, **96**, 388—390).—Aquatic plants placed in a vessel containing air gradually absorb the oxygen. Aëro-aquatic plants (the experiments being carried out with members of the family *Nymphœaceœ*) growing in a deep vessel produce submerged leaves containing gas absorbed through the roots. One of these leaves supplied, under water, with water impregnated with carbonic anhydride, gave out no oxygen, but became yellow and transparent at the end of several days. A leaf of the white waterlily, the stalk of which was introduced under a bell-jar, was exposed to sunlight in water charged with carbonic anhydride; a large quantity of oxygen was disengaged, ceasing at the end of about a couple of days. Under the most favourable circumstances as much as 1 litre was emitted in three hours. The disengagement increased with the temperature up to a maximum at 35°. Scratches made on the surface of the leaf arrested the disengagement of gas, the solution of carbonic anhydride killing the green protoplasma. Two leaves, the stalks of which were connected with caoutchouc tube, gave no evolution of gas when plunged into water impregnated with carbonic acid. The author believes that in submerged plants the decomposition of carbonic acid ceases as soon as the oxygen liberated in the vessels of the plant reaches a certain tension, and that the disengagement takes place only when a leaf becomes detached; the broken surface allowing the oxygen to escape, and so preventing the increase of tension. In the case of the *Nelumbium*, the leaves of which retain a layer of air over their surface, scarcely any gas is emitted, either from their leaves or broken stalks, but if the layer of air be removed with a brush a considerable disengagement of oxygen takes place by the stalk. The *Pontederiaceæ* emit but very little gas. Tulips, hyacinths, &c., can be grown in closed vessels, where their leaves obtain no carbonic anhydride, and their whole nourishment must come from the bulb. From these and his former experiments (*Compt. rend.*, 1877), the author believes that in a normal condition the special respiration of the green parts of plants does not play as important a *rôle* in its life as is generally ascribed to it. L. T. T.

Proportion of Nitrogen in the Form of Amides, Albumin, and Nucleïn in different Feeding Stuffs. By W. KLINKENBERG (*Zeits. Physiol. Chem.*, 6, 155—165).—In ascertaining the nutritive value of vegetable foods and feeding stuffs, the quantitative determination of the different forms of nitrogenous constituents is of great importance. Some of these, as, for example, nitrates, amides, and alkaloïds, are of subordinate value in this respect, and as A. Stutzer has shown (*Jour. für Landwirthsch.*, 1880, 195, 435), only a certain amount of the proteïds are rendered available for the purpose of nutrition by the digestive ferments.

Miescher first demonstrated the existence of nitrogenous matters insoluble in the gastric juice at the ordinary temperature of the body in the nuclei of pus corpuscles, to which constituent he gave the name of nucleïn. Nucleïn combinations may be assumed to exist generally diffused throughout the animal and vegetable kingdoms; they contain, in addition to the elements C, H, N, O and S, also phosphorus as a characteristic constituent, and having a different chemical constitution from albuminates soluble in the gastric juice, doubtlessly play a perfectly distinct physiological *rôle*.

Owing to its insolubility, nucleïn is worthless for nutrition, and hence in determining the value of foods in this respect, a separate estimation of nucleïn from soluble proteïds is essential.

In his experiments, the author followed the process of A. Stutzer (*loc. cit.*, pp. 103, 190). He gives the results arrived at by this method in the separate determination of the nitrogenous constituents of feeding stuffs, such as poppy cake, earth-nut cake, rape and cotton cake, rice-meal, beer grains, and flesh-meal; the results are tabulated below, the numbers showing percentage proportions of nitrogen occurring in different forms of combinations:—

	Not precipitated by hydrated cupric oxide.	Precipitated and insoluble; and by gastric juice are rendered	
		Soluble.	Insoluble.
Poppy cake	6·49	82·17	11·34
Sesame cake	1·50	92·06	6·41
Soja-bean	9·50	86·18	4·29
Earth-nut cake	4·54	90·91	4·55
Linseed	8·50	78·89	12·58
Rape cake, 1	12·77	74·46	12·77
,, 2	8·33	79·33	12·34
,, 3	9·23	76·80	13·97
Copra cake	6·74	85·75	7·51
Cotton cake	4·35	86·97	8·68
Rice-meal, 1	7·07	72·27	20·66
,, 2	5·77	77·09	17·14
Beer grains	—	79·83	20·17
Flesh-meal	4·53	93·30	2·17

D. P.

Loss and Gain of Nitrogen in Arable Land. By P. P. Déhérain (*Compt. rend.*, **96**, 198—200).—The author gives the results of experiments extending over seven years. The crops raised were maize (for fodder) and potatoes, the different plots of land being subjected to different treatment. One series of plots was freely manured with farmyard manure, another was treated with sodium nitrate or ammonium sulphate, whilst the third was left totally unmanured.

Each crop was weighed and a sample analysed, and from the numbers thus obtained the quantity of nitrogen contained in the whole crop was calculated.

The author draws the following conclusions from the results which he obtained: i. The loss of nitrogen in arable land is due not only to its removal by vegetation, but also, and in a larger measure, to the oxidation of nitrogenous organic matter: the loss being greater the oftener the land is tilled. ii. When the land is not disturbed by tillage, the air penetrates less, oxidation is more restricted, and the gain of nitrogen exceeds the loss. iii. A soil is more easily enriched by being allowed to remain in meadow than by lavishing manure upon it.

L. T. T.

Analytical Chemistry.

Estimation of Phosphorus by the Molybdate Method. By E. TAUBER (*Landw. Versuchs.-Stat.*, **28**, 333—341).—The object of this investigation was to study the action of ammonium nitrate on the phosphomolybdate of ammonia. The formula given by Fresenius was used in preparing the nitro-molybdate solution, and the first point investigated was whether the addition of ammonium nitrate rendered the use of more or less ammonium molybdate necessary. The experiments showed that in every case a considerable saving of molybdate was effected, and that the precipitate thus produced was more flocculent and less liable to stick to the sides of the glass vessels than phosphomolybdate thrown down in the usual way; the precipitation takes place much more quickly in presence of ammonium nitrate, one hour's standing being sufficient for complete precipitation.

The solubility of the precipitate in ammonium nitrate is very little greater than in molybdate, and the former can be safely used to wash the precipitate, the first 100 c.c. of wash-water producing no sensible error, and being in nearly all cases quite sufficient for the purpose; a drop or two of nitric acid may be added with advantage, 100 c.c. of acidified dilute ammonium nitrate solution (100 grams to the litre) dissolving from 0·1—0·2 milligram of phosphoric acid.

A gradual addition of the magnesium mixture is to be recommended in all cases, with continued stirring; otherwise a small quantity of magnesium chloride is carried down with the precipitate, and the results come out too high. After heating the pyrophosphate over a Bunsen flame, a yellow tinge is generally still observable; this is due to the presence of a trace of molybdic acid, which may be completely driven off by heating over the blowpipe; the change in weight is, however, very small, and may almost be neglected. J. K. C.

Examination of Butter. (*Dingl. polyt. J.*, **247**, 350—351.)—For testing butter according to Reichert's method (*ibid.*, **231**, 478), Munier melts the sample on a water-bath, allows the melted mass to settle, and pours it on a warm filter. 2·5 grams of the filtered butter are weighed into a flask, and treated with 5 c.c. of a solution containing 20 g. caustic potash in 100 c.c. of alcohol (70 per cent.); on warming a soap is formed. The last traces of alcohol are removed by drawing air through the flask, after which the soap is dissolved in 50 c.c. water, treated with 20 c.c. dilute phosphoric acid and distilled, adding a few pieces of pumice to avoid bumping; 50 c.c. of the filtered distillate are then titrated with decinormal ammonia solution. D. B.

Recognition of Suint in Suet and other Fats. By L. MEYER (*Dingl. polyt. J.*, **247**, 305—306).—The author had occasion to examine suet adulterated with as much as 30 per cent. distilled suint; one sample contained nothing but fatty acids from suint, the quantitative determination of glycerol showing only 0·2 per cent. 1 g. of fat required 169·8 mg., and 1 g. of separated fatty acids 170·8 mg. of potassium hydroxide for saponification, so that the sample consisted exclusively of free fatty acids. The fatty acids were separated by saponification with alcoholic potash-ley, the alcohol being expelled by evaporation, and the soaps decomposed with sulphuric acid. Their melting point was 41·8°, solidifying point 40°, whilst the original fat melted at 42·1°, and solidified at 40°. The presence of cholesterin contained in the grease of sheep's wool was detected in these samples in the following manner. The separated fatty acids were saponified with caustic potash; the resulting soap was treated with ether, which extracts cholesterin. The ethereal solution was evaporated and treated with hydrochloric acid and ferric chloride, when a violet-red colour changing to blue was obtained, characteristic of cholesterin. For detecting suint in suet, the latter is saponified, the soap treated with ether, and the ethereal residue tested for cholesterin. By this method it is possible to find 5 per cent. of suint mixed with suet or other fats. D. B.

Examination of Oil-cakes. (*Dingl. polyt. J.*, **247**, 351—352.) —In order to determine whether oil-cake contains mustard seeds, Dirks recommends the oxidation of the extracted oil of mustard with an alkaline solution of potassium permanganate, and precipitation of the sulphuric acid thus formed with barium chloride. Mustard oil treated in this manner gives 31·1—31·6 per cent. sulphur; 15 grams oil-cake from black mustard gave 0·4729 barium sulphate, corresponding with 1·34 per cent. mustard oil. Oil-cake from winter rape yielded 0·17—0·19 per cent. oil of mustard; the seeds of turnips gave 0·033—0·038 per cent., and pressed cake from white mustard seeds 0·018 per cent. mustard oil. D. B.

Microscopic Investigation of Dyed Cotton Fabrics. By R. MEYER (*Ber.*, **16**, 455—457).—Cotton goods which have been dyed by means of the albumin process can easily be distinguished from articles which have been printed with soluble dyes, by means of the microscope. For example, if a piece of cotton is first treated with a solution of lead acetate, and afterwards with a chromate, the fibres are uniformly coloured. But if the goods have been printed with a mixture of precipitated lead chromate and albumin, and the colour fixed by steaming, the fibres themselves appear colourless under the microscope, but patches of coloured albumin are attached to the fibre.

W. C. W.

Estimation of the Reducing Power of Urine, and of the Extractive Matter which it contains. By ETARD and C. RICHET (*Compt. rend.*, **96**, 855—858).—In an acid solution, bromine is without action on urea, creatinine, hippuric acid, and xanthine, but attacks uric acid and extractive matter. In alkaline solution, bromine acts on all these compounds, and it is usual to estimate the volume of nitrogen given off by this reaction. Since, however, the nitrogenous organic substances other than urea either give off no nitrogen at all, or only a very small quantity, this method gives no information as to the total amount of organic matter present. Better results are obtained by estimating the reducing power of these bodies by means of a standard solution of alkaline hypobromite, which is added in excess, and the excess determined by means of a standard acid solution of stannous chloride, potassium iodide and starch being used as indicator. The difference (which is always considerable) between the reducing action of the urine on the standard hypobromite and the amount of urea calculated from the volume of nitrogen given off by the ordinary method, furnishes some measure of the reducing action of the other substances in the urine. Titration of an acid solution of the urine by standard bromine-water, the excess being determined by standard stannous chloride, gives the amount of uric acid and unoxidised extractive matter.

The ratio between the reducing action of urine on hypobromite and its reducing action on bromine-water in acid solution varies greatly for different individuals, but for the same individual oscillates between very narrow limits, even during long periods of time. In no case is it possible to predict the total reducing power of urine from the amount of urea which it contains. C. H. B.

Technical Chemistry.

A New Photographic Paper. By C. Cros and A. Vergeraud (*Compt. rend.*, **96**, 254—255).—To sensitise the paper, it is steeped in a bath of 2 grams ammonium dichromate and 15 grams glucose in 100 c.c. water, and dried: the developing solution is 1 gram silver nitrate, 10 grams acetic acid, and 100 c.c. water. The image is of a blood-red colour when dried quickly before the fire, deep brown if dried exposed to the air in bright day- or sun-light, and is blackened by hydrogen sulphide. Treated with a bath of copper and potassium sulphites, an intense neutral-black image is obtained. L. T. T.

Preparation and Purification of Carbon for Electric Lighting. By Jacquelain (*Ann. Chim. Phys.* [5], **27**, 537—554).—The author's endeavours have been directed towards the preparation of carbon having the density and conducting power of gas-carbon without its earthy and siliceous impurities. To remove these impurities, gas-carbon may be submitted to three different processes:—

1. Treatment with dry chlorine gas at a bright red heat for 30 hours. This removes silica, metallic oxides, and hydrogen, and was the process employed by the author to prepare pure carbon for Dumas' atomic weight determinations. It is more troublesome on a large scale.

2. Treatment with fused potash or soda. The alkali must not be too strong nor the temperature too high; Na_2O with three equivalents of water answers well. An immersion of three hours is gene-

rally sufficient, after which the carbon is washed with water, then with dilute hydrochloric acid, and finally with water.

3. Immersion in hydrofluoric acid diluted with twice its weight of water for 24—48 hours at a temperature of 15—25°.

The gas-carbon may be submitted to either of these processes after being cut into sticks or pencils. In order to restore the carbons, from which the impurities have been removed, to their original compactness, they are carbonised by being strongly heated for a few hours in the vapour of some heavy hydrocarbon, a portion of the carbon from the latter being deposited in the pores.

Pure graphitoid carbon may be prepared directly by passing the vapour of some heavy hydrocarbon through a fireclay tube raised to a temperature of 1000—1200° C. Two arrangements of apparatus for this purpose are described and figured by the author. Hydrocarbons with high boiling points answer best, and gas tar is the most suitable for use on a commercial scale. The author gives a table showing the comparative results obtained by using purified and unpurified natural and artificial carbon electrodes for the arc light. The steadiness of the light and durability of the carbons are in direct proportion to their hardness, density, and purity. The best results were obtained with Siberian graphite (sp. gr. 2·3, whilst gas-carbon is 1·9) purified by treatment with hydrofluoric acid, by which process the percentage of ash was reduced from 8·674 and 5·184 to 0·767 and 0·900. J. M. H. M.

Variation of the Amount of Ammonia in Rain-waters. By A. Houzeau (*Compt. rend.*, **96**, 259—260).—The author points out that the influence both of light and heat tends to reduce the amount of ammonia present in waters, and attributes this diminution not to volatilisation, but to absorption by the organic matter present in the water. L. T. T.

Preparation and Testing of Cement. (*Dingl. polyt. J.*, **247**, 257—258.)—Roth prepares cement from bauxite by mixing blast furnace slag with the requisite quantity of lime and bauxite, moulding the mixture into bricks, and burning and grinding the latter. In testing Portland cement for slag-dust, Heintzel states that the composition of the cement and impurities, especially blast furnace slag, may vary as follows:—

	Portland cement.	Slags.
SiO_2	21—25 per cent.	30—35 per cent.
Al_2O_3	3—8 ,,	10—16 ,,
Fe_2O_3	3—4 ,,	—
FeO	—	2—4 ,,
Mn_2O_3	traces	—
MnO	—	traces—4 ,,
CaO	58—64 ,,	40—50 ,,
MgO	1—4 ,,	2—6 ,,
SO_3	1—2 ,,	traces—1 ,,
S	traces—0·5 ,,	1—2 ,,
Alkalis	1—3 ,,	2 ,,

By mixing an average cement with 25 per cent. of average slag, a mixture of the following composition is obtained:—

SiO_2.	Al_2O_3.	Fe_2O_3 and FeO.	Mn_2O_3 and MnO.	CaO.	MgO.	SO_3.	S.	Alkalis.
25·4	7·4	3·6	0·8	58·0	3·0	1·4	0·6	2·0

Although the small amount of lime and the comparatively large percentage of silica, manganese, and sulphur point to the presence of impurities, the differences in the chemical composition do not suffice to condemn the cement as being adulterated with slag-dust. The sp. gr. of Portland cement is less than that of slag-dust; 1 litre cement shot loosely into the measure weighs 1288 grams, and when shaken down, 1840 grams, slag-dust 1100 and 1500 grams respectively. Under the microscope, Portland cement forms porous lava-like grey granules, slag-dust vitreous sharp-edged white or greenish granules. Pure Portland cement extemporaneously mixed with 33·3 per cent. of its own weight of water forms a liquid paste, whilst slag-dust requires 40—45 per cent.

In conclusion, it is stated that unless all the above-mentioned points are considered, it is impossible to recognise with certainty the nature of the impurity. D. B.

Hydraulic Silica and its Functions in Hydraulic Cements. By E. LANDRIN (*Compt. rend.*, **96**, 156—158 and 379—380).—If a solution of potassium silicate be decomposed with an acid, and the precipitate well washed and ignited at a dull red heat, pure silica, insoluble in acids, and to which the author gives the name *hydraulic silica*, is obtained. This silica, when mixed with two or three times its weight of lime, has the property of setting under water. In the *hydraulic cement* thus obtained, the silica becomes again soluble in acids, the quantity becoming soluble increasing with the duration of immersion. Quartz or any other hard substance may be added to the mixture without affecting its setting power. This property of the silica thus obtained is not due to its fine state of division, as the silica obtained in the preparation of hydrofluosilicic acid, although an equally fine powder, does not possess this power. Hydraulic silica plays the part of a puzzolana, removing lime from its aqueous solution, and the author considers that it is to the presence of this silica that puzzolanas owe this latter property. The author has detected the presence of hydraulic silica in many natural cements. Calcium aluminate when present in cements, although slowly dissolved by water, and thus not adding much to the *permanent* hardness of hydraulic cements, aids very considerably in the setting process by protecting the cement from the too rapid action of the water.

The second paper is a reply to Le Châtelier (see next Abstract), upholding the author's own claims to priority, especially with regard to the following points:—That hydraulic silica does not owe its peculiar properties to its fine state of division; that although insoluble in acids it is slowly acted on by lime; that it possesses the property of removing lime from water; and that the puzzolanas owe their hydraulic properties to its presence. L. T. T.

Hydraulic Silica. By H. Le Châtelier (*Compt. rend.*, **96**, 255—256).—The author contends that most of Landrin's results (see last Abstract) have been anticipated by Vicat, de Caudemberg, Rivot, Berthier, &c. L. T. T.

Relative Oxidisability of Cast and Malleable Iron and Steel. By Gruner (*Compt. rend.*, **96**, 195—197).—The author has tried the oxidising action of weak acid, sea-water, and moist air on various kinds of steel and iron. The experiments were made on plates 1 decimetre square, both surfaces being exposed. The plates were weighed carefully before and after the experiments. The loss of weight is given in grams for the 2 square decimeters of surface of the plates.

In *moist air*, ordinary steel lost 3—4 grams in eight days; that containing chromium lost more; that containing tungsten less. All kinds of cast iron were less oxidised than steels, white specular iron (containing 20 per cent. manganese) losing least.

In *sea-water*, cast iron is more strongly attacked than steel, specular iron being most acted on. In nine days, steel lost 1—2 grams; specular iron, 7 grams; Bessemer black cast iron, 3·5 grams; and cast iron containing phosphorus, 5 grams. Tempered steel is less affected than annealed; soft steels than those containing manganese or chromium; and those containing tungsten less than ordinary steels with the same percentage of carbon. These results show that the use of iron or steel containing manganese should be avoided for coating of vessels.

In *acidulated water* (0·5 per acid), grey cast iron dissolves more and white specular iron less rapidly than steel. In three days (the acid being renewed each day), Bessemer black cast iron (3—4 per cent. manganese and 1—2 per cent. silicon) lost 15·9 grams; grey cast iron containing phosphorus, 8·9; white specular iron, 1·5; pure cast iron, 0·8; soft steel, 0·1—0·4; soft carburetted steels, 0·8—1·1; manganese steel, annealed hard, 1·6; and the same steel tempered, 4·1 grams.

It is thus clear that the action of acidulated water on irons and steels does not give a true measure of their power of resisting the corroding action of the air and sea-water. L. T. T.

Plastering of Wines; Rapid Estimation of Cream of Tartar. By P. Pichard (*Compt. rend.*, **96**, 792—793).—In a saturated aqueous or alcoholic solution of potassium hydrogen tartrate containing potassium hydrogen sulphate, free tartaric acid can only liberate a quantity of sulphuric acid, not exceeding one-twelfth of the total amount. In similar solutions, potassium sulphate and chloride precipitate potassium hydrogen tartrate, the amount precipitated increasing with the quantities of the potassium salts. The chloride acts more energetically than the sulphate, precipitation being complete when the amount of the latter approaches saturation. This property may be utilised for the rapid estimation of cream of tartar in ordinary non-plastered wines. Sodium chloride produces no precipitate under similar conditions, and consequently the addition of sea-salt or sea-water to wines does not diminish the amount of cream of tartar which they contain. Calcium tartrate is less soluble in aqueous or alcoholic solutions saturated with potassium hydrogen tartrate than in the same solutions from which this latter salt has been removed. In an aqueous or alcoholic solution, equivalent quantities of free sulphuric acid and potassium hydrogen sulphate dissolve equal quantities of calcium tartrate. The addition of an excess of calcium tartrate to a saturated aqueous or alcoholic solution of potassium hydrogen tartrate containing potassium hydrogen sulphate, converts a portion of the latter salt into normal sulphate, and produces a precipitate of cream of tartar. The true cause of the diminution of cream of tartar in plastered wines is the impossibility of saturating with this salt a liquid containing a certain quantity of potassium sulphate. C. H. B.

Influence of Barley on the Fermentation Process. (*Dingl. polyt. J.*, **247**, 350).—According to Thausing, the observation of the important part which a certain amount of proteïds in barley plays is of comparatively recent origin. Richness in starch, conditions productiveness of barley, and in order to obtain a wort which will form a good nutrient for yeast, the presence of a sufficient quantity of albuminoïds is absolutely necessary. During the germination of barley, the proteïds act on the starch, and from them the peptones are formed. Barley containing little proteïd matter gives malt, the starch in which it is difficult to convert into sugar. According to Lintner, barley should contain at least 10·5 per cent. proteïds to produce a good beverage. D. B.

Defecation of Beet-juice with Strontium Saccharate. (*Dingl. polyt. J.*, **247**, 304—305.) — For defecating beet-juice or other saccharine juice, Scheibler uses strontium saccharate, separated at a boiling heat, or the solution out of which strontium hydroxide has separated on cooling. For the saturation, carbonic anhydride is employed. The separated sludge is made into bricks with sawdust or small coal, burnt, and the strontium oxide recovered, or it is subjected to dry distillation, ammonia, tar, and combustible gases being obtained. From the solution, the strontium hydroxide is separated in the usual manner, the insoluble residue being treated with carbonated alkalis for the removal of phosphoric acid, and converted into strontium oxide by ignition. In order to prevent the loss of substances valuable as manures, it is preferable to treat the juice first with lime, lime sludge manure being produced, and then to defecate the filtrate with strontium saccharate. D. B.

Action of Certain Metals on Oils. By A. Livache (*Compt. rend.*, **96**, 260—263).—Chevreul has shown that under certain circumstances metals have a considerable influence on the oxidation of oils, and that when spread over the surface of a plate of lead, linseed oil becomes rapidly siccative. The author has investigated the action on oils of lead, copper, and tin when in a state of very fine division.

The lead used was precipitated from its saline solution by zinc, washed with water, alcohol and ether, and dried in a vacuum. Moistened with oil and exposed to air, an increase of weight rapidly took place, the increase being greater and more rapid the more siccative the oil employed, and also approximately proportional (except in the case of cotton-seed oil) to the increase of weight of their respective fatty acids when exposed to the air for a long time. This will be seen from the following table:—

Oil in contact with lead.	Increase of weight. After two days. per cent.	Increase of weight. After seven days. per cent.	Increase of weight of corresponding fatty acid exposed to the air for eight months. per cent.
Linseed	14·3	—	11·0
Walnut	7·9	—	6·0
Poppy	6·8	—	3·7
Cotton-seed....	5·9	—	0·8
Beech-nut	4·3	—	2·6
Colza	—	2·9	2·6
Sesamé........	—	2·4	2·0
Earth-nut	—	1·8	1·3
Rape-seed	—	2·9	0·9
Olive	—	1·7	0·7

That this action is due to the metal and not to the greater surface exposed to the air, was proved by substituting other powdered substances for lead, when no increase of action took place, and also by conducting the experiments with lead out of contact with the air, when the oil was rendered equally siccative. Cloetz has shown that all the glycerol is destroyed in the preparation of drying oils. The author finds that in contact with glycerol precipitated lead becomes oxidised at the expense of the glycerol, and passes into solution. The drying oil prepared by the action of lead is much less coloured than that prepared in the ordinary way, and the author believes that this process might be advantageously used commercially in the preparation of drying oils, and in the detection of adulteration.

L. T. T.

Investigations on Milk. (*Dingl. polyt. J.*, **247**, 306—307.)—Vieth found that when milk is kept for two days at 10—15°, it lost 0·3 per cent. dry substance; at 19—21° the loss was equal to 0·78 per cent., whilst in four days the loss amounted to 1·0 and 1·92 per cent. respectively. This loss is probably due to alcoholic fermentation; it has not, however, been proved whether and to what extent the other constituents in milk take part in this rapid decomposition. Referring to the changes which milk undergoes whilst it is in the hands of the seller, Vieth states that for all practical purposes the alteration in the percentage of fat is too small to be taken into account. D. B.

Scherft's Preserved Milk. By W. FLEISCHMANN and A. MORGEN (*Landw. Versuchs.-Stat.*, **28**, 321—332).—Scherff's method of preserving milk consists in heating it under two to four atmospheres pressure at 100—120° for one or two hours. Prepared in this way, it differs from fresh milk in being much less amenable to the action of rennet, and on being acidified or becoming sour it does not yield a coagulum consisting of large compact lumps, but a mass of loose finely divided flakes. This difference in behaviour has been explained by assuming that during the heating process part of the albumin has undergone a change, and been converted into peptone. In order to ascertain the accuracy of this view, the various samples of ordinary and prepared milk were made use of, and the amount of albumin determined in each by Ritthausen's method, both before and after treatment with pepsin; the filtrates were also examined for peptones after coagulation with acetic acid.

The experiments showed that the albuminoïds in milk do not undergo any decomposition when treated by Scherff's process; no bodies of a peptoid character being found in milk thus prepared: the latter seems, however, to contain albumin in an already coagulated state, and caseïn which cannot be curdled by rennet. The albuminoïds in prepared milk are also less easily acted on by pepsin than those of fresh milk. J. K. C.

Preservation of Milk. (*Dingl. polyt. J.*, **247**, 376—378.)—According to A. Mayer sourness is accelerated when milk is heated at 45°, but retarded if heated for 24 hours at 55°; the milk, however, assumes a burnt taste. Milk treated with boric acid, common salt or salicylic acid, and preserved at 16°, behaved in the following manner:—

	Sourness after	Coagulation after
With 0·02 per cent. boric acid......	30 hours	47 hours.
,, 0·04 ,, ,, ...	35 ,,	47 ,,
,, 0·06 ,, ,, ...	56 ,,	60 ,,
,, 0·02 ,, salt	26 ,,	30 ,,
,, 0·04 ,, ,, ...	26 ,,	32 ,,
,, 0·06 ,, ,, ...	26 ,,	34 ,,
,, 0·02 ,, salicylic acid ..	33 ,,	58 ,,
,, 0·04 ,, ,, ..	47 ,,	82 ,,
,, 0·06 ,, ,, ..	144 ,,	does not coagulate after eight days.
Without addition	25 ,,	28 hours.

Mayer preserves milk by adding 0·08 per cent. sodium benzoate or 0·04 per cent. boric acid, warming at 50° for three hours, and transferring the milk to closed vessels. According to Biedert milk can be preserved for a long time by boiling it for two hours at 100° with exclusion of air.

Meissl (*ibid.*, **245**, 142) mentions that the changes undergone by milk on keeping are due to the long-continued interaction of the separate milk constituents, neither decay nor fermentation being observable. Loew (*Ber.*, **15**, 1482) rejects this explanation, because when previously heated at 120° for some time, milk remains permanently unchanged.

For the preparation of condensed milk, it is recommended to use partially creamed milk, which decomposes less readily. D. B.

Preparation of Blue and Violet Dye-stuffs. (*Dingl. polyt. J.*, **247**, 396.)—According to Casella and Co. (Ger. Pat. 20,850), indophenol is prepared by warming α-bromonaphthol on a water-bath with an aqueous solution of dimethylparaphenylendiamine, adding carbonated or caustic soda to the mixture so that the liquid remains alkaline. A blue precipitate is formed, which is separated by filtration. The filtrate contains leuco-indophenol, and yields further quantities of indophenol by introducing air into the solution or adding oxidising agents. The various processes for preparing indophenol were applied to the following phenols: Orthocresol, paracresol, resorcinol, orcinol, β-naphthol; and the diamines, paraphenylendiamine, monethylparaphenylendiamine, diethylparaphenylendiamine (symmetrical), dimethylparaphenylendiamine, mono- and di-isobutylparaphenylendiamine, mono- and di-amylparaphenylendiamine, paratoluylendiamine, xylendiamine, and diethylparaphenylendiamine (symmetrical); the colouring matters formed did not, however, supersede the typical products in fineness, yield, or cheapness. D. B.

A New Method of Manufacturing Paper-pulp. By G. ARCHBOLD (*Ber.*, **16**, 350—351).—Straw or wood is digested for 12 hours in dilute milk of lime; it is then saturated with sulphur dioxide under a pressure of 4 atmospheres, which effects a complete disintegration of the mass in one or two hours. The mass is washed with water and subjected under pressure to the action of 3 per cent. of calcium chloride and 0·5 per cent. of aluminium sulphate dissolved in a small quantity of water. After a final washing, the product resembles cotton wool in appearance, and can be used for the manufacture of the finest quality of paper. W. C. W.

Cause of the Acid Reaction exhibited by some Kinds of Paper. By HAERLING (*Dingl. polyt. J.*, **247**, 382).—The author rejects Feichtinger's statement (*ibid.*, **247**, 218) that all papers sized with resin contain free sulphuric acid, as the method used for sizing does not admit of the presence of free sulphuric acid in paper. The method consists in adding resin-soap, prepared by dissolving resin in soda-ley, to the paper pulp and precipitating with normal aluminium sulphate, so that the precipitate of alumina in combination with resin forms the size. In the presence of free acid, resin only would be precipitated, and the paper not sized, but merely impregnated with resin particles which would render it useless for writing or printing purposes. Feichtinger admits the presence of aluminium sulphate, but appears unable to prove, without further investigation, whether the sulphate exists in paper as normal or basic salt. The author mentions that this question is answered by the above method, for when normal aluminium sulphate is precipitated with an excess of sodium hydroxide, a basic precipitate must be formed. Moreover, the assumption of the simultaneous presence of free sulphuric acid and basic aluminium salt contradicts the laws of chemistry.

D. B.

Waterproof Paint for Stones, &c. (*Dingl. polyt. J.*, **247**, 396.) —This paint is prepared by fusing equal parts of aluminium palmitate and colophony, or mixing aluminium palmitate with wax, and dissolving in caustic soda and water. A solution resembling soap is formed, which is used for wall painting, &c. After drying, the paint is washed with a weak aqueous solution of aluminium sulphate, which renders it insoluble. D. B.

General and Physical Chemistry.

Spectra of Carbon Compounds. By K. WESENDONCK (*Ann. Phys. Chem.*, **17**, 427—467).—The paper describes the spectra produced by electrical discharges through the rarefied vapours of certain compounds of carbon and hydrogen, or of these elements combined with nitrogen and oxygen. Common to all of these compounds are two quite different kinds of spectra, the difference having relation to the nature of the electrical discharge. Tables of the author's determinations of the positions of the several lines and bands attributed to carbon are given in the paper. He considers that his researches go to prove that the spark spectrum of bands described by Swan is due to carbon itself separated from its compounds in a sufficient quantity and at a sufficiently high temperature, for which it is necessary that a comparatively large quantity of electricity shall pass each unit of section in the unit of time. On the other hand, the channelled spectrum (called by Watts the second) must be ascribed to oxide of carbon. The bands ζ and θ of Watts are due to a nitrogen-compound of carbon, for they never occur except when nitrogen is present.

R. R.

Observations of Infra-red Spectra by Means of Phosphorescence. By H. BECQUEREL (*Compt. rend.*, **96**, 1215—1218).—The author has continued his observations of the infra-red region of various spectra by projecting them on phosphorescent substances (*Compt. rend.*, **96**). The solar spectrum shows four broad telluric bands, the mean wave-lengths of which in ten-millionths are 9300, 10,820, 12,300, and 14,700. The last band was observed by Fizeau and Foucault in 1847. When the sun is low on the horizon, the band at 9300 is very broad and dark; the bands at 10,820 and 12,300 are also intense, and the interval between them is less luminous. The variations in the band 14,700 are difficult to observe. Near A are the five bands observed by Brewster and Gladstone, viz., 7620—7645, 7850—7900, 7995—8020, 8100—8140, and 8240—8310. The variations in this region and in the luminous spectrum are less marked than those of the broad bands in the infra-red.

Water.—With a layer of water 1 mm. in thickness, there is absorption from the extreme infra-red to about wave-length 13,000, and the bands are visible at 9300 and 12,300. With greater thicknesses of water, the bands at 9300 and 12,300 become broader and more intense, and with a thickness of 1 cm. absorption extends from the extreme infra-red up to wave-length 10,820, where it terminates sharply, and the band at 9300 is still visible. A layer of water 0·5 m. in thickness gives general absorption of the infra-red up to wave-length 9300.

Earth-metals.—The absorption-spectrum of solutions of didymium gives in the infra-red three intense bands of wave-lengths 7305—7560, 7820—8190, and 8720—8900. With very dilute solutions the bands are narrower, and have mean wave-lengths of 7430, 7960, and 8720. The solutions examined showed other bands in addition to those of water. Two intense bands at about 10,100 and 11,800 respectively appear to be due to samarium, whilst the origin of two other weaker bands at 8400 and 9100 is uncertain. Solutions of erbium and holmium free from didymium show the band at 8110 attributed to holmium by Soret, and another weaker band at 8900.

Certain solutions of copper salts absorb the whole of the infra-red region. Nickel chloride absorbs the visible red, but is transparent to that portion of the infra-red which is not absorbed by water.

The author has also applied this method to the study of radiation-spectra, and will describe his results in a subsequent paper.

C. H. B.

Lockyer's Dissociation Theory. By W. Vogel (*Ann. Phys. Chem.* [2], **19**, 284—287).—The author has on a former occasion taken exception to Lockyer's dissociation theory, and has pointed out that photographs bring out a fifth hydrogen line very close to the Fraunhofer calcium line H′. This line was probably confounded by Huggins with its neighbouring calcium line, and its presence, taken in connection with the absence of the calcium line H″ in the photographs of the spectra of the so-called white stars, was one of the principal arguments brought forward by Lockyer. Attention is also drawn to the researches of Liveing and Dewar, which have conclusively proved that certain magnesium and calcium lines are brought out only in the presence of some foreign substance, hydrogen, for example (compare Abstracts, 1882, 249—252, 253—255); therefore any arguments drawn from the presence of certain iron lines in sunspots and their absence in the protuberances cannot be regarded as conclusive, in that the former only may afford a medium for the development of the lines. Lastly, the author quotes experiments of Hagenbach on the absorption-spectrum of chlorophyll, and of Kundt on the absorption-spectrum of gases, which have established the fact that lines are under certain conditions displaced in the direction of the red end of the spectrum. The gaseous medium of the sun's envelope might effect such a displacement of the iron lines, and cause the conclusions drawn from the observations to be erroneous. V. H. V.

Molecular Refraction. By E. Wiedemann (*Ann. Phys. Chem.*, **17**, 577—580).—The mathematical discussion of the refractive indices of the several sulphur substitution-derivatives of ethyl carbonate, $CO_3(C_2H_5)_2$, shows that with sulphur, as with oxygen and carbon, when the several bonds of affinity are engaged by the same carbon-atom, there is a greater atomic refraction than when they are divided amongst different carbon-atoms. R. R.

Variation of the Indices of Refraction of Water and Quartz with the Temperature. By H. Dufet (*Compt. rend.*, **96**, 1221—1224).—A transparent solid with parallel faces is placed in a liquid contained in a vessel with rectangular sides. A beam of parallel rays is allowed to pass through the liquid, and half of the beam passes through the solid from a slit of suitable width. When the transmitted beam is decomposed by a prism, Talbot's fringes are perceived.

The position of these fringes varies with the temperature, and from the variations the difference between the refractive indices of the solid and liquid at different temperatures can be deduced. Since the refractive index of the glass from Saint Gobain does not sensibly vary with the temperature, this glass was employed for determining the variations in the refractive index of water, and by substituting for the glass a plate of quartz, the variations in the index of the latter could then be determined. The number obtained for the variation of the ordinary index of quartz between 20° and 40° was $-0{\cdot}0000050$, a number almost identical with that obtained by Fizeau, 0·0000055, between slightly different limits of temperature. C. H. B.

Fluorescence of Iodine Vapour. By E. LOMMEL (*Ann. Phys. Chem.* [2], **19**, 356—358).—The phenomenon of fluorescence has hitherto been observed only with liquid and solid substances. The author has examined several highly coloured vapours, as nitrogen peroxide, chlorine, bromine, and sulphur, but without result. Iodine vapour, however, displays a remarkable green fluorescence, which is best observed when sunlight, concentrated by a lens, is thrown on a glass globe filled with not too dense vapours of iodine, and the emerging beam filtered through green glass. If blue glass be used the fluorescence will be very feeble, and it disappears altogether if red glass is used. The fluorescent spectrum displays itself in the red, orange, yellow, and green from the line 35 to the line 60 in the Bunsen scale, and is most marked in the orange. The author further established that iodine vapour does not absorb the ultra-violet rays.

V. H. V.

Theory of Phosphorescence. By B. RADZISZEWSKI (*Ber.*, **16**, 597—601).—The author has shown (*Annalen*, **203**, 305) that the phosphorescence of organic bodies is produced by the action of active oxygen in alkaline solution. He divides such phosphorescent bodies into two groups, the first of which contains hydrocarbons (*e.g.*, the terpenes, &c.) which phosphoresce on the addition of an alkali, whilst the second group contains aldehydes and bodies which yield aldehydes when treated with alkalis. In the case of group I the *active* oxygen is produced by the action of sunlight, and in the case of group II by the decomposition of the aldehyde by the alkali. The phosphorescence of fats is probably attributable to the same cause, namely, the decomposition of the acids $C_nH_{2n-2}O_2$ into salts of fatty acids and aldehydes. The author is of opinion that phosphorescence in organisms is also due to the same cause, and in favour of this view he mentions the presence of an alkaline basic substance and of a fatty body in such organisms. He also shows the presence of *active* oxygen in such organisms (*Pelagia noctiluca*) by placing them on porous plates moistened with potassium iodide and starch-paste, and with tincture of guaiacum. A. K. M.

Researches on Statical Electricity. By V. DVOŘÁK (*Ann. Chem. Phys.* [2], **19**, 325—340).—The author has made a series of observations on the electric discharge of Leyden batteries consisting of glass plates between thin layers of silver. The form of this discharge is dependent not only on the thickness of the silver layer, but also on the intensity of the charge and the distance of the electrodes. The first part of the discharge consists of a large number of sharply-defined ripples, disposed concentrically around the electrode; the second portion consists of thin branches containing only traces of silver, and in the third portion, which is colourless and transparent, silver is wholly absent. If the silver be coated by a layer of some insulating material, as varnish or oil, the ripples are generally absent, and the radiating branches diverge immediately from the electrodes; the colour of the discharge is golden or even brown. If the varnish layer be made too thick the glass plate is frequently shattered by the discharge. On substituting thin layers of graphite for the silver the discharge took a different form, the ripples were perpendicular to the direction of the discharge. Layers of a mixture of a pulverulent conductor, as finely divided graphite, with stearic acid, give a discharge, the form of which the author compares to a series of needles inserted in the positive pole; olive oil, turpentine, gave similar discharges.

The author on examination considers Riess's theory as regards the electric action of flames untenable. According to Riess two different cases of electrostatic action of flames must be distinguished—first, of substances which only glimmer, as carbon; secondly, of inflammable substances, which form a conducting column of hot gas. In the first case, the electrostatic action will arise from a series of solid points, but in the second case from a series of gaseous points.

The author quotes experiments to demonstrate that in the first case the action is derived from a series of gaseous points in a heated column. He further proves that the electric repulsions, normal to the surface of a gaseous column, scatter the electrified particles in all directions, so that the whole environment of the flame is filled with electrified particles. This fact offers an explanation of the well-known phenomena of the removal of electricity from an electrified body and the charge of a conductor by means of a flame.

V. H. V.

The Units of Electricity and Magnetism. By R. Clausius (*Ann. Phys. Chem.*, **17**, 713—719).—The author expresses the relations between the unit of magnetism and the electrostatic and electrodynamic units respectively by the following general equations, which are independent of the units of measurement:—

$$[m_d] = [e_d L T^{-1}]$$
$$[m_s] = [e_s L T^{-1}].$$

R. R.

Electromotive Force of certain Galvanic Combinations. By F. Braun (*Ann. Phys. Chem.*, **17**, 593—642).—Full details are given in this paper of measurements of the electromotive force of galvanic elements formed of dry chlorine, bromine, or iodine, with platinum for one metal, and zinc, lead, silver, mercury, or aluminium for the other, also with carbon opposed to silver or platinum. The experiments furnish data for the determination of the fraction of the total energy of combination that is converted into current energy in the several chemical processes concerned, which in the second part of the paper include cases where the electrolyte consists of aqueous solutions. The author calls in question the validity of Exner's experiments and views on the relation between chemical actions and the production of electricity. R. R.

Reply to the Observations of Reynier on Bichromate Batteries. By TROUVÉ (*Compt. rend.*, **96**, 1048).—The author corrects some of the numbers given in his paper (this vol., 700). The consumption of zinc by the battery of 12 elements was 0·912 kilo., or double the amount given in the paper, which is the value for 6 elements. Each battery of 6 elements had an intensity of 18 ampères in short circuit, with a resistance of 0·0016 ohm for each element, when the solutions were fresh. The E.M.F. given, 1·9 vols., is the value for one element. C. H. B.

Substitution of Hydrogen Peroxide for Nitric Acid in Galvanic Batteries. By A. KÖNIG (*Ann. Phys. Chem.*, **17**, 347—349).—The author has examined the electromotive force and other conditions of Grove and Bunsen cells in which a 2·25 per cent. solution of hydrogen peroxide replaced the nitric acid, as proposed by Landolt. Their electromotive force is less than that of the ordinary cells, and their internal resistance four to five times greater, when the hydrogen peroxide solution is not acidulated: when it is acidulated, the peroxide is much more quickly consumed. Considering the present cost of the hydrogen peroxide solution, the author believes that Landolt's proposal cannot be adopted advantageously. R. R.

Secondary Batteries. By G. F. BARKER (*Chem. News*, **47**, 196—199).—After a sketch of the history of secondary batteries from the time of Gautherot, 1801, until the present day, the author proceeds to explain the construction, the theory, and the chemistry of Planté's and Faure's batteries, and points out that the latter differs from the former in that the lead oxide is "put on" and not formed on, thus saving time. The power stored in these batteries is represented by the peroxide formed; the force obtained is never equal to the theoretical quantity on account of various interfering influences, such as diffusion, counter-currents set up by the formation of secondary products, *e.g.*, lead sulphate, from the action of the sulphuric acid upon both the metallic lead and the oxide; this local action is always going on. A great defect in batteries of secondary cells, is the inequality of action and varying storage capacity of the individual cells, and therefore care should be taken not to use weak or exhausted charges along with strong fresh ones. Planté's battery is less liable to local action, and is more permanent than Faure's. The author describes the charging of these batteries by means of a dynamo and also a "cut out" apparatus, which consists of a coil with a moveable core, which, when the current flows, is drawn in, and presses on a spring, which then makes the contact between the machine and the secondary batteries; if, however, the current from the dynamo becomes weaker than that from the batteries the reverse action takes place, the spring pushes back the core, and the circuit is broken. The secondary battery is a useful regulator in electrical lighting, for if a battery of sufficient electromotive force be placed in multiple circuit with the machine and lamps, it acts as an equaliser, and destroys entirely pulsations due to inequalities in the working of the motive power; and should the latter fail altogether, the light would still be supplied from the stored force of the batteries. The average electromotive force of a single cell, in the author's battery of 32 cells, was about 2 volts. D. A. L.

Electric Researches. By C. FROMME (*Ann. Phys. Chem.* [2], **19**, 300—319).—The author was led to suspect that the peculiar phenomena observed when platinum is the positive pole in a chromic or nitric acid battery, were possibly due to the property of this metal of absorbing and of condensing hydrogen (this vol., p. 697). He has accordingly examined the electric properties of platinum and palladium when containing hydrogen.

Before the experiment, the palladium was freed from traces of oxide and of hydrogen; the measurements of E.M.F. were made with open circuit. The ratio of the E.M.F. of the Zn-Pt to the Zn-Pd element was found to be 1 : 0·934.

The first form of the experiment adopted to determine the electric properties of hydrogenised platinum and palladium, consisted in introducing the metals into sulphuric acid saturated with hydrogen; under these conditions the E.M.F. of the Pt | H_2SO_4 element had a constant value of 0·71 Daniell, while that of the Pd | H_2SO_4 element was at first 0·92 Daniell, and then it slowly decreased. The difference in behaviour the author explains by the greater readiness with which platinum condenses hydrogen on its exterior surface, while palladium absorbs the hydrogen into its interior.

In other experiments, the metals saturated with hydrogen were introduced into sulphuric acid, free from the gas; the E.M.F. of the combination Zn | H_2SO_4 | Pt was about 18 per cent. less than the same combination with the pure metal, after eight minutes the difference was only 8 per cent. In the case of palladium the E.M.F., after a polarisation of short duration, reaches a minimum value of 0·75 Daniell.

The author further examined with a rheostat the E.M.F. of the combinations Zn | H_2SO_4 | Pt and Zn | H_2SO_4 | Pd (the acid and the metals being free from hydrogen), and established that the relation of the E.M.F. of Pt and Pd decreased from 1·07, and then increased to 1·14; when the resistance decreased from ∞ to 0; if the resistance of the rheostat be ∞, then with greater resistance in the circuit the E.M.F. of the Pd element, but with less resistance the E.M.F. of the Pt element is the greater.

The author then proceeds to offer an explanation of the phenomena of the variation of the E.M.F. in the chromic and nitric acid batteries; the well-known property of palladium of absorbing hydrogen is sufficient to account for these variations, but in the case of platinum the evidence is not so clear. When a Grove's element is first closed, a layer of hydrogen gas appears at the surface of the metal, but it subsequently disappears; this hydrogen is subject to two opposing forces, the one from the nitric acid tending to oxidise the hydrogen, the other from the platinum tending to condense the gas upon the surface of the metal, and of absorbing it into its interior. If at the outset the platinum contains no hydrogen, then the latter force preponderates, and to a greater extent, the more dilute the acid, and the greater the intensity. With a greater concentration of acid, or with less intensity of current, these conditions are reversed. Sometimes the platinum condenses a portion of the hydrogen, while another portion is oxidised by the acid, and as a necessary consequence the E.M.F. falls; when it reaches a minimum then the thickness of the hydrogen layer no longer increases, and all the gas is oxidised by the acid. As soon as the hydrogen condensed on the surface begins to combine with the platinum molecules on the surface of the metal, then the E.M.F. increases in proportion as the attraction of the hydrogen for the platinum decreases, while that of the hydrogen for the oxygen increases. The E.M.F. never attains its former value, on account of the hydrogen absorbed by and combined with the platinum. During the opening of the circuit the E.M.F. suddenly rises until it reaches a maximum, while the hydrogen on the surface of the metal is oxidised, and the combined hydrogen is separated off. Shaking the platinum causes the hydrogen to be given off from its surface, while a rise of temperature of the acid diminishes the evolution of the oxygen; the effects produced by these changes in the conditions will act in an opposite direction. The similar phenomena observed in the chromic acid battery cannot be attributed entirely to the absorptive power of platinum for hydrogen. The author supposes that the chromium sesquioxide, the product of the oxidation of the hydrogen by the chromic acid, forms a compound with the platinum; this supposition is not based on any facts, but it appears to the author that no other explanation is sufficient. When the combination Zn | H_2SO_4 | H_2CrO_4 | Pt is closed a portion of hydrogen is oxidised, while another portion, the quantity of which is dependent on the intensity of the current, is taken up by the platinum, as no hydrogen is evolved in the free state. The chromium sesquioxide partly combines with the sulphuric acid, and partly forms a combination with the platinum, and this latter causes the decrease of the E.M.F., which again increases when the evolved hydrogen turns out the chromium sesquioxide, and in its turn combines with the platinum. V. H. V.

Researches on the Heat Changes at the Poles of a Voltameter. By E. Edlund (*Ann. Phys. Chem.* [2], **19**, 287—299).—In the year 1869, the author propounded the view that when a current passes through an electromotor in the same direction as that of the electromotor, a quantity of heat disappears proportional to the product of the E.M.F. by the intensity of the current; conversely if the current is in the opposite direction, an equal quantity of heat is produced. If in a closed circuit a current is formed of one or more E.M.Fs., then these forces destroy a quantity of heat equal to the sum of the heats caused by the resistance of the circuit. The total heat production of the current is therefore *nil*, inasmuch as on the passage of the current through the circuit an amount of heat is produced equal to that required by the E.M.F. Sir William Thomson, however, considers that the sum of the heat evolved by the resistance is equal to the quantity of heat produced by the chemical changes within the battery; but if the author's view be accepted these quantities bear no intimate relation to one another. The author has carried on experimental investigations on this point, and has succeeded not only in establishing that his proposition satisfactorily explains the observed phenomena, but also in some cases he has calculated the value of the heat changes. His work has received further confirmation at the hands of J. Thomsen, Braun, and Hoorveg. In the present communication, the author proposes a method by which it is possible to decide whether the heat consumed by the E.M.F. is greater or less than that evolved by the chemical changes, without a separate estimation of the latter. Salts of copper, zinc, silver, cadmium, and lead were used as electrolytes, and the electrodes were of the same metal as that present in the salt. Taking for example copper sulphate with electrodes of copper, and assuming a current of intensity i passed through, then the heat evolved from the resistance of the liquid is gi^2, where g is a constant. At the anode, copper sulphate is formed, and an amount of heat required, which can be expressed by ki, where k is a constant. But as the anode is the seat of an E.M.F., a quantity of heat is consumed, expressed by ei where e is the E.M.F. At the kathode, where copper is separated, there is a heat absorption equal to $-ki$, and therefore the sum of the heat changes at the anode is equal to $gi^2 + ki - ei$, and at the kathode, $gi^2 - ki + ei$. In experiment gi^2 must be eliminated, and the reading of the instrument made dependent on the difference between ki and ei, and the current must pass through the electrolyte only for a short time, in order to prevent any marked variation in the neighbourhood of the electrode. If the current be passed through an electrode A, then the rise of temperature at the point of junction with the circuit is equal to $f(gi^2 + ki - ei)$, where f is a constant, and at B is $f'(gi^2 - ki + ei)$ where f' is another constant. If the rise of temperature is not the same in both cases, then the swing of the galvanometer is proportional to the difference between them, and so $f(gi^2 + ki - ei) - f'(gi^2 - ki + ei) = a$. If the current be reversed, so that B is the positive pole, then there is a different swing b in the galvanometer, so $f'(gi^2 + ki - ei) - f(gi^2 - ki + ei) = b$. Hence it follows that $ki - ei = \left(\frac{a + b}{2}\right)(f + f')$. If $a + b$ is positive, then the heat produced by the chemical change is greater than that consumed by the E.M.F.; if the sum is negative, then this relation is reversed. The author proves by his experiments, the details of which are given in the original paper, that in Daniell's cell the E.M.F. consumes an amount of heat equal to that produced by the chemical process. On the other hand, with solutions of silver nitrate and sulphate with silver electrodes, the E.M.F. between the metal and the salt solution consumes a greater quantity of heat than that set free in the formation of the salt, and therefore $\frac{a + b}{2}$ has a negative value; the same obtains with lead acetate and lead.

V. H. V.

Effect of Absorbed Gases on the Electrical Conductivity of Carbon. By J. PROBERT and A. W. POWARD (*Chem. News*, **47**, 157). The authors have measured the electrical conductivity of specimens of a porous variety of carbon in different gases at different pressures, and have observed that the conductivity is not constant for a given temperature, but varies with the chemical nature and density of the absorbed gas. Quantitative experiments are in progress.

D. A. L.

Unipolar Conductivity of Solid Bodies. By J. BRAUN (*Ann. Phys. Chem.* [2], **19**, 340—352).—This paper is merely a comparison of the work of the author and Meyer on the unipolar conductivity of psilomelane, together with a description of the apparatus used.

V. H. V.

Electrical Conductivity of Silver Haloïd Salts. By W. KOHLRAUSCH (*Ann. Phys. Chem.*, **17**, 642—654).—At temperatures above their melting point, silver chloride, bromide, and iodide conduct electricity much better than sulphuric acid. The order of conductivity is chloride, bromide, iodide. The resistance of the chloride and bromide is increased when they solidify, and rises quickly by cooling, until at 20° it has more than a million times its former value. Silver iodide, on the other hand, does not on solidifying change its resistance in the least at first, but the resistance increases rapidly at the temperature (145°) at which it passes from the amorphous to the crystalline state.

R. R.

Fluidity and Galvanic Conductivity. By C. STEPHAN (*Ann. Phys. Chem.*, **17**, 673—701).—The experiments described in this paper relate to solutions of salts in mixtures of alcohol and water, and they lead to the following conclusions :—In such solutions of $NaCl$, KCl, $LiCl$, NaI, and KI, the conductivity is determined by the coefficient of friction. The conductivity increases with increase of the proportion of salt less rapidly than is the case with aqueous solutions. The temperature coefficients of conductivity correspond nearly with those of fluidity. The conductivity of the alcoholic solutions may be expressed by multiplying that of the corresponding aqueous solutions by a factor depending only on the solvent, and the same for all the salts. In passing from pure water to a mixture of equal parts of water and alcohol, the conductivity remains very nearly proportional to the fluidity of the solvent. With a larger proportion of alcohol, the conductivity is behind.

R. R.

Platinum-water Pyrometer. By J. C. HOADLEY (*Chem. News*, **47**, 171).—The apparatus here described is for the measurement of temperatures above the range of the mercurial thermometer up to the melting point of platinum, by means of the method of mixtures, platinum and water being the substances employed. The pyrometer consists of an inner cell (for the water) 4·25 inches in diameter and height, with a bottom in form of a spherical segment of 4·25 inches radius, made of brass plate 0·01 inch thick, nickel plated and polished on both sides; and an outer case 8 inches diameter, 8·5 inches deep, of

16 oz. copper nickel plated, in the inside, with a hopper-shaped top of the same metal. The inner cell is connected with the outer case by three vulcanite bands screwed together, which also insulate it. The joints between the metal and vulcanite are made tight with asphaltum varnish. The cover of the inner cell consists of two nickel-plated brass plates separated by a ring of vulcanite which both connects and insulates them; these plates are bound together by a vulcanite tube. When this cover is on, the water in the cell is surrounded by polished nickeled brass insulated from all other metallic connections by vulcanite. The space between the inner cell and outer case is filled with eider-down. Brass tubes pass through the cover for the admission of a thermometer. The agitator is a perforated concave disc of brass made to conform with the bottom of the cell, with a narrow rim turned up all round; the stem as far as the under side of the cover is of perforated brass tube, the upper part a vulcanite tube and passes through the vulcanite tube previously mentioned; in agitating, it is not necessary to draw the brass tube out beyond the exterior vulcanite tube of the cover. The thermometer is passed down the internal tube, and to protect this instrument this tube should be surrounded externally with a brass wire cage, and should have a tuft of wool at the bottom inside; the thermometer itself should be protected by a small band of india-rubber. Very accurate thermometers must be used. The best heat-carriers are platinum balls; the author uses three varying sizes: one 1·1385 inch diameter weighing 4800 grains; another 0·9945 inch diameter = 2800 grains; and the third 0·7894 inch diameter = 1400 grains. A less expensive heat-carrier made of iron covered with platinum may be used for temperatures up to about 1500° F. When in use, the heat-carriers are placed in small graphite crucibles, which are placed, for further protection, in a firebrick case; two are used together, one as a check on the other. The temperature of the water in the cell is carefully taken, and an instant before "pouring" the heat-carrier from the crucible, the cover and agitator are both lifted together, so that the rim of the latter is on a level with the sloping top of the apparatus; the agitator then receives the hot ball without doing injury to the apparatus: as soon as the temperature of the water is constant, the degree is noted and the result calculated from tables, &c. Several precautionary measures have to be taken before making an experiment: thus the calorific capacity in terms of water of the cell, of the inside plate of the cover, of the metallic portions of the agitator, of the part of the thermometer exposed to the temperature during the reading, also the amount of water of certain temperature, must be accurately known, care being taken to note loss occasioned by contact with air, by radiation, and by evaporation during the time the water is poured from one vessel to another; again, the amount of heat communicated to the eider-down must not be overlooked. Compared with the mercurial thermometer, the author believes this pyrometer to be more accurate, although less convenient. For temperatures up to 900° F. it is only equalled by a suitable air thermometer. For temperatures up nearly to the melting point of platinum it is without a rival. The author's sample of platinum began to melt below 2950° F. D. A. L.

Radiation from Silver at the Solidifying Point. By J. VIOLLE (*Compt. rend.*, **96**, 1033—1035).—The radiation from molten silver, as measured by its effect on a thermopile, remains constant during the actual process of solidification. It therefore constitutes a convenient secondary standard for spectro-photometric measurements, &c.

C. H. B.

Specific Heats of Gases at High Temperatures. By VIEILLE (*Compt. rend.*, **96**, 1218—1231).—Observations of the pressures developed by the explosion of a mixture of hydrogen and oxygen, or cyanogen and oxygen, with certain proportions of nitrogen, oxygen, hydrogen, and carbonic oxide, show that at temperatures as high as 2700° the molecular specific heats at constant volume of these four gases are identical, if it is assumed that their coefficients of dilatation remain constant. The results of some of the experiments seem to indicate that the specific heats of these gases attain a limit at about 3500°.

The pressures developed by the explosion of mixtures of cyanogen and oxygen indicate that the temperature of explosion of $CN + O$ is 3927°, whilst that of $CN + O_2$ is 5320°. This last number is probably too high in consequence of dissociation; but the first may be regarded as accurate, and is nearly 1000° higher than the temperatures which are generally regarded as actually attainable by combustion.

C. H. B.

Some Relations between Temperatures of Combustion, Specific Heats, Dissociation, and Pressure of Explosive Mixtures. By BERTHELOT (*Compt. rend.*, **96**, 1186—1191).—In calculating the temperature of combustion of an explosive mixture, it is necessary to take into account the amount of dissociation and the variation in the specific heats of the gases concerned. It is possible to calculate the temperature of combustion and the amount of dissociation in the case of gases which combine without change of volume, if only the total heat of combination and the pressure developed is known; or the maximum and minimum possible limits of the temperature of combustion can be calculated with no other datum but the pressure developed. Generally, in a reversible system, *i.e.*, a system in which dissociation tends to reproduce the original constituents, we have, starting from 0°,

$$t = 273\left(\frac{P}{H}\,\frac{1}{1 - k + kg} - 1\right),$$

where t is the temperature of combustion, P the pressure developed, H the initial pressure, g the ratio of the volume of the products when completely combined to the volume of the same bodies when completely dissociated, and k the fraction actually combined. If the initial temperature τ is higher than 0°, then P must be replaced by $P\left(1 + \frac{\tau}{273}\right)$. When there is no dissociation this formula becomes

$$t_1 = 273\left(\frac{P}{H}\,\frac{1}{g} - 1\right),$$

which gives one of the limits of temperature, the other being obtained by making $k = 0$ when we have

$$t_2 = 273\left(\frac{P}{H} - 1\right).$$

When combination takes place without change of volume, the two limits are identical, and the temperature is at once obtained from the pressure developed.

If the heat of combination is divided by the temperature of combustion, the quotient is the mean quantity of heat restored by the system for each degree between 0° and the temperature of combustion; this quantity the author terms the *apparent specific heat of the system.* If there is no dissociation, it will be the mean specific heat of the compound, and by comparing it with the specific heat of the same substance at the ordinary temperature it can be ascertained whether the specific heat varies, and, if so, what is the amount of variation. If, on the other hand, there is dissociation, the apparent specific heat is a complex quantity made up of the specific heat of the compound, the specific heats of its constituents, and the heat developed by the combination which takes place during cooling. If the specific heats of the compound and its constituents can be measured in any other way, then the amount of dissociation can be calculated from this complex quantity.

The maximum limit of dissociation can be calculated in any case. The specific heat of compound gases usually increases with the temperature, and by multiplying its value at the ordinary temperature into t, the known temperature of combustion, or t_2, the lower of the two calculated limits, the product is the smallest quantity of heat compatible with the formation of that proportion of the compound which gives rise to the observed pressure. The ratio of this quantity to the total heat of combination gives the maximum limit of dissociation. It must be borne in mind that all these calculations only hold good for gases which obey the ordinary laws of expansion and compressibility: they are not applicable to a gas like chlorine, which expands abnormally at high temperatures. It is also necessary to distinguish between *reversible systems*, in which the compound formed can reproduce the original bodies by dissociation, and *non-reversible systems*, in which this is not the case.

In order to apply these principles, the author has made a number of experiments with combustible *isomeric mixtures*, *i.e.*, mixtures of the same elements associated in different ways in the initial mixtures, but producing the same final system by combustion: for example, $CH_4 + O_4$ and $CO + 2H_2 + O_3$, $C_2H_6 + O_7$, $C_2H_4 + H_2 + O_7$, $C_2H_2 + 2H_2 + O_7$, $C_2H_6O + O_6$, and $2CO + 3H_2 + O_5$. In calculating the temperature-limits it is necessary to take into account the dissociation of the water and carbonic anhydride into hydrogen, oxygen, and carbonic oxide. If g represents the condensation corresponding with the formation of these two compounds, the formulæ for the temperature-limits are

$$t_1 = 273\left[\frac{P\left(1 + \frac{\tau}{273}\right)}{H}\frac{1}{g} - 1\right];\quad t_2 = 273\left[\frac{P\left(1 + \frac{\tau}{273}\right)}{H}\frac{g_1}{g} - 1\right].$$

The results of these experiments will be detailed subsequently.

C. H. B.

Basis of Thermo-chemistry. By L. Meyer (*Annalen*, **218**, 1—12).—No simple connected theory of chemical change has hitherto been based on thermo-chemical investigations, notwithstanding their number and the trustworthiness of the constants deduced from them; indeed many chemists would even consider that such a generalisation is for the present not ripe for discussion. For although many observations are in direct accordance with the mechanical theory of heat, yet from time to time facts are brought forward apparently in direct contradiction to it; as the validity of this theory cannot be doubted, such discrepancies probably arise from wrong methods of its application. According to the author's opinion, the retention of old and baseless hypotheses hampers the framing of a thermo-chemical theory; such, for example, is the conception that the atoms are particles of mass endowed with a power of attraction through space, although it is least highly probable that attraction, as we conceive it, is produced by a certain movement of smaller particles, arising from pressure or impact. The satisfaction of these attractions or affinities is not then correlated with a conversion of potential into kinetic energy, but the combinations and also the separations of the affinities are merely a conversion of one form of kinetic energy into another. Again, it is often tacitly assumed that the atoms are particles at rest, more especially in the more or less established generalisation that in absence of disturbing circumstances the final result of a chemical change is the combination of those affinities which evolve the greatest heat in their satisfaction. If, on this assumption, 2 atoms, A and B, are attracted, and, by their mutual impact combine with one another, then their potential energy is converted into kinetic, which either wholly or partially assumes the form of heat. Supposing, then, a third atom, C, whose attraction for A is greater than that of B, to be brought into such a condition that it can oust B, then the kinetic energy evolved as heat is equivalent to the potential energy between A and C diminished by the work done in the separation of A and B. A decomposition of the compound AC by B is practically excluded, and also every chemical change which is associated with a consumption of heat.

But atoms and molecules are not at rest: for, not only is every molecule in motion as a whole, but each of its constituent atoms is likewise moving, the movement of the latter being so far limited that no individual atom can be separated from the others which form the molecule.

The form and force of the movement is dependent on the nature of the substance, temperature, and space occupied by a given quantity of it. Although no ultimate conclusion can be arrived at as to the actual form of the motion, yet it can *à priori* be suspected that it is either of such a kind that the *vis viva* remains the same, or alternately increases and decreases at the expense of the potential energy. The former case would obtain when the several atoms describe a circle around some centre of gravity, the latter when the path described is an ellipse: if the latter represent the form of motion, then the readiness of decomposition of the molecule is dependent on the relative position of the atoms in a given unit of time; and it is thus possible that one and the same compound by the action of one and the same substance is in certain cases decomposed, and in others unaltered without any perceptible difference in the external conditions, especially temperature. Then for the decomposition of a compound AB by C, it is not even necessary that in any given position the attraction between A and B should be less than that between B and C, for it is a possible case that while A and B are indefinitely apart from one another, C strikes with such velocity on A that it ousts B from the sphere of action. Whether, after such a decomposition, the kinetic energy of the system is greater or less than before is dependent upon whether C or B possesses the greater affinity for A, but *for effecting* the decomposition it is not necessary that B should possess the greater, for C can compensate a less degree of affinity by a greater *vis viva.* In accordance with this view not only the decomposition of AB by C, but the re-formation of AB from AC and B is possible. Finally, the possibility and ease of a chemical combination is dependent, not upon the force of the affinities, but upon other properties of atoms and molecules and upon external conditions.

The author also remarks that there is no fundamental distinction between positive and negative heat-change: for the combination of two atoms could scarcely be dissolved without their kinetic energy taking some part in work done in overcoming the affinities, but the loss of energy will be marked by the heat developed in the newly formed affinities. The final heat-change observed in a chemical reaction is the mixed result of intimately associated circumstances, and does not probably afford a true representation of the energy of the satisfied or dissociated affinities; this change, as also change of volume and refractive index, is dependent not upon the mutual attraction or affinity of the combining substances, but upon their individual nature and their relative quantities.

In conclusion, the author considers that the science of thermochemistry requires to be thoroughly reviewed, and the recorded observations, although of manifestly great service, must not be considered as affording a final solution of the problems involved.

V. H. V.

Neutralisation of Glycollic Acid by Bases. By DE FORCRAND (*Compt. rend.*, **96**, 582—583).—The glycollic acid was prepared by the action of zinc-dust on a solution of oxalic acid. Its heat of solution in water is − 2·76 cal. between 8° and 10°. Determinations of the heats of formation of its salts gave the following results:—

					Cal.
Potassium glycollate,	$2C_2H_4O_3$,	dissolved	+ K_2O,	dissolved	+ 27·48
Sodium glycollate,	$2C_2H_4O_3$,	,,	+ Na_2O,	,,	+ 27·20
Ammonium glycollate,	$2C_2H_4O_3$,	,,	+ $2NH_3$,	,,	+ 24·46
Barium glycollate,	$2C_2H_4O_3$,	,,	+ BaO,	,,	+ 27·80
Strontium glycollate,	$2C_2H_4O_3$,	,,	+ SrO,	,,	+ 28 00
Calcium glycollate,	$2C_2H_4O_3$,	,,	+ CaO,	,,	+ 27·80
Lead glycollate,	$2C_2H_4O_3$,	,,	+ PbO,	solid	+ 15·10
Magnesium glycollate,	$2C_2H_4O_3$,	,,	+ MgO,	,,	+ 27·42
Copper glycollate,	$2C_2H_4O_3$,	,,	+ CuO,	,,	+ 15·22
Zinc glycollate,	$2C_2H_4O_3$,	,,	+ ZnO,	,,	+ 20·80

C. H. B.

Salts of Glycollic Acid. By DE FORCRAND (*Compt. rend.*, **96**, 710—713).—The author has determined the heats of solution of glycollic acid and sodium glycollate in varying quantities of water. The results obtained with glycollic acid may be represented by the formula $Q = -0{\cdot}012 \frac{1{\cdot}452}{n}$, where n represents the number of H_2O mols. originally united with the acid: starting with from 18 to 20 H_2O, the formula $Q = -\frac{1{\cdot}93}{n}$ is sufficient. The results with sodium glycollate are represented by the formula $Q = 0{\cdot}213 - \frac{33{\cdot}652}{n + 19{\cdot}515}$. The heat of combination of the acid and base in concentrated solutions, calculated from these data, differs but little from the heat of combination in dilute solutions, a result similar to that obtained in the case of strong acids. Themochemical measurements show that acid glycollates can be formed even in dilute solutions, and that compounds can be formed at the expense of the alcoholic function of the glycollic acid, as in the case of lactic acid. The salts of glycollic acid may be divided into three groups: (1), neutral salts, stable in presence of water; (2), acid salts, decomposed to a great extent by water; (3), basic salts, which have the characteristics of both neutral salts and of alcoholates, and which, like the acid salts, are partially decomposed by water. C. H. B.

Heat of Combination of Glycollates. By D. TOMMASI (*Compt. rend.*, **96**, 1139—1140).—Reply to Forcrand (this vol., p. 708, and preceding Abstract).

Ammonium Hydrosulphide and Cyanide. By ISAMBERT *Ann. Chim. Phys.* [5], **28**, 332—349).—The author, in the course of his investigations on the substances whose vapours occupy twice the volume of a molecule of hydrogen, has studied more particularly the vapour of ammonium hydrosulphide and cyanide, as likely to afford cases bearing on the general problem.

The author at first measured at various temperatures the tension emitted by ammonium hydrosulphide in presence of the ammonia compound of calcium chloride, $CaCl_2,4NH_3$, whose partial dissociation has already been made the subject of experiment. If at any temperature T the latter emitted ammonia of tension F, and the former a vapour of tension $2f$, then, were the ammonium hydrosulphide vaporised without decomposition, the tension of the mixture would be $F + 2f$; but it would be $F + f$ if the dissociation of the salt were complete, and an intermediate number in the case of partial decomposition. But experiment did not confirm any of these *à priori* suppositions; the tension of the mixed vapours was even less than $F + f$, which corresponds to the complete decomposition. The author proceeding to investigate the cause of this phenomenon, found that in the presence of an inert gas, hydrogen or nitrogen, the pressure exerted is the sum of the pressures of the gas and the vapour of the hydrosulphide; but if ammonia or hydrogen sulphide be substituted for the inert gas, the same general law does not hold good. For the total pressure exerted is less than the sum of the tensions, this diminution being due either to an absorption of the gas, hydrogen sulphide or ammonia, by the hydrosulphide, or to a diminution of the tension of the vapour of the salt by the presence of these gases. Experiments are quoted to confirm this latter view.

The numerical results of the tensions of the vapour of the salt in the presence of one of its constituent gases, proved that the gases, ammonia and hydrogen sulphide, exert the same pressure in the mixture, whether in a state of combination or not, the pressure of one of the gases being inversely proportional to the pressure of the other. This empirical law can be expressed by an equation $\frac{P^2}{4} = (h + x)x$, in which P is the tension of the hydrosulphide in a vacuum, h, the pressure of the gas introduced in excess, and $2x$ the tension of the hydrosulphide in the presence of this excess h of one of its constituent gases. This formula has been applied by Horstmann to cases in which a solid compound, as ammonium chloride, is resolved by heat into equal volumes of its constituent gases.

Owing to the difficulties presented in the investigation of ammonium hydrosulphide, the author turned his attention to the study of the vapours of ammonium cyanide. He made a series of determinations at the same temperatures of the tensions of vapours of (1), hydrocyanic acid; (2), ammonium cyanide; (3), ammonium cyanide in presence of more or less considerable excess of hydrocyanic acid; (4), of ammonium cyanide in presence of a known excess of ammonia. In the third of these cases, in which the hydrocyanic acid is in excess, the total pressure is independent of the quantity in excess of the acid, and in all cases is equal to that which would have been exerted, had the ammonium cyanide been absent altogether. This doubtless arises from the non-volatilisation of the ammonium cyanide in presence of the hydrocyanic acid—a view which has been put forward by Engel and Moitessier to explain analogous cases; or from a diminution of the tension of vapour of hydrocyanic acid in presence of the cyanide, this diminution being compensated by the tension of the cyanide. In the presence of ammonia in excess, the cyanide behaves exactly as the hydrosulphide, and observations on the tension of the mixed gases agree with those deduced from the formula given above. In order to decide between the hypothesis of Engel and Moitessier and that of the author, a small quantity of gaseous hydrochloric acid was introduced into the vessel containing the ammonium cyanide and excess of hydrocyanic acid. White vapours were thus produced, which prove that the ammonium cyanide is partially decomposed into ammonia and hydrocyanic acid. Analyses of the mixed vapours confirmed this fact. The view propounded by the author is the more correct, and the tension of ammonium cyanide in presence of hydrocyanic acid can be calculated according to Horstmann's formula. From this study of the vapour of ammonium cyanide, no conclusion can be drawn as regards the composition of the vapour of this salt; for although certain experiments seem to militate against the decomposition of the salt when vaporised, yet the whole investigation is beset with so many difficulties that the conclusions cannot be considered as final. V. H. V.

Wave of Explosion. By BERTHELOT and VIEILLE (*Ann. Chim. Phys.* [5], **28**, 289—331).—The authors, in the course of experiments on explosives, were led to examine the velocity of propagation of explosion in gases, varying the conditions of the phenomenon, such as the pressure of the gases, their nature and relative proportion, and the form, dimensions, and material of the containing vessels. The investigations have revealed a new kind of undulatory movement, the wave of explosion, which consists of a certain regular surface, wherein is developed the chemical transformation and its concomitant alteration of temperature and pressure; this surface, once produced, is transmitted layer by layer, throughout the entire mass, by successive shocks of the gaseous molecules, with a gradual increase of vibration, due to the heat developed by the chemical combination. The effects produced are comparable to an exaggerated sonorous vibration, although it is to be observed that an explosion gives rise to an isolated characteristic wave, while sound is produced by a periodic succession of similar waves. The following are the principal characteristics of the wave of explosion:—(1.) It is propagated uniformly; (2), its velocity is dependent on the nature of the explosive mixture, and not on the material of the containing vessel; (3), its velocity is independent of pressure; these two latter facts prove that the wave of explosion is regulated by the same general laws as the wave of sound; (4), the theoretical relation existing between the velocity of the wave of explosion and the chemical nature of the gas is difficult to establish, for the former is dependent upon the temperature and *vis viva* of the gaseous molecules, which vary with different systems. However, if the total energy of the gas at the moment of explosion depends on its initial temperature and the heat disengaged during the combination, then these two data determine the *vis viva*, and consequently the absolute temperature of the system, which is proportional to the *vis viva* $\frac{1}{2}m\theta^2$, *i.e.*, the *vis viva* communicated to the molecule is none other than the heat energy developed in the reaction. At 0°, the gas produced by the reaction contains a quantity of heat q, equal to $273c$ (c being the specific heat); at the moment of combination it contains, in addition to this, a quantity of heat Q, disengaged by the reaction. The *vis viva* of the translation θ of the molecules $= \frac{1}{2}m\theta^2$, in the former and latter conditions are in the ratio $\frac{Q + q}{q}$, consequently $\theta_1 = \theta_0 \sqrt{\frac{Q + q}{q}}$, a formula which the authors have verified by experiment.

In order to investigate the properties of this explosive wave, a tube about 40 m. long was filled with the detonating mixture at known pressure; the mixture was ignited at one of the extremities of the tube by an electric spark, and the flame produced destroyed the connection of two electric circuits. The interval of time elapsing between the interruption of these two currents was measured by a Le Boulengé chronograph. With the aid of this apparatus, which is described at length in the original memoir, the authors carried on experiments in order to determine whether the velocity of the explosive wave is dependent upon the position, length, and material of the tube, when opened or closed at both or one end, on the initial pressure of the gaseous mixture, and its composition. It was found in the cases of mixtures of hydrogen or carbonic oxide with oxygen, that the velocity is independent of the position of the tube, whether horizontal or vertical, of the material, whether of lead or caoutchouc, of its diameter, and also whether one or both ends were closed or opened. The velocity is also independent of the initial pressure of the gases.

Tables are given of the velocity of the explosion in mixtures of hydrogen, carbonic oxide, acetylene, ethylene, ethane, methane, and cyanogen, with the necessary quantity of oxygen, and the experimental results compared with those deduced from the formula $\theta_1 = \theta_0 \sqrt{\frac{Q + q}{q}}$:—

Mixture.	Velocity calculated in meters per second.	Velocity found in meters per second.
Hydrogen and oxygen	2831	2810
Carbonic oxide	1941	1089
Acetylene................	2660	2482·5
Ethylene	2517	2209·5
Ethane..................	2483	2363
Methane	2427	2287
Cyanogen................	2490	2195

In the case of the hydrocarbons and cyanogen, the velocity found is less than that calculated according to the above formula; in the case of carbonic oxide the formula is not applicable. It is evident that the velocity is independent of the relation between the volumes of the combustible gas and the oxygen, and of the initial and final volumes.

Results are also given of experiments with a mixture of two combustible gases with oxygen, of a combustible gas with a gas which supports combustion, of isomeric mixtures of hydrogen and hydrocarbons with oxygen, which produce finally the same quantities of carbonic anhydride and water. The influence of the presence of an inert gas as nitrogen is also investigated. As a result of these various forms of experiment, it may be stated generally that the velocity of translation of the gaseous molecules, which preserves the whole of the *vis viva* corresponding to the heat disengaged in the reaction, can be regarded as the limit of maximum velocity of propagation of the wave of explosion. This velocity is diminished by the presence of an inert gas, and in the case of carbonic oxide seems to be dependent upon another law.

With a slightly different form of apparatus, the authors examined the conditions necessary for the production of the explosive wave, and of the state of the gases immediately preceding their detonation. It is thus shown that the velocity of the wave increases rapidly up to a point distant about 5 cm. from the point of inflammation of the explosive mixture; from that point the velocity for each interval of space is practically constant. Experiments with mixtures of carbonic oxide and oxygen with nitrogen showed that for detonation at least 60 per cent. of carbonic oxide are necessary, but for combustion only 20 per cent.; and in mixtures of oxygen and hydrogen 22 per cent. of hydrogen are required for detonation, and 6 per cent. for combustion. It is further noticed that a mixture of cyanogen with nitric oxide detonates violently, when ignited by a spark, but burns quietly when lit by a match. The various results obtained all point to the conclusion that the phenomenon of the explosive wave is quite distinct from that of ordinary combustion, each being marked by well-defined limits, which the authors denominate the *régime* of detonation and of combustion respectively. The transition from one to the other is accompanied by violent molecular movements. V. H. V.

Affinity Values of Carbon. By A. Geuther (*Annalen*, **218**, 12—13).—The researches of Röse on the mixed alkyl salts of carbonic acid (Abstr., 1881, 251) have established that the affinity values of carbon are equal; the author with his pupils has carried on investigations on the acetals, taking as the starting point the so-called ethylene oxychloride and aldehyde chloride. But it was found that the latter alone possessed the power of forming mixed acetals, and thus of affording a basis for the investigation of the "carbonic oxide" affinities. V. H. V.

Specific Gravity and Chemical Affinities of Elements in Various Allotropic Modifications. By W. Müller-Erzbach (*Annalen*, **218**, 113—120).—The author would generalise into a law the well-known facts that elements, when prepared by different processes, possess different atomic volumes and chemical affinities, and thus to bring forward further corroboration of his law of "smallest volumes" (Abstr., 1882, 137). This law states that chemical reactions are intimately connected with contraction of mass, inasmuch as the reactions are the more violent the smaller the volumes occupied by the combinations resulting from it. In many cases, one form of an element at a given temperature passes into another, but this molecular change is a particular case of the interaction of two substances, differing merely from it in that the reacting bodies are of the same and not of different kind.

The author in the original paper adduces various examples of the differences in chemical behaviour and atomic volume of the allotropic modifications of sulphur, selenium, phosphorus, carbon, silicon, boron, arsenic, and tin. Of these eight elements, there are only two, sulphur and selenium, which do not display a higher degree of chemical affinity associated with a lower specific gravity; in the remaining cases, this conclusion is most marked, and in no case is greater affinity associated with higher specific gravity.

The author considers that the relation affords a fresh corroboration of his law that the energy of a chemical reaction is dependent upon the volumes occupied by the resultant substances; conversely if by the combination of two chemically analogous substances allotropic modifications are formed, then the lower its specific gravity the more easily is it decomposed into another form. V. H. V.

Constitution of Hydrated Salts. By E. Wiedemann (*Ann. Phys. Chem.*, **17**, 561—576).—The dilatometrical method has been applied by the author in an investigation of the changes of volume undergone by certain hydrated salts when gradually heated in the solid state. His experiments show that changes of constitution take place before fusion. Two new modifications of magnesium sulphate may thus be recognised.

These results have certain relations to other researches. Thus, for example, before we can determine the tensions, we must first ascertain whether or not the salt changes in constitution within the given range of temperature; and again in researches on the heat of solution, &c., it is necessary to know the precise constitution of the salts at the temperature in question. R. R.

Inorganic Chemistry.

Chlorine Hydrates. By E. Maumené (*Chem. News*, **47**, 145—146).—The author publishes the following in reply to Ditte's note (this vol., p. 550). He finds that the hydrate formed by passing a rapid current of chlorine through water at 5° is of a pale yellow colour, and after being drained and pressed between filter-paper, has the composition $Cl_2,12H_2O$. If this hydrate is enclosed in a bent tube according to Faraday's directions for obtaining liquid chlorine, deep yellow crystals may be seen bordering upon the liquefied gas; these crystals vary in composition. When formed in presence of excess of chlorine, they have the constitution $Cl_2,4H_2O$, whilst when produced in presence of much of the solution, they have a variable constitution approximating to $Cl_2,7H_2O$. They are produced and remain as long as the solution of chlorine is hot enough to prevent an absorption of chlorine. According to the author's theory, chlorine when in presence of about an equal weight of water, can combine with an equal weight of it or 72 parts, the crystals formed being $Cl_2,4H_2O$. When, however, the water is in excess, the $Cl_2,4H_2O$ in its turn combines with an equal weight or 144 parts of water, *e.g.*, $Cl_2,12H_2O$.

Lastly, these two hydrates can combine together in equal weights, and the result is that $Cl_2,12H_2O$ combines with $2(Cl_2,4H_2O)$, forming $Cl_6,20H_2O$ or $Cl_2,6{\cdot}67H_2O$, or the hydrate bordering on $Cl_2,7H_2O$. From this it will be readily seen how Faraday found a hydrate containing $Cl_2,10H_2O$. D. A. L.

Liquefaction of Oxygen and Nitrogen; Solidification of Carbon Bisulphide and Alcohol. By S. Wroblewski and K. Olszewski (*Compt. rend.*, **96**, 1140—1142, and 1225—1226).—Liquid ethylene boils at − 102° to 103° under a pressure of one atmosphere, and not at − 105° as is generally stated. This temperature is above the critical point of oxygen, but by the rapid evaporation of liquid ethylene in a vacuum, a temperature as low as − 136° can be obtained. At this temperature oxygen liquefies under a moderate pressure, the numbers obtained being as follows:—

Temperature.	Pressure at which oxygen liquefies.
− 131·6°	26·5 atmos.
− 133·4°	24·8 ,,
− 135·8°	22·5 ,,

Liquid oxygen is colourless, transparent, and very mobile; it forms a very distinct meniscus.

Nitrogen does not liquefy at − 136° even under a pressure of 150 atmos., but if the pressure is somewhat slowly released, care being taken not to diminish it below 50 atmos., the nitrogen liquefies completely and forms a colourless transparent liquid with a very distinct meniscus; it evaporates very rapidly.

Carbonic oxide has been liquefied in a similar manner. It forms a colourless liquid with a distinct meniscus.

Carbon bisulphide solidifies at about − 116°, and melts at about − 110°. Alcohol becomes viscous like oil at about − 129°, and solidifies to a white mass at about − 130·5°.

All these low temperatures were measured with a hydrogen thermometer. C. H. B.

Action of Heat on Sulphuric Monochloride and Dichloride. By K. Heumann and P. Köchlin (*Ber.*, **16**, 602—608).—The readiness with which sulphuric dichloride, SO_2Cl_2, is decomposed by phosphorus, arsenic, and antimony has been pointed out by the authors (Abstr., 1882, 1262). When its vapour is passed through a glass tube at a dull red heat, it is completely decomposed into sulphurous anhydride and chlorine. This decomposition is further confirmed by vapour-density determinations made at high temperatures. In aniline vapour (184°) normal results are obtained, whilst in sulphur vapour (442°) the dissociation is complete. Many vapour-density determinations of sulphuric monochloride, $SO_2(OH)Cl$, have been made by different chemists, and different explanations given of the way in which this body is decomposed. The authors have experimented at 184° and at 442°, and they find that at the latter temperature the vapour-density is 2·09 instead of 4·04, the dissociation being nearly complete at 184°. The decomposition probably takes place thus:—

$$2SO_2(OH)Cl = SO_2 + Cl_2 + SO_3 + H_2O.$$

A. K. M.

Pyrosulphuric Chloride. By D. KONOWALOFF (*Compt. rend.*, **96**, 1059—1062, and 1146—1148).—A reply to Ogier (this vol., p. 646).—Pyrosulphuric chloride carefully purified by fractional distillation, whether prepared from carbon tetrachloride and sulphuric anhydride, from sulphuric monochloride and phosphoric pentoxide, or from sulphuric anhydride and sulphur chloride, boils at 153°, and has the density 7·3. It is very difficult to purify pyrosulphuric chloride from sulphuric monochloride by the action of even large quantities of phosphoric anhydride, and it is better to prepare it from perfectly anhydrous materials. C. H. B.

Combination of Phosphoric Acid with Silica. By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **96**, 1052—1054).—Silica obtained by the decomposition of silicon fluoride by water is added to fused metaphosphoric acid, and the fused mass extracted with boiling water, when transparent colourless octohedrons are obtained, which have no action on polarised light. These crystals are rarely distorted by unequal development of the faces, but their angles are sometimes slightly truncated. They scratch glass, have a sp. gr. of 3·1 at 14°, and melt on platinum before the blowpipe to a colourless glass which does not devitrify on cooling. The crystals have the composition SiO_2, 29·37; P_2O_5, 69·91; Al_2O_3, 0·57, corresponding with the formula SiO_2,P_2O_5. Phosphates of zirconia and other dioxides can probably be formed in the same way. The solubility of different phosphates in metaphosphoric acid furnishes a method of acting on these phosphates with silica under conditions favourable to the formation of crystallised silicates. C. H. B.

Phosphates. By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **96**, 1142—1144).—Orthophosphates, pyrophosphates, and the intermediate phosphates can be obtained in crystals by fusing metaphosphates with metaphosphoric acid mixed with progressively increasing quantities of trisilver phosphate. If this method is applied to the phosphates of sesquioxides, double salts are obtained containing both the sesquioxide and silver oxide, the latter being easily displaced by an alkaline base. The formation of double compounds of the types $2M_2O_3,Ag_2O,4P_2O_5$, and $2M_2O_3,2Ag_2O,5P_2O_5$ almost always accompanies the formation of simple phosphates of the sesquioxides.

Aluminium metaphosphate crystallises in pseudo-cubic crystals from fused metaphosphoric acid containing a small quantity of trisilver phosphate, but if the silver phosphate is present in notable proportion, birefractive crystals which act strongly on polarised light are obtained in addition to the metaphosphate. These crystals are formed exclusively by fusing 2 parts alumina with 4·6 parts metaphosphoric acid and 8 parts silver phosphate, and the same result is obtained by fusing aluminium metaphosphate with about three times its weight of silver phosphate. The double phosphate thus obtained has the composition $2Al_2O_3,Ag_2O,4P_2O_5$, and forms colourless perfectly transparent crystals derived from rhombic prisms. It is not very stable in the fused mixture, and the presence of a slight excess of metaphosphoric acid causes the formation of monoclinic crystals of aluminium pyrophosphate, $Al_2O_3,2P_2O_5$, free from silver. The presence of an excess of silver phosphate converts the original crystals or the pyrophosphate into acute octohedrons, apparently derived from a monoclinic prism, and having the composition $2Al_2O_3,3P_2O_5$.

Ferric and chromic oxides and the corresponding amorphous phosphates yield similar results when treated in a similar manner. The double salt $2Fe_2O_3,2Ag_2O,5P_2O_5$ forms highly refractive slightly rose-coloured rhombic prisms. The salt $2Cr_2O_3,2Ag_2O,5P_2O_5$ forms deep emerald-green crystals derived from a monoclinic prism, and macled in the same manner as sphene. Uranium sesquioxide yields similar compounds. C. H. B.

Action of Sulphur on Alkaline Phosphates. By E. FILHOL and SENDERENS (*Compt. rend.*, **96**, 1051—1052).—Finely divided sulphur has no action in the cold on solutions of trisodium or tripotassium phosphate, but if the solutions are heated, a notable quantity of alkaline polysulphide and thiosulphate is formed. In moderately concentrated solutions, trisodium phosphate is converted in less than two hours into disodium phosphate, in accordance with the equation $6Na_3PO_4 + 3H_2O + S_n = 2Na_2S_n + Na_2S_2O_3 + 6Na_2HPO_4$. When a solution containing 52·82 grams of disodium phosphate per litre is heated with sulphur in sealed tubes at 100° for more than 300 hours, it is entirely converted into sesquisodium phosphate (Abstr., 1882, 693). This reaction would seem to indicate that phosphoric acid is a sesquibasic acid of mixed function. C. H. B.

Bromapatites and Bromowagnerites. By A. DITTE (*Compt. rend.*, **96**, 846—849).—The author has prepared several bromapatites in addition to those previously described (this vol., p. 648). They were obtained by heating the metallic bromide with a small quantity of ammonium phosphate at the lowest possible temperature, out of contact with the air. If the apatite is required free from the corresponding wagnerite, a mixture of metallic bromide and sodium bromide must be used. The proportion of sodium bromide must not exceed a certain limit, otherwise the apatite will be decomposed. In this way, the bromapatites of barium, strontium, manganese, and lead were obtained. They all crystallise in transparent prisms or plates belonging to the hexagonal system, and are readily soluble in dilute nitric acid. They have the general formula $MBr_2,3(M_3P_2O_8)$, where M represents one atom of a dyad metal.

The corresponding brom-mimetites were obtained by substituting ammonium arsenate for ammonium phosphate. They crystallise in transparent prisms or plates belonging to the hexagonal system.

Barium, strontium, and lead bromovanadinites were obtained by adding vanadic acid to the fused bromides, care being taken to avoid the presence of reducing gases. They crystallise in hexagonal prisms or plates, and are soluble in dilute nitric acid.

Bromarsenio-manganese wagnerite, $MnBr_2,Mn_3As_2O_8$, is obtained by adding ammonium arsenate to a large excess of the fused metallic bromide. It forms rose-brown transparent prisms, easily soluble in dilute nitric acid. The corresponding phosphate is obtained in a precisely similar manner. Similar compounds are apparently obtained from magnesium bromide, but they are always mixed with a large proportion of magnesia, formed by the decomposition of the bromide.

C. H. B.

Iodo-apatites. By A. DITTE (*Compt. rend.*, **96**, 1226—1229).—The iodo-apatites cannot be obtained by means of the iodides of the alkaline-earths, since these are decomposed when fused, but by employing double iodides of the alkalis and alkaline-earths, carefully regulating the proportions of the mixtures, preventing access of oxygen to the fused salt, and taking care not to prolong the fusion more than is necessary, the author has succeeded in obtaining iodophosphates, iodoarsenates, and iodovanadates of barium, strontium, and calcium, closely resembling in crystalline form and other properties the corresponding chlorine- and bromine-compounds.

C. H. B.

Antimonious Sulphide in Aqueous Solution. By H. SCHULZE (*J. pr. Chem.* [2], **27**, 320—332).—The author has recently (this vol., p. 295) pointed out the existence of a soluble colloïdal modification of arsenious sulphide, and now shows that a similar modification of antimonious sulphide can be obtained. It can be prepared from antimonious oxide in a manner similar to that described for the arsenic-compound, but, owing to the sparing solubility of antimonious oxide in water, that method is very troublesome. Good results were obtained with solutions of tartar emetic, sulphuretted hydrogen giving a deep red coloration, but no precipation in solutions containing $\frac{1}{200}$ of that salt. The best results, however, were obtained with a solution of antimonious oxide in tartaric acid (4·3 grams Sb_2O_3 per litre = 5 grams Sb_2S_3). On saturating this solution with sulphuretted hydrogen, it assumes a very deep nearly blood-red colour, is completely clear by transmitted light, but appears brownish-red and turbid by reflected light, and shows strong fluorescence. Strong solutions when viewed in a thin layer are yellowish-red in colour, and with dilution the yellow tint becomes more pronounced. The analytical results show that the dissolved substance is the trisulphide. The colloïdal properties are well marked. It can be readily separated from crystalloïds by dialysis. The solution is tasteless, and on evaporation leaves a brownish-red varnish of hydrated antimonious sulphide. It is much less readily converted spontaneously into the insoluble form than is colloïdal arsenious sulphide, but, like the latter, is readily precipitated by addition of acids or salts. The author considers it very probable that many other substances usually regarded as insoluble may be found capable of existing in solution in the colloïdal form. He is at present investigating what appears to be a soluble modification of selenium. A. J. G.

Production of Crystallised Vanadates in the Dry Way. By A. DITTE (*Compt. rend.*, **96**, 1048—1051).—The reactions which take place between substances dissolved in fused salts obey the same laws as in other solutions, and just as water can decompose certain double salts, so a fused salt can decompose the compounds which are formed in it. For example, in the artificial formation of apatites, &c. (this vol., p. 648), the particular reaction which takes place is determined by the relative proportions of the haloïd alkaline salt and the haloïd salt of the alkaline earth, and the proportions necessary for the production of a particular compound are different in the three cases of chlorides, bromides, and iodides. By taking advantage of this fact, the author has prepared the following crystallised vanadates. *Barium vanadate*, BaO,V_2O_5, obtained by heating vanadic acid with sodium bromide and a very small quantity of barium bromide, forms yellowish brilliant transparent crystals, which melt at a red heat, and are only slightly soluble in water. *Strontium vanadate*, $3SrO,V_2O_5$, by heating vanadic acid with a mixture of sodium and strontium iodides, forms yellowish transparent plates. *Lead vanadate*, $PbO,2V_2O_5$, obtained in a similar manner, forms short yellow transparent crystals easily soluble in dilute nitric acid. *Zinc vanadate*, $2ZnO,V_2O_5$, is obtained in orange-red prisms by fusing vanadic acid with a mixture of 5 parts sodium bromide and 1 part zinc bromide, and extracting the residue with water. The crystals are slightly soluble in water, and melt at a red heat. *Cadmium vanadate*, CdO,V_2O_5, obtained in a similar manner, forms brilliant transparent slender yellowish needles which melt at a bright red heat. *Manganese vanadate*, $2MnO,V_2O_3$, obtained by fusing vanadic acid with a mixture of equal parts of manganese and sodium bromides, and treating the slowly cooled mass with water, forms large brilliant fragile brown needles, soluble with difficulty in cold dilute nitric acid, but soluble in the hot acid. *Nickel vanadate*, $3NiO,V_2O_5$, obtained by heating small quantities of vanadic acid and nickel bromide with a large excess of sodium bromide, and treating the fused mass with water and dilute nitric acid, forms green prismatic needles, sometimes much flattened. These crystals do not melt at a bright red heat, are insoluble in hot nitric acid, and are but slowly attacked by fused potassium carbonate, but dissolve easily in hydrogen potassium sulphate. C. H. B.

Reduction of Tungsten Compounds. By O. FREIH (*Ber.*, **16**, 508—511).—When tungsten trioxide solutions are reduced with zinc, the final product of the reaction is tungsten dioxide. The reduction does not proceed as readily as in the case of molybdenum trioxide. The author finds that it is advisable to employ tolerably strong hydrochloric acid (27 per cent.). The solution first becomes blue, then black, dark green, and finally a dark red.

It undergoes partial oxidation in the air. If titrated according to Zimmermann's method (*Annalen*, **213**, 304), the dioxide can be very exactly estimated. In a solution containing oxide equivalent to 6·89 per cent. of oxygen, the mean of six determinations made by the author was 6·886 per cent. He employs the following method for estimating small quantities of tungsten trioxide. The solution of the salt in a small quantity of water, containing not more than 0·1 gram WO_3, is heated on a water-bath and immediately treated with 70—80 c.c. of 27 per cent. hydrochloric acid, after which 14—15 grams of stick zinc are added. The iron contained in the zinc must be previously determined. As soon as the red colour is observed, the flask is cooled, and the contents poured into a porcelain basin containing an excess of potassium permanganate and manganese sulphate (40 c.c.) and dilute sulphuric acid (70—100 c.c.). After washing out the flask the whole is diluted to about a litre, an excess of ferrous sulphate solution is added, and the solution is titrated with permanganate. The mean of eight experiments made by the author on solutions containing 78·91 per cent. WO_3, was 78·93 per cent. J. I. W.

Borotungstates. By D. Klein (*Compt. rend.*, **96**, 1054—1056).—The addition of concentrated hydrochloric acid to the dense mother-liquor obtained by the action of boric acid on a solution of neutral sodium tungstate (*Compt. rend.*, **94**, 1070), precipitates a white crystalline *boroquatuordecitungstate*, $14WO_3,B_2O_3, 2Na_2O,4H_2O + 25Aq$, which was previously described as a boroduodecitungstate. It dissolves in water, and on gradual evaporation crystallises in hexagonal prisms. The corresponding acid could not be obtained. The tribarium salt, $14WO_3,B_2O_3,3BaO,5H_2O$, and the tripotassium salt, $14WO_3,B_2O_3,3K_2O + 22Aq$, crystallise in needles; the trisilver salt, $14WO_3,B_2O_3,3Ag_2O,7H_2O + Aq$, is amorphous. Some of the properties of these and of the double sodium barium and sodium strontium salts, have been described in a previous paper (this vol., p. 23), but some of the formulæ given were inexact. These boroquatuordecitungstates, or more briefly, *borotungstates*, are decomposed by boiling acids with formation of a tungstoborate, and tungstic hydrate.

The potassium boroduodecitungstate previously described (*Compt. rend.*, **91**, 495), yields with barium chloride a double salt,

$$12WO_3,B_2O_3,3BaO,K_2O + 28Aq,$$

which was erroneously described as a barium boroduodecitungstate; it forms large quadratic crystals. The mother-liquors from potassium boroduodecitungstate deposit rectangular tables of the composition $12WO_3,B_2O_3,4K_2O + 21Aq$. They are decomposed by boiling hydrochloric acid, and probably belong to a new class of salts. Boroduodecitungstic acid, obtained by decomposing the insoluble mercurous salt with hydrochloric acid and mercury, can only be concentrated by heat up to a certain limit, beyond which it splits up into tungstoboric acid and tungstic hydrate.

The action of boric acid on ammonium paratungstate yields a very dense liquid, which continually loses ammonia when heated, and on cooling deposits oblique prisms, and a saccharoïd crystalline mass belonging to a new class of borotungstates.

When sodium paratungstate is treated with three-fourths its weight of boric acid and the solution concentrated, a non-crystallisable mother-liquid is obtained, from which another new class of borotungstates can be prepared. The barium salt forms rhombic prisms. C. H. B.

Organic Chemistry.

Preparation of Paraffins. By B. Köhnlein (*Ber.*, **16**, 560—563).—The author finds that when normal propyl iodide is heated with pure anhydrous aluminium chloride at 130—140° in a sealed tube from which the air has previously been exhausted, pure propane is formed. Isobutyl iodide, when treated in a similar manner, yields pure butane. Ethyl iodide yields ethane. The method appears to be of universal applicability for the preparation of the paraffins of the C_nH_{2n+2} series.

J. I. W.

"Reaction Aptitudes" of the Halogens in Mixed Haloïd Ethers. By L. Henry (*Compt. rend.*, **96**, 1062—1064, and 1149—1152).—The experiments described in this paper were undertaken with a view to ascertain in what order radicles X, X′, X″, combined with the hydrocarbon residue C_nH_m, and having equivalent or analogous functions, are affected by a foreign body Y, to the action of which they are susceptible.

Ethylene Chlorobromide.—The action of various metallic reagents, such as potassium hydroxide, sodium ethylate, potassium acetate, potassium thiocyanate, silver nitrate, &c., in equivalent proportions, resulted in the formation of a metallic bromide, and different organic compounds. In a few cases only were traces of a metallic chloride formed, whence it appears that metallic reagents have an exclusive or almost exclusive preference for the bromine in ethylene chlorobromide. The reaction with silver nitrate is particularly well marked. The reaction of alcoholic solutions of ethylene chlorobromide and silver nitrate, in molecular proportion, gives a white bulky precipitate of pure silver bromonitrate, Ag_2BrNO_3, and a mixture of ethylene chloronitrate, $C_2H_4Cl.NO_3$, and ethylene chlorobromide, only half the latter being decomposed; in order to completely decompose the ethylene chlorobromide, 2 mols. silver nitrate must be used. This reaction furnishes an easy method of preparing silver bromonitrate, and the formation of this compound in this way indicates that the molecule of silver nitrate is $\begin{array}{c}AgNO_3\\ |\\ AgNO_3\end{array}$.

Ethylene Chloriodide.—The reactions with this compound are rendered less distinct by the secondary changes, due to the action of the group CH_2Cl on the metallic iodide at first formed; in the initial reactions, however, metallic reagents shown an exclusive or almost exclusive preference for the iodine. With silver nitrate, silver iodonitrate is formed, resembling the bromonitrate in its properties.

Ethylene Bromiodide.—With this compound, the secondary changes are still more marked, a considerable quantity of iodine being always liberated, in consequence of the decomposition of the metallic iodide at first formed, by the action of the group CH_2Br which is more active in this respect than the group CH_2Cl. Metallic reagents show a marked preference for the iodine.

The experiments with ethylene chlorobromide and ethylene bromiodide, show that there is a greater difference between the "reaction aptitudes" of chlorine and bromine than between those of bromine and iodine. C. H. B.

Reconversion of Nitro-Glycerol into Glycerol. By C. L. Bloxam (*Chem. News*, **47**, 169).—The author has observed that nitroglycerol is decomposed by alkaline and alkaline earthy sulphides; thus, when an alcoholic solution of nitro-glycerol is shaken with alcoholic potassium hydrogen sulphide, considerable rise in temperature take place, the solution becomes red, a large quantity of sulphur separates, and the nitro-glycerol is converted into glycerol. With potassium or yellow ammonium sulphide, the reaction is less vigorous; in the latter case a qualitative examination of the products of decomposition proved the presence of glycerol, ammonium nitrite and sulphur, the reaction can therefore be thus expressed: $C_3H_5(NO_3)_3 + 3NH_4HS = C_3H_5(OH)_3 + 3NH_4NO_2 + S_3$. With calcium sulphide, the reaction is much slower than in the other cases, and more agitation is required; the reduction, however, is complete in a few minutes. D. A. L.

Ethylidene Oxychloride. By H. Laatsch (*Annalen*, **218**, 13—38).—Ethylidene oxychloride, $C_4H_8OCl_2$, first obtained by Lieben by the action of dry hydrochloric acid on aldehyde, is isomeric with dichlorethyl oxide, one of the products of the action of chlorine on alcohol; to the latter, Lieben assigned the formula $CH_2Cl.CHCl.O.CH_2Me$, and to the former the constitution $(CHClMe)_2O$. The formation of alcohol and ethyl iodide affords a confirmation of the presence of the ethyl-group in dichlorether, whilst the production of acetic acid by the action of water indicates the presence of a methyl-group. To determine the constitution of ethylidene oxychloride is the object of the present communication.

Alcohol forms, with ethylidene oxychloride, aldehyde, hydrochloric acid, and aldehyde ethyl chloride, thus, $C_4H_8Cl_2O + 2C_2H_5O.2(C_2H_4O + EtCl) + H_2O$; sodium ethylate, free from alcohol, gives alcohol and diethylacetal, whilst sodium ethylate containing alcohol gives, besides diethylacetal, ethylideneoxyethyl alcoholate, $C_4H_8(OEt)_2O$, derived from ethylidene oxychloride by the replacement of 2 atoms of chlorine by two ethoxyl-groups. This latter compound is a colourless liquid (b. p. 153°, sp. gr. = 0·891), sparingly soluble in water, and undergoing a gradual decomposition into diethylacetal and aldehyde. Similarly, sodium methylate, propylate, isobutylate, and isoamylate, gave their corresponding ethylidene oxyalcoholates, the physical properties of which are collected in the following table:—

	Formula.	Boiling point.	Specific gravity.
Methyl compound..	$C_4H_8(OMe)_2O$	126	0·953
Propyl............	$C_4H_8(OPr^\alpha)_2O$	184	0·895
Isobutyl	$C_4H_8(OC_4H_9)_2O$	174	0·879
Isoamyl	$C_4H_8(OC_5H_{11})_2O$	226	0·874

The author studied further the action of various alcohols on these derivatives, and obtained in every case a mixture of two acetals, and not a so-called mixed acetal. Thus—

$C_4H_8(OMe)_2O$ and amyl alcohol gave dimethyl and diamyl acetal.
$C_4H_8(OC_5H_{11})_2O$ and methyl alcohol gave dimethyl and diamyl acetal.
$C_4H_8(OPr^{\alpha})_2O$ and amyl alcohol gave dipropyl and diamyl acetal.
$C_4H_8(OPr^{\alpha})_2O$ and methyl alcohol gave dimethyl and dipropyl acetal.
$C_4H_8(OC_4H_9)_2O$ and methyl alcohol gave dimethyl and diisobutyl acetal.
$C_4H_8(OC_5H_{11})_2O$ and ethyl alcohol gave diethyl and diamyl acetal.

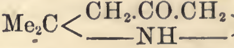
Inasmuch as the action of water on ethylidene oxychloride gives aldehyde and hydrochloric acid, it appears that its constitution is expressed by the formula $(CHClMe)_2O$, *i.e.*, that it is the ether of monochlorethyl alcohol, or the analogue of aldehyde ethyl chloride, $CH_3.CHO,EtCl$, in which one hydrogen-atom in the ethyl-group is replaced by chlorine. V. H. V.

Action of Bromine on Amines in Alkaline Solutions. By A. W. HOFMANN (*Ber.*, **16**, 558—560).—On treating a solution of a primary monamine in hydrochloric acid with alkaline bromine, a nitrogen bromine compound is obtained which contains 2 atoms of bromine. The amines of the propyl and butyl series yield compounds analogous to the bodies $MeNBr_2$ and $EtNBr_2$. Hexylamine and octylamine undergo the same reaction.

When a secondary amine is subjected to the same treatment, if it contains two alcohol-radicles, the primary amine will be formed. If, however, it contains a divalent alcohol-group, a nitrogen bromine compound is formed, which contains only 1 atom of bromine. The formation of piperidine and conine derivatives has been previously described (*Ber.*, **14**, 2725, and **15**, 767). If the conine-derivative be treated with an acid, a base closely resembling conine is formed; it differs from it, however, in containing 2 atoms less hydrogen. The compound, $C_8H_{15}N$, boils at 158°, and is a tertiary base. It also differs from conine in yielding a picrate which is sparingly soluble. On treatment with an alkali, the conine-derivative yields a secondary base, $C_8H_{14}\dot{:}NH$, of the same composition as the preceding. It boils at 173°, and forms a sparingly soluble platinochloride. Reducing agents convert both this and the preceding base into conine; on allowing the reduction to continue, the conine is reduced, yielding octylamine and octane. The new derivatives of conine complete the series of amines containing 8 atoms of carbon :—

Collidine	$C_8H_{11}N$.
Tropidine	$C_8H_{13}N$.
New conine-derivative ..	$C_8H_{15}N$.
Conine	$C_8H_{17}N$.
Octylamine	$C_8H_{19}N$.

When piperidine is treated in the same manner as conine, it yields bromine and oxygen intermediate products, one of which, $C_5H_7Br_2NO$, resembles the body $C_5H_3Br_2NO$, previously described by the author (*Ber.*, **12**, 986). J. I. W.

Triacetonamine. By E. FISCHER (*Ber.*, **16**, 649—650).—If Heintz's formula  $Me_2C{<}\begin{matrix}CH_2.CO.CH_2\\ \text{——}NH\text{——}\end{matrix}{>}CMe_2$ (Abstr., 1880, 102) is correct, this body must be closely related to tropine, and should yield hydroxytetramethylpiperidine by reduction. By the action of a mixture of phosphorus pentachloride and phosphorus oxychloride on triacetonamine hydrochloride, a chlorinated basic substance is obtained, having an odour like that of conine; ammonia and an oily body being simultaneously formed. It is readily volatile in steam, and forms a crystalline platinochloride, sparingly soluble in water. When triacetonamine is heated with twice its weight of sulphuric acid at 160°, and the product allowed to cool, a crystalline mass is obtained, from which on addition of water and alkali, an oil separates which in its odour resembles piperidine; it consists of a mixture of bases readily volatile in steam, and forming a crystalline hydrate when cooled. The *hydrochloride* crystallises in white needles, melting at 293°, and readily soluble in alcohol. The numbers obtained on analysis agree approximately with the formula $C_9H_{17}N,HCl$.

A. K. M.

Test for Acetal. By M. GRODZKI (*Ber.*, **16**, 512).—When acetal is acted on by acids in presence of water, it yields aldehyde and alcohol. A dilute aqueous solution treated with normal sodium hydroxide solution and normal iodine solution yields a clear colourless liquid; on acidifying, however, a dense precipitate of iodoform is obtained. 1 c.c. of a tenth per cent. solution of acetal gives a perceptible amount of iodoform.

J. I. W.

Constitution of Nitrosomalonic Acid. By V. MEYER and A. MÜLLER (*Ber.*, **16**, 608—611).—In support of Meyer and Ceresole's formula $(COOH)_2C\colon N.OH$ for nitrosomalonic acid, the authors state that they have obtained this body from mesoxalic acid and hydroxylamine, $(COOH)_2CO + NH_2.OH = H_2O + (COOH)_2C\colon N.OH$. The mesoxalic acid is neutralised with soda, a solution of hydroxylamine nitrate added in excess, together with the equivalent quantity of sodium carbonate, and the whole allowed to stand for some days. Solution of silver nitrate is then added, and the precipitate decomposed by hydrochloric acid; the aqueous solution thus obtained is evaporated over sulphuric acid or in a current of air, and the nitrosomalonic acid crystallised from ether. It melts at 120°, and explodes when heated on platinum foil. When its aqueous solution is warmed, it decomposes with evolution of carbonic anhydride and formation of hydrocyanic acid. A further proof of the above formula is afforded by the reduction of benzylnitrosomalonic acid by hydriodic acid, the benzyl-group being split off as benzyl iodide, whilst if the formula $(COOH)_2C(NO).C_7H_7$ were correct, amidobenzylmalonic acid should be formed. The conclusions drawn by the authors are, that isonitroso-bodies are always formed by the action of nitrous acid on the group CH_2, and also on CH when united with easily replaceable radicles, whilst *true* nitroso-bodies are formed when CH is united with difficultly replaceable radicles.

A. K. M.

Derivatives of Meconic Acid containing Nitrogen, and their Conversion into Pyridine. By H. Ost (*J. pr. Chem.* [2], **27**, 257—294).—In a previous paper by the author (Abstr., 1879, 708), two isomeric acids, amidopyromeconic acid and pyromecazonic acid, were described; the investigation of the latter acid is continued in the present paper.

Pyromecazonic acid, $C_5H_3NO(OH)_2$, is best prepared by the reduction of oxypyromecazonic acid (*loc. cit.*) with hydriodic acid; it crystallises in well-formed rhombic nearly quadratic tables, having characteristic striation parallel to the longer axis. It is readily soluble in concentrated acids and in alkalis, the latter solutions oxidise with great readiness on exposure to air; the acid, when mixed with barium chloride and ammonia, gives a precipitate, at first colourless, but which quickly assumes a fine blue colour in contact with air, the reaction being very delicate. *Bromopyromecazonic acid*, $C_5H_2BrNO(OH)_2$, is obtained as a crystalline precipitate on adding bromine to pyromecazonic acid suspended in water and well cooled. It is insoluble in nearly all solvents, but little soluble in boiling water; it dissolves readily in concentrated hydrochloric acid, from which the *hydrochloride* crystallises in long needles; these lose the hydrochloric acid on treatment with water, or on heating at 100°. With ferric chloride, silver nitrate, and ammoniacal barium chloride, the free acid gives the same reaction as pyromecazonic acid. *Diacetylpyromecazonic acid*, $C_5H_3NO(O\overline{Ac})_2$, is obtained by long heating of pyromecazonic acid with excess of acetic anhydride at 150—200°. It crystallises in small prisms, melts at 153—155°, gives no reaction with ferric salts, and is reconverted into pyromecazonic acid by evaporation with water, or better, with hydrochloric acid.

Pyromecazone, $C_5H_3NO \colon O''_2$, a quinone-like body, is obtained by careful oxidation of pyromecazonic acid with nitric acid. It is insoluble in ether, but readily soluble in cold water; it gives no coloration with ferric chloride, but gives a crimson precipitate with barium chloride and ammonia. On crystallisation from ethyl alcohol, colourless needles of the alcoholate, $C_5H_3NO_3,EtOH$, are obtained; this and the corresponding methylate, $C_5H_3NO_3,MeOH$, lose alcohol on exposure over sulphuric acid, leaving a brownish-red residue of partially decomposed pyromecazone. On boiling with alcohol or water, pyromecazone is decomposed with formation of brown amorphous products; on heating it explodes; in aqueous solution it imparts a dark violet colour and most unpleasant odour to the skin. Sulphurous acid readily reconverts it into pyromecazonic acid.

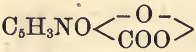
Nitropyromecazone, $C_5H_2NO(NO_2)O_2 + H_2O$, is obtained, in nearly colourless compact prisms, by the action of nitric acid on a solution of pyromecazonic acid in glacial acetic acid. It dissolves readily in water, the solution on standing or on gentle heating evolves carbonic anhydride, and deposits yellow crystals of nitropyromecazonic acid; a much better yield is obtained, however, by reduction with sulphurous acid.

Nitropyromecazonic acid, $C_5H_2NO(NO_2)(OH)_2$, crystallises from hot water, in which it is but partially soluble, in golden-yellow plates, which are not decomposed at 200°. It gives a strong blood-red coloration with ferric chloride, and has a strongly acid reaction. The *sodium* salt, $C_5H_3N_2O_5Na$, crystallises in anhydrous broad yellow needles, and is slowly decomposed on evaporation with water. A cold aqueous solution of pyromecazone on standing deposits small brilliant octohedrons, possibly of the *hydrate* $C_5H_5NO_4$; a satisfactory analysis could not be obtained, owing to contamination by decomposition products.

Hydroxycomenamic acid, $C_5H_2NO(OH)_2.COOH$, obtained by Reibstein (Abstr., 1882, 197) by the action of aqueous ammonia at 150°, on hydroxycomenic acid, can also be prepared by the direct oxidation of comenamic acid. It must be regarded as a carboxylated pyromecazonic acid, as it is resolved on heating at above 150° into carbonic anhydride and pyromecazonic acid; its reactions with ferric chloride and ammoniacal barium chloride are similar to those of the latter.

Bromhydroxycomenic acid, $C_6HBrNO(OH)_2.COOH + 2H_2O$, is obtained by the action of bromine on an aqueous solution of hydroxycomenic acid. It crystallises in very fine needles, is sparingly soluble in cold water, and reduces silver salts.

Azoncarboxylic acid, $C_5H_2ON(O_2)''.COOH + 2H_2O$, is obtained by the oxidation of an ethereal solution of hydroxycomenamic acid with nitric acid; it crystallises in orange-red tables, is readily soluble in water and hot alcohol, sparingly in glacial acetic acid, and is insoluble in ether. It imparts a colour to the skin similar to that given by pyromecazone. Sulphurous acid readily reduces it to hydroxycomenamic acid; water partially effects the same reduction, but the greater part of the substance is resinified.

Comenamic acid, $C_5H_3NO(OH).COOH$, is best obtained by heating comenic acid with aqueous ammonia in an open vessel. It is not decomposed by boiling with solutions of the alkalis; fusion with potash converts nearly the whole of its nitrogen into cyanogen. With ammoniacal barium chloride it gives a white precipitate of the *basic salt*,  $C_5H_3NO<\begin{matrix}-O-\\COO\end{matrix}>Ba$, which assumes a greenish tint on long standing. Oxidised with nitric acid, it yields hydrocyanic and oxalic acids; with potassium permanganate it gives hydroxycomenamic and oxalic acids; and with bromine-water it yields oxalic acid and small quantities of bromhydroxycomenamic acid. Ethyl comenamate, when heated with excess of acetic anhydride at 220°, yields an unstable volatile acetyl compound, and a substance, $C_8H_7NO_3$, crystallising in small prisms melting at 261°, and nearly insoluble in water.

Pyrocomenamic acid, $C_5H_4NO.OH + H_2O$, is obtained together with carbonic anhydride by heating comenamic acid with hydriodic acid at 270°. It crystallises in large colourless needles, is moderately soluble in water and hot alcohol, insoluble in ether, chloroform, or carbon bisulphide; it decomposes at above 250°, without previous fusion. With ferric chloride, it gives an intense violet coloration. It has a slightly acid reaction, and dissolves in alkalis, but does not appear to yield crystalline compounds with them. It unites readily with acids; the *hydrobromide*, $C_5H_5NO_2,HBr$, crystallises in prisms, and is readily soluble in water.

Nitrisodipyromeconic acid (Abstr., 1879, 708), after standing for some months in closed vessels, is partly changed into an isomeric compound, which crystallises in colourless needles with 2 mols. H_2O, is sparingly soluble in hot water, gives an intense dark coloration with ferric chloride, and reduces silver salts. Treatment with tin and hydrochloric acid does not convert it into pyromecazonic acid.

Comenamic acid, when heated with phosphoric chloride in a vessel provided with a reflux condenser, yields an amorphous substance (probably $C_5H_3Cl_3N.COCl$), which is reconverted into comenamic acid by heating with water. By reduction with tin and hydrochloric acid, it is converted into the *aldehyde* of *dihydrohydroxypyridinecarboxylic acid*, $C_5H_5N(OH).COOH$, crystallising in anhydrous well-formed short transparent prisms, or with 1 mol. H_2O in long prisms, which effloresce in air. It is sparingly soluble in cold water, gives the same reaction as comenamic acid with ferric chloride, and readily reduces ammoniacal silver solution. By the further action of phosphoric chloride on comenamic acid it is converted into a mixture of pentachloro- and hexachloro-picoline, the reaction having to be assisted towards the close by heating at 250° in sealed tubes; small quantities of monochlorhydroxypyridinecarboxylic acid, $C_5H_2ClN(OH).COOH$, and of an acid, $C_8H_8ClNO_4$, are also formed. *Hexchlor-α-picoline*,

$$C_5HCl_3N.CCl_3,$$

can be separated from the mixture by fractional solidification and recrystallisation from alcohol; it is formed almost exclusively if a still larger excess of phosphoric chloride (6—7 mols.) and a temperature of 280—290° be employed in the reaction. It crystallises in large colourless acute-angled prisms, melts at 60°, is readily soluble in hot alcohol, insoluble in water, acids, or alkalis. It has a faint odour, not, however, like that of pyridine.

Monochlor-α-picoline, C_6H_6ClN, is obtained by the action of hydriodic acid on the mixture of penta- and hexa-chloropicoline; it boils at 164—165° (uncorr.), is readily volatile in steam, has a sp. gr. of 1·146 at 20°, and can be obtained by cooling in large colourless prisms melting at 21°. It has a strong pyridine-like odour, is sparingly soluble in water, readily in alcohol and ether. It has basic properties, reacts strongly alkaline, and dissolves readily in acids. The *hydrochloride*, C_6H_6ClN,HCl, crystallises in anhydrous prisms, readily volatilises at 100°, and is decomposed into its constituents when heated with water. The *platinochloride*, $(C_6H_6ClN),H_2PtCl_6$, crystallises in anhydrous prisms or needles, and is sparingly soluble in cold water.

Chloriodopicoline, C_6H_5ClIN, prepared by digesting monochloropicoline with iodine and caustic soda solution, crystallises in colourless prisms, apparently rhombic, is insoluble in water, soluble in alcohol, and can be distilled in steam. It has basic properties. The *hydrochloride* is sparingly soluble in water; the *platinochloride* crystallises in plates. By the long-continued action of hydriodic acid at 270° on chloropicoline, very small quantities of a base richer in hydrogen and free from chlorine is obtained. It appeared to have the formula $C_6H_{13}N$ (methylpiperidine), but could not be obtained in a pure state.

By heating the mixture of penta- and hex-chloropicoline with sulphuric acid (80 per cent. strength) for about an hour in a vessel provided with a reflux condenser, dichloropicolinic acid, dichlorhydroxypicolinic acid, and monochlorhydroxypicolinic acid are formed, the first and third of these being derived from the pentachloropicoline, the second from hexchloropicoline. They are best separated by precipitation with water, and treatment of the dried precipitate with chloroform, in which dichloropicolinic acid dissolves, whilst the nearly insoluble hydroxy-acids are converted into calcium salts, of which that of the dichlorhydroxy-acid is sparingly soluble in water, whilst that of the monochlorhydroxy-acid is readily soluble.

Dichloropicolinic acid, $C_5H_2Cl_2N.COOH + H_2O$, crystallises in slender needles, melts with decomposition at 180°, is sparingly soluble in cold water and ether, readily in hot water, in alcohol, or in hot chloroform. It volatilises appreciably at 100°, does not give any coloration with ferric chloride, nor unite with dilute mineral acids. The *sodium salt*, $C_5H_2Cl_2N.COONa$, crystallises in plates or needles, sparingly soluble in cold water; the *potassium salt*, $C_5H_2Cl_2N.COOK$, crystallises like the sodium salt; the *ammonium salt* forms rectangular plates; the *barium* and *calcium salts* are insoluble. Dichloropicolinic acid is readily reduced by sodium-amalgam; in alkaline solution, all the nitrogen is evolved as ammonia; in acid solution no ammonia is formed; no crystalline products are obtained in either case.

Tetrahydromonochloropicolinic acid, $C_5H_7ClN.COOH$, is obtained as hydrochloride by the action of tin and hydrochloric acid on dichloropicolinic acid. The free acid crystallises in brilliant rectangular plates, melts at 265—270°, previously blackening, and is readily soluble in water. The *hydrochloride*, $C_6H_8ClNO_2,HCl$, crystallises in readily soluble acute-angled tables and prisms. The copper salt is characteristic, precipitating in bundles of blue prisms.

Monochloropicolinic acid, $C_5H_3ClN.COOH + H_2O$, obtained by the action of hydriodic acid dissolved in glacial acetic acid on dichloropicolinic acid at 140—150°, crystallises in acute-angled prisms or needles. It loses its water of crystallisation and sublimes pretty readily at 100°, and melts at 168°. It is sparingly soluble in cold water, readily soluble in hot water and in alcohol, moderately soluble in ether. It does not unite with acids. The *barium salt*,

$$(C_5H_3ClN.COO)_2Ba + 2H_2O,$$

crystallises in sparingly soluble plates; the calcium, copper, lead, and silver salts are also nearly insoluble.

By heating dichloropicolinic acid with hydriodic acid for three days at 155—160°, it is converted into hexahydropicolinic acid and an acid agreeing in all particulars with the *picolinic acid obtained directly from picoline* by Weidel (Abstr., 1880, p. 268).

Hexhydropicolinic acid, $C_5H_{10}N.COOH$, is the main product of the action of hydriodic acid on mono- or di-chloropicolinic acids; addition of ordinary phosphorus prevents the formation in the reaction of any of the acids containing less hydrogen. It forms a syrup readily soluble in water. The *hydrochloride* crystallises in warts, and is also very soluble; the *platinochloride*, $(C_6H_{11}NO_2)_2,H_2PtCl_6 + 2H_2O$ crystallises in orange- to brownish-red apparently rhombic prisms; it is readily soluble in water.

Dichlor-α-hydroxypicolinic acid, $C_5HCl_2N(OH).COOH + H_2O$, obtained as previously mentioned, crystallises in fine interlaced needles, or in small hard prisms. It melts with decomposition at about 282°, gives a pale yellowish-red coloration with ferric chloride, and has an acid reaction. Its salts are mostly soluble. The *calcium salt*, $(C_5HCl_2N[OH].COO)_2Ca$, is sparingly soluble in water, either hot or cold; it forms pale yellow star-like crystals of silvery lustre. The free acid is not reduced by boiling with aqueous hydriodic acid, nor by tin and hydrochloric acid; sodium-amalgam reduces it to a syrup soluble in alcohol. By heating at 200—210° with hydriodic acid dissolved in glacial acetic acid, it is converted into *α-hydroxypicolinic acid*, $C_5H_3N(OH).COOH$; this crystallises with 1 mol. H_2O in long needles, or less frequently in anhydrous short needles, melts at 267°, is not volatile, dissolves readily in hot water and alcohol, and is insoluble in ether. It gives a reddish-brown coloration with ferric salts, a white precipitate with silver salts; it does not reduce silver salts. The *copper salt* is sparingly soluble; the characteristic *barium salt*, $(C_6H_4NO_3)_2Ba + H_2O$, is precipitated on adding barium chloride to neutral or ammoniacal solutions of the acid; it can be crystallised from hot water in obtuse-angled prisms and needles. The *calcium salt*, $(C_6H_4NO_3)_2Ca$, crystallises in short prisms or rhomboidal tables, and is moderately soluble in water; the *basic potassium salt*,

$$C_5H_3N(OK).COOK + H_2O,$$

separates in groups of needles on adding ether-alcohol to a solution of the acid in concentrated potash. A *hydrochloride* crystallising in slimy needles appears to exist. The further action of hydriodic acid at above 220° leads to the formation of other acids (richer in hydrogen ?) and elimination of ammonia.

Monochloro-β-hydroxypicolinic acid, $C_5H_2ClN(OH).COOH + H_2O$, whose preparation has been already given, crystallises in thick needles, melts with decomposition at 257°, and is more soluble in water than the dichlor-α-hydroxy acid; it reacts strongly acid and gives a yellowish-red coloration with ferric salts. The *calcium salt*,

$$(C_6H_3ClNO_3)_2Ca + 4H_2O,$$

crystallises in hard rhombic tables. Heated at 200° with hydriodic acid dissolved in glacial acetic acid, it yields *β-hydroxypicolinic acid*, $C_5H_3N(OH).COOH$, crystallising with 1 mol. H_2O in brilliant rectangular plates, and melting at 250°. The β-acid is more soluble in water and alcohol than its isomeride, is insoluble in ether, and gives a yellowish-red coloration with ferric chloride, much paler than that given by the α-acid. It is not volatile. The *barium salt*,

$$(C_6H_4NO_3)_2Ba + 2H_2O,$$

crystallises in small tables; it is sparingly soluble in water, but is more soluble than the salt of the α-acid. The *hydrochloride* crystallises in fine thick prisms.

On heating comenic acid with phosphoric chloride in a vessel provided with a reflux condenser, and subsequently adding water, an acid of the formula $C_5HCl_2O_2.COOH$ (m. p. 217°) is obtained; at higher temperatures (280—290°) the reaction takes another course, hexachlorethane and perchloromecylene being formed, together with oily products not yet separated.

Perchloromecylene, C_5Cl_8, crystallises from alcohol in compact acute-angled prisms, melts at 39°, is readily soluble in alcohol, insoluble in water, has a camphor-like odour, volatilises slowly in a current of steam, and boils at 270° with evolution of chlorine. A. J. G.

Oxidising Action of Dilute Nitric Acid on Metaisobutyltoluene. By W. KELBE (*Ber.*, **16**, 619—621).—The author obtains an acid containing the same number of carbon-atoms as the hydrocarbon oxidised, so that it must be either metaisobutylbenzoic acid, $CHMe_2.CH_2.C_6H_4.COOH$, or metatolylisobutyric acid, $C_6H_4Me.CH_2.CHMe.COOH$, the latter being in the author's opinion the more probable. It crystallises from light petroleum in needles melting at 91—92°. A. K. M.

Symmetrical Tribromaniline. By L. GATTERMANN (*Ber.*, **16**, 634—636).—It is generally stated that symmetrical tribromaniline does not form salts. In an attempt to obtain higher substitution derivatives, the author prepared tribromaniline by the action of bromine on aniline sulphate, dissolved the product in benzene, and added bromine as long as a precipitate was produced. Hydrobromic acid was evolved, and a mass of small white needles obtained consisting of *tribromaniline* (symmetrical) *hydrobromide*. It is insoluble in benzene, xylene, light petroleum, ether, and alcohol, melts at 190° with partial decomposition, but can be sublimed unchanged, forming long white needles. It is moderately stable in dry air, whilst water and alkalis rapidly decompose it. The same body is also obtained by passing dry hydrobromic acid into a solution of symmetrical tribromaniline in benzene. By the action of hydrochloric acid, the corresponding *hydrochloride* is formed crystallising in needles. It is far less stable than the hydrobromide, and loses the greater part of its hydrochloric acid by exposure to the air. A. K. M.

Gallocyanins. By KÖCHLIN (*Chem. News*, **47**, 170—171).—When an alcoholic solution of nitroso-dimethylaniline hydrochloride is allowed to react with the tannins or gallic acid, colouring matters are obtained, which the author calls *gallocyanins*.

These colours resist light and various reagents better than alizarin violets do. Neither concentrated hydrochloric acid nor caustic soda (38° B.) changes the tone of the violets fixed with chrome. These colours are faster against chlorine when the dyed material is prepared with stannate, whilst they resist light better on unprepared cloth. Yellow or maize discharges may be produced by printing the violet over a chrome-orange design saturated with dichromate, and after cleansing, taking the pieces through lukewarm oxalic acid at 25 grams per litre. The addition of alizarin in proportion of 1—30 strengthens the colour without sensibly affecting its tone; in other proportions, olives and loutres are produced.

Gallocyanin from gallic acid, *gallic gallocyanin*, is crystalline with metallic lustre; its best solvents are ammonia, soda, and the acid sulphites. Hydrogen sodium sulphite in excess, however, decomposes it, forming an orange colouring matter and an insoluble substance; at the best, the solvent action of sodium hydrogen sulphite is very slow. Gallic gallocyanin dyes woollens and silks violet-blue. This dye, like alizarin, requires double mordants for fixing it on cotton; with aluminous mordants it dyes violets; with those of iron blacks. In dyeing, tin, chrome, cobalt, or nickel may be used; with the other oxides, the violet does not stand soaping at a boil.

Catechin gallocyanin gives redder shades than gallic gallocyanin. It is fixed in the same manner, and dyes violets with alumina and iron which bear soaping well.

Morine or *Morintannic Gallocyanin* is green. In printing it is fixed with chromium acetate. With mordants of chrome, tin, alumina, and iron, it dyes olives, which are exceedingly fast against soap.

Ammonium hydrogen sulphite easily dissolves and reduces it, thus forming a vat in which goods may be dyed by immersion and subsequent oxidation in the air, precisely as with indigo. D. A. L.

Action of Ethyl Chloracetate on Primary Diamines. By J. Zimmermann and M. Knyrim (*Ber.*, **16**, 514—516).—One of the authors has previously shown (*Ber.*, **15**, 518) that when metaphenylenediamine is acted on by ethyl chloracetate, the ethyl salts of metaphenylenediglycocine and phenylenediamine hydrochloride are obtained. Since the glycocine could not be obtained by the direct action of chloracetic acid on phenylenediamine, the authors have endeavoured to saponify the ethyl salt in order to separate it. On treating ethyl phenylenediglycocine with strong hydrochloric acid, the authors obtained the hydrochloride of phenylenediglycocine

$$C_6H_4(CH_2NH.COOH,HCl)_2.$$

They were unable to obtain either the free base or a platinochloride. The crystals of the hydrochloride are freely soluble in water.

When paraphenylenediamine is treated with ethyl chloracetate, it yields a product similar to the meta-compound. It crystallises from water in colourless or brown needles, $C_6H_4(CH_2NH.COOEt)_2$, melting at 83°. It is easily soluble in hydrochloric acid, and like the meta-compound, yields a hydrochloride of the glycocoll

$$C_6H_4(CH_2.NH.COOH,HCl).$$

It crystallises from hydrochloric acid in colourless plates, and does not yield a platinochloride.

Orthophenylenediamine when treated like its isomeride yields a body crystallising in long yellow needles (m. p. 135°), which have not yet been analysed.

When toluylenediamine is acted on by ethyl chloracetate, it yields ethyl toluylenediglycocine, which crystallises from light petroleum in glassy greenish crystals, and from water in bright yellow needles melting at 70°. This salt could not be saponified with hydrochloric acid. J. I. W.

Cyanic Acid Derivatives of the Three Isomeric Phenylenediamines. By E. Lellmann (*Ber.*, **16**, 592—593).—The author has shown (this vol., p. 324) that the thiocyanates of the three phenylenediamines, exhibit different chemical changes. He now finds that the corresponding cyanates are all converted alike into phenylenedicarbamides, the action taking place much more readily than in the case of the thiocyanates. *Orthophenylenedicarbamide*, $C_6H_4(NH.CONH_2)_2$, is obtained on mixing solutions of orthophenylenediamine hydrochloride and potassium cyanate, and can be purified by crystallisation from hot dilute alcohol. It crystallises in needles melting at 290°, is readily soluble in alcohol, water, and in glacial acetic acid, sparingly in chloroform, benzene, and ether. *Metaphenylenedicarbamide* has been described by Warder (*Ber.*, **8**, 1180). *Paraphenylenedicarbamide* crystallises in plates having a silvery lustre; when heated these decompose without melting. A. K. M.

Compounds of the Hydrazines with the Ketones. By H. Reisenegger (*Ber.*, **16**, 661—664).—Fischer (*Annalen*, **190**) has described compounds of the hydrazines with the aldehydes; Meyer and Petraczek (*Ber.*, **15**, 2783) similar compounds of the aldehydes with hydroxylamine; whilst Meyer and Janny (Abstr., 1882, 1047) showed that hydroxylamine likewise formed compounds with the ketones. The author finds that the hydrazines also combine with the ketones, the products being unaltered by potash, although readily decomposed by acids, with formation of the original substances. By the action of phenylhydrazine on acetone, *acetonephenylhydrazine* is produced, and can be purified by heating on a water-bath to drive off the excess of the acetone, then shaking with water and extracting with ether; the latter is evaporated, the residue dried with potassium carbonate, distilled in a vacuum, and finally allowed to stand over sulphuric acid to get rid of traces of ammonia. Its formation is thus shown:—$PhN_2H_3 + COMe_2 = PhN_2HCMe_2 + H_2O$. It has no action on Fehling's solution. On adding sodium nitrite to a cold solution in dilute sulphuric acid, diazobenzenimide, $C_6H_5N_3$, is precipitated. *Acetophenonephenylhydrazine*, $PhN_2HCPhMe$, is obtained by warming a mixture of acetophenone and phenylhydrazine, washing the crystalline product with dilute acetic acid, and crystallising from alcohol. It forms slender white needles melting at 105°, sparingly soluble in water and cold alcohol, readily in ether. Fehling's solution readily decomposes it. When a mixture of acetophenone and dimethylhydrazine is heated for some hours at 100° in sealed tubes, *acetophenonedimethylhydrazine*, Me_2N_2CPhMe, is formed as an oil which does not reduce Fehling's solution. It distils at 165° under a pressure of 190 mm. On heating œnanthaldehyde with phenylhydrazine at the temperature of a water-bath, water is given off with the formation of a body of the formula $PhN_2H.C_7H_{14}$. It is a yellowish coloured oil, boiling at 240° under a pressure of 77 mm., and not solidifying at $-20°$. Fehling's solution has no action on it, whilst boiling with acids decomposes it into aldehyde and hydrazine. Chloral and phenylhydrazine react very violently at the ordinary temperature with evolution of hydrochloric acid and formation of a semi-carbonised product. A crystalline body can, however, be obtained if the base is dissolved in ether and the chloral added to the cooled solution which is then evaporated to a fifth of its volume and precipitated with light petroleum. The slender white needles obtained are very unstable, so that no analysis has been made. A. K. M.

Amarine and Furfurine. By R. Bahrmann (*J. pr. Chem.* [2], **27**, 295—320).—The author finds the best method of preparing amarine to be that of Bertagnini (*Annalen*, **88**, 127). The melting point is 113°, not 100°, as previously stated. An ethereal solution of amarine, mixed with an equivalent quantity of acetic chloride, gives an amorphous white precipitate of *amarine acetyl chloride*,

$$C_{21}H_{18}N_2,\overline{Ac}Cl.$$

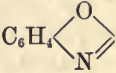
It is very unstable, a solution in cold absolute alcohol begins to decompose in the course of a few minutes, diacetylamarine being precipitated, whilst amarine hydrochloride remains in solution. *Diacetylamarine*, $C_{21}H_{16}(\overline{Ac}_2)N_2$, is thus obtained in white flocks consisting of a network of microscopic needles melting at 268°. It is only sparingly soluble in hot alcohol (0·5 gram in 7 litres), insoluble in water, ether, benzene, and chloroform. It does not react with moderately concentrated acids or alkalis. Benzoic chloride and amarine unite directly in ethereal solution, the resulting *amarine benzoyl chloride*, $C_{21}H_{18}N_2,\overline{Bz}Cl$, forms a white indistinctly crystalline precipitate, which is more stable than the acetyl compound; its alcoholic solution, however, decomposes on long standing, but amarine hydrochloride was the only definite compound isolated from it. By the action of benzoyl chloride on an alcoholic solution of amarine, amarine chloride and a substance of the formula $C_{21}H_{16}N_2\overline{Bz}.OEt$, crystallising in small white needles, were obtained. On treating a cold ethereal solution of amarine with ethyl chlorocarbonate, amarine hydrochloride and diethyl amarinedicarboxylate, $C_{21}H_{16}N_2(COOEt)_2$, are precipitated and can be separated by crystallisation. The latter salt is readily soluble in hot alcohol, sparingly soluble in ether, insoluble in water. The alcoholic solution has a neutral reaction. Heated with alcoholic ammonia in sealed tubes at 100° for some days, it is converted into a base of the formula $C_{21}H_{16}N_2(COOEt).CONHEt$. This crystallises in small rosettes of silky needles, is very soluble in alcohol, has a strong alkaline reaction, and gives crystalline salts with acids. The hydrochloride, $C_{27}H_{27}N_3O_3,HCl$, crystallises in brilliant prisms, and is readily soluble in hot water or hot alcohol. The platinochloride,

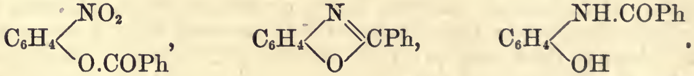
$$(C_{27}H_{27}N_3O_3)_2,H_2PtCl_6 + H_2O,$$

forms orange-coloured crystals. The author considers that his results best agree with the constitutional formula assigned to amarine by Claus (this vol., p. 204).

Acetic chloride and furfurine unite to form an unstable molecular compound, quickly decomposing in alcoholic solution into furfurine hydrochloride and monacetylfurfurine.

Benzoylethoxy-furfurine, $C_{15}H_{11}O_2N_2\overline{Bz}(OEt)$, is obtained by the action of alcohol on the precipitate formed by addition of benzoic chloride to an ethereal solution of furfurine. It crystallises in groups of microscopic needles, melts at about 290°, and can be sublimed. It is moderately soluble in chloroform or glacial acetic acid, very sparingly soluble in alcohol, insoluble in ether or water, and does not unite with acids or bases. By the action of ethyl chlorocarbonate on furfurine, *diethyl furfurinedicarboxylate*, $C_{15}H_{11}O_3N_2(COOEt)_2$, is obtained; it crystallises in hard brilliant prisms, melts at 124°, is soluble in hot alcohol, sparingly soluble in water, and insoluble in ether. A. J. G.

Anhydro-compounds. By W. Böttcher (*Ber.*, **13**, 629—634).—Hübner and Stünkel (*Annalen*, **210**, 384) have described the preparation of anhydrobenzamidophenol,  $C_6H_4\langle{}^{O}_{N}\rangle CPh$, by the reduction or orthonitrophenol benzoate by means of tin and hydrochloric acid, and subsequent decomposition of the resulting tin compound by hydrogen sulphide. They did not, however, succeed in obtaining the intermediate compound, orthamidophenol benzoate. The author finds that if hydrogen sulphide is passed into the cold alcoholic solution of the tin compound, the anhydro-body is obtained nearly pure; if into a hot solution, a mixture of the latter with *benzamidophenol*, $C_{13}H_{11}NO_2$, is formed, from which the anhydro-compound can be extracted by means of light petroleum. Benzamidophenol can also be obtained from the anhydro-compound by heating its alcoholic solution with hydrochloric acid for two days on a water-bath. The liquid assumes a red colour, and on cooling deposits reddish-coloured shining plates, melting at 165°. That this body has the constitution $HO.C_6H_4.NH\overline{Bz}$, and not $NH_2.C_6H_4.O\overline{Bz}$, is shown by its ready solubility in alkalis, from which it can be reprecipitated by acids. It also agrees in its properties with Hübner's orthobenzamidophenol. The apparently anomalous change of position of the benzoyl-group from its union with oxygen (in orthonitrophenol benzoate) to nitrogen is readily explained when anhydrobenzamidophenol is regarded as the intermediate product, thus:—



A. K. M.

Nitro- and Amido-derivatives of Benzenesulphonanilide and Benzenesulphonparatoluide. By E. Lellmann (*Ber.*, **16**, 594—597).—*Benzenesulphonorthonitranilide*, $C_6H_5.SO_2.NH.C_6H_4.NO_2$, is obtained when benzenesulphonic chloride (1 mol.) is added to a solution of nitraniline (2 mols.) in a little benzene, and the whole warmed on a water-bath. The liquid is separated from the nitraniline hydrochloride, which is washed with light petroleum. It forms yellowish coloured plates insoluble in light petroleum and in benzene. In moist air, it decomposes with evolution of hydrochloric acid, also when heated to 155° or by contact with water or alcohol. After heating the filtrate from the nitraniline salt to drive off the benzene and petroleum and allowing it to stand in a desiccator, benzenesulphonorthonitranilide is obtained, and can be purified by crystallisation from hot petroleum. It forms yellow plates melting at 104°, and readily soluble in alcohol, glacial acetic acid, chloroform, and benzene.

Benzenesulphonmetanitranilide crystallises in bright yellow needles, melting at 131—132°, readily soluble in alcohol, glacial acetic acid, chloroform, and benzene.

Benzenesulphonparanitranilide forms yellow crystals melting at 139°, and is readily soluble in alcohol, benzene, and glacial acetic acid, more sparingly in chloroform and light petroleum. *Benzenesulphonmetanitroparatoluide*, $C_6H_5SO_2.NH.C_6H_3Me.NO_2$, is obtained by the action of nitric acid (sp. gr. 1·43) on benzenesulphonparatoluide and precipitation by water, also by the action of benzenesulphonic chloride and benzene on metanitroparatoluidine. It crystallises from hot alcohol in cubes melting at 99°.

Benzenesulphonmetadinitroparatoluide,

$$C_6H_5.SO_2.NH.C_6H_2Me(NO_2)_2,$$

is produced by the action of nitric acid of sp. gr. 1·47 on benzenesulphonparatoluide. It crystallises from hot alcohol in dense yellowish prisms melting at 178°, and from hot benzene in wedge-shaped crystals containing 1 mol. benzene. It is readily soluble in hot alcohol and in benzene, sparingly in cold alcohol. *Benzenesulphonorthamidoanilide*, $C_6H_5.SO_2.NH.C_6H_4.NH_2$, obtained by the reduction of the corresponding nitro-compound, crystallises from 50 per cent. alcohol in long colourless needles melting at 168°, and is sparingly soluble in water, readily in alcohol, glacial acetic acid, and in chloroform. The *hydrochloride*, $C_6H_5.SO_2.NH.C_6H_4.NH_2,HCl$, separates from water in large dense anhydrous crystals. *Benzenesulphonmetamidoparatoluide*, $C_6H_5.SO_2.NH.C_6H_3Me.NH_2$, crystallises from dilute alcohol in long colourless needles melting at 146·5°. It is readily soluble in alcohol and in glacial acetic acid, sparingly in water. A. K. M.

Metanitrophenylthiocarbimide. By H. STEUDEMANN (*Ber.*, **16**, 548—551).—When metanitrothiocarbanilide, prepared according to Losanitsch's method, is dissolved in hot acetic anhydride, and the solution, after addition of water, is boiled for a short time, metanitrophenylthiocarbimide separates as a heavy oil, which solidifies on cooling. The crystals are pressed between filter-paper to remove admixed phenylthiocarbimide, and after being distilled by steam are obtained colourless (m. p. 58°). When solid it has no odour; but on melting evolves the characteristic smell of thiocarbimides. It is freely soluble in ether, glacial acetic acid, and alcohol, and only slightly soluble in water. It can be obtained in fine white needles by adding water to a solution in alcohol until a precipitate just begins to form. When an alcoholic solution is heated with aniline, metanitrodiphenylthiocarbimide is formed. With metanitraniline, it yields yellow crystals of metadinitrodiphenylthiocarbimide,

$$CS(NH.C_6H_4.NO_2)_2,$$

melting at 160°. When treated with alcoholic ammonia, it forms metanitromonophenylthiocarbimide crystallising in lemon-coloured crystals melting at 157—158·5°. When metanitrophenylthiocarbimide is dissolved in boiling alcohol, it is converted into nitrophenylethylurethane (m. p. 115°). Phenylthiocarbimide undergoes a similar change only when heated in a sealed tube at 110—115°. If methyl alcohol is employed, the corresponding methylurethane is obtained in glittering colourless needles melting at 119—120°. J. I. W.

Conversion of Phenols into Nitriles and Carboxylic Acids. By V. Merz (*Ber.*, **16**, 512—513).—Weith and Merz have shown (*Ber.*, **10**, 746) that the monohaloïd derivatives of benzene hydrocarbons yield the corresponding nitriles when heated with cyanides of metals. The conversion of phenols into nitriles has not been investigated since Scrugham's research in 1854 (*Jahresber.*, 605). At the instigation of the author, Heim has studied the action of potassium cyanide on the neutral phosphates of phenols under the influence of heat. In all cases nitriles are formed which by saponification yield the corresponding acids. He has, in this manner, prepared benzoic acid, ortho- and para-toluic acids, and the two naphthoic acids from triphenyl, ortho- and para-tricresol, and α and β trinaphthyl phosphates respectively. Traces of higher nitriles are formed. J. I. W.

Reduction of Substituted Phenols. By F. Pfaff (*Ber.*, **16**, 611—616).—With the view to obtain monobromoresorcinol, the author brominated metanitrophenol, reduced the product with tin and hydrochloric acid, and then by means of the diazo-reaction obtained a body which he found to be resorcinol, and not a bromine-derivative as he expected. The elimination of the bromine takes place during the reduction by the tin and hydrochloric acid, and can also be effected by stannous chloride. By the reduction of the methyl ether of bromometanitrophenol, metamidoanisoïl is produced. The potassium-derivative of monobromometanitrophenol, $C_6H_3Br(NO_2).OK + 2H_2O$, is a red body which loses its water of crystallisation over sulphuric acid, at the same time becoming brown. The sodium-derivative,

$$C_6H_3Br(NO_2).ONa + H_2O,$$

is yellowish-red and does not change colour on becoming anhydrous. By the action of ammonium sulphide on dinitrometaxylene, the author has prepared nitroxylidine, and from this by the diazo-reaction nitroxylenol, $C_6H_2Me_2(NO_2).OH$. The latter forms yellow crystals melting at 95°. A. K. M.

Phenol-derivatives. By L. Henry (*Compt. rend.*, **96**, 1233—1235).—*Phenyl monochlorethyl oxide*, $PhO.CH_2.CH_2Cl$, is obtained by the action of ethylene chlorobromide on an alcoholic solution of potassium phenate. It is a colourless solid, with an agreeable phenolic odour, and a sharp taste. It is quite insoluble in water, but dissolves easily in alcohol, ether, &c. It melts at 25°, and boils without decomposition at 221° under a pressure of 754 mm.; the fused mass on cooling crystallises in thick elongated hexagonal lamellæ belonging to the monoclinic system. Since it contains the group CH_2Cl, it has the properties of the haloïd ethers, and reacts readily with metallic and hydrogenised compounds. Alcoholic potash converts it into the compound $C_2H_4(OC_6H_5)_2$.

The corresponding bromine-derivative has been described by Weddige (Abstr., 1881, 1136). It melts at 39° and boils between 250° and 260° with partial decomposition.

The isomeric *ethyl-monochlorphenyl oxide*, $EtO.C_6H_4Cl$, was described by the author some years ago (*Bull. Acad. Bruxelles*, 1869, 566).

Ethylene phenyl-ethyl oxide, $PhO.CH_2.CH_2.EtO$, is obtained by the action of alcoholic potash on the preceding compound in sealed tubes. It is a limpid liquid, insoluble in water, with an agreeable ethereal odour differing from that of other phenol-derivatives. It boils at about 230° without decomposition; sp. gr. at 11° = 1·018. This compound is obtained more easily by the action of alcoholic potash on phenyl-monobromethyl oxide, but in this case the reaction is not so simple, a notable quantity of a more volatile liquid boiling at about 170° being also produced. This liquid is colourless, insoluble in water and in solutions of caustic alkalis, and reacts energetically with bromine; it is probably *oxyphenyl ethylene*, $CH_2 \colon CH.OPh$, but has not yet been analysed.

Phenylmonobromallyl oxide, $PhO.CH_2.CBr \colon CH_2$, is obtained by the action of alcoholic potassium phenate on monobromallyl bromide boiling at 142°. It is a limpid colourless liquid, which becomes yellowish after some time. It has a feeble phenolic odour, a sharp and bitter taste, and is insoluble in water. It boils at about 240°, with slight decomposition: sp. gr. at 11° = 1·4028.

Phenylpropargyl oxide or *Propargylic phenol*, $PhO.C_3H_3$, cannot be obtained from allylic phenol, $PhO.C_3H_5$ (*Ber.*, 1872, 455), but is prepared by the action of alcoholic potash on the preceding compound. It is a colourless liquid, becoming brown after some time, with a feeble propargylic odour and a sweet sharp taste. It is insoluble in water, and boils at about 210°, but has no fixed boiling point, and undergoes alteration on ebullition, being probably polymerised; sp. gr. at 6° = 1·246.
C. H. B.

Nitro-derivatives of Resorcinol. By R. BENEDIKT (*Ber.*, **16**, 667—668).—A reply to Typke.

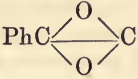
Benzil. By M. WITTENBERG and V. MEYER (*Ber.*, **16**, 500—508).—The constitutions of benzoïn and of the bodies nearly related to it are generally expressed by the following formulæ:—

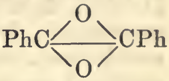
$Ph.CO.CHPh(OH)$. Benzoïn.	$CH_2Ph.CO.Ph$. Deoxybenzoïn.
$CHPh(OH).CHPh(OH)$. Hydrobenzoïn.	$Ph.CO.CO.Ph$. Benzil.

There is little doubt that the above formula of deoxybenzoin is correct, and that it is a mixed ketone of benzoic and phenylacetic acids. The formula for benzil does not explain how the characteristic decomposition into benzilic acid can take place.

Action of Heated Lead Oxide on Benzil.—The ordinary formula places benzil in close relationship to phenanthraquinone. When benzil vapour is passed over heated lead oxide benzophenone is obtained. The authors have carefully determined the boiling point of benzil, and find it to be 346—348° (corr.).

Action of Heated Lead Oxide on Phenanthraquinone and Benzoïn.—When phenanthraquinone is heated with lead oxide, it yields diphenylene ketone (m. p. 83—84° C). Benzoïn under similar circumstances yields benzophenone, as was to be expected, since benzil is formed as an intermediate product.

According to V. Meyer's rule, it is to be expected that by the action of hydroxylamine on benzil only such oxygen-atoms as are present in carbonyl-groups will be replaced by the group $=N—OH$. The oldest formula of benzil,  $\mathrm{PhC}\overset{\diagup O \diagdown}{\underset{\diagdown O \diagup}{\text{———}}}\mathrm{CPh}$, does not admit of any reaction taking place.

Action of Hydroxylamine on Benzil.—By treating an alcoholic solution of benzil with a concentrated aqueous solution of hydroxylamine, a body crystallising in small white quadratic plates is obtained melting at 130—131°. It has the composition $C_{14}H_{11}O_2N$ or Ph.CN(OH).COPh. This result puts the formula  $\mathrm{PhC}\overset{\diagup O \diagdown}{\underset{\diagdown O \diagup}{\text{———}}}\mathrm{CPh}$ out of the question. It is equally incompatible with the ordinary formula, because only one oxygen-atom has been replaced.

In order to show that the hydroxylamine reaction takes place in the benzoïn series in the same manner as with other ketones, and that the groups CO—CO are both replaceable like a single CO-group, the authors have made the following experiments:—

Action of Hydroxylamine on Benzoïn.—An alcoholic solution of benzoïn was mixed with an aqueous hydroxylamine solution, and allowed to stand for a week. The product was a snow-white powder consisting of microscopic prisms (m. p. 151—152°) of the composition $C_{14}H_{13}NO_2$. The reaction proceeds according to the equation—

$$\mathrm{Ph.CO.CHPh.OH + NH_2OH = H_2O + Ph.CN(OH).CHPh.OH.}$$

Action of Hydroxylamine on Glyoxal.—According to the ordinary formula benzil may be looked upon as a diphenylated glyoxal. Glyoxal, however, when acted on with hydroxylamine, takes up two atoms of nitrogen, therefore benzil cannot be represented by the formula of a substituted glyoxal. On treating an aqueous solution of glyoxal with hydroxylamine, a colourless body crystallising in transparent well-formed rhombic plates (m. p. 178°) is obtained. It can easily be sublimed, and dissolves readily in hot water, alcohol, and ether. Its aqueous solution is slightly acid. When boiled with acids it yields hydroxylamine. Its composition is $C_2H_4N_2O_2$. The authors propose to call it glyoxime. The reaction proceeds as follows:—

$$COH.COH + 2NH_2OH = 2H_2O + H.CN(OH).CN(OH).H.$$

Glyoxime bears a close relationship to the so-called acetoximic acids. The authors propose that they should be termed "glyoximes." The five known members of the series would then be—

Glyoxime........	H.CN(OH).CN(OH).H, glyoxime.
Acetoximic acid ..	Me.CN(OH).CN(OH).H, methylglyoxime.
Homologous acetoximic acids ..	Me.CN(OH).CN(OH).Me, dimethylglyoxime.
	Me.CN(OH).CN(OH).Et, methylethylglyoxime.
	Me.CN(OH).CN(OH).$\overline{Bz}$, methylbenzylglyoxime.

When silver nitrate is added to an aqueous solution of glyoxime, neutralised with ammonia, a silver salt is obtained, $C_2N_2O_2H_3Ag$. It is a white powder, which decomposes on heating.

As a result of their investigations, the authors conclude that benzil contains only one carbonyl-group, and they think that it should be regarded as a lactone with a formula like

$$C_6H_4<\begin{matrix}CHPh\\ -CO-\end{matrix}>O.$$

J. I. W.

Decomposition of Benzil by Potassium Cyanide. By F. Jourdan (*Ber.*, **16**, 658—660).—By the action of potassium cyanide on benzil in the presence of alcohol, a brownish-red solution is obtained, becoming semi-solid on cooling. On treating it with water, a solid body and an oil are obtained, the former being benzoïn, whilst the latter consists of benzaldehyde and ethyl benzoate. If methyl alcohol is used, methyl benzoate is formed, the other products being the same. This reaction may be explained by the benzil taking up the elements of alcohol with formation of benzaldehyde and ethyl benzoate, the production of benzoïn being due to a secondary reaction between the potassium cyanide and benzaldehyde. The same reaction takes place if a concentrated solution of sodium carbonate is used in the place of the alcohol, the benzil decomposing into benzaldehyde and benzoic acid. All compounds containing the group CO—CO appear to decompose in the same way, furil yielding a deep blue coloured liquid, which changes to reddish-brown, the solution containing furfuraldehyde and ethyl pyromucate, the evanescent blue colour being due to furoïn. Isatin is not altered by potassium cyanide, which fact is against the presence of the group CO—CO, and in accordance with Baeyer and Œconomides' formula for this body (this vol., p. 202). A. K. M.

Action of Acetic Chloride on Benzaldehyde in Presence of Zinc-dust. By C. Paal (*Ber.*, **16**, 636—639).—The author previously stated (this vol., p. 62) that this reaction yielded a body of the formula $C_9H_8O_2$, which gave dibenzyl when treated with amorphous phosphorus and hydriodic acid, and stilbene when distilled with zinc-dust. By the action of sodium-amalgam on its alcoholic solution at 70—80°, hydrobenzoïn and acetic acid are produced, from which it is concluded that the substance is hydrobenzoïn-diacetate, $CHPh(O\overline{Ac}).CHPh(O\overline{Ac})$, the half molecule of which, $C_9H_9O_2$, differs but slightly from the formula previously given, $2Ph.COH + 2\overline{Ac}Cl + Zn = ZnCl_2 + CHPh(O\overline{Ac}).CHPh(O\overline{Ac})$. It melts at 134—135°, *i.e.*, some degrees higher than previously stated. A direct comparison of this body with hydrobenzoïn diacetate prepared from benzoïn shows that the two are identical. A. K. M.

Ethyl Phthalylacetoacetate. By E. Fischer and H. Koch (*Ber.*, **16**, 651—652).—By the action of phthalic chloride on ethyl sodacetoacetate the following reaction takes place even at the ordinary temperature:—

$$C_6H_4(COCl)_2 + 2NaC_6H_9O_3 = 2NaCl + C_6H_{10}O_3 + C_6H_4 \vdots (CO)_2 \vdots C_6H_8O_3.$$

Ethyl phthalylacetoacetate, $C_6H_4 \vdots (CO)_2 \vdots C_6H_8O_3$, crystallises in colourless prisms melting at 124°; it yields phthalic acid when boiled with dilute sulphuric acid. A reaction similar to the above also takes place between succinic chloride and ethyl sodacetoacetate.

A. K. M.

Displacement of the Sulphonic-group by Chlorine. By W. Kelbe (*Ber.*, **16**, 617—619).—The action of bromine on metaisocymenesulphonic acid has been previously described by the author. He finds that chlorine acts in the same way, although more energetically. Chlorine is passed into an aqueous solution of cymenesulphonic acid, kept cool with ice, until a considerable quantity of chlorine hydrate has formed. The vessel is then well closed and heated to 40° in a water-bath, when the chlorine hydrate disappears, whilst an oily body is formed, which becomes crystalline on standing. It can be purified by crystallisation from boiling alcohol, from which it separates in long needles melting at 158·5°. Tetrachlorocymene, C_6Cl_4MePr, thus obtained is a very stable body, being only slowly attacked when heated with concentrated nitric acid in sealed tubes. Chromic mixture, nitric acid, and potassium permanganate have no action on it, whilst chromic anhydride in acetic acid completely oxidises it. Bromine has no action at ordinary temperatures, but at 150° a thick oil is produced solidifying to a resin-like mass. If the ethereal extract of the latter is treated with potash to remove hydrobromic acid, the ether distilled off, the residue dissolved in alcohol, and an alcoholic solution of potassium acetate added, potassium bromide separates, and a filtrate is obtained which gives a resinous precipitate on being diluted with water; this after treatment with alcoholic potash and oxidation with dilute nitric acid at 150°, yields an acid, the barium salt of which corresponds with

$$(C_6Cl_4Me.C_2H_4.COO)_2Ba + 3H_2O \text{ or } (C_6Cl_4Pr.COO)_2Ba + 3H_2O.$$

The liquid separated from the chlorocymene contained trichlorocymenesulphonic acid, the sodium salt of which, $C_6Cl_3MePr.SO_3Na$, crystallises in plates. By the action of bromine on an aqueous solution of the latter a bromine-derivative, probably $C_6Cl_3BrMePr$, is produced, crystallising in long needles. A. K. M.

Barium Paratoluenesulphonate. By W. KELBE (*Ber.* **16**, 621—622).—This salt crystallises in two forms, according to the temperature of the solution from which it crystallises. Above 30° it separates in anhydrous plates, and below this temperature in needles containing 3 mols. H_2O. A. K. M.

Action of Aluminium Bromide on Symmetrical Dibromethylene and Benzene. By R. ANSCHÜTZ (*Ber.*, **16**, 622—623).—Demole has shown (Abstr., 1880, 158) that the action of aluminium chloride on benzene and dibromethylene (b. p. 87—92°) yields unsymmetrical diphenylethylene. From dibromethylene boiling at 110—111°, benzene and aluminium bromide, the author obtains *dibenzyl*, which proves the *symmetrical* character of the higher boiling dibromethylene. Small quantities of anthracene are also formed. A. K. M.

Rosaniline Colouring Matters. By R. MELDOLA (*Chem. News*, **47**, 133 and 146).—The author has succeeded in preparing:—*Tri-β-naphthyl-pararosaniline*, $(C_6H_4.NH\beta C_{10}H_7)_3C.HO$, by heating the rosaniline base with excess of β-naphthylamine at a temperature slightly above the melting point of the latter for 15—20 minutes in presence of a small quantity of benzoic or acetic acid, the rich blue melt thus obtained can be purified and converted into sulphonic acids in the usual manner. It dyes silk or wool deep blue. Diphenylpararosaniline, $(C_6H_4.NHPh)_2C(HO).C_6H_4.NH_2$, is formed by the direct oxidation of a mixure of 1 mol. paratoluidine with 2 mols. diphenylamine. These substances are dissolved in glacial acetic acid, and are heated with the requisite quantity of As_2O_5.

A naphthyl-derivative of rosaniline analogous to diphenylamine-blue is produced by heating β-naphthyl-phenylamine, $NHPh\beta C_{10}H_7$, with oxalic acid or any of the oxidising substances which transform diphenylamine into its blue. This also can be converted into a sulphonic acid, which dyes silk or wool a green shade of blue. α-Naphthyl-phenylamine does not readily yield a blue with oxalic acid, whilst no colour is obtained either with di-α-naphthylamine or di-β-naphthylamine by similar treatment. D. A. L.

Derivatives of α-Naphthoic Acid. By P. BOESSNECK (*Ber.*, **16**, 639—642).—α-Cyanonaphthalene is prepared by distilling a mixture of dry sodium naphthalenesulphonate (3 parts) and potassium ferrocyanide (2 parts), heating the distillate on a water-bath to volatilise the ammonium carbonate which is formed, and then fractioning. To prepare naphthoic acid, the cyanide is mixed with an equal volume of concentrated hydrochloric acid, and heated in sealed tubes at 200°. The product is treated with ammonia, filtered, the acid then precipitated by hydrochloric acid, and finally crystallised from alcohol.

The conversion of α-naphthylglyoxylamide into the corresponding acid is best effected by heating it with dilute hydrochloric acid for about an hour and extracting with ether. *Naphthylglyoxylic acid* (m. p. 113·5°) is readily soluble in water, ether, alcohol, and benzene, sparingly in light petroleum and carbon bisulphide. With sulphuric acid, its benzene solution gives a reaction similar to that of phenylglyoxylic acid (Abstr., 1880, 67) assuming a brownish-red coloration, changing to brown. On the addition of water, the colouring matter remains dissolved in the benzene, forming a carmine-coloured layer. α-Naphthoic cyanide and α-naphthylglyoxylamide do not show this reaction. By the action of sodium-amalgam on a slightly alkaline solution of α-naphthylglyoxylic acid, *α-naphthylglycollic acid*,

$$C_{10}H_7.CH(OH).COOH,$$

is produced, crystallising in plates. *α-Naphthylacetic acid*,

$$C_{10}H_7.CH_2.COOH,$$

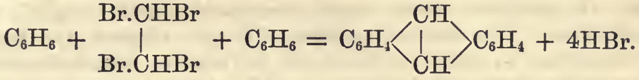
is formed when α-naphthylglyoxylic acid is heated with amorphous phosphorus and hydriodic acid for some hours at 160°. It is sparingly soluble in cold water, readily in hot water, from which it crystallises in long silky needles melting at 131°. It also dissolves readily in ether, alcohol, glacial acetic acid, and in benzene. *α-Naphthylacetamide*, $C_{10}H_7.CH_2.CONH_2$, is insoluble in cold water, but crystallises from hot water in slender needles melting at 180—181°. It is soluble in benzene, carbon bisulphide, and ether, and readily in glacial acetic acid. On distilling it with phosphorus pentoxide, a yellowish-brown oil is obtained which is apparently *α-naphthylacetonitril*, $C_{10}H_7.CH_2.CN$, boiling above 300°. *α-Naphthylethenyldiphenyldiamine*,

$$C_{10}H_7.CH_2.C(NPh)NHPh,$$

is obtained by the action of phosphorus trichloride (2 mols.) on a mixture of naphthylacetic acid (3 mols.), and aniline (6 mols.). It is soluble in ether, benzene, light petroleum, and in acids, and crystallises from dilute alcohol in colourless needles melting at 130·5°. *α-Naphthylmethenyldiphenyldiamine*, $C_{10}H_7.C(NHPh):NPh$, from naphthoic acid, forms silky needles melting at 183·5°, and in its solubility resembles the last-named body. A. K. M.

Synthesis of Dihydronaphthoic Acid. By v. H. PECHMANN (*Ber.*, **16**, 516—517).—When benzyl acetoacetate is treated with from 8—10 parts of concentrated sulphuric acid, to which a small quantity of water has previously been added, and the mixture, after being allowed to stand for several hours, is poured into cold water, a fine white crystalline powder is thrown down. After recrystallisation from ether, it gives numbers on analysis which correspond with the formula $C_{11}H_{10}O_2$. The body possesses the properties of a dihydronaphthoic acid. It dissolves in a dilute solution of sodium carbonate with evolution of carbonic anhydride. It yields a bromine additive compound, and on oxidation with either nitric acid or potassium permanganate, it gives phthalic acid. When heated in a test-tube, it distils almost entirely without decomposition. Distilled with soda-lime it yields carbonic anhydride and a liquid hydrocarbon of the composition $C_{10}H_{10}$, boiling at 199—201°; this appears to be identical with the dihydronaphthalene obtained by Berthelot by the action of hydriodic acid on naphthalene. J. I. W.

New Synthesis of Anthracene. By R. ANSCHÜTZ and F. ELTZBACHER (*Ber.*, **16**, 623—624).—Anthracene is formed by the action of aluminium chloride on a solution of acetylenetetrabromide in benzene. Its formation may be explained by the following equation:—



$$C_6H_6 + \begin{matrix}Br.CHBr\\ |\\ Br.CHBr\end{matrix} + C_6H_6 = C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

A. K. M.

Liquid Terebenthene Hydrochlorides. By P. BARBIER (*Compt. rend.*, **96**, 1066—1069).—Lævogyrate terebenthene dissolved in twice its volume of alcohol was saturated with hydrochloric acid gas, left at rest for twelve hours, the hydrochloride precipitated by addition of water, dried over calcium chloride, and distilled in a vacuum In this way a monohydrochloride is obtained which forms a colourless, slightly oily liquid, boiling at 120° under a pressure of 0·045 mm. Its lævorotatory power, $[\alpha]_D = -6° 51'$; sp. gr. at 0° = 1·016; refractive index for D = 1·4826 at 12·5°. When heated with alcoholic potash in a sealed tube at 180°, it yields a colourless mobile liquid of the composition $C_{10}H_{16}$, with an odour which at first resembles that of the amyl compounds, but changes to that of lemons after exposure to air. The lævorotatory power of this hydrocarbon, $[\alpha]_D = -19° 9'$; b. p. = 157°; sp. gr. = 0·8812; index of refraction = 1·4692. When treated with hydrochloric acid gas, it yields a mixture of liquid and solid monohydrochlorides.

Lævogyrate terebenthene was treated with hydrochloric acid gas at 100°, and the product fractionated in a vacuum. In this way a perfectly colourless liquid hydrochloride is obtained, which boils at about 120° under a pressure of 0·04 mm., and yields no precipitate when placed in a mixture of ice and salt. Its lævorotatory power $[\alpha]_D = -29°$; sp. gr. at 0° = 1·017; index of refraction = 1·4083. When heated with alcoholic potash in a sealed tube at 150° for twelve hours, it yields a colourless, very mobile liquid hydrocarbon of the composition $C_{10}H_{16}$, with an odour recalling that of lemons. It boils at 157°; sp. gr. at 0° = 0·8815, at 12° = 0·8724; refractive index for D = 1·4704; lævorotatory power $[\alpha]_D = -40°$. When treated with hydrochloric acid gas, it yields a mixture of a solid and a liquid monohydrochloride. The solid hydrochloride is dextrogyrate.

C. H. B.

Essence of Angelica Root. By L. NAUDIN (*Compt. rend.*, **96**, 1152—1154).—When the root of *Angelica officinalis* is distilled in vapour of water, a colourless, mobile liquid is obtained of sp. gr. 0·875 at 0°. It turns yellow on exposure to light, and absorbs oxygen from the air, being slowly converted into a resin. When boiled, it is polymerised, but at higher temperatures the polymerides split up into light liquids which have not yet been examined. By fractionation in a vacuum, a colourless, very mobile liquid boiling at 166° is isolated. It has the composition of the terpenes, does not alter when exposed to light, and has a somewhat pungent odour; sp. gr. at 0° = 0·870. Its dextrorotatory power for a thickness of 200 mm. is + 5° 29′. When heated at 100° in sealed tubes for 30 days, its rotatory power sinks to + 4° 1′; it becomes slightly yellow and less mobile, and its odour is more pungent. Ordinary terebenthene treated in the same way does not alter in rotatory power by 1′. At 160° the terpene from angelica root becomes viscous in a few hours, especially in presence of sodium. It yields a liquid monohydrochloride, but no solid monohydrochloride. The author proposes for this terpene the name of β-terebangelene, in order to distinguish it from the isomeride obtained from angelica seeds, which boils at 175°, and is far more readily altered by the action of heat.

The author concludes that essence of angelica root consists of a single terpene, which, in the commercial product, is mixed with polymerides formed during distillation. The proportion of polymerides increases with time; a sample two years old had become viscous in a closed vessel exposed to light. C. H. B.

Action of Zinc Chloride on Camphor. By A. REUTER (*Ber.*, **16**, 624—629).—The author distils camphor and zinc chloride according to Fittig's method, treats the distillate with strong soda solution to separate the phenols, and then with concentrated sulphuric acid, the mixture being well cooled. From the soda solution, he obtains orthocresol and other higher-boiling phenols. On mixing the sulphuric acid extract with water an oil separates containing camphor, and a body probably identical with Schwanert's camphrene (*Annalen*, **123**, 298). The residual mixture of hydrocarbons was distilled over sodium, converted into sulphonic acids, and the latter purified by means of the barium and sodium salts. It contained toluene, pseudocumene, cymene, and laurene, and also some hydrocarbon oil (probably paraffins) insoluble in sulphuric acid. A. K. M.

Gentianose. By A. MEYER (*Zeits. Physiol. Chem.*, **6**, 135—138). —The roots of *Gentiana lutea*, *pannonica*, *punctata*, and *purpurea* are used in the preparation of gentian brandy. The freshly sliced roots are for this purpose added to water, allowed to ferment, and distilled. The relatively large proportion of alcohol in the product is suggestive of the presence of a considerable amount of some fermentescible substance in the roots. The author sought for this presumably saccharine constituent in the expressed juice of *Gentiana lutea*, gathered in September. The roots yielded 50 per cent. of juice. From this juice was obtained by treatment with 95 per cent. alcohol, fractional precipitation by ether, and subsequent slow crystallisation, a crystalline body which the author names *gentianose*. It occurs in small colourless crystals having a faintly sweet taste, easily soluble in water. Melting point, 210°.

On the addition of yeast fermentation at once begins. Concentrated sulphuric acid carbonises the substance, as in the case of cane-sugar. Fehling's solution is not reduced by it. Analysis gives the formula $C_{36}H_{66}O_{31}$. The other properties of gentianose would appear to place it near cane-sugar. D. P.

Nitroquinolines. By W. La Coste (*Ber.*, **16**, 669—677).—The only nitroquinoline previously known is that described by Koenigs (*Ber.*, **12**, 448), and shown by Bedall and Fischer (*Ber.*, **15**, 683) to be the ortho-compound. The author has attempted to prepare isomerides by heating the nitranilines with glycerol, sulphuric acid, and nitrobenzene. From paranitraniline the corresponding nitroquinoline, $C_9H_6N.NO_2$ $[N : NO_2 = 1 : 6]$ is obtained. It crystallises from water or dilute alcohol in colourless slender silky needles, melting at 149—150°, and subliming without decomposition. It is sparingly soluble in cold alcohol or water, much more readily on heating, is readily soluble in dilute acids and in benzene, whilst ether and light petroleum dissolve it but slightly. The *platinochloride*, $C_9H_6N.NO_2,H_2PtCl_6$, forms a yellow crystalline precipitate. Nitroquinoline combines with methyl iodide at 100° with formation of the compound $C_9H_6N.NO_2,MeI$, which crystallises in groups of reddish-yellow needles, readily soluble in hot water, less so in warm alcohol. *Amidoquinoline*, obtained by the reduction of the above nitro-compound, crystallises from water with 2 mols. H_2O. It is readily soluble in alcohol and in ether, more sparingly in water and in light petroleum. When anhydrous it melts at 114°, and can be sublimed unchanged. The *hydrochloride*,

$$C_9H_6N.NH_2,2HCl,$$

forms large prisms of vitreous lustre, which readily dissolve in water to a deep yellow solution. The *platinochloride*,

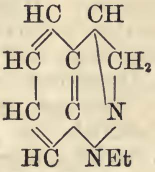
$$C_9H_6N.NH_2,H_2PtCl_4 + 2H_2O,$$

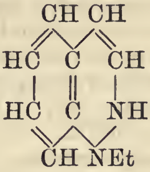
is obtained as a yellow crystalline precipitate. By the action of picric acid on the hydrochloride, the compound $C_9H_6N.NH_2,2C_6H_2(NO_2)_3.OH$ is produced, crystallising in woolly needles. *Dimethylamidoquinoline*, $C_9H_6N.NMe_2$, is prepared from dimethylamido-paraphenylenediamine (from paranitrosodimethylaniline). It melts at 54—56°, and boils at about 335°. It is readily soluble in alcohol, ether, and benzene, but on evaporating the solution it separates as an oil. With picric acid it forms a sparingly soluble compound, $C_9H_6N.NMe_2,C_6H_2(NO_2)_3OH$, crystallising in slender reddish-yellow needles, which melt at 215°, with decomposition, and explode when suddenly heated. When it is heated with methyl iodide, $C_9H_6N.NMe_2,MeI$ is obtained, crystallising in long red shining needles, and on boiling the latter with silver chloride and then adding platinic chloride, a yellow crystalline precipitate, $(C_9H_6N_2Me_3)_2PtCl_6$, is produced. Orthonitraniline yields a nitroquinoline identical with that obtained by the nitration of quinoline, whilst with metanitraniline an entirely different reaction takes place. In the latter case phenanthroline (Abstr., 1882, 1111) is formed, together with small quantities of hydroxyphenanthroline, $C_{12}H_7(OH)N_2$. The latter melts at 159—160°, dissolves readily in dilute sodium

hydroxide solution, from which it is reprecipitated by carbonic anhydride; it is also readily soluble in warm alcohol or benzene, and crystallises from the latter in colourless shining needles. The platinochloride, $C_{12}H_7N_2.OH,H_2PtCl_6 + H_2O$, forms a yellow crystalline precipitate.
A. K. M.

Action of Phthalic Anhydride on Quinoline. By E. JACOBSEN and C. L. REIMER (*Ber.*, **16**, 513—514).—The authors claim the priority over Traub in the discovery of a yellow colouring matter produced by the action of phthalic anhydride on quinoline. They found that other quinoline bases, such as pyridine, would yield similar colouring matters, and one of them took out a patent for their production in November, last year. The analytical results obtained by the authors differed somewhat from those published by Traub. They state that their experiments have shown that quinoline obtained from coal-tar differs widely from that prepared by Skraup's method.
J. I. W.

Quinazole-compounds. By E. FISCHER and H. KUZEL (*Ber.*, **16**, 652—656). — In an attempt to prepare ethylhydrazincinnamic acid from nitrosoethylamidocinnamic acid by treatment with zinc-dust and acetic acid, the authors have obtained an acid of the formula $C_{10}H_{11}N_2.COOH$, which is decomposed by heat into carbonic anhydride, and a base, $C_{10}H_{12}N_2$. The latter (*ethylquinazole*) bears no resemblance to the hydrazines, but in many reactions shows a similarity to quinoline. To prepare *ethylquinazolcarboxylic acid*, $C_{10}H_{11}N_2.COOH$, an excess of zinc-dust is added to an alcoholic solution of the nitrosamine (Abstr., 1881, 599), and acetic acid gradually added, the temperature being maintained first at 40°, and towards the end of the operation at 60—70°. The product is filtered, the solution evaporated, and the residue treated with water and dilute sulphuric acid. On agitating with ether and evaporating, an oil is obtained, which, after treatment with dilute sulphuric acid, gradually becomes crystalline. It can be purified by boiling its chloroform solution with animal charcoal, and adding light petroleum when the acid separates in dense brown crystals, and after recrystallisation from water forms colourless plates, melting at 131°. It is sparingly soluble in water, readily in alcohol, ether, and alkalis. *Ethylquinazole* is obtained by heating the above in an oil-bath at 180—190°, until the decomposition is nearly complete, then at 230°, and finally distilling, its boiling point being 234—235° at a pressure of 741 mm. When cooled by a freezing mixture, it solidifies, forming large plates melting at 30°. It is readily soluble in alcohol and in ether, sparingly in water; it is volatile in steam, has a penetrating odour resembling that of quinoline, and a sharp taste. It forms readily soluble salts, which are decomposed by water; the *sulphate*, $C_{10}H_{12}N_2,H_2SO_4$, is obtained in long needles on adding ether to its alcoholic solution; the *platinochloride*, $(C_{10}H_{12}N_2)_2,H_2PtCl_6$, is sparingly soluble in water, and crystallises from dilute hydrochloric acid in orange-yellow prisms; the *picrate* is also sparingly soluble in water and in alcohol. It yields white crystalline precipitates with silver nitrate and mercuric chloride, nearly insoluble in cold water. Fehling's solution, mercury and silver oxides have no action on it even on boiling; neither has nitrous acid nor boiling acetic anhydride. The formation of this base from nitrosoethylamidocinnamic acid is most easily explained on the assumption that its formula is I, whilst its similarity to quinoline suggests either of the formulæ II or III :—


I.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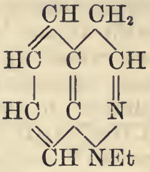

III.

A. K. M.

Piperidine and Pyridine. By A. W. Hofmann (*Ber.*, **16**, 586—591).—Previous experiments on the action of bromine on piperidine (*Ber.*, **12**, 984) led the author to assume a relationship between the latter base and pyridine. This has since been established by Königs (Abstr., 1880, 404), who obtained pyridine by the oxidation of piperidine, and also by Schotten (Abstr., 1882, 983), who obtained dibromopyridine by the action of bromine on piperidine. The author, by modifying his former experiments, has succeeded in obtaining pyridine from piperidine. He combines the latter with acetic anhydride, and gently warms the resulting compound (1 mol.) with bromine (2 mols.). Hydrobromic acid is evolved, whilst a colourless distillate, consisting of acetic bromide and its substitution-derivatives, passes over, leaving a syrupy residue in the retort. On treating the residue with alkali and steam-distilling, an alkaline aqueous distillate and an oily layer, together with crystals of dibromopyridine, are obtained. After recrystallisation from alcohol the latter melts at 112°, and boils at 222°. On adding potassium hydroxide to the aqueous distillate, an oily layer separates, consisting of pyridine mixed with unaltered piperidine. The latter is readily separated by treatment with acetic anhydride, and then distilling, when nearly pure pyridine is obtained. The oily portion of the steam distillate contains monobromopyridine, C_5H_4BrN, which the author previously obtained by the bromination of pyridine. It forms a platinochloride, $(C_5H_4BrN)_2,H_2PtCl_6$, crystallising in flat needles, and an aurochloride, $C_5H_4BrN,HAuCl$, crystallising in plates.

An attempt to reverse the process, and to obtain piperidine from pyridine, was unsuccessful. Pyridine was heated with concentrated hydriodic acid, when normal pentane and ammonia were produced.

A. K. M.

Oxidation of Piperidine. By C. Schotten (*Ber.*, **16**, 643—649).—The author has shown (this vol., p. 220) that an acid of the formula $C_7H_{15}O_2N$ (for which he now suggests the name *coninic acid*) is produced by the action of nitric acid on conylurethane. Under similar conditions, piperylurethane (Abstr., 1882, 983) yields *piperidinic acid*, $C_4H_9O_2N$, homologous with the latter; its *hydrochloride*, $C_4H_9O_2N,HCl$, forms dense hygroscopic prisms, readily soluble in water and in alcohol; its platinochloride, $(C_4H_9O_2N)_2,H_2PtCl_6$, forms large shining prisms. If urea is added to the nitric acid to moderate its action, *nitrodehydropiperylurethane*, $C_5H_7(NO_2)N.COOEt$, is produced, crystallising in yellowish needles or prisms, melting at 51·5°, and soluble in hot water or in alcohol. It is not readily acted on by acids, whilst alkalis dissolve and decompose it even in the cold. When it is treated with tin and hydrochloric acid and the solution is then heated with concentrated hydrochloric acid in sealed tubes above 100°, an oil is obtained, which is probably dehydropiperidine. On adding bromine to its solution in glacial acetic acid, it forms a *bromhydroxyl-derivative*, $C_5H_7(NO_2)N(HOBr).COOEt$, which crystallises in prisms melting at 157°. *Piperylmethylurethane*, $C_5H_{10}N.COOMe$, is prepared in the same way as the ethyl-compound (*loc. cit.*), and forms a colourless liquid (b. p. 201°), having a slight and agreeable odour. It is heavier than water, in which it is sparingly soluble, and can be boiled with alkalis or with hydrochloric acid without decomposition. It yields a *nitrodehydro-derivative*, $C_5H_7(NO_2)N.COOMe$, which crystallises in yellowish needles melting at 102—103°, and by the action of bromine on this a body is obtained melting at 130°. By the action of bromine on piperylethylurethane, the compound

$$C_5H_7BrN(HOBr).COOEt$$

is produced, crystallising in short hard shining prisms, which melt at 140°. If twice as much bromine is used as is necessary to form this body, dibromopyridine is produced. A. K. M.

New Crystalline Colouring-matter in Urine. By P. Plosz (*Bied. Centr.*, 1883, 208).—The alkaline fermented urine was acidified with hydrochloric acid, aërated until it became red, then extracted with chloroform, which removed indigo, as well as red acicular crystals or rhombic plates. This substance is probably a skatole derivative.
E. W. P.

Metahæmoglobin. By F. Hoppe-Seyler (*Zeitschr. Phys. Chem.*, **6**, 166—174).—The author has already (**2**, 150) described certain experiments of his, which he believes to prove beyond doubt that metahæmoglobin, a name given by him to a product of the decomposition of the colouring-matter of the blood, must be regarded as a compound of albumin and hæmatin, the view of several observers, that it is a higher oxidation stage of arterial blood pigment, being erroneous.

The present article is occupied with a defence of his previous statements against the opinion of A. Jäderholm (*Zeitschr. für. Biolog.*, **16**, 1), that metahæmoglobin is a higher oxide (peroxide). D. P.

Nucleïn. By W. Klingenberg and A. Stutzer (*Bied. Centr.*, 1883, 204—206).—Miescher considers that the substance found in yolk, and the red blood-corpuscles of goose-blood, called nucleïn by Hoppe-Seyler, is a grouping of nucleïn compounds, and is not identical with the nucleïn of pus. Klingenberg has investigated the nucleïn of fodder, and by means of the proportion P : N, finds that the nucleïn of poppy, earthnut, rape, and cotton cake is the same, whilst that of palm nut is very different; the proportion P : N : S (1 : 6·97 : 0·88) found by Klingenberg agrees with that found by previous investigators. Stutzer reports the presence of nucleïn in yeast and mildew; of 100 parts of the nitrogen in mildew, 40·75 are as nucleïn; whilst in yeast only 26·09. E. W. P.

Physiological Chemistry.

Researches on Digestion in the Stomach. By A. Kietz (*Bied. Centr.*, 1883, 208).—During the first hour of digestion, lactic acid is not present in notable quantities, but the acid present is hydrochloric; the appearance, sooner or later, of free acid is dependent on the quantity and quality of the food, as well as on the idiosyncrasy of the individual. E. W. P.

Reaction of the Living Mucus-lining of the Stomach. By L. Edinger (*Bied. Centr.*, 1883, 207).—By injection of sodium-alizarin, which causes the death of the animal experimented upon, it is shown that the majority of the glands of the stomach are acid during digestion; the lining itself is not always acid, and whilst the lumen of a gland may be acid, the interior parts may be alkaline or neutral.
E. W. P.

Digestibility of Meat. By P. Hönigsberg (*Bied. Centr.*, 1883, 208).—Experimenting with artificial stomach juice, the author finds that of the albumin in raw meat 39·7 per cent. is converted into peptone, in boiled 26·6 per cent., in roasted meat 48 per cent.
E. W. P.

Digestibility of Caseïn from Heated Milk. By M. Hoffmann (*Bied. Centr.*, 1883, 208).—More peptones are formed by the digestion of caseïn from boiled than from unboiled milk, and most from caseïn obtained from milk which has been subjected to Becker's process.
E. W. P.

Decomposition of Digestive Ferments. By J. N. Langley (*Bied. Centr.*, 1883, 209).—Hydrochloric acid and gastric juice destroy the power of the saccharifying ferment of the parotid. Dilute alkaline carbonates destroy pepsin, and in presence of trypsin, these carbonates are more energetic. The ferment of rennet is destroyed by a 1 per cent. solution of sodium hydroxide and by trypsin; consequently, neither ptyalin nor rennet ferment can exist in the intestines. A glycerol extract of the pancreas is rendered inactive by hydrochloric acid, and trypsin in acid solution decomposes pepsin.
E. W. P.

Fattening of Calves. By K. v. Langsdorff (*Bied. Centr.*, 1883, 168—170).—Thirty-four sets of experiments were instituted to ascertain whether or not it was most advantageous to feed calves for the butcher with skim milk (with additional food), or with whole milk. The results are greatly in favour of skim milk. E. W. P.

Feeding of Cattle with Dry Fodder. (*Bied. Centr.*, 1883, 167.) —Seven oxen were fed from May to end of August on hay and aftermath; in addition to this from June onwards they received a ration of oats; the expenses of food and attendance being reckoned at 2396 M, each 50 kilos. live weight was put on for 3·7 M—a satisfactory result. The average daily gain in weight was 1·57 kilos.

E. W. P.

Digestibility of Meadow-hay and Wheat-bran treated with Hot and Cold Water. By G. KÜHN and others (*Landw. Versuchs.-Stat.*, **29**, 1—2 and 1—241).—This voluminous paper contains a report of numerous experiments carried on by the reporter and various assistants at the station of Möckern during 1877 to 1881, in order to ascertain whether the treatment of meadow-hay with hot and cold water and hot and cold infusions of wheat-bran had any influence on its digestibility. The subject is considered of considerable importance in Germany, and the authors enter into very minute details, which occupy 91 closely-printed tables.

The general idea of the experiments was to analyse the fodder and excreta, keeping a record of the gain and weight of the six oxen employed as experimental animals.

The stall arrangements were carefully made, the mangers freely accessible and moveable, with arrangements for collecting the uneaten fodder; the floor of each stall was of asphalt and inclined towards the centre; a cut stone channel running along all the stalls was so disposed that it received the solid excrement; this was carefully swept into a receptacle from which samples were daily drawn for analysis, but the urine was allowed to escape.

The methods employed were simple. The hay, as brought in from the different sources of supply, was spread in thin layers one over the other, on a dry clean granary floor, and, when all stored, was well trodden down; a section, therefore, was a fair specimen of the whole; the daily rations of the oxen were so cut, and then put through an ordinary chaffcutter and filled into sacks, during the filling of which a certain number of handfuls were taken to make up the sample for analysis, which was then dried in the water-bath and exposed to the air and the proportion of dry matter determined. The bran was sampled in a similar manner. The dung was well mixed in its receptacle, and samples carefully drawn and dried with like precautions. The chemical examination of both fodder and dung was confined to the estimation of ash, indigestible fibre, fat, and nitrogen in the dried samples so prepared, according to usual methods.

Fifty-one tables give the daily variations in the food, drink, and weight of the animals, their solid evacuations, temperature of stalls, increase of weight, &c., with remarks as to the progress of the experiments as affecting each animal.

The most interesting points are: the daily ration of dry hay was 10 kilos. with the occasional addition of 2 kilos. of bran prepared in various ways, steeped either in hot or cold water in different proportions. The amount of water taken by the animals depended greatly on the wet or dry state of the fodder, but the amount of dry substance contained in the daily yield of dung was very regular. In table after table, the average of 10 days is given as 3·5 to 3·6 kilos., quite as regular, apparently, as the quantity of food given. The percentage of mineral matter in the dry substance of the hay was 7·79 to 8·89 per cent.; in the wheat-bran 6·79 to 7·08; and in the dung 12·37 to 18·23 per cent. The nitrogen in the hay 1·71 to 1·96; in the bran 2·35 to 2·54 per cent.; and in the dung 1·78 to 2·31 per cent.

The fatty matter extracted by ether from the hay was 2·69 to 2·98 per cent., from the bran 4·41 to 5·12 per cent., the dung 3·20 to 4·39 per cent.

The greater part of the remainder of the paper is occupied with tabular comparisons of the experiments with each other, possible sources of error from the constitutions of the different beasts, and similar details, the results of the whole series of experiments being of a negative character. The conclusions drawn by the experimentalists themselves will be sufficient:—

1. The mere damping of hay, immediately before feeding, either with cold water or cold bran infusion, in quantity insufficient to satisfy the animal's thirst, has no effect on the digestibility of fodder.

2. The saturation of the bran with 30 kilos. of cold water and the damping of the hay with the mixture has no effect on the digestion either of the hay or the bran, if done immediately before the feeding.

3. The steeping of the bran for a period of 24 hours in cold water does not influence the digestion of the fodder, so long as it has not been so much moistened that the thirst of the cattle is not more than half satisfied by it, and that they drink half their usual supply of water; if this limit is passed, and the desire of the animals for water does not induce them to take nearly 50 per cent. of their usual quantity, the digestibility of the fodder becomes sensibly reduced.

4. The scalding of the bran with boiling water is injurious, and renders the mixed fodder indigestible, in proportion to the initial temperature of the water used and the length of time it remains heated.

5. The use of an infusion of bran as a drink, without previous admixture with the fodder, does not appear to exercise any influence on the digestion.

6. The diminution of the digestibility of the fodder, when treated with boiling water, is attributed by the authors to the action of heat on the albumin of the bran and not on the raw proteïd matter of the hay.

The authors conclude by saying, that although the experiments in question refer only to two kinds of fodder, they believe that similar results would be arrived at with other foods, but they specially exempt from their caution not to treat the fodder with water, the case of inferior kinds of food, which by such treatment might be rendered more agreeable and appetising. J. F.

Results of the Suppression of Perspiration of Animals. By Ellenberger (*Bied. Centr.*, 1883, 173).—It is generally supposed that when perspiration is partly suppressed by means of a coating of varnish, the animal dies. Ellenberger has investigated this matter, employing horses, dogs, &c., as subjects, and finds that the above statement is incorrect. Only weakly animals die, as also those from which the hair or wool has been removed immediately before the varnishing. Sheep suffer most from the operation, but the varnishing of one-eighth to one-fourth of the skin is not dangerous. Swine are but slightly affected, as also dogs; but tar must not be employed, or they suffer by licking themselves. With horses, the temperature falls 1·5° by removal of the hair, but after the constitution has recovered itself, no harm ensues. In six out of seven experiments, an increase of urea was noticed, but albuminous urine was never observed. E. W. P.

Peptone the Source of Sugar in the Liver. By J. SEEGEN (*Bied. Centr.*, 1883, 206).—Feeding with peptone or injection of the same raises the percentage of sugar in the liver. E. W. P.

Alteration in the Secretion of Milk under the Influence of Drugs. By STUMPF (*Bied. Centr.*, 1883, 171).—Goats were experimented on. When potassium iodide was administered, the yield of milk was reduced, while the percentage of fat and sugar was raised; salts and albuminoïds were unaltered; reaction became alkaline. Small doses of lead acetate produced no change of composition or yield; the same negative results were obtained with morphine. Pilocarpin at first only reduced the sugar. Sodium salicylate considerably raised the yield. Alcohol did not alter the yield, but the solids increased, whilst the sp. gr. decreased. When beer was given, the sp. gr. fell, but the fat rose in quantity, as did also the sugar.

E. W. P.

Behaviour of Blood when Deprived of Oxygen. By ZWEIFEL (*Bied. Centr.*, 1883, 207).—If the oxygen be removed artificially from the blood, decomposition immediately sets in; also, blood so treated acts injuriously on animals. E. W. P.

Observations on a Dog with Biliary Fistula. By F. RÖHRMANN (*Bied. Centr.*, 1883, 207).—The presence or absence of fistula had no effect on the weight of the dog. The absence of bile produced a non-absorption of fat, yet fat continued to be deposited on the body, so that it would appear as if bile were absolutely essential for the assimilation of fat. E. W. P.

Formation and Decomposition of Tyrosine. By C. BLENDERMANN (*Bied. Centr.*, 1883, 209).—Experimenting on himself, the author found that tyrosine produced phenol in the urine, but no excess of oxyacids; in a rabbit, phenol and oxyacids in large proportions were found, as also two new derivatives of tyrosine, tyrosine-hydantoïn, and oxyhydroparacumaric acid. E. W. P.

Adipocere. By ERMAN (*Bied. Centr.*, 1883, 209).—Adipocere formed during life forms fat, and is not a decomposition-product of albuminous tissue. E. W. P.

Poisoning of Cattle by Earth-nut Cake. By ANACKER (*Bied. Centr.*, 1883, 210).—Examination showed that the death of the cattle arose from the presence in the cake of mildew, sand, small stones, croton and castor oils. E. W. P.

Insensibility arising from a Deficiency of Oxygen in the Air. By W. WALLACE (*Chem. News*, **47**, 158).—The author is of opinion that the feeling of depression or suffocation resulting from breathing the air of a badly ventilated chamber is due not so much to carbonic anhydride as to the diminution in the quantity of oxygen. He supports this view by figures and by a case of death from suffocation in a confined space where the oxygen was being quickly absorbed, whilst carbonic anhydride was simply produced from the breathing of the victim; on analysis, the atmosphere in question proved to be principally nitrogen. D. A. L.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Character of Living Protoplasm. By O. LOEW (*Bied. Centr.*, 1883, 211).—The silver reaction for living protoplasm is not due, as Reinke and Mori suppose, to aldehyde, as it takes place in the presence of spirogyra which contain neither aldehyde nor chlorophyll; neither does this reaction occur with every green or chlorophyll-free plant, nor even with the same plant under every circumstance of growth. It occurs only when the protoplasm contains a lecithin compound, whereby the chemical resistance is increased so that change does not follow immediately after the first attack on the cells. E. W. P.

Autoxidation in Plant Cells. By J. REINKE (*Bied. Centr.*, 1883, 178—181).—The researches of others to which reference is made point to the following conclusions: In every live cell autoxydators (*i.e.*, substances which at low temperatures by the decomposition of water oxidise themselves by taking up molecular oxygen) are formed; during the oxidation of autoxydators, hydrogen peroxide is formed; hydrogen peroxide under the influence of diastase, &c., may act as energetically as atmospheric oxygen. The locality in colourless cells where oxidation occurs is in the peripheral layer of the protoplasm; here hydrogen peroxide is formed, which, however, does not become free, but is immediately employed in oxidising hydrocarbons. The first compounds which it will attack are the readily oxidisable matters which have been formed by the combined action of water and molecular oxygen on the autoxydators; this explains the presence of colouring matters in beet and potato juices, which do not appear so long as there are living cells; this formation of colouring matter is noticeable when a potato is grated and exposed to the air. E. W. P.

Colour and Assimilation. By T. W. ENGELMANN (*Bied. Centr.*, 1883, 174—178).—Former investigations in which the activity of bacteria in the presence of oxygen evolved through the aid of chlorophyll was made the measure of assimilation, showed that for green cells the disengagement of oxygen was greatest when the red rays between B and C (Fraunhofer) and the blue near F, were allowed to fall on those cells. These rays being thus more readily absorbed by chlorophyll, the question arose as to whether a similar relationship existed between absorption and assimilation when cells containing plasma or another colour were employed. To answer this question, yellowish-brown cells (Diatomaceæ), bluish-green (Oscillaria) and red (Floridaceæ) were introduced into the solution containing bacteria; it was then found that the maxima of absorption exactly coincided with the maxima of evolution of oxygen, and *vice versâ*. The details are as follows:—

Green Cells.—Maximum of assimilation and absorption in the red between B and C, in the blue at F, whilst the minimum occurs in the green between E and *b*.

Yellowish-brown Cells.—First maximum in the red between B and C, and again at D $\frac{1}{2}$E, the minimum being found in the orange and yellow.

Bluish-green Cells.—No absolute maximum is found in the red, although the absorption is high here, but it is found in the yellow; comparatively feeble is the action of the blue and green rays.

Red Cells.—The maximum (in gaslight) occurs in the green, a second maximum at B, C, and a minimum at C $\frac{1}{2}$D. From these experiments it is evident that chlorophyll is not the only substance which assimilates. It is not improbable that these colouring matters (chromophyll) are mixtures of chlorophyll with other assimilating substances. E. W. P.

Formation of Starch from Sugar. By J. BÖHM (*Bied. Centr.*, 1883, 212).—After reference to previous communications, experiments on plants are described, which prove that starch may be deposited in chlorophyll and etiolin cells, which would not otherwise contain starch, and this will occur if the plant be supplied with cane- or starch-sugar, the quantity deposited being affected by the concentration of the sugar solution. Some leaves, as those of *Allium* and asphodel, which normally contain no starch, will not convert sugar into starch. The roots of seedlings also take up sugar.

E. W. P.

Experiments on the Value of Various Fodders for Cows. By F. WALTHER (*Bied. Centr.*, 1883, 210).—Feeding some cows with cotton cake meal and others with rye bran, proved the superiority of the former food for the production of butter. When cotton cake and grains were compared with cocoanut cake and grains, the first mixture produced less milk, and somewhat less butter.

E. W. P.

Rice and Earth-nut Meal as Food for Milch Cows. By W. WOLDE (*Bied. Centr.*, 1883, 170).—Rice meal is here shown to be less costly, more productive of milk, and more palatable than earth-nut meal. E. W. P.

Nitrogenous Constituents of Malt, Wort, Beer, and Bread. By F. Ullik (*Bied. Centr.*, 1883, 201—203).—From the examination of malt and wort, the author concludes that normal malt contains no ready-formed peptones, the principal portion of the soluble nitrogen being present as amides: peptones appear first in the wort, but the quantity is unimportant; the quantity of the various nitrogenous compounds present is dependent on the quality of the malt.

Examination of three kinds of beer showed that amides were in larger proportion than peptones, and albuminates were absent. Further, the feeding powers of these three are compared with that of bread. To obtain the necessary amount of albuminoïds (118 grams, Voit), a man must consume of the weaker beer examined 154·7 litres; or 1 kilo. bread contains the same quantity of albuminoïds as 64·6 litres beer.

E. W. P.

Fermentation of Cellulose. By F. Hoppe-Seyler (*Ber.*, 16, 122—123).—Experiments recorded by Popoff (*Pflüger's Archiv.*, 10, 113) have already shown the probability that the ferments present in the mud of cesspools are capable of decomposing cellulose into carbonic acid and marsh gas. The author has succeeded in proving the reaction.

A small portion of mud from a cesspool, purified by levigation, and containing a known amount: (1) of total organic matter; (2) of cellulose insoluble in alcohol, ether, dilute hydrochloric acid, and dilute soda-lye, was placed on a weighed filter, the paper of which contained a known proportion of cellulose, and enclosed in a bottle containing distilled water. The evolved gases were collected over mercury. The arrangement was left so for 13 months, during many of which it was kept in darkness. Atmospheric air was excluded during the whole time, and the pressure of the gas in the apparatus was always more than an atmosphere.

Up to the time of the report, many litres of gas had been obtained, 20 to 25 c.c. being obtained daily at a temperature of 20° C.; the evolution still continues. The amount of carbonic anhydride obtained is more than double the quantity which the organic matter in the mud alone should yield, and as there is nothing else but the filter-paper present, it must necessarily be derived therefrom. The evolved gas consists of about 50 per cent. in volume of carbonic anhydride, 45 per cent. marsh gas, and a little hydrogen.

The author remarks on the very large extent of the earth's surface in which this process of fermentation must be going on, inasmuch as all cultivated ground, and all meadow and forest land, where favourable temperature exists, must contain the elements necessary for it. He is at present engaged in researches on the subject in connection with the reduction of gypsum, the formation of carbonate and sulphide of iron, and the production of nitrous acid in presence of ammonia and oxygen.

J. F.

Influence of Organic Manures on the Temperature of the Soil. By F. Wagner (*Bied. Centr.*, 1883, 150—152).—The temperature of the soil is not wholly dependent on the heat derived from the sun, but also from the heat evolved by the condensation of aqueous vapour, and the decomposition of organic matter. Concerning this last source, investigations have been made to ascertain the heating effect of the fresh and rotten dung of various animals, as also of green manures and stubble. The rise of temperature is in proportion to the amount of manure, to a certain extent to the temperature of the soil, and to the amount of moisture present, but only so far as the evaporation of that moisture does not counteract the heating produced, and so long as there remains a sufficiency of oxygen in the crevices of the soil. A fall of the external temperature to 10° arrests the production of heat. The more readily decomposition is effected, the greater is the rise in temperature; all added material, such as lime, which assists decomposition, aids in raising the temperature, and it is also requisite that the manure be evenly distributed. The maximum heating effect occurs immediately after the introduction of the manure, but heat is generated for from four to twelve weeks. Bean straw and horse dung are most effective, there having been an increase in temperature of 2·8° and 1·0° respectively. E. W. P.

Application of Insoluble Phosphates to Soils. By M. FLEISCHER and R. KISSLING (*Bied. Centr.*, 1883, 155—161).—In the first portion of this paper we find that the action of moorland soils when mixed with insoluble phosphates is to render a portion of that phosphate soluble in water, amounting in one case to 5·5 per cent. of the total phosphoric acid; at the same time, a portion is reduced to the dicalcium salt, and in one compost heap as much as 17 per cent. of the total acid was brought into this form. The observations also show that as the ratio between soil and phosphate is widened, so does the amount of soluble salt increase, and although an increase occurs as time goes on, yet there is a limit, after which soluble phosphate becomes "reduced." In the second portion, we find the influence exerted by added salts as kainite, gypsum, &c., on the solubility of phosphates in peaty soil. Ammonium sulphate was most energetic, but the authors put its action on one side, as the sample was crude and contained free acid. Potassium sulphate was very effective, whilst Chili saltpetre and kainite were far less so. This assisting action of potassium sulphate seems to increase with each addition of the salt. E. W. P.

Ash of Pistia Stratiotes: "Páná Salt." By C. J. H. WARDEN (*Chem. News*, **47**, 133—134).—*Pistia stratiotes*, known as "taka panna," in Bengalee and Hindoostanee, is found floating on stagnant pools of water in most parts of India, resembling in appearance half-grown lettuce plants; the saline matter obtained from the ash is called "páná salt." To prepare this salt, the matured plants are dried and incinerated, the ash thus obtained is percolated with water, and the saline solution is evaporated to dryness. Páná salt is almost entirely used for medicinal purposes. A specimen of the plant yielded the following results on analysis. The plant was dried at 130°, exposed to a temperature below redness, exhausted with boiling distilled water, and the insoluble residue incinerated until free from carbon. Total ash, 31·4583 per cent.; 6·1426 per cent. being soluble and 25·3463 insoluble. A sample of páná salt was slightly deliquescent, had alkaline reaction, and looked like dirty common salt. Dried at 130° it contained—

	Per cent.
Potassium chloride	73·0916
Potassium sulphate	22·6130
Potassium carbonate	traces
Sodium carbonate	0·4727
Calcium sulphate	0·5874
Magnesium sulphate	0·2574
Iron oxide and alumina	0·0982
Sand and silica	0·3673
Organic matter	0·3575
Water	1·8674
Nitrates, nitrites, phosphates, bromine, iodine	Nil
	99·7125

This analysis shows that water-weeds may contain a large amount of saline matter. It is hence probable that these plants have the power of removing saline matter from water, as well as indirectly oxidising the dissolved organic matter. For this reason, it is desirable to allow water-weeds to grow in Indian tanks (which are very liable to pollution), but only during the cold season, when direct oxidation proceeds slowly; in the hot season, however, it is advisable to keep the surface of the water clear of weeds, so as to expose it to the heat, light, and air, in order to facilitate direct oxidation, which is rapid at high temperatures. In the case of wells in India, the mouths are generally raised above the level of the ground, so that the water must percolate through a certain depth of soil and is thus rendered innocuous; if sewage does gain access, it retains its virulence for a long time; the author attributes this to the low temperature of the water, to the absence of light and plant life, and to the stagnation of the atmosphere. D. A. L.

Manuring Sugar-beet. By A. TSCHUSCHKE (*Bied. Centr.*, 1883, 161—163).—Five sets of experiments show that a mixture of saltpetre and superphosphate brings the highest yield of roots, but that saltpetre alone produces the heaviest root, whilst superphosphate alone produces a root having the highest quotient of purity. Of two samples of roots, Schlesian is better as regards yield, individual weight, and quotient than Little Wanzleben. E. W. P.

Analytical Chemistry.

Preparation of Hydrogen Sulphide from Coal-gas. By J. TAYLOR (*Chem. News*, **47**, 145).—"Hydrogen sulphide may be prepared very easily, and sufficiently pure for ordinary analytical purposes, by passing coal-gas through boiling sulphur." For this purpose the sulphur is placed in a retort, through the tubulure of which a bent glass tube, connected with the gas supply, passes below the surface of the sulphur, the neck of the retort being inclined upwards and connected with a wash-bottle, to which is attached the flask containing the solution to be treated. The apparatus is worked by an aspirator which serves both to regulate the flow of gas and also as a receptacle for unused gas. The gas-supply tube may be advantageously perforated with several small holes at the end dipping under the sulphur. During working hours the sulphur is kept hot by means of a burner, so that it can be quickly raised to boiling when required. The author claims cleanliness, cheapness, and convenience for this method.

D. A. L.

Litmus, Methyl-orange, Phenacetolin, and Phenol-phthaleïn as Indicators. By R. T. THOMSON (*Chem. News*, **47**, 135—137).—A continuation of the paper already abstracted (this vol., 682).

XI. *Effect of Sodium Silicate.*—With this substance, *litmus* and *methyl-orange* give good results, and the end-reaction is very distinct in both cases. *Phenacetolin* results are good, but the colour-change is not so; a dark pink is developed, which becomes yellowish and indistinct towards the end. *Phenol-phthaleïn* gives very low results. The titration of sodium silicate, $Na_2Si_4O_9$, gave the following results:—

Indicator.		c.c. of normal acid consumed.	Gram Na_2O found.
Litmus		15·05	0·466
Methyl-orange		15·10	0·468
Phenacetolin		15·00	0·464
Phenol-phthaleïn	cold	12·70	0·393
	boiled	13·50	0·418

XII. *Effect of Alumina.*—The experiments were made with caustic soda-solution of average strength, containing about 8 per cent. of alumina. With *litmus*, more acid is required than when alumina is absent, and the end-reaction is not very distinct. With *methyl-orange*, no permanent change in colour takes place until the alumina first precipitated is redissolved, and the results show that almost all the alumina is estimated along with the soda. With *phenacetolin* and *phenol-phthaleïn*, the actual amount of soda is found; the alumina, however, renders the end-reaction slightly obscure. The results are as follows:—For each test 50 c.c. of the solution containing 0·775 gram Na_2O and 0·103 gram Al_2O_3 (= 0·186 gram Na_2O) was employed.

Indicator.	c.c. normal acid consumed.	Gram Na_2O found.
Litmus....................	25·25	0·782
Methyl-orange.............	30·70	0·951
Phenacetolin	25·05	0·776
Phenol-phthaleïn	25·00	0·775

XIII. *Effect of Sodium and Potassium Nitrite.*—These salts are neutral to *litmus*, *phenacetolin*, *phenol-phthaleïn;* and with *methyl-orange* no permanent colour is produced in moderately dilute solutions (1·70 gram KNO_2 in 100 c.c.), probably owing to the decolorising effect of the nitrous acid, and even in a solution containing 0·085 gram of nitrite in 100 c.c. the pink colour disappears in a few minutes, leaving a pale yellow colour.

XIV. *Determination of Soda in Borax.*—For this purpose, *methyl-orange* is admirably adapted, the final colour-change being sharply defined, and the results are good. With *litmus* and *phenacetolin* the change of colour is slow, and therefore the end-reaction is indistinct. *Phenol-phthaleïn* is quite useless. The results obtained were as follows:—1·683 gram $Na_2B_4O_7$ = 0·516 gram Na_2O were used for each test.

Indicator.		c.c. normal acid consumed.	Gram Na_2O found.
Litmus		16·65—16·60	0·516—0·514
Methyl-orange		16·70—16·65	0·518—0·516
Phenacetolin..............		16·70—16·60	0·518—0·514
Phenol-phthaleïn	cold	7·60— 7·80	0·235—0·242
	boiled ..	11·00—11·30	0·341—0·350

XV. *Determination of Free Sulphuric, Nitric, and Hydrochloric Acids.*—From previous experiments (*loc. cit.*, 684) it is obvious that these acids may be determined by a standard caustic alkali in the presence of these indicators, excepting, of course, by ammonia with phenol-phthaleïn. Sodium carbonate can be used for titration in the cold with *methyl-orange*, and a small quantity of carbonate should always be used with phenacetolin in order to obtain the dark pink end-reaction.

XVI. *Determination of Free Oxalic Acid.*—*Litmus* and *phenol-phthaleïn* are well adapted for this purpose, the end-reactions being very well defined and the results exact. With *methyl-orange*, the pink colour is soon completely destroyed, whilst the phenacetolin colour does not develop well, therefore neither of these two indicators are of use for the titration of oxalic acid. The results obtained are tabulated below:—0·900 gram $H_2C_2O_4$ for each test.

Indicator.	c.c. normal NaHO consumed.	Gram $H_2C_2O_4$ found.
Litmus	20·0	0·900
Methyl-orange	18·0	0 810
Phenacetolin................	19·8	0·891
Phenol-phthaleïn	20·0	0·900

XVII. *Determination of Acetic Acid.*—The acetic acid solution employed contained 100 grams of acetic acid (sp. gr. 1·0472 at 15°

= 35·02 per cent. $C_2H_4O_2$) per litre. 50 c.c. were used for each titration. The caustic alkali used was standardised with normal sulphuric acid. With *litmus*, the final change of colour is uncertain, sodium acetate being alkaline to this indicator, and can only be ascertained either by comparing with blue litmus solution of the same strength as that operated on, or by using paper; the results are the same in both cases. Neither *methyl-orange* nor *phenacetolin* are adapted for the titration of acetic acid. *Phenol-phthaleïn*, on the other hand, answers admirably, sodium acetate is neutral to it, the end-reaction is delicate and sharply defined, and is not affected by dilution, therefore when the acetic acid is to be determined in dark-coloured liquids (such as some vinegars) they may be highly diluted before titration so as not to interfere with the phenol-phthaleïn colour. The results are as follows:—

Indicator.	c.c. normal NaHO consumed.	Gram $C_2H_4O_2$ found.
Litmus............	29·15—29·15	1·749—1·749
Methyl-orange......	3·50	0·210 (printed 2·10)
Phenacetolin	27·80	1·668
Phenol-phthaleïn ..	29·20—29·20	1·752—1·752

XVIII. *Determination of Tartaric Acid.*—With *litmus*, the result is good, but the change of colour is slow. *Methyl-orange* gives very low results; whilst those with phenacetolin are very slightly below the truth. *Phenol-phthaleïn* again is prominent with its delicate end-reaction and good results. The following are the results obtained, 1·5 grams $C_4H_6O_6$ being used for each test:—

Indicator.	c.c. normal NaHO consumed.	Gram $C_4H_6O_4$ found.
Litmus............	20·00—20·00	1·500—1·500
Methyl-orange	16·00	1·200
Phenacetolin	19·85	1·488
Phenol-phthaleïn ..	20·00—20·00	1·500—1·500

XIX. *Determination of Citric Acid.*—The solution employed contained 14 grams of citric acid (containing 8·53 per cent. of water, although carefully dried) per 200 c.c. The normal soda was standardised by normal sulphuric acid, standardising with citric acid being too laborious, entailing as it does the testing for impurities, and tedious estimation of water (compare Grosjean, Trans., 1883, p. 332). *Litmus* either as solution or as paper, is not so good for the titration of citric acid when the soda has been standardised with sulphuric acid, sodium citrate being alkaline to litmus. Neither is *methyl-orange* or *phenacetolin* of any value for this purpose. *Phenol-phthaleïn*, however, gives good results, and a sharply defined end-reaction. The results obtained were as follows:—20 c.c. of the solution = 1·2806 grams $C_6H_8O_7$ being used for each experiment.

Indicator.	c.c. normal NaHO consumed.	Gram $C_6H_8O_7$ found.
Litmus............	19·7—19·7	1·2608—1·2608
Methyl-orange	9·0	0·5760
Phenacetolin	17·2	1·1000
Phenol-phthaleïn ..	20·0—20·0	1·2800—1·2800

Some lime-juice was titrated with the following results:—

Indicator.	c.c. normal soda consumed.	Grams of $C_6H_8O_7$ per oz.
Litmus............	13·00—13·05	36·40—36·54
Phenol-phthaleïn ..	13·25—13·25	37·10—37·10

In this case, 10 c.c. of the lime-juice were diluted to 150—200 c.c., as the yellow colour would otherwise interfere with the reaction; as it is, the colour-change is not quite so delicate as with a colourless solution, although it can be easily recognised. D. A. L.

Use of Rosolic Acid as an Indicator; Additional Notes on the Use of Phenol-phthaleïn and Methyl-orange. By R. T. Thomson (*Chem. News*, **47**, 184—186).—This paper is simply an addition to those which the author has lately published (preceding Abstract and this vol., p. 683). In the absence of any interfering agent rosolic acid is a very delicate indicator, the complete change from pale yellow to deep pink being very sharp. For *the determination of alkali in potassium or sodium hydroxide, carbonate, and hydrogen carbonate*, this indicator is extremely delicate, provided the carbonic anhydride when present is boiled off. *Sodium or potassium sulphate, chloride, nitrate, sulphite, thiosulphate*, and *nitrite* are neutral to rosolic acid. *In the presence of ammonium salts*, 0·2 c.c. of normal sodium hydroxide are required to develop fully the deep pink colour; it is therefore not recommended for the titration of free ammonia. In *sodium sulphide*, the whole of the sodium can be accurately estimated; the end-reaction is very sharp, provided the liberated hydrogen sulphide is boiled off.

Effect of Sodium Phosphate.—The disodium phosphate is strongly alkaline; the monosodic salt is neutral to rosolic acid. The whole of the alkali in sodium silicate can be determined with this indicator; but in order to get a good end-reaction, the experiment must be done with a boiling solution. With *alumina*, rosolic acid behaves in much the same way, and gives results similar to litmus. Rosolic acid is not fitted for the determination of soda in borax. It is, however, an excellent and delicate indicator for the determination of free *sulphuric, hydrochloric, nitric, and oxalic acids*, either by standard soda or potash. It is not well adapted for determination of tartaric acid, and is useless for the titration of acetic and citric acids.

When phenol-phthaleïn is used for the determination of citric and acetic acids, the titration should be done in the cold; for the sodium salts of these acids, although neutral in the cold, have a slightly alkaline reaction when hot. The author again points out that phenol-phthaleïn is not trustworthy in the presence of ammonia or ammonium salts. The author has devised the following method for the valuation of potassium or sodium phosphate and phosphoric acid; it is based on the fact that when normal sodium phosphate is titrated with sulphuric acid, the neutral point with methyl-orange is reached when the monobasic phosphate NaH_2PO_4 is formed, whilst the phenol-phthaleïn neutral point is the dibasic phosphate Na_2HPO_4 stage. To work the method, 5 to 10 grams of the sample dissolved in 80 c.c. of water is mixed with normal sulphuric acid, or, in the case of phosphoric acid, with soda, until the faintly acid reaction with methyl-orange is obtained; carbonic acid, if present, is expelled by boiling; and the cool solution is now titrated with sodium hydroxide, phenolphthaleïn being the indicator, until the neutral (or mono-acid) point is reached: the result thus obtained is one-third of the total phosphoric acid present. Good results have been obtained, but somewhat lower than by the magnesia mixture gravimetric method. D. A. L.

Determination of Caustic Alkalis in presence of Alkaline Carbonates; and of Calcium Hydrate in presence of Calcium Carbonate. By G. LUNGE (*Chem. News*, **47**, 188).—The author uses phenacetolin as indicator, and in the case of the lime determination, he drops in normal acid until a permanent yellow coloration is established. For caustic soda, he proceeds in the manner recommended by Thomson (this vol., 682). D. A. L.

Determination of Zinc as Sulphide. By R. MACARTHUR (*Chem. News*, **47**, 159).—The author proceeds in the following manner:—The solution to be analysed is nearly neutralised, then rendered alkaline with ammonia, acidified with acetic acid, and the zinc precipitated with hydrogen sulphide. The precipitate is washed by decantation with hydrogen sulphide solution containing ammonium acetate, collected on a filter, dried, and ignited in an atmosphere of hydrogen sulphide. For this purpose the crucible containing the zinc sulphide is supported in a No. 6 Hessian crucible, which has two holes drilled in it; one at the bottom for the Bunsen burner, and one in the side for the hydrogen sulphide supply, which is kept up briskly during the ignition. D. A. L.

A New Test for Titanium and the Formation of a New Oxide of the Metal. By E. JACKSON (*Chem. News*, **47**, 157).—Hydrogen peroxide gives rise to a yellow or orange colour in solutions of titanic oxide in hydrochloric or sulphuric acid: this reaction is extremely delicate. By it $\frac{1}{50000}$ of a gram of titanium oxide, or conversely $\frac{1}{2500000}$ of a gram of hydrogen peroxide, can be easily detected. This colour is due to a new oxide of titanium; it is destroyed by reducing agents, or by potassium permanganate or by heating; in the last two cases oxygen is evolved. It is not affected by potassium chromate. With alkalis, a pale lemon-coloured precipitate is thrown down; but on redissolving in dilute hydrochloric acid, the colour is restored to its original intensity. The reaction does not take place in presence of much hydrofluoric acid; ferric chloride should also be absent, as the yellow colour of the iron salt masks the titanium coloration. The composition of this oxide has not yet been definitely determined, the results obtained being discordant. By means of this reaction, titanium has been detected in coal ash, in sawdust, in seed of French bean, in the ash of cotton-seed cake, and in some soils.

D. A. L.

Water Analysis. By L. W. McCay (*Chem. News*, **47**, 195).—In using Tidy's permanganate method for estimating the organic purity of waters, the author has always experienced a difficulty in ascertaining the precise moment of the disappearance of the blue colour of the iodised starch; to avoid this he has adopted the use of ammonium ferrous sulphate. The solutions he employs are—(1.) 0·395 gram permanganate in 1000 c.c. pure water. (2.) 4·90 grams ammonium ferrous sulphate in 975 c.c. water and 25 c.c. concentrated sulphuric acid. From several experiments, the author is assured that the method is very good; the results are not only constant, but also agree well with duplicate analyses done by Tidy's method. The advantages claimed for the method are—(1.) The abolition of the blue colour difficulty. (2.) Saving of time. (3.) Two solutions only are required. (4.) The amount of chemically pure water necessary is reduced to a minimum. The ammonium ferrous sulphate solution keeps very well in the dark. D. A. L.

Sulphuric Acid in Sherry. By E. Borgmann (*Ber.*, **16**, 601—602).—An analysis of a soil producing the best sherry is given. It contains 0·1578 per cent. sulphuric acid, which is insufficient to account for the amount of acid frequently found in this wine.

A. K. M.

Estimation of Sugar in Urine. By Worm-Müller (*Bied. Centr.*, 1883, 207).—5 c.c. of urine in a beaker are boiled, and simultaneously a mixture of 1—3 c.c. copper sulphate solution (2·5 per cent.) with alkaline Rochelle salts (100 grams in 1000 c.c. normal sodium hydrate) is boiled for the same time in another beaker. After 20—25 seconds, the boiling is interrupted, and the two are mixed.

E. W. P.

Employment of Magenta with Sulphurous Anhydride as a Microchemical Test for Aldehyde. By O. Loew and T. Bockorny (*Bied. Centr.*, 1883, 212).—This reagent is uncertain, for when it is exposed to the air, sulphurous oxide volatilises, and a red solution is left, the colour being similar to that produced by acetone; it cannot, therefore, be safely used for the detection of aldehyde in protoplasm as proposed by Mori. E. W. P.

New Test for Aldehydes. By F. Penzoldt and E. Fischer (*Ber.*, **16**, 657—658).—Pure crystallised diazobenzenesulphonic acid is dissolved in cold water (about 60 parts) with the addition of a little soda-solution, and the substance to be tested (also mixed with dilute alkali) is added, together with a little sodium-amalgam. After standing for 10—20 minutes, a reddish-violet colour is produced, resembling that of fuchsine. A liquid containing 1 part benzaldehyde in 3000 will show this reaction. Chloral and benzoïn do not give the colour, whilst acetone and ethyl acetoacetate produce a deep red coloration without the characteristic violet hue which is, however, produced by grape-sugar. The colour is destroyed by long exposure to the air, and is changed by the addition of an acid. A. K. M.

Estimation of Humus in Soils. By G. Loges (*Bied. Centr.*, 1883, 147—150).—Warington and Peake's results are corroborated. Although chromic acid oxidises organic matter, yet all the carbon cannot be estimated as carbon dioxide by its means, seeing that acetic acid is formed. A table of analytical results shows the wide difference which exists between the results obtained by chromic acid and by the ignition process. E. W. P.

Technical Chemistry.

Action of Water on the Lime of Theil. Existence of a New Compound, "Pouzzo-Portland." By E. Landrin (*Compt. rend.*, **96**, 1229—1232).—The author has already shown (this vol., p. 712) that the absorption of lime by hydraulic silica tends to the formation of the compound $3SiO_2,4CaO$. For this compound he proposes the name *Pouzzo-Portland.*

If 1 gram of the lime of Theil is agitated with 2 litres of water free from carbonic acid for 10 or 12 days by means of a mechanical agitator, a portion of the lime is dissolved. The composition of the original lime was:—Carbonic anhydride and water, 4·40; part soluble in water, 41·21; part insoluble in water, 54·39 = 100. The composition of the soluble and insoluble portions was as follows:—

	SiO_2.	Fe_2O_3 and Al_2O_3.	CaO.	MgO.
Soluble portion....	4·70	1·05	35·10	0·36 = 41·21
Insoluble portion ..	21·70	1·95	30·06	0·68 = 54·39

From these figures it is evident that the part soluble in water consists of (1) a large excess of free lime, which in actual practice will either be converted into carbonate by the carbonic anhydride existing in the air or water, thus forming a protecting envelope to the mortar, or will dissolve in the water if the latter contains too little carbonic anhydride to form calcium carbonate, or if on the other hand it contains sufficient carbonic anhydride to form soluble calcium bicarbonate; (2) soluble calcium aluminate; (3) silica held in solution by the alkali.

If it is admitted that the alumina is combined with the lime in the most basic form, the composition of the insoluble portion may be thus expressed:—

Silica	21·70	Pouzzo-Portland	48·58
Lime	26·88		
Lime	3·18	Calcium aluminate	5·13
Alumina and ferric oxide	1·95		
Magnesia			0·68
			54 39

This insoluble portion when dried at dull redness has the property of setting and gradually hardening, like the best Portland cement. Nodules of very similar composition, but containing a slightly higher proportion of calcium aluminate, are formed during the roasting of the lime at Theil, and can be separated after slaking the lime, since they are not disintegrated by the water. They yield excellent Portland cement.

When mixtures of lime with different varieties of silica in the proportion required to form Pouzzo-Portland are heated to bright redness in a gas-carbon crucible for a time varying with the nature of the silica, the fused but non-vitrified mass yields an artificial Pouzzo-Portland which generally splits up and falls to powder as it cools. It is completely soluble in hydrochloric acid, and when moistened with the smallest possible quantity of water and immersed under water, it sets in from 15 to 16 hours, acquiring a hardness which, however, is scarcely equal to that of Spanish white. If, however, the water is charged with carbonic acid, the cement after some hours acquires a hardness equal to that of the hardest stone. C. H. B.

Hardening of Cements. By H. Le Chatelier (*Compt. rend.*, **96**, 1056—1059).—Whenever a body occurs in the nascent state in contact with one of its solvents and in quantity greater than can normally exist in solution, a supersaturated solution is formed. To this law there may, however, be exceptions. The author extends to other cements his theory of the setting of plaster of Paris (this vol., p. 712), and details experiments which prove that supersaturated solutions are formed when calcium sulphate is treated with a saturated solution of potassium sulphate, zinc oxide with a concentrated solution of zinc chloride, and lime with a concentrated solution of calcium chloride.

When fused calcium aluminates are treated with a large excess of water, alumina and lime dissolve in varying proportions, generally different from those in which they exist in the original aluminate. From hydrated aluminates on the other hand, water dissolves no alumina. The solutions of aluminates gradually deposit the whole of the alumina and part of the lime in the form of crystalline hydrated aluminates of variable composition. The aluminates exist in solution in a state of supersaturation. The proportion of alumina originally dissolved is greater the smaller the proportion of lime in the anhydrous aluminate; the precipitation of the hydrated aluminates on the other hand is more rapid the greater the quantity of lime contained in the anhydrous aluminate and consequently in the solution.

When a solution of any aluminate is mixed with an equal volume of lime-water, precipitation commences in a few seconds, and is complete after some hours. The precipitate consists of tufts of elongated microscopic crystals radiating from a central point; if precipitation is very slow, the precipitate forms small, compact spheroliths. This precipitate has the composition $Al_2O_3,4CaO,12H_2O + 9H_2O$, and is identical in appearance with the crystals formed in the setting of aluminous cements. It loses $9H_2O$ at 40°. C. H. B.

Chemistry of the Bessemer Converter. By J. E. STEAD (*Chem. News*, **47**, 159—162).—The author points out that the Bessemer converter is by far the most important metallurgical instrument of modern times, and this importance has been increased by the discovery of the basic or Thomas-Gilchrist process; for by this improvement immense quantities of phosphoric pig-iron, previously considered unfit for making steel, have been rendered available for the Bessemer process. In this paper, the chemistry of the converter is discussed, and the two processes, the acid and basic, compared (compare this vol., 402—404).

Firstly, for lining purposes, the material must be able to resist a very high temperature, and must be sufficiently plastic when damp, so as to hold together when placed in the converter; the ganister therefore should contain about 6 per cent. of alumina. Potash and soda should be avoided, as they render the mixture more fusible. The following figures show the percentage composition of linings:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.
A good mixture for "acid" lining ..	91·2	6·0	1·70	0·25	0·25	0·38	0·32
A "basic" lining..	11·4	4·5	3·46	49·91	30·27	—	—

The "basic" lining is prepared by calcining bricks made from finely ground magnesian limestone until all carbonic anhydride is expelled, and the substance has shrunk to about half the original size; it is then ground to a rough powder, and mixed with 9 to 10 per cent. of boiled coal-tar free from water. Water would slake the lime, and cause the lining to crack. The mixture of tar and basic material may be thrown in plastic lumps into an annular space formed inside the vessel by the introduction of an iron cage, within which a fire is placed. The basic mixture soon becomes hot, melts, fills up the space, and finally becomes quite hard; or it may be cast and baked into bricks in iron moulds, whereupon the tar cakes, and the mixture may be transformed into solid bricks, which after the removal of the moulds, are simply built round the inside of the converter.

The following analyses of the metal charged during the "acid" process show that there is more sulphur now than formerly:—

	C.	Mn.	Si.	S.	P.
Metal used 15 years ago..	3·5—4·0	0·1—1·0	2·0—3·0	0·01—0·05	0·03—0·10
Ditto now ..	3·0—4·0	0·1—1·0	2·0—3·0	0·05—0·15	0·03—0·10

But manganese is now added in larger quantities, and this metal neutralises the injurious effect of the sulphur, which would otherwise render the steel red short (*ibid.*, 404).

The primary object of the "acid" converter is to rid the metal of its carbon and silicon. The following tables are the result of analyses of samples taken after varying periods of exposure in the converter :—

	P. c. at start.	After 5 mins.	After 10 mins.	After 15 mins.	After 20 mins.	After 25 mins.
C	3·50	3·60	3·3	3·25	2·0	trace
Si......	2·25	1·00	0·5	0·20	0·1	trace
Mn	1·00	0·35	0·2	trace	—	—

Another sample series—

C	3·50	3·60	3·30	2·5	1·0	trace
Si......	3·00	1·75	0·25	0·9	0·7	0·5
Mn	0·75	0·25	trace	—	—	—

Generally, then, the manganese is the first to go, the silicon next, and the carbon last; and, this being the case, the oxygen towards the end has nothing else to work on but the carbon, which is quickly burnt, and therefore the large carbonic oxide flame at the mouth of the vessel drops suddenly, and the "blower" knows that the operation is complete. When large quantities of silicon are present, as in the second case above, the rapid oxidation causes great increase of heat (this can be reduced by putting in cold scrap or pig-iron), and under these circumstances the carbon is attacked before all the silicon is gone, so that, towards the end of the operation, the work for the oxygen is divided. In this case the carbonic oxide flame, instead of falling suddenly, fades gradually away, and the "blower" knows that silicon is present in the "bath," and continues to blow until brown fumes (iron oxide) appear, showing that iron is being burnt. Of course the apparent increase of some substances in some of the stages in the above figures is due simply to the decrease of the other constituent or constituents. It is evident that the proper adjustment of temperature for casting is of great importance if uniformly solid and homogeneous steel is to be obtained: for if it be too high, the carbon will be oxidised and blowholes will be formed.

The metals for the "basic" process are commonly of the following composition :—

	C.	Mn.	Si.	S.	P.
No. 1	3·35	0·60	1·30	0·15	1·75 p.c.
No. 2	3·50	1·00	1·00	0·12	2·75 ,,

The chief feature is the high percentage of phosphorus. From 15—17 per cent. of well-burnt lime is put in with the charge; otherwise the lining would soon be destroyed by the silicon and phosphoric anhydride produced: the process is really based on the removal of these acids by the alkali. The approximate rates of disappearance of impurities from phosphoric pig-iron during the blow are given below :—

	P. c. at start.	After 5 mins.	After 10 mins.	After 15 mins.	After 18 mins.
Carbon......	3·50	3·55	2·35	0·07	trace
Silicon......	1·50	0·50	0·09	trace	—
Manganese ..	0·71	0·56	0·27	0·12	trace
Phosphorus..	1·57	1·60	1·43	1·22	0·08
Sulphur	0·16	0·14	0·13	0·12	0·10

Remarks.—Si disappears first; C next; Mn next: P does not appear to be much attacked until the C is all oxidised.

The author explains the action in the converter in the following manner: The oxygen coming in at the bottom combines with all the constituents forming a highly basic iron oxide cinder. This cinder passing upwards through the column of metal which is in violent agitation, brings about the reactions described in the equations:—Air + nFe = FeO + N, air and iron giving iron oxide and nitrogen; $2FeO + Si = SiO_2 + Fe_2$; $FeO + Mn = MnO + Fe$; $6FeO + 2P = FeO,P_2O_5 + 5Fe$; $FeO,P_2O_5 + 6C = Fe + P_2 + 6CO$; $FeO,P_2O_5 + 3Si = 3SiO_2 + P_2 + Fe$. From these changes it is apparent that in the ordinary way whilst carbon and silicon are present, phosphorus cannot be removed; this can, however, be effected in shallow "baths," or if the tuyeres blow on the surface of the molten mass, for then the cinder comes directly in contact with a quantity of lime which is ready to combine with the silica and phosphoric anhydride as soon as they are formed, producing calcium phosphate which is not reduced, either by the carbon in the iron or by carbonic oxide. In Richard's process some of the excess of oxygen in the "basic" steel is removed by adding fluid hæmatite pig containing silicon. From this point onwards the two processes work alike. Spiegeleisen is added to the blown metal to replace the carbon and manganese (and in case of "acid" steel to remove surplus oxygen) necessary to convert it into malleable steel. Spiegeleisen analyses gave following results:—

	C.	Mn.	Si.	S.	P.
Old German ..	4·50	10·00	0·50	trace	0·10 p.c.
New English ..	5·20	20·00	0·50	trace	0·10 „

The following equations explain why phosphorus is not removed in the "acid" converter:—$3CaO,P_2O_5 + 3SiO_2 = 3CaO,SiO_2 + P_2O_5$; $FeO,P_2O_5 + SiO_2 = P_2O_5 + FeO,SiO_2$; $P_2O_5 + 5Fe = 5FeO + P_2$ Results from the analysis of the slags from the two processes were as follows:—

	FeO.	Fe_2O_3.	K.	Al_2O_3.	MnO.
"Acid" process	15·62	1·57	—	1·02	5·33
"Basic" „	9·13	—	—	2·10	4·32

	SiO_2.	CaO.	MgO.	S.	P_2O_5.
"Acid" process	75·70	0·94	0·09	0·01	Nil
"Basic" „	16·60	47·08	4·62	0·12	16·03

Loss in Bessemer converting is greatly due to projections from the nose of the vessel being carried away as rubbish. Analysis of several Bessemer projections yielded results as follows:—

Fe.	Fe_2O_3.	Mn.	C.	Si.	Sand.	P.	S.
70·30	14·50	0·11	1·01	0·63	13·18	0·05	0·06 p.c.

The amount of iron burnt is only 2 per cent; a certain quantity is always lost in the slag which, being great in the basic process, occasions a greater loss. The respective yields are about: "acid," 88·5; "basic," 85 per cent. of the metal charged. Analyses of the steels from—

	Fe.	C.	Mn.	Si.	S.	P.	Cu.
"Acid" process ..	98·33	0·35	1·11	0·08	0·06	0·05	0·02
"Basic" ,, ..	98·46	0·35	1·01	0·03	0·11	0·04	trace

The "basic" process is making rapid progress commercially, especially on the Continent. D. A. L.

Purification of Molasses. By GUNDERMANN (*Bied. Centr.*, 1883, 215).—A solution of bone charcoal or crude calcium phosphate in hydrochloric acid is added to the molasses, and then milk of lime in excess; the precipitate of calcium phosphate carries down with it all the organic calcium salts. E. W. P.

Manufacture of Sugar without the Aid of Bone-charcoal, Sand, or Sulphurous Anhydride. By H. PELLET and A. DUBAELE *Bied. Centr.*, 1883, 200).—After careful treatment with lime and carbonic anhydride, the solution is passed through Puvrez's filter, made of strong sacking 2 m. long and 0·3 mm. broad, which lies horizontally in a channel; in the supporting channel or gutter are holes through which the liquid passes clear and pure. A second evaporation and filtration is necessary. E. W. P.

Prevention of Boiler Explosions. By TRÉVES (*Compt. rend.*, **96**, 1043—1046; see also this vol., 250).—Many disastrous boiler explosions are undoubtedly caused by superheating of the water, which is frequently due to the fact that the water is kept at the boiling point during the night in order to economise heat. This prolonged gentle ebullition expels all the air from the water and brings it into a condition in which it is particularly liable to become superheated. The author proposes to furnish boilers with a T-tube about 4 cm. in diameter, the horizontal part being about 2 decimeters from the bottom of the boiler. The under side of the horizontal tube is perforated by a number of small cups, and, before firing up in the morning, air is driven into the tube until all the water is expelled, this being effected when the manometer attached to the air-pump registers a somewhat higher pressure than the pressure of the steam in the boiler. The small cups filled with air constitute "surfaces of evaporation," from which ebullition proceeds regularly. The best plan is to provide each boiler with a thermo-manometer, in addition to the air-pipe, and to inject air whenever the temperature of the water rises 5° or 6° above the temperature corresponding with the pressure registered by the manometer. This latter plan is the only one that can be adopted on board ship. C. H. B.

Explosive and Dangerous Dusts. By T. W. Tobin (*Chem. News*, **47**, 149—153).—Amongst many observations and experiments, the author points out that mill fires or explosions generally take their rise in the dust-shaft or its vicinity, which is due to the fact that, month after month streams of dry air are urged through them bearing along with it the dry flour-dust; at last a spark comes, ignites it, and sets fire to the mill.

He shows by an experiment, in which he allows flour to fall down a hollow shaft 7 feet high, perforated so as to admit plenty of air, and with a Bunsen burner alight at the bottom, that, as soon as the flour reaches the flame, instantaneous combustion of the contents of the shaft ensues. The microscopical appearances of several dangerous dusts, such as flour, starch, "wheat dust-room" dust, consisting of minute particles of starch, husk, fractured gluten cells, the beard, &c., lycopodium, and wood-dust from axe-handle factory are described, and experimental illustrations of their dangerous character are given. The great importance of the humidity of the atmosphere is insisted on, and, from a series of observations, he shows that whereas the atmospheres of the grinding and bolting floors are generally moister, that of the dust-shaft is always drier than the external atmosphere; the humidity of the grinding and bolting-rooms is due to the evaporation from the flour caused by the heat of the rollers; the dryness of the air of the dust-shaft is caused by the hygroscopic nature of the flour-dust. Again, the pressure of the atmosphere bears an interesting relation to the question of dangerous dust, for the higher the barometer the more dust particles will be buoyed up. Finally, he suggests that dust-rooms should be built of brick, and all communicating doors, shafts, &c., made of iron. The dry shoots, shafts, and dust-rooms should be daily, if practicable, charged with steam, and the mill should be kept free from superfluous dust and flour. The hygrometer should be used, and its readings attended to. Care should be taken not to overcharge the air with dust in dry weather when the air is dense; and naked flames should never be used in the mill.

D. A. L.

General and Physical Chemistry.

Atmospheric Absorption in the Infra-red of the Solar Spectrum. By W. W. Abney and R. Festing (*Proc. Roy. Soc.*, **35**, 80—83).—The authors allude to the importance attached to a study of atmospheric absorption in relation to its meteorological bearings. They describe observations on the absorptions in the infra-red of the solar spectrum at London and on the Riffel at an altitude of 8500 feet in relation to atmospheric moisture. On a fairly dry day the banded absorptions occur principally between λ 9420 and λ 9800, with a fainter absorption between λ 8330 and λ 9420, only on a cold day with a N.E. wind these absorptions nearly disappear. When the air is almost saturated with water, no ray beyond λ 8330 can be photographed; with a difference of 3° between the wet and dry bulb thermometers, the spectrum extends to λ 9420. Precisely similar absorptions may be produced by interposing between a source of light giving a continuous spectrum and the slit of the spectroscope, layers of water 1 foot and 3 inches thick respectively. From a comparison of the spectra it is quite easy to deduce the moisture present at a given temperature.

According to the accepted view, the presence of vapours of certain thicknesses give rise to linear absorptions, which increase in intensity and number until there is finally produced a total absorption. But in the case of absorption in the solar spectrum a different condition obtains; the linear absorptions are not thus increased in number and intensity, except so far that the blackness of the lines is increased by the blackness of the banded absorptions. Further, the Fraunhofer lines from λ 9420 to λ 9800 are so irregularly distributed that it is impossible to conceive that they are all caused by water-vapour, yet they are equally darkened by the absorption-band of water-vapour. However this may be, the authors' experiments show that the absorptions seem to result from a water-stuff existing in some form in the atmosphere. V. H. V.

Note on the Absorption of Ultra-violet Rays by Various Substances. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **35**, 71—74).—The authors have made a series of observations, in addition to those recorded by Hartley, Soret, and Chardonnet, on the absorption of the ultra-violet rays. The source of light was the spark of an induction coil between iron electrodes, as offering an almost continuous spectrum in the ultra-violet region, with a sufficient number of breaks and conspicuous lines to serve as points of reference. The spectra were all photographed.

Chlorine in small quantity shows a single absorption-band from N (λ 3580) to T (λ 3020), in larger quantities bands from H (λ3968) to λ 2755, from λ 4415 to λ 2665, and from λ 4650 to λ 2630. Bromine-vapour in small quantity absorbs light up to L (λ 3820), with large quantities the absorption increases to P (λ 3360); liquid bromine in a very thin film is transparent for a band between λ 3650 and λ 3400. Iodine-vapour tolerably dense absorbs all below λ 4300, the absorption gradually diminishing to λ 4080; iodine dissolved in carbon disulphide transmits light between G and H. Sulphurous anhydride produces an absorption-band between R (λ 3179) and λ 2630, and a greater absorption extending on the less refrangible side to O. Hydrogen sulphide produces complete absorption above λ 2580; carbon bisulphide vapour an absorption-band between P and T, shading away at each end; liquid carbon tetrachloride an absorption-band with a maximum about R, extending from Q (λ 3285) to S (λ 3045). Chlorine peroxide gives a succession of nine shaded bands at equal intervals between M and S. A plate of mica shows absorption from S (λ 3100), increasing above U (λ 2947), and reaching a maximum at λ 2840. A thin film of silver transmits a band of light between λ 3380 and λ 3070; a thin film of gold produces a slight absorption throughout the whole spectrum.

The authors endeavoured to apply the photometric method by means of polarised light to the comparison of intensities of ultraviolet rays. On taking photographs of the spectrum of the iron spark through a pair of Foucault's prisms at various inclinations between the planes of polarisation of the two prisms, it was found that for the whole range between the position of parallelism and an inclination of 80° there was no sensible difference of effect on the photographic plate; but for inclinations between 80—90° there is an increasing diminution, as the planes of the polariser and analyser were more nearly at right angles. V. H. V.

Reversal of Hydrogen Lines. By G. D. Liveing and J. Dewar (*Proc. Roy. Soc.*, **35**, 74—76).—From the concentration of the radiation of hydrogen into a few lines, it is *à priori* to be expected that the absorption of light of the same refrangibility would be correspondingly strong, and therefore that the lines would be easily reversed; but owing to the small mass of hydrogen which can be raised to incandescence at any time, the reversal of the lines has not hitherto been noticed.

If a short induction spark be taken in hydrogen between aluminium or magnesium points, no reversal is noticeable, but on increasing the pressure by half an atmosphere the lines expand, and a dark line is seen in the middle of F; at two atmospheres the reversal is most marked. With a dispersion of more than one prism the reversal of C may also be noticed. The authors have before observed that the C and F lines are visible in the arc of a De Meritens machine taken in hydrogen, but in the arc of the Siemens machine only the former can be detected. If, instead of taking the arc in hydrogen, drops of water are allowed to fall into the arc taken in air in a lime crucible, each drop produces an explosive outburst of the hydrogen lines, usually much expanded, but without reversal. The effect produced resembles that of an outburst of hydrogen in the solar atmosphere.

V. H. V.

Order of Reversibility of Lithium Lines. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*, **35**, 76).—From former observations the authors have concluded that of the lithium lines the blue is more easily reversed than the orange. In the present note it is pointed out that such is not really the case, for when a considerable quantity of lithium is introduced into the arc, a second blue line is developed near to, but more refrangible than the well-known blue line, so as to produce the appearance of a reversal of the latter. Of these lines, the ordinary line λ 4604 is the more readily and persistently reversed. Hence the order of reversibility is as follows:—red, orange, blue, green, violet. V. H. V.

Chemistry of Storage Batteries. By E. FRANKLAND (*Proc. Roy. Soc.*, **35**, 67—70).—The author at first alludes to the variety of opinion as regards the chemical changes occurring during the charging and discharging of storage batteries, some authorities maintaining that the effects are dependent on the occlusion of oxygen and hydrogen gas on the plates, whilst others consider that lead sulphate plays an important part. To test the former opinion, the author twisted two plates of lead into a corkscrew form, filling the gutter of the screw with red lead; the plates were introduced into dilute sulphuric acid, and charged in the usual way. On heating these plates, and collecting the gas evolved, it was found that mere traces of gases were expelled, thus showing that the occluded gases are not the important agent of the cell. It was observed, as regards the function of the lead sulphate, that, in charging a storage cell, a considerable amount of sulphuric acid disappears, which is accompanied by a deposit of lead sulphate. The deposit formed is not however sufficient to account for the total acid which has disappeared.

As the charging proceeds the strength of the acid ceases to diminish, and afterwards increases, this change continuing until the maximum charge has been reached, and oxygen and hydrogen gases are evolved from the positive and negative plates respectively, derived from the electrolysis of hexbasic sulphuric acid according to Bourgoin's equation—

$$H_6SO_6 = \underbrace{SO_3 + 3O}_{\text{On + plate.}} + \underbrace{3H_2}_{\text{On − plate.}}$$

On discharging the cell the phenomena are reversed, the sp. gr. of the acid decreasing to the point from which it began to increase on the charging of the cell. From these observations the author concludes that in charging the battery the following changes occur:—(1.) The electrolysis of hexbasic sulphuric acid. (2.) The reconversion of the evolved sulphuric anhydride into the corresponding acid. (3.) The chemical action on the coating of the positive plate, $PbSO_4 + O + 3H_2O = PbO_2 + H_6SO_6$. (4.) The action on the negative plate, $PbSO_4 + H_2 + 2H_2O = Pb + H_6SO_6$. In the discharge of the storage battery the two former changes of the charging are repeated, while upon the coating of the positive, formerly the negative electrode, the chemical change is as follows:—$PbO_2 + H_2 = PbO + H_2O$, while upon the other, formerly the positive electrode, the change occurring is $Pb + O + H_6SO_6 = PbSO_4 + 3H_2O$. According to the author's conception, the real formation of the cell consists in the more or less thorough decomposition of those portions of the lead sulphate comparatively removed from the conducting metallic nucleus of the lead. Lead sulphate has a low specific conductive power, while the far better conductors, lead peroxide and spongy lead, seem to bring the outlying portions of the coating under its influence.

The above experiments indicate a means of ascertaining the amount of stored energy without discharging the cell; for if the sp. gr., and therefore the strength of the acid be known in its uncharged and charged conditions, it is merely necessary to take the sp. gr. at any time to ascertain the proportion of the charge. Preliminary experiments showed that each increase of 0·005 in the sp. gr. corresponded with a storage of 20 ampères per hour obtainable at discharging.

V. H. V.

Scrivanow's Chloride of Silver Element. (*Dingl. polyt. J.*, **248**, 128.)—This element, although of great power, is too expensive for practical purposes, as, owing to its rapid exhaustion, it requires frequent treatment. It consists of a prism made of gas coal, which is covered with pure argentous chloride over its entire surface. This prism is contained in a solution of potassium or sodium hydroxide (1·30° to 1·45° B.), *i.e.*, dissolved in 30 to 40 per cent. of water. As active electrode, a zinc cylinder or plate is used, which is placed within a suitable distance from the carbon electrode. All loss of silver is prevented by enclosing the carbon in asbestos paper or fibre. When the element has been used up, *i.e.*, when all argentous chloride has been reduced, it suffices to immerse the carbon in a bath consisting of 100 parts by weight of nitric acid, 5 to 6 hydrochloric acid, and about 30 water. Potassium chlorochromate and nitric or sulphuric acid also forms a suitable mixture for a bath. This cell is distinguished from other chloride of silver cells by the use of an alkaline solution.

D. B.

Effects of Temperature on the Electromotive Force and Resistance of Batteries. By W. H. PREECE (*Proc. Roy. Soc.*, **35**, 48—62).—The author gives a brief summary of the experiments during the last forty years on the influence of temperature on galvanic cells, and of the various views held as to the causes producing the variations. Some experimenters, as Faraday, attributed the increase of intensity to improved conductivity of the liquids in the cell, while others, as De la Rive and Daniell, maintained that the effect was due to an increase of chemical energy. But in all the various researches the influence of temperature upon the E.M.F. has not been quantitatively separated from its influence on the internal resistance; but both factors must be taken into account, for the variation in intensity may arise either from a variation of E.M.F. or internal resistance, or from a mixed variation of both together. The cells experimented with were the Daniell, two fluid and one fluid "bichromate" and the Leclanché, being the forms generally used for telegraph; these cells were introduced into a larger vessel containing water, which could be warmed to the temperature required. A Daniell's cell at 14° C. was taken as the standard. The following methods were adopted to measure the E.M.F. and resistance; the charge or discharge of a small condenser ($C = 3$ microfarad) through a galvanometer of low resistance is an accurate measure of the E.M.F., and therefore $e = E\frac{d}{D}$ in which E and e are the E.M.F.'s of the standard and the examined cell, D and d the charge deflections. To measure the resistance the charge deflection d is first noted, and then the cell is shunted through a coil of resistance, and thus reducing the E.M.F. affecting the condenser, and a discharge d' is noted; then if b is the resistance of the cell, $b = r\frac{d'}{d-d'}$.

Variation of E.M.F.—Experiments proved that when a Daniell's cell is heated to a gradually increasing temperature up to 100°, the E.M.F. decreases at first rather abruptly, but then more gradually until a point was reached about 64°, when it begins to increase. The E.M.F., however, remains unaltered on cooling the cell from 100° to ordinary temperatures. These results are probably due to a thermoelectric action set up within the battery from the difference of temperature of the inner and the outer cell.

In the "bichromate" cell the E.M.F. decreases gradually with rise of temperature, and conversely increases with its fall. The E.M.F. of the Leclanché is practically unaltered by change of temperature.

Variation of Internal Resistance.—The results of the experiments observed that (i) on heating a Daniell's cell from 0—100° the resistance decreases at first abruptly, then more gradually until it becomes rather less than one-third of its original value; (ii) on cooling the cell the resistance increases, but at a greater rate than it decreases while being heated; (iii) if the cooled down cell be left undisturbed, the resistance of the cell gradually diminishes until it arrives at the same value which it had before being heated up; (iv) at any temperature the resistance is less the more concentrated the copper sulphate solution. In the case of the "bichromate" and Leclanché cell, the resistance diminishes with the rise and increases with the fall of temperature.

From these results it follows that changes of temperature do not practically affect the E.M.F., but only the internal resistance of the batteries. The results obtained with the Daniell's cell explain the discrepancies of measurements obtained with it, and the uncertainty of its intensity when placed in exposed positions. V. H. V.

Electric Resistance of Carbon Contacts. By S. Bidwell (*Proc. Roy. Soc.*, **35**, 1—18).—The phenomenon of diminution of resistance of carbon contacts with increase of pressure has long been known; in the present communication it is systematically investigated.

The author arrives at the following results with carbon contacts :—Changes of pressure produce proportionately greater changes of resistance with small than with great initial pressure, and with weak than with strong currents. Changes of current produce proportionately greater changes of resistance with weak than with strong currents, and with light pressures than with heavy pressures. The resistance of carbon contact, reduced by an increase of pressure, returns to its former value on removal of the pressure. The passage of a current, whose intensity does not exceed a certain limit, causes a permanent diminution of resistance, which is greater the stronger the current; but if that limit is exceeded, the resistance is greatly and permanently increased.

In the case of bismuth and probably other metallic currents, with a given pressure, the weaker the current the higher will be the resistance. Increase of intensity of the current is accompanied by a fall in the resistance, and if the current be reduced to its original strength, the resultant change in the resistance will be small. Increased pressure produces a greater diminution in the resistance with small pressures than with great pressures, and with weak than with strong currents. In some cases on increasing the pressure, the metallic contacts fused together.

The above observations throw light on the superiority of carbon over metals in the microphone; the metallic contacts, unlike those of carbon, do not recover their original resistance, and the initial effect of pressure upon resistance is more marked with carbons than with metals.

A metal microphone might be used, but the fundamental tone produced would be marked by the superimposed vibrations of its particles. V. H. V.

Thermometric Measurements. By J. M. CRAFTS (*Bull. Soc. Chim.* [2], **39**, 196—205, and 277—289).—The author remarks at the outset that the progress made in the purification and preparation of chemical substances has not been accompanied by any appreciable improvement in thermometric measurements. In these communications the author gives an account of a series of experiments on the commonly employed methods of fusion and ebullition, with a view of facilitating the construction of thermometers, of examining their behaviour, and of rendering the method of observation precise.

In the thermometers from the best sources the author observed residual errors of 0·015°—0·04° degree. When the scale is divided into tenths of a degree, in ordinary thermometers differences of length of 0·1°—0·5° degree in contiguous sections of 25 degrees. As these variations rarely compensate one another, it is not rare to find thermometers which require corrections amounting to several fractions of a degree.

In determining the value of a degree from the points 0° and 100°, it is most important to follow an invariable order in the observation of these points. After the point 100° has been fixed, the zero point must be determined by quickly cooling and placing the thermometer in pounded ice, or preferably snow, which has remained for some time in contact with distilled water. But even after adopting all the necessary precautions, the value of a degree may vary owing to the displacement of the zero point, which causes a change in various proportions of all the constants. In the original paper examples are given to show that the elevation of zero of 1·24 to 2·6° may cause an increase in the interval 0—100° of 0·04 to 0·9 degree. On the other hand, a depression of the zero point may be effected by heating a thermometer at various temperatures for a prolonged time, and then leaving it to cool in the air, and these depressions will necessarily increase all the constants of the thermometer when referred to the zero point. After such a depression has been effected, the thermometer, slowly at ordinary temperatures, but more quickly when warmed slightly, tends to revert to its original readings.

A considerable elevation of the zero point, 10° to 26°, is produced by heating the thermometer for a week at 355°, which is caused by the expansion of the glass bulb after it has been blown out and then suddenly cooled.

The elevation of zero in a thermometer maintained at ordinary temperatures diminishes gradually and ceases to be appreciable after five or ten years. Similarly variations produced by protracted heating tend towards constant limit; thus, for example, a thermometer may be heated for several days at 300°, or for several months at 100° without causing a variation in the effect produced by heating to 355°.

From the facts detailed above, it is necessary to heat a thermometer required for ordinary experiments for a week in boiling mercury, the whole of the stem being enclosed in the vessel; after this treatment, the points 0° and 100° will have a permanent value.

The author further remarks that thermometers with a limited range, from 200° to 300° for example, cannot be graduated with the same degree of precision, for the determination of the fixed points 0 and 100 becomes impossible, owing to the falling of the mercury within the reservoir. In order to fix definite points above 100°, the author suggests the use of naphthalene and benzophenone, substances which can be obtained in a state of purity; the former boils at 218°, and the latter at 306° under normal pressure; in a table in the original memoir, the boiling points of these two substances under various pressures are given.

In a thermometer which has been thoroughly deprived of air, the phenomenon of volatilisation of mercury can be observed at 100°; the column of mercury gradually descends, and after about 15 minutes the variation is about 0·01—0·02 degree. If the zero point is redetermined after each warming, no error is caused by the descent of the mercury. In all cases the mercury with which the thermometer is filled must not only be purified but boiled for a long time to rid the instrument of bubbles of air which cling persistently to the sides of the bulb and stem.

The changes of barometric pressure may in ordinary cases be neglected, but it is necessary to take account of the differences of pressure dependent upon the horizontal or vertical position of the column of mercury in the stem of a long thermometer. But this factor cannot safely be neglected for second determination under reduced pressures, when the thermometer is immersed in the vapour; in these cases it is preferable to introduce a thermometer in a tube sealed at its lower extremity, and communicating directly with the atmosphere.

In conclusion, the author points out the errors in determination of boiling and melting points. In the former, errors frequently arise from a too hasty observation; to ensure accuracy the whole stem must be immersed in the vapour, and distillation must be carried on for at least ten minutes before the whole of the stem acquires the temperature of its environment.

To determine fusing points it is preferable to plunge the thermometer into the melting substances and to observe the changes of temperature during complete solidification: when the quantity of substance does not admit of this method of procedure, the usual process must be adopted.

In the memoirs, tables of corrections are given for converting readings of ordinary thermometers and those with limited scale, into readings of the hydrogen thermometer. V. H. V.

Combustion of Gaseous Mixtures. By MALLARD and LE CHATELIER (*Bull. Soc. Chim.* [2], **39**, 268, 269—277, and 369—377).—A continuation of the authors' investigations, *vide* p. 542.

The authors' remark that the curves of their registering manometers do not give, owing to loss of heat, exactly the curves of pressure produced by the combustion. For the maximum pressure recorded by the curve is affected by the cooling in the interval of time during which the combustion is propagated through the cylinder, and while the manometer arrives at equilibrium. If the combustion be instantaneous, this latter factor could be neglected, but as the propagation of the combustion lasts about $\frac{1}{10}$ second, there is a certain and unknown loss. As a correction for this loss, deduced from the loss of pressures observed during cooling after the combustion, gives too high a value, whilst the maximum of the curves gives too low a value, the mean of these two limits may be taken as fairly exact. If then the pressure due to combustion be known, and if it be admitted that at high temperatures the coefficient of expansion of all gases is the same, then the temperature of combustion can be calculated from the formula $\frac{T}{T^0} = \frac{\pi}{\pi^0}$, provided that no dissociation takes place.

In the original paper a table is given of the temperatures of combustion of various mixtures of carbonic oxide and oxygen with excess of nitrogen, carbonic anhydride, and steam, of hydrogen and oxygen with excess of hydrogen, oxygen, nitrogen, and steam, of hydrogen and chlorine with excess of chlorine, hydrogen and steam, and of mixtures of cyanogen and air sufficient for the burning of the carbon into carbonic oxide.

Specific Heats.—From the temperatures of combustion the mean specific heats at constant volume can be calculated according to the formula $Q = (mc + m'c' + \ldots)(\theta - \theta_1)$. It follows, as a necessary consequence of the authors' experiments, that the specific heats of the permanent gases, hydrogen, oxygen, nitrogen, and carbonic oxide, which are equal to one another at ordinary temperatures, are equal to one another at 200°, for equal volumes of carbonic oxide, nitrogen and oxygen added to an excessive mixture of carbonic oxide and oxygen, give the same temperature of combustion; the same result holds good in mixtures containing hydrogen.

From the temperature attained in the combustion of a mixture of carbonic oxide and oxygen, the specific heat of carbonic anhydride can be calculated, provided that no dissociation takes place. The authors estimate that at a temperature of 2000° about 5 per cent. of the anhydride is dissociated; if allowance is made for this, the most probable value for the mean specific heat of this gas referred to a molecular volume of 22·22 litres between 1° and 2000°, is 13·2. If the mean specific heat of carbonic anhydride be known, that of steam at the same temperature can be determined, for it is only necessary to compare the temperatures of combustion of hydrogen and carbonic oxide each mixed with such an excess of a permanent gas that the temperatures produced by the combustions is the same. Experiments give the number 12·8 as the value for the mean specific heat of the molecule of steam at 2000°. Similarly the specific heats of the permanent gases can be deduced by the same method; the authors find this value to be 7·5 at 2000°, or 50 per cent. more than the mean specific heat at 0°.

Law of Variation of Specific Heats.—The authors have endeavoured to establish a law of variations of specific heats by comparing the values found at 2000° with the values at two lower temperatures, 100° and 200° for example. The equation is of the form $C_\theta = a + b\theta + C\theta^2$, of which b and c are given by a graphical construction. For carbonic anhydride the experiments of Regnault and Niedermann give the constant a, while c is fixed by those of the authors; the law of variation of the specific molecular heat is represented by the formula $C_\theta = 6{\cdot}3 + 0{\cdot}0056 + 0{\cdot}0000011\theta^2$. Similarly, the law of variation of the specific heat of steam is expressed by the formula $C_\theta = 5{\cdot}9 + 0{\cdot}0037\theta + 0{\cdot}00000015\theta^2$, and those of the permanent gases by the formula $C_\theta = 5 + 0{\cdot}00062\theta^2$.

If the law of variation of specific heat were known for any temperature, the degree of dissociation of a gaseous compound could be deduced from these data; the authors calculate by prolonging the curve of variation to 8000°, that 40 per cent. of carbonic anhydride and 10 per cent. of steam is dissociated at that temperature. Their calculation is in direct accordance with the experiments of Crafts on carbonic anhydride.

The velocity of propagation of flame varies according to the nature and proportion of the mixed gases, their temperature, and their internal agitation. The authors have examined the phenomenon by three different methods: firstly, by causing the gas to flow through a minute orifice, igniting the jet of gas, and diminishing the velocity gradually until the flame passes through the orifice: this method, provided that the experiments are made under strictly comparable conditions, gives accurate results. The second method consists in passing the gas into a tube closed at one end and open at the other, where it is ignited; the time required for the passage of the gas through the length is measured. In the third method the velocity is measured by an arrangement by which the passage of the flame causes an electric current to attract an electromagnet, and thus cause a registration to be made on a smoked cylinder. But as this method only records intervals greater than one-hundredths of a second, a pneumatic arrangement was substituted whereby the pressures produced set in motion a Marey's registering drum.

The walls of the tubes and orifices exert a cooling action on the flame, which diminish its velocity of propagation; this effect is the more marked the narrower the tubes, but is independent of the material of the tube. Vibratory movements produced by the propagation of the combustion always produce a considerable but irregular acceleration of the combustion. To eliminate as far as possible this source of error, measurements of the velocity of transmission should be made at the anterior portion of the tube. The authors have made a series of experiments of the velocity of combustion of various mixtures of methane with air with or without addition of nitrogen or carbonic anhydride, of hydrogen and coal-gas with air, of carbonic oxide with oxygen, of hydrogen with oxygen and chlorine.

An increase of temperature increases the velocity; thus a detonating mixture of hydrogen and air having at 20° a velocity of propagation of 3·50 m., at 100° C. has a velocity of 4·30 m. The authors have confirmed Schloesing and Montdésir's observations on the enormous velocity of the combustion when the detonating mixture is ignited at the closed and not at the open end of the tube; a velocity of 300 m. per second was obtained by a detonating mixture of hydrogen and air. As the method of ignition affects the agitation of the gas, and, consequently, the velocity of the propagation of the flame, an explanation is offered of different phenomena presented by explosions in coal mines. For some time the flame travels slowly with no noise or mechanical effect, while at other times a violent detonation is produced accompanied by a wreck of every obstacle in the passage of the flame. The first of these phenomena would be caused by the ignition of the fire-damp at the open end of the gallery, while the latter to its ignition at the bottom or closed end of the gallery.

The authors' experiments give further support to the evidence brought out in inquiries into accidents in coal mines, that the wire gauze of the Davy lamp is insufficient to prevent an explosion if the lamp is placed in a current of air sufficiently strong to blow the detonating mixture through the gauze.

In certain experiments the authors noticed that the flame of a detonating mixture which had been lighted at the end of the tube was sometimes spontaneously extinguished, owing doubtless to a very violent agitation of the gas within the tube and the admixture of a sufficient quantity of cold gas to prevent the production of the chemical change. Probably a similar explanation holds good as regards the experiment of Schützenberger on the combustion in endiometers of gases containing a small proportion of hydrogen. V. H. V.

Notice on the Atomic Weights. By A. Butlerow (*Bull. Soc. Chim.* [2], **39**, 263—268).—A short time ago Schützenberger announced that in the analysis of certain hydrocarbons he obtained numbers which on calculation led to a sum of hydrogen and carbon greater than the weight of the original substance. In the present notice the author proposes to offer some explanation of the abnormal result. Rejecting the hypotheses (1) that the absolute mass of the substance is increased by the transformation of some form of energy into matter; (2) that the absolute mass remaining the same, its weight has been increased by an increase of intensity of gravity, there is then left the conjecture that the absolute value assigned to the atom varies within certain and probably narrow limits. If it be admitted, for example, that the value of the atom of carbon descends temporarily to 11·8, then the molecular weight of carbonic anhydride will become 43·8, instead of 44. Then there will be about one-hundredth of carbon in excess, if, starting from a carbonic anhydride of the former molecular weight, the weight of the carbon be calculated from the latter molecular weight. The author has undertaken experiments with a view of determining how far the atomic weight may vary under different conditions; the examples selected are white and red phosphorus, and the formation of mercuric chloride from the combination of the two elements with or without exposure to light. Though the investigations of Stas have established that atomic weights are not expressed by whole numbers, yet as the deviations are so small it is impossible to consider them accidental, and thus to regard Prout's hypothesis as devoid of any value. In other cases, as for example the laws of Boyle and Mariotte, the numbers furnished by experiment, from which the law has been deduced and expressed in a simple form, are approximately equal to, but not identical with the numbers required by the law. The atomic weight of an element is the representation of a certain ponderable quantity of matter, the bearer of a determinate quantity of chemical energy: as in other forms of energy its quantity is far from being determined exclusively by the mass of matter, it is at least possible that the same principle may hold good for chemical energy, although within certain narrow limits. Carbonic anhydride would not be a compound containing absolutely carbon and oxygen in the proportion of 31·92 [32] of the latter to 11·97 [12] of the former, but may contain a relative proportion of carbon varying from 11·8 to 12. These varieties of carbonic anhydride would up to a certain point still constitute the same chemical compound; its general properties, and especially its chemical functions, would remain the same.

In conclusion the author asks whether such a supposition, although bold, is entirely devoid of probability. V. H. V.

Special Form of Gasometer. By L. G. de Saint Martin (*Bull. Soc. Chim.* [2], **39**, 377—384).—The author has devised a gasometer differing from the usual form by a special arrangement of the water reservoir, which, instead of consisting of a simple cylinder, is formed of two concentric cylinders of nearly the same diameter. The smaller or interior, closed at the top, fills the cavity of the exterior nearly completely, so that between the two there is a small annular space filled with water or some other isolating liquid.

By this arrangement only a small quantity of water is required, so that secondary chemical reaction or solution becomes practically impossible. The author also describes an arrangement of the gasometers whereby gas from the one can be made to bubble through a purifying apparatus, and then to pass into the other. Thus to obtain pure nitrogen air from one gasometer is deprived of its oxygen by passing through sodium hyposulphite, and the gas nitrogen enters the second gasometer. By a similar method carbonic oxide can be purified from carbonic anhydride. The arrangement can also be used for a study of the chemical changes during respiration, air being supplied to the patient for inspiration from the one, while the expired gases pass into the other gasometer. V. H. V.

Inorganic Chemistry.

Activity of Oxygen in Presence of Nascent Hydrogen. By F. Hoppe-Seyler (*Ber.*, **16**, 117—123).—The author refers to previous experiments on this subject (this Journal, Abstr., 1880, 3), whereby he has shown the energy of oxidation in presence of nascent hydrogen. His experiments were then made with the alloy of palladium and hydrogen, and also with metallic sodium, and the conclusions arrived at were, that hydrogen in that state when brought into contact with the indifferent oxygen of the atmosphere, causes oxidation of the most active character, accompanied by the production of water. This fact is of the greatest importance in physiological researches, accounting for many processes in the animal economy. Circumstances prevented continued experiments, but they have lately been resumed. In the meanwhile Traube has published papers in opposition to the author's views (this Journal, Abstr., 1882, 795), casting doubts on the accuracy of his deductions.

Traube brings forward the production of hydrogen peroxide by the action of palladium-hydrogen alloy on oxygen, and seeks to explain the blue coloration of potassium iodide and starch solution by some unknown reaction of the palladium on the hydrogen peroxide. The author does not lay great weight on the objection, as he simply mentioned the hydrogen peroxide in passing, and its presence is unnecessary to the reaction. He criticises the failure of Traube to reproduce his experiments, and repeats that he founds his conclusions respecting the activity of oxygen (1) on the production of a blue colour by the palladium-hydrogen compound when in contact with oxygen and potassium iodide starch solution; (2.) The power of those substances to oxidise indigo-carmine solution to yellow. (3.) The oxidation of oxyhæmoglobin to metahæmoglobin. (4.) Oxidation of ammonia to nitrous acid. These reactions occur regularly except when ignited palladium is substituted for the hydrogen alloy of the metal; neither are they produced with dilute pure and neutral solutions of hydrogen peroxide, whether palladium is present or not. St. Claire-Deville and Debray have already briefly described a decomposition of formic acid by means of rhodium and iridium black, which offers an interesting parallel to the decomposition of that acid by the mud of cesspools, a little of which, when air is excluded, is capable of breaking up almost unlimited quantities of calcium formate into calcium carbonate, carbonic acid and hydrogen; the same reaction takes place with rhodium black; its behaviour resembles that of a ferment, as it comes out of the reaction unaltered. The author has convinced himself that in presence of oxygen the hydrogen from the formic acid gives rise to increased activity in the oxygen, turning the iodide of potassium and starch-solution blue, and oxidising the indigo solution; the presence of free ammonia or its carbonate completely prevents the reaction.

Rhodium black, obtained by the action of formic acid on rhodium hexchloride and sodium chloride evidently contains hydrogen, and resembles the palladium alloy.

Rhodium black decomposes hydrogen peroxide with violence into water and indifferent oxygen, whether hydrogen is present in the rhodium or not.

The action of rhodium black as a ferment is the more interesting because it is an absolutely insoluble substance, and it suggests that there may exist other insoluble ferments. This is the author's conviction, and he thinks that he will soon be in a position to show that they play a very important part in the living body. J. F.

Specific Gravities of Solutions of Ammonia and Ammonium Carbonate. (*Dingl. polyt. J.*, **247**, 504.)—From a suggestion by Lunge, J. H. Smith was led to determine the sp. gr. of pure ammonia solutions (standardised with normal hydrochloric acid and methyl orange) at 14° by means of a pycnometer; the results are compared with water and reduced to a vacuum:—

Sp. gr. at 14°.	Percentage of ammonia (NH_3), according to						
	Smith.	Carius.	Wachsmuth.	Otto.	Ure.	Dalton.	Davy.
0·8933	31·0	31·8	29·9	—	27·8	24·0	27·6
0·9116	23·8	24·6	23·8	—	23·1	19·5	23·6
0·9246	20·8	20·2	19·7	—	19·4	16·4	19·8
0·9400	15·1	15·4	15·0	—	14·7	12·9	15·5
0·9536	11·7	11·7	11·3	11·5	11·3	10·2	11·8
0·9780	5·1	5·2	4·9	5·2	5·0	4·5	—

Solutions of commercial ammonium carbonate, which contained 31·3 per cent. NH_3, 56·6 per cent. CO_2, and 12·1 per cent. H_2O, corresponding approximately with the formula

$$H.NH_4.CO_3 + NH_4.CO_2.NH_2$$

gave—

Degrees. Tw.	Sp. gr. at 15°.	Per cent. ammonia carbonate.	Change of the sp. grs. for + 1°.	Degrees. Tw.	Sp. gr. at 15°.	Per cent. ammonia carbonate.	Change of the sp. grs. for + 1°.
1	1·005	1·66	0·0002	15	1·075	22·25	0·0006
2	1·010	3·18	0·0002	16	1·080	23·78	0·0006
3	1·015	4·60	0·0003	17	1·085	25·31	0·0006
4	1·020	6·04	0·0003	18	1·090	26·82	0·0007
5	1·025	7·49	0·0003	18	1·095	28·33	0·0007
6	1·030	8·93	0·0004	20	1·100	29·93	0·0007
7	1·035	10·35	0·0004	21	1·105	31·77	0·0007
8	1·040	11·86	0·0004	22	1·110	33·45	0·0007
9	1·045	13·36	0·0005	23	1·115	35·08	0·0007
10	1·050	14·38	0·0005	24	1·120	36·88	0·0007
11	1·055	16·16	0·0005	25	1·125	38·71	0·0007
12	1·060	17·70	0·0005	26	1·130	40·34	0·0007
13	1·065	19·18	0·0005	27	1·135	42·20	0·0007
14	1·070	20·70	0·0005	28	1·140	44·29	0·0007

D. B.

Formation of Nitrous Acid in the Evaporation of Water. By A. SCHEURER-KESTNER (*Bull. Soc. Chim.* [2], **39**, 289).—The author observes that the formation of nitrous acid in the evaporation of water, to which attention has recently been called by Warington (this Journal, Trans., 1882, 351), was noticed many years ago by Schoenbein. The following characteristic experiment made by Schoenbein is quoted; a piece of filter-paper is cut into two parts, of which one is moistened with water free from nitrous acid, and allowed to dry. Then this part will give the reactions for nitrous compounds, whilst the other half will give no reaction.

V. H. V.

Action of Microcosmic Salt on Various Oxides. By K. A. WALLROTH (*Bull. Soc. Chim.* [2], **39**, 316—322).—Berzelius and others have remarked that beads of microcosmic salt, when saturated with various metallic salts, become opaque on cooling, from separation of minute crystals of phosphate of sodium and the introduced metal. The author has isolated these salts by dissolving the metallic oxides in microcosmic salt heated to a bright red heat; the glass so formed is maintained in a state of fusion until the crystals have separated out. On cooling, the mass is digested with water, and then with dilute hydrochloric acid.

Phosphates of Dyad Metals.—*Cadmium sodium phosphate*, $CdNa_2P_2O_7$, is a white crystalline salt, soluble in dilute acids, melting into a transparent glass. The manganese salt, $MnNa_2P_2O_7$, forms prismatic crystals, soluble in acids, melting into an amethyst glass; the *zinc* salt, $ZnNa_2P_2O_7$, crystallises in tables, soluble in acids; the *calcium* salt, $Ca_{10}Na_{16}(P_2O_7)_9$, is a crystalline powder, melting into a white enamel; the *magnesium* salt, $Mg_{10}Na_{16}(P_2O_7)_9$, forms transparent prisms, melting into a transparent glass; the *cobalt* salt, $Co_{10}Na_{16}(P_2O_7)_9$, crystallises in cherry-red prisms, and melts into a transparent blue glass; the *nickel* salt, $Ni_{10}Na_{16}(P_2O_7)_9$, forms yellow prisms, melting into a brown clear glass; the *beryllium* salt, $BeNaPO_4$, forms hexagonal tables, sparingly soluble in cold acids, and infusible; the *copper* salt, $Cu_3Na_6(PO_4)_4$, is a bluish crystalline powder which melts into a green transparent glass.

Phosphates of Triad Metals.—The *bismuth* salt, $Bi_4(P_2O_7)_3$, forms hexagonal tables, decomposed by water; it melts into a white enamel; the *chromium* salt, $Cr_2Na_2(P_2O_7)_2$, is a brilliant green powder, infusible and insoluble in acids; the *aluminium* salt, $Al_2Na_2(P_2O_7)_2$, crystallises in prisms, insoluble in acids, fusible into a clear glass; the *cerium*, *lanthanum*, and *yttrium* salts, of formula $M_2Na_2(P_2O_7)_2$, crystallise in infusible microscopic prisms, insoluble in cold, readily soluble in warm acids; the *erbium* salt, $Er_2Na_2(P_2O_7)_2$, forms rhombic infusible prisms of a rose colour, sparingly soluble in dilute acids; the *ytterbium* salt, $Yb_2Na_2(P_2O_7)_2$, is a white powder resembling the erbium salt; the *didymium* salt forms minute crystals, infusible and insoluble in acids.

Phosphates of Tetrad Metals.—The *thorium* salt, $Th_2Na(PO_4)_3$, forms clinorhombic prisms, infusible and insloube in acids; the tin and titanium salts have a composition similar to that of the thorium salt.

It will be seen from the above that the dyad metals with the exception of copper and beryllium, and triad metals with the exception of didymium, form pyrophosphates, while the tetrad metals form orthophosphates.
V. H. V.

Specific Gravity of Sulphuric Acid. (*Dingl. polyt. J.*, **248**, 91).—Lunge and Naef (*Chem. Ind.*, 1883, 37) give the following table of the specific gravities of very concentrated sulphuric acids at 15°, the numbers having been reduced to a vacuum and compared with water at 40°. The numbers marked† have been directly observed; the remainder were determined by interpolation:—

Percentage of H_2SO_4.	Pure acid. Sp. gr.	Commercial acid from Uetikon.	
		Sp. gr.	Baumé.
90·00	1·8185	1·8202	65·1°
†90·20	1·8195	—	—
†90·29	—	1·8219	—
91·00	1·8241	1·8254	65·4
†91·48	1·8271	—	—
92·00	1·8294	1·8306	65·6
†92·83	1·8334	—	—
93·00	1·8339	1·8346	65·8
94·00	1·8372	1·8374	65·9
†94·09	—	1·8375	—
†94·84	1·8387	—	—
95·00	1·8390	1·8397	66·0
†95·26	—	1·8404	66·0
†95·97	1·8406	—	—
96·00	1·8406	—	—
97·00	1·8410	—	—
97·70	1·8413	—	—
97·75	—	1·8468(1)	66·2

Percentage of H_2SO_4.	Pure acid. Sp. gr.	Commercial acid from Uetikon.	
		Sp. gr.	Baumé.
98·00	1·8412	—	—
†98·39	1·8406(2)	—	—
†98·66	1·8409(3)	—	—
99·00	1·8403	—	—
†99·47	1·8395	—	—
†100·00	1·8384	—	—

(1.) Acid from Griesheim, prepared by direct evaporation on a large scale.

(2.) Prepared by mixing acid of ordinary strength with acid containing anhydride.

(3.) Prepared by direct evaporation. D. B.

Preparation of Selenium on a Large Scale. By H. BORNTRÄGER (*Dingl. polyt. J.*, **247**, 505).—It is known that when seleniferous pyrites is used for the manufacture of sulphuric acid, selenium is found in the various stages of the process. For the recovery of selenium, the following method is recommended: A set of chambers is connected with a Glover tower, besides having the nitric acid cascades. Chamber acid alone runs over the tower, the nitric acid being introduced by means of the cascades. Thus, a turbid Glover acid is obtained which has a deep red colour, owing to the presence of selenium. It is clarified in leaden tanks, and after decantation the red deposit is washed with hot water and dried at 100°. The following is an analysis of this deposit (from Spanish pyrites of Rio Tinto):—

Fe_2O_3 and SiO_2.	Se.	As_2O_3.	$PbSO_4$.
8·20	12·60	0·13	76·30

The dried deposit is heated to redness in closed clay retorts provided with receivers, when a black metallic sublimate of selenium is obtained, which is washed with concentrated soda-ley to remove arsenious and selenious acids, and finally with water. Pure selenium dissolving completely in sulphuric acid is obtained. D. B.

Atomic Weight of Didymium. By P. T. CLEVE (*Bull. Soc. Chim.* [2], **39**, 289—330).—The author has determined the atomic weight of didymium in samples of the oxide separated by fractional precipitation from lanthanum oxides (cf. p. 553). The pure oxide thus obtained was converted into the sulphate, and the proportion of the oxide in the salt was determined. A series of ten estimations gave 58·0905 per cent. of Di_2O_3. Another series of seven gave 58·0895 per cent.; the former value the author considers the more exact. Adopting for oxygen the atomic weight $15·9633 \pm 0·0035$, and for sulphur the number $31·984 \pm 0·012$, the atomic weight of didymium is $Di = 142·124 \pm 0·0326$, a number which may practically be taken as 142.

The author notes that this value differs from those obtained by other chemists, and from the number 147, which he himself obtained in 1874. This discrepancy he attributes to the presence in former samples of didymium oxide of samarium, the existence of which has to the present time been unknown. V. H. V.

Basic Sulphates of Copper. By S. U. Pickering (*Chem. News*, **47**, 181—184).—In previous communications the author has shown that the metals, iron and aluminium, do not form as many basic sulphates as they were supposed to do. He has now examined the basic sulphates of a metal belonging to a different class, viz., copper, and has found not six but only two basic sulphates of this metal. The one, $6CuO,2SO_3 + 5H_2O$, is precipitated in small quantity when a neutral solution of copper sulphate is boiled, the precipitation being complete in 10 minutes. In this manner from 0·37 to 2·5 per cent. of the copper present can be precipitated, the quantity increasing with the dilution of the solution. The second basic sulphate, $4CuO,SO_3$, is formed when a solution of copper sulphate is precipitated with less than 1·5 mol. of potassium hydroxide to 1 mol. of copper sulphate, or with sodium acetate, or when copper hydrate (dried at 100° C.) or the precipitate obtained by adding excess of potash to copper sulphate is digested with a 10 per cent. solution of copper sulphate. This basic sulphate is very sparingly soluble in water (0·017 gram in 1000 c.c.). When, however, the solution is boiled, it becomes dark, owing to the separation of copper hydroxide. It remains unaltered when exposed to air or boiling water. This latter property serves as a test for the sulphate $4CuO,SO_3$, for those containing more CuO soon become blackened when boiled with water. No definite basic sulphate is formed either by heating normal copper sulphate, or by diluting an ammonio-copper sulphate solution. D. A. L.

Rehydration of Ferric Oxide. By C. F. Cross (*Chem. News*, **47**, 239).—The method of experimenting was the same as described (*ibid.*, **44**, 101). From the experimental observation the author shows that the ferric oxide obtained by drying the ordinary precipitated hydrate at 100°, when exposed to a saturated atmosphere and a somewhat regular temperature, gradually becomes rehydrated. The observations extended over 192 days, the temperature varying from 15° to 22°. The rehydration does not take place so readily when the temperature fluctuates, so as to cause evaporation and condensation from or upon the portion enclosed in the saturated atmosphere.

D. A. L.

Gold Compounds. By P. Schottländer (*Annalen*, **217**, 312—380).—According to Weber, *hydrogen gold chloride*, $AuHCl_4$, crystallises with 3 mols. H_2O, and according to Thomsen (*Ber.*, **10**, 1633), with $4H_2O$. The author who evaporates the aqueous solution containing some free hydrochloric acid over lime and sulphuric acid, obtains crystals which, after being pulverised and exposed for months over sulphuric acid, contain $3H_2O$. On gradually adding silver carbonate suspended in water to a warm solution of hydrogen gold chloride in excess, carbonic anhydride is evolved and a brown precipitate produced. On heating the filtrate with an excess of silver carbonate at 100°, a second precipitate is obtained, from which the excess of silver carbonate can be removed by means of dilute nitric acid. Both precipitates contain gold oxide and silver chloride approximately in the proportion of 1 mol. of the former to 8 mols. of the latter, besides variable amounts of undecomposed gold chloride. To prepare *potassium gold bromide*, precipitated gold (20 parts) and a solution of potassium bromide (12·5 parts) in twenty-four times its weight of water are brought together in a capacious vessel and bromine (30 parts) added, the bottle being then well stoppered and allowed to stand in a warm place until the gold is dissolved; the solution is evaporated on a water-bath, and the product recrystallised from water. It forms monoclinic crystals, readily soluble in water, sparingly in the presence of potassium bromide. Ether decomposes it, taking up gold chloride, and leaving a residue of potassium bromide. By the action of sulphurous anhydride on an alcoholic solution of the dried salt, a gold-coloured solution is obtained, whilst potassium bromide is precipitated together with a little sulphate. When the filtrate is evaporated in a desiccator containing lime, sodium hydroxide and zinc chloride, two-thirds of the gold are precipitated, forming a lustrous layer on the glass, whilst the solution contains free hydrobromic acid, sulphuric acid, and an oily body, probably ethyl bromide. By the action of potassium carbonate on a boiling aqueous solution of potassium gold bromide, a brownish-red precipitate is obtained, which, after being washed with boiling water and dried at 100—108°, has a composition corresponding with the formula $16Au_2O_3,3K_2O,2KBr,15H_2O$. From the filtrate containing potassium bromide, an orange-yellow substance is also obtained, to which the author assigns the formula $20Au_2O_3,3\frac{1}{2}K_2O,2KBr,xH_2O$. By the action of hydrogen potassium carbonate, a bright reddish-yellow solution is obtained, the colour of which almost disappears on boiling. The solution contains potassium bromide and carbonate and a bright yellow amorphous body, which is probably a compound of gold oxide with potash. By the action of manganese acetate on gold chloride solution, a black precipitate is produced containing the whole of the gold. If atmospheric oxidation is carefully avoided during the preparation and drying of this precipitate, it can be dissolved in hydrochloric acid without evolution of chlorine. Its composition is not perfectly definite and its constitution is doubtful. The author assumes it to be a *molecular mixture* of metallic gold with manganese dioxide and monoxide, *e.g.*, $6Au + 9MnO_2,MnO,2H_2O$, the gold and manganese dioxide being in the proportion of two atoms of the former to 3 mols. of the latter; whilst if oxidation has taken place, the proportion of dioxide is greater, $6Au + 10MnO_2,H_2O$, the compound losing a molecule of water for each oxygen-atom absorbed. Gold can be extracted from this substance by shaking it with mercury; concentrated sulphuric acid does not dissolve it, whilst a mechanical mixture of gold and manganese dioxide can be dissolved in this acid; concentrated potash solution takes up nothing even on boiling; concentrated solution of potassium cyanide dissolves the whole of the gold and part of the manganese, forming potassium gold cyanide and potassium manganese cyanide, and leaving a black residue. On boiling with glycerol and concentrated soda-solution, gold separates out, whilst a violet solution is formed, from which alcohol precipitates the glycerol compound previously described by the author (*Annalen*, **155**, 230). Aqueous ammonia has no action; nitric acid (sp. gr. 1·4) dissolves part of the gold and manganese, although no oxidation takes place On digesting with a concentrated solution of sodium thiosulphate for some days at about 60°, a part of the gold dissolves, forming the double salt $Au_2S_2O_3,3(Na_2S_2O_3),4H_2O$, which is precipitated on adding alcohol. In sealed tubes at 100° only traces of this double salt are formed, the solution being found to contain manganese, sulphurous and sulphuric acids, and the residue to consist of a mixture of gold, manganese (probably as MnO), and sulphur. By the action of manganese acetate on gold chloride in presence of ammonium chloride in the cold, the gold is only partially precipitated, and on treating the precipitate with hydrochloric acid, a bright yellow crystalline body is produced, containing gold, chlorine, and the elements of ammonia; it explodes on heating, though not by concussion or friction. A hydrated oxide of gold of the formula $Au_3O_2(OH)_2$ is obtained by the decomposition of the sulphate $AuSO_4$ (see below) by water. In its properties it does not agree with the compound described by Prat (*Compt. rend.*, **70**, 840). It forms a crystalline black powder, which is not acted on by boiling potash-solution, whilst hydrochloric acid or nitric acid decomposes it into metallic gold and trioxide, the latter dissolving and forming a salt. *Hydrated gold trioxide* has been prepared by the author by different methods, but in no case has he obtained a product corresponding with the formula $Au(HO)_3$ generally given; the highest percentage of water obtained corresponds with the formula $Au_4O_3(OH)_6$, and the lowest with AuO.OH; and he thinks it probable that the latter would always be formed if the product were exposed long enough in a vacuum over sulphuric acid, or dried at a somewhat higher temperature. The compound, $HNO_3,Au(NO_3)_3,3H_2O$, is obtained by mixing gold hydroxide with nitric acid (3·6 parts) of sp. gr. 1·492 at 20°, and then heating on a water-bath until a clear yellow solution is obtained, which is separated from traces of reduced gold, and finally surrounded by a freezing mixture to promote crystallisation. It forms large gold-coloured triclinic crystals, which deliquesce in moist air. It melts at 72—73° with evolution of nitric acid, and on further heating, the normal salt $Au(NO_3)_3xH_2O$ is probably formed. At 100° it loses 50 per cent. of its weight, with formation of a basic nitrate, $Au_4O_5(NO_3)_2,2H_2O$. A third nitrate (*auryl nitrate*), $5(AuO,NO_3) + H_2O$ (?), is obtained by dissolving gold hydroxide in nitric acid of sp. gr. 1·4, filtering through asbestos, and evaporating at reduced pressure over lime and soda. When a solution of gold nitrate and potassium nitrate in nitric acid is allowed to crystallise, a double salt of the formula $HNO_3,Au(NO_3)_3,2KNO$ is obtained, crystallising in plates. A gold sulphate (*auryl sulphate*), AuO,HSO_4, is produced by heating the corresponding nitrate with concentrated sulphuric acid at about 200°, forming a yellow crystalline powder; it absorbs water from the air, with production of sulphuric acid and gold hydroxide. Potassium gold sulphate, $KAu(SO_4)_2$, is formed when hydrogen potassium sulphate is dissolved in a solution of auryl sulphate, and the liquid evaporated at 200°; it forms a bright yellow crystalline salt which is somewhat more stable than auryl sulphate. A silver gold sulphate can be obtained in the same way. A gold sulphate of the formula $AuSO_4$ is obtained on evaporating a solution of auryl sulphate nearly to dryness at 250°, the crystals thus obtained being dried on porous plates in a lime desiccator; it forms lustrous scarlet prisms, which rapidly absorb water from the air, with partial decomposition. The author is of opinion that the gold in this and in corresponding salts is a true *dyad* analogous to mercury, and that such compounds should not be regarded as combinations containing both monad and triad gold. A. K. M.

Atomic Weight of Manganese. By J. Dewar and A. Scott (*Proc. Roy. Soc.*, **35**, 44—48).—The results of determinations of the atomic weight of manganese may be divided into two classes; the one giving approximately the number 55, the other the number 54. The former has resulted from analysis of the chloride and carbonate, and conversion of the monoxide into sulphate, or sulphate into sulphide; the latter from the analysis of the oxalate and reduction of the red oxide into the monoxide.

The authors discuss the errors inherent in these processes; the chloride and bromide are apt to contain traces of a manganic salt, are very hygroscopic, and are liable to retain traces of the halogen acids. Researches into the oxides of manganese have established that they are difficult to obtain in a definite form. From the molecular weight of carefully prepared specimens of the chloride and bromide, the respective atomic weights of manganese were found to be 54·97 and 54·91. Silver permanganate was finally selected as being readily freed from impurities by recrystallisation, as anhydrous, and not in any way hygroscopic, and as not liable to contain excess of any of its constituents. The first method adopted consisted in reducing the salt in a current of hydrogen, and weighing the residual silver and manganese monoxide; but the results showed great variation, the errors being due probably to the occlusion of hydrogen, and suspension of the oxide in the oxygen evolved. Better results were obtained by reducing the salt with sulphurous acid, sodium or potassium formate, potassium nitrite, and determining the silver by precipitation with potassium bromide. Rejecting the use of sulphurous acid as causing the formation of sparingly soluble silver sulphide or sulphate, the mean atomic weight was found to be 55·038 ($O = 16$, $Ag = 107·93$). Another element is therefore added to those whose atomic weights have been found to be approximately whole numbers.

V. H. V.

Mineralogical Chemistry.

Application of Organic Acids to the Examination of Minerals. By H. C. Bolton (*Chem. News*, **47**, 251—252).—In previous communications (*ibid.*, **34**, 249, and Abstr., 1881, 62, 642) the author has shown that citric acid can decompose minerals almost as well as hydrochloric acid does; and has described experiments in which the finely powdered minerals were exposed to the action of the citric acid solution sometimes for a few hours in the cold, and at other times for a few minutes at a boiling temperature. The experiments described in this paper were conducted at the ordinary room temperature, 60—70° F., and the time of exposure was prolonged. Some 200 minerals were examined, but a few representative specimens only have been selected for description. The progress of decomposition was noted at periods varying from a few days up to more than two years. A solution of citric acid concentrated in the cold was used in all the experiments. The following are the representative observations:—

In the *sulphide* group chalcocite showed signs of decomposition at the end of ten days, and at the expiration of several months gave a partial solution of a green colour. Ullmanite showed signs of decomposition in two days, and in a month gave a very dark-coloured solution. Arsenical pyrites was attacked in a few days; iron pyrites in eight days; a month later gave a reddish-yellow solution, with the reactions for iron and sulphuric acid; copper pyrites behaved in a similar manner, giving, of course, copper, instead of iron reactions; 1 gram of this mineral lost 11 per cent. of its weight after 14 months' contact with the acid solution. Smaltite was attacked in eight days, and sulphuric acid could be detected in the coloured solution. Tetrahedrite was strongly attacked in about four months. Cinnabar, orpiment, argentite, and pyrargyrite completely resisted the action of the acid solution.

Oxides.—In this group experiments were made only on those minerals which resisted the acid solution on boiling; of these, magnetite and limonite were strongly attacked in eight days, hematite only after several months.

Silicates.—Datolite was decomposed after 24 hours, yielding gelatinous silica. Hornblende, pyroxene, almandite, epidote, vesuvianite, and serpentine were decomposed in eight days, and after a month, hornblende, almandite, and epidote yielded coloured solutions and slimy silica, whilst serpentine gave gelatinous silica. After 14 months' contact with the acid solution, hornblende and pyroxene were completely decomposed, giving dark brown solutions full of floating silica; serpentine, on the other hand, yielded a dry gelatinous mass. Actinolite is not so readily decomposed as common black hornblende.

Of *felspars*, labradorite yields the most readily, being decomposed in eight days; in a few months slimy silica is formed. Tourmaline and staurolite are attacked after four or five months, the latter forming a solution coloured by iron, whilst slimy silica separates. Orthoclase and oligoclase show signs of decomposition after eight months, but the decomposition of albite is doubtful. Talc and kyanite appear to resist the action of citric acid. Muscovite and biotite yield very slowly. After two years' subjection to the acid solution, minute scales of mica separate, and some slimy silica appears in the slightly coloured solution.

As these results probably bear important relation to the disintegration of rocks by the action of the humus acids, the author has gone somewhat into detail, and finally gives the following *rough* generalisation of his observations:—

Table showing approximate relative Disintegration of Rock-forming and Associated Minerals by Citric Acid in Solution.

Quickly decomposed.	Slowly decomposed.	Very slowly decomposed.	Not decomposed.
Carbonates. Phosphates. Prochlorite. Chrysolite. Nephelite.	Serpentine. Pyroxene. Hornblende. Labradorite. Garnet. Epidote. Vesuvianite. Pyrites. Limonite. Magnetite. Gypsum (?).	Orthoclase. Oligoclase. Albite (?). Biotite. Muscovite. Tourmaline. Staurolite. Hæmatite.	Quartz. Corundum. Spinel. Beryl. Fluorite. Barite. Talc (?). Kyanite (?).

D. A. L.

Separation of Minerals according to the Degree of Cohesion. By BÜTTGENBACH (*Dingl. polyt. J.*, **248**, 112).—The separation of minerals on a large scale has hitherto been effected mainly by the differences in their density, and also by magnetic means. The author suggests separating minerals or ores by the difference in the degree of brittleness and firmness. Starting with the well-known fact that by casting two minerals of different degrees of hardness against a solid body, the one is crushed to pieces whilst the other remains intact or is broken into large pieces, he devised a practical method of separating ores on a large scale according to their cohesive degrees. In his experiments pyrites and zinc blende were used. The mixture was introduced into Vapart's disintegrating mill, in which the ores are cast three times against the sides of the cylinder before they leave the apparatus. The mass was then sifted through separating drums, when it was found that the particles which passed through the finer sieves consisted chiefly of zinc blende, whilst the larger pieces left behind were pyrites. D. B.

Analysis of some Minerals. By A. B. GRIFFITHS (*Chem. News*, **47**, 169—170).—The author has found considerable quantities of tungsten in a sample of ferromanganese ore from the neighbourhood of Casa Branca, Portugal, whilst in two samples of brown hæmatite from the same locality, in one he detected traces of titanium (sp. gr. of ore = 4·102), in the other traces of both titanium and selenium. The following is an analysis of a nodule of copper ore from the northern part of Nova Scotia; it is found in grey nodules, which often contain anthracite bands:—

Cu.	S.	Fe_2O_3,Al_2O_3.	Sand, &c.	CaO.	MgO.	Mn.	Total.
64·101	25·639	3·891	5·790	0·201	0·137	0·221	= 99·98

From these results he calculates the formula Cu_5S_4 or $Cu_2S(CuS)_3$; its sp. gr. = 4·392.

An analysis of a Dresden syenite yielded the following results:—

SiO_2.	Al_2O_3.	K_2O.	Na_2O.	FeO.	MgO.	CaO.	H_2O.	P_2O_5.	Total.
60·020	16·663	6·504	2·410	7·207	2·509	3·585	1·100	trace	= 99·998

D. A. L.

Magnetic Property of Platinum Ore. By T. Wilm (*Ber.*, **16**, 664—667).—The author has examined a large number of specimens of platinum ore, and finds that nearly all are magnetic. From an ore containing 76·07 per cent. platinum, 55·15 per cent. was separated by means of a comparatively weak magnet, and this magnetic portion contained as much as 69·23 per cent. platinum, so that practically no purification can be effected in this way; neither does the magnet afford any criterion as to the adulteration of platinum ores with iron. For the latter purpose the author recommends warming the ore with pure hydrochloric acid, when no gas will be evolved if the ore is not adulterated. A. K. M.

An Ammonio-phosphatic Deposit in the Vicinity of Cape Town. By A. B. Griffiths (*Chem. News*, **47**, 239).—The deposit is brown, in a powdered condition, and contains nodules resembling ordinary guano in appearance. A microscopical examination revealed the presence of diatomaceæ and a few spongy spicules; and by a chemical examination a specimen of the deposit was found to contain 70·21 per cent. ammonium compounds, 17·5 per cent. phosphates, and 3·3 per cent. nitrogen. D. A. L.

Artificial Hausmannite. By A. Görgeu (*Compt. rend.*, **96**, 1144—1146).—Hausmannite can be obtained artificially by fusing manganous chloride for several hours in a moist oxidising atmosphere. This can be effected by filling a porcelain crucible about 3 cm. in height with one-third its volume of anhydrous manganese chloride, placing this crucible in a larger one about 5 cm. in height, and covering the latter with a piece of platinum foil, which extends beyond its edges, but only rests on it at a few points. The crucibles are then heated over a Bunsen flame in such a way that no reducing gases enter the crucibles. The temperature should be somewhat high, but not high enough to cause a rapid evolution of vapours of the chloride. An experiment requires at least five or six hours, and should not be interrupted, but manganous chloride should be added to make up for loss by volatilisation, &c. When the evolution of hydrochloric acid has almost ceased, the crucibles are left to cool, the lighter particles removed by elutriation, and the heavier crystals washed with boiling water until free from chlorine. The crystals thus obtained are identical with natural hausmannite in composition, form, colour, specific gravity, hardness, &c.

The formation of hausmannite is due to the combined action of moisture and oxidising gases on the manganous chloride. Moist carbonic anhydride or dry air yields no hausmannite when it acts on the fused chloride.

In presence of chlorides of potassium, sodium, calcium, and barium the crystals obtained are smaller, but they do not contain a notable quantity of the foreign bases. In such cases, however, the salt must be fused in a platinum crucible.

Cobalt chloride also yields crystals when treated in a similar manner. C. H. B.

Organic Chemistry.

A New Product of the Slow Combustion of Ether. By E. Legler (*Annalen*, **217**, 381—386).—When ether vapour is oxidised in a current of air by means of red-hot platinum, and the products of the imperfect combustion are condensed, a liquid is obtained which yields by slow evaporation over sulphuric acid a body forming rhombic crystals and melting at about 51°. It is soluble in water, alcohol, ether, and chloroform, with slight decomposition, its solution rapidly becoming acid, although the crystals themselves have a neutral reaction. It volatilises slowly at ordinary temperatures, detonates slightly when suddenly heated, and also very faintly when struck. The constitution of this body is not understood, its formula being apparently $C_{11}H_{33}O_{21}$. On the addition of alkalis to its aqueous solution, hydrogen is evolved, whilst formic acid and methaldehyde are produced; with ammonia it yields oxygen, formic acid, and methaldehyde, and with ammoniacal lead solution, oxygen and lead dioxide. It liberates iodine from potassium iodide, especially in presence of sulphuric acid, and with lead oxide it yields detonating gas. The dioxides of lead and manganese are reduced, with evolution of gas and formation of formates of these metals; with acids however it shows greater stability. A. K. M.

Action of Carbonic Oxide on Steam. By L. Maquenne (*Bull. Soc. Chim.* [2], **39**, 308—309).—The formation of carbonic anhydride observed in the decomposition of formic acid, either by the electric discharge or by heat, led the author to conclude that carbonic anhydride and hydrogen are the resultants of the action of carbonic oxide on steam. This view is further supported by the fact that the proportion of carbonic anhydride increases with the time of action.

Its change also follows as a necessary deduction from thermochemical data, for the heat of combustion of carbonic oxide with oxygen exceeds that of hydrogen by five heat-units.

In one set of experiments the author sealed up carbonic oxide with water in tubes through which the electric discharge could be passed, and found that 96·97 per cent. of the theoretical quantity of hydrogen and carbonic anhydride were formed. The reaction never becomes complete, owing to the dissociation of the carbonic anhydride. A similar result was obtained when tubes containing carbonic oxide and water were heated at 250—275°, and even at as low a temperature as 150° the transformation into carbonic anhydride and hydrogen is practically complete. From these observations the author concludes that the system $CO_2 + H_2$ is stable at any temperature below that at which carbonic anhydride is dissociated, and that carbonic oxide is a more powerful reducing agent than hydrogen. V. H. V.

Compounds of Benzotrichloride with Phenols and Phenylamines. By A. DOEBNER (*Annalen*, **217**, 223—269).—Most of the results described in this paper have already appeared in this Journal (Abstr., 1880, 239 and 644; 1881, 165; 1882, 956). From diethylaniline and benzotrichloride a green dye, $C_{27}H_{32}N_2$, is produced corresponding with malachite-green. The *sulphate*, $C_{27}H_{32}N_2,H_2SO_4$, forms crystals of a golden lustre, readily soluble in water and in alcohol. The double salt with zinc chloride, $(C_{27}H_{32}N_2,HCl)_2,ZnCl_2,2H_2O$, crystallises in reddish-brown needles or in gold-coloured prisms, readily soluble in cold water. The free base is slightly soluble in water, readily in alcohol; on reduction it yields a leuco-base, $C_{27}H_{34}N_2$ (m. p. 62°), which crystallises in large colourless needles possessing a vitreous lustre; it is sparingly soluble in water, readily in alcohol, ether, and benzene; the platinochloride, $C_{27}H_{34}N_2,H_2PtCl_6,3H_2O$, is obtained as a colourless crystalline precipitate.

On heating the base $C_{27}H_{32}N_2$ with concentrated hydrochloric acid at 180°, it suffers a decomposition similar to that of malachite-green, yielding diethylbenzoylaniline, $C_6H_4.\overline{Bz}NEt_2$, and diethylaniline, the former crystallising in rhomboidal prisms melting at 78°; it is insoluble in water, sparingly soluble in cold alcohol, but readily in hot alcohol and in ether.

Similar green dyes have also been obtained by the action of benzotrichloride on the following tertiary amines:—Dibutylaniline, diamylaniline, methylethylaniline, methylamylaniline, and methyldiphenylamine. Para-derivatives, such as dimethylparatoluidine, appear not to yield green dyes. A. K. M.

Action of Nitric Acid on Phenols. By W. STAEDEL (*Annalen*, **217**, 153—181).—*Action on Ethyl Orthocresol.*—When ethyl orthocresol is slowly added to ten times its weight of well cooled nitric acid (sp. gr. 1·505), ethyl dinitro-orthocresol is formed. It crystallises from alcohol in bright orange-coloured needles melting at 51°, which become dark coloured on exposure to sunlight. They dissolve easily in benzene, carbon bisulphide, and ether. On treatment with alcoholic ammonia they are decomposed, dinitrotoluidine being formed (m. p.

208°). When nitric acid of sp. gr. 1·48 is employed, ethyl mononitro-orthocresol is formed. It crystallises from alcohol in straw-coloured needles melting at 71°. They are soluble in ether and benzene, and are not attacked by alcoholic ammonia even when heated at 180°. The mononitro-body is always accompanied by a small quantity of the dinitro-body.

Ethyl-dinitro-orthocresol from Ethyl-mononitro-orthocresol.—When the mononitro-compound (m. p. 71°) is treated with nitric acid of sp. gr. 1·6°, it is converted into ethyl dinitro-orthocresol. The same substance is formed when the liquid, ethyl metanitro-orthocresol, is slowly added to nitric acid (sp. gr. 1·5) and the mixture allowed to stand for three hours.

Dinitro-orthocresol is formed whenever ethyl orthocresol is nitrated. It varies in quantity directly with the temperature of the mixture during the experiment. *The barium salt*, $C_{14}N_4O_{10}H_{10}Ba + 3\frac{1}{2}H_2O$, forms fine reddish-yellow needles soluble in hot water. The crystals were observed to be mixed with a salt in the form of bright yellow warty masses, which proved to be a salt of ethyl-dinitro-orthocresol. The barium salt when heated for four hours at 70—80° loses its water of crystallisation, and assumes a blood-red colour. *The sodium salt* does not crystallise well. *The free acid* crystallises from dilute alcohol in canary-yellow coloured needles melting at 85—86°. *The ammonium* and *magnesium salts* form yellow needles which are soluble in water. *The silver salt* is a brownish-red, and the *lead salt* a yellow precipitate.

Ethyl-metacresol.—When ethyl-metacresol is treated with nitric acid in a similar manner to the ortho-compound, it yields a mononitro-derivative, which crystallises from alcohol in colourless needles melting at 54°. It is not decomposed when heated at 100° with alcoholic ammonia.

Ethyl-paracresol dissolved in glacial acetic acid yields on nitrating an ethyl mononitroparacresol. A different reaction takes place when acetic acid is not present, and the ethyl salt is very cautiously added to small quantities of well-cooled nitric acid. When the reaction is complete, the mixture is poured into a large quantity of water or, preferably, on to ice. A yellowish-white precipitate is formed which gradually agglomerates. On treating it with soda-solution, a portion dissolves, and the remainder is obtained as a dark-coloured oil which solidifies on cooling. The soluble portion consists of dinitrocresol. The insoluble oil crystallises from alcohol in long white opaque needles which, after drying over sulphuric acid, melt at 72·5—75°. They consist of ethyl-dinitroparacresol, and are turned brown by sunlight.

Dinitroparacresol crystallises from alcohol in glittering yellow needles melting at 85°. It is sparingly soluble in water, more soluble in alcohol, ether, and benzene. It is precipitated from an alcoholic solution on addition of water as a yellow flocculent precipitate. *The sodium salt*, $C_7H_5N_2O_5Na$, is obtained by neutralising it with sodium carbonate. It crystallises from an aqueous solution in red needles, which, on drying over sulphuric acid, lose water and assume an orange-yellow colour. *The barium salt*, $(C_7H_5N_2O_5)_2Ba$, is obtained by boiling the dinitro-compound with barium carbonate. It crystallises in yellow needles which are very sparingly soluble in water and alcohol. *The* *potassium salt*, $C_7H_5N_2O_5K$, is formed when a solution of the barium salt is boiled with a dilute solution of potassium sulphate. It crystallises from water in red iridescent anhydrous needles. *The silver salt*, $C_7H_5N_2O_5Ag$, obtained by treating the potassium salt with silver nitrate, crystallises from an aqueous solution in dark-red needles. *The ammonium salt*, $C_7H_5N_2O_5NH_4$, is obtained by boiling the barium salt with ammonium sulphate. It crystallises from water in the anhydrous as well as in the hydrated form. *The ethyl salt*, $C_7H_5N_2O_5Et$, obtained by acting on the silver salt with ethyl iodide, crystallises in long colourless needles (m. p. 75°), soluble in alcohol and ether. It is identical with the salt obtained direct from ethyl paracresol. *The methyl salt*, $C_7H_5N_2O_5Me$, crystallises in nearly colourless needles melting at 122°.

Nitration of Ethyl- and Methyl-naphthol.—Ethyl-trinitro-α-naphthol, $C_{10}H_4(NO_2)_3.OEt$, is formed when ethyl-α-naphthol is cautiously added to ten times its weight of nitric acid (sp. gr. 1·52) which is well cooled by ice. The nitro-product crystallises from alcohol in glittering yellow needles which melt at 148°. They dissolve freely in glacial acetic acid, but only sparingly in chloroform, ether, and benzene. *Ethyl-trinitro-β-naphthol*, $C_{10}H_4(NO_2)_3.OEt$, prepared in a similar manner to the α-compound, crystallises from glacial acetic acid in large yellow needles melting at 186°. They are only sparingly soluble in alcohol, chloroform, and benzene.

Methyl-trinitro-α-naphthol, $C_{10}H_4(NO_2)_3.OMe$, is prepared in a similar manner to the above salts. It crystallises from glacial acetic acid in yellow plates which melt at 128°.

Methyl-trinitro-β-naphthol, $C_{10}H_4(NO_2)_3.OMe$, crystallises from glacial acetic acid in small colourless needles which melt at 213°, and are almost insoluble in alcohol, benzene, chloroform, and ether.

Trinitronaphthylamine, $C_{10}H_4(NO_2)_3.NH_2$.—When the above-mentioned ethyl and methyl salts are heated in a sealed tube at 50° with alcoholic ammonia, they yield trinitronaphthylamine. It crystallises from toluene in small glittering yellow plates which melt between 240° and 266°.

Trinitronaphthalene.—The trinitronaphthylamine, obtained from ethyl trinitro-β-naphthol as above, was converted into trinitronaphthalene. By decomposing the diazo-compound with hot alcohol in the usual way the product crystallised from nitric acid gave two kinds of crystals, one forming glittering yellow plates melting at 210°, the other crystallising in cubes melting at 181°. Trinitronaphthylamine, obtained from methyl trinitro-β-naphthol on similar treatment, yields yellow needles melting at 210°.

Nitro-product of Benzylphenol.—This and the following nitro-bodies were prepared by the general method. After continued treatment with ether, it forms a yellowish-grey crystalline powder, which is only soluble in boiling toluene and glacial acetic acid. It is a mononitrobenzyl dinitrophenol, $C_6H_3(NO_2)_2.O.CH_2.C_6H_4.NO_2$. It crystallises from glacial acetic acid in small orange-yellow needles.

The nitro-product of benzyl-paracresol consists of three substances melting at 70°, 85°, and 181°. The first is paranitrobenzyl nitrate. That melting at 85° is dinitroparacresol. The third forms white needles, and probably is the neutral nitro-product of benzyl paracresol. *The nitro-product of benzyl-orthocresol* is mononitrobenzyl dinitro-orthocresol, $C_6H_2Me(NO_2)_2.O.CH_2C_6H_4.NO_2$. When crystallised from boiling alcohol it forms slender colourless needles melting at 145°.

J. I. W.

Nitrophenols and Nitrocresols. By W. STAEDEL (*Annalen*, **217**, 182—217).—When *mononitrobenzyl-dinitrophenol* is heated in a sealed tube at 100° with alcoholic ammonia for 4—5 hours, it forms paranitrobenzyl alcohol, which crystallises in brown needles melting at 91°. Dinitraniline is also obtained. It crystallises from a mixture of alcohol and ether in brownish-yellow crystals melting at 174°, and is orthoparadinitraniline.

On heating *mononitrobenzyl-dinitro-orthocresol* with alcoholic ammonia at 120—130°, dinitrotoluidine and paranitrobenzyl alcohol are obtained. The former is insoluble in water, but crystallises from alcohol and toluene in small yellow needles with a blue fluorescence, and melting at 209°. The latter crystallises from water in light-yellow needles melting at 91°.

Ethyl-dinitro-orthocresol is partially decomposed by alcoholic ammonia in the cold. The reaction, however, is more complete when the mixture is heated at 140—160° in a sealed tube for three hours. A dinitrotoluidine (m. p. 208—209°), identical with that obtained from mononitrobenzyl-dinitroorthocresol, is formed.

Ethyl-dinitroparacresol is easily converted into dinitrotoluidine by alcoholic ammonia. It is obtained in yellowish-red crystals melting at 167—168°. The author shows that it is identical with the dinitrotoluidines obtained by Beilstein and Kuhlberg (m. p. 166°), and by Tiemann (m. p. 168°) (*Ber.*, **3**, 219). Since, on oxidation with chromic acid and subsequent treatment with ammonia, dinitrotoluidine yields chrysanisic acid, the constitution of ethyl dinitroparacresol must be $C_6H_2Me(NO_2)(OEt)(NO_2)$ [1 : 3 : 4 : 5].

Preparation of Symmetric Dinitrotoluene.—When a solution of dinitrotoluidine in absolute alcohol is boiled, with a stream of nitrous fumes passing through it for 12 hours, it remains unaltered. When it is heated with amyl nitrite for 18 hours, the dinitrotoluidine is attacked and nitrous fumes are given off. On adding alcohol to the mixture when cold, it becomes milky, and a heavy oil gradually separates out. The filtrate from the oil when distilled yields a dark-coloured liquid having a smell resembling that of amyl compounds. On distilling with steam, it passes over in yellow oily drops. It is probably a new product. The aqueous distillate deposits on cooling yellow needle-shaped crystals of dinitrotoluene (m. p. 90—91°). Beilstein and Kuhlberg state that nitrous acid does not act on dinitrotoluidine in concentrated nitric acid. The author finds that on passing nitrous acid into a well cooled mixture of dinitrotoluidine and pure concentrated nitric acid, a reaction takes place. All unaltered dinitrotoluidine can be separated by pouring the mixture into boiling absolute alcohol, and then cooling quickly. On filtering into twice its volume of water, the solution deposits a reddish-yellow precipitate which, after treatment with ammonia and crystallisation from water, yields bright yellow needle-shaped crystals of dinitrotoluene, melting at

90—91°. They are sparingly soluble in light petroleum, freely soluble in warm alcohol and carbon bisulphide, and in cold chloroform and ether. They crystallise with 1 mol. of benzene, and, when anhydrous, sublime without decomposition. When treated with chromic mixture the crystals become colourless, and then melt at 92—93°. On oxidation with chromic mixture, dinitrotoluene yields dinitrobenzoic acid melting at 201°, and identical with Cahours's acid. The author states that the ethyl salt is very readily prepared by dissolving the free acid in a small quantity of absolute alcohol, adding a few drops of strong sulphuric acid, heating for a few minutes on a water-bath, and finally treating the mixture with water: the precipitated salt crystallises well from alcohol, and melts at 90°. The above-mentioned derivatives of paracresol have the constitution—

Dinitroparacresol (m. p. 84—85°), $C_6H_2Me(NO_2)(OH)(NO_2)$ [1 : 3 : 4 : 5].
Dinitroparatoluidine (m. p. 167—168°), $C_6H_2Me(NO_2)(NH_2)(NO_2)$ [1 : 3 : 4 : 5].
Dinitrotoluene (m. p. 91°), $C_6H_3Me(NO_2)(NO_2)$ [1 : 3 : 5].

Symmetric Dinitrotoluene from Dinitro-orthotoluidine.—When dinitro-orthotoluidine is treated in a similar manner to dinitrotoluidine it yields dinitrotoluene, melting at 91°. The latter is absolutely identical with that obtained from dinitroparatoluidine.

Symmetric Nitrotoluidine, $C_6H_3Me(NO_2)(NH_2)$ [1 : 3 : 5].—When dinitrotoluene is treated with an alcoholic solution of ammonium sulphide it is reduced, symmetric nitrotoluidine being formed. It crystallises from water in red needles, melting at 98°.

Symmetric toluylenediamine is produced when dinitrotoluene is reduced with tin and hydrochloric acid. It forms a tin double salt with the composition $C_6H_2Me(NH_2)_2,2HCl + SnCl_2$. The author obtained the free base in the form of a syrupy liquid, boiling at 285°, but was unable to get it to crystallise. The sulphate forms violet crystals, soluble in water. The platinochloride crystallises in rusty-coloured needles.

The knowledge that symmetric dinitrotoluene is formed by removing the amido-group of dinitro-orthotoluidine, leads to the conclusion that the above derivatives of orthocresol have the following compositions:—

Dinitro-orthotoluidine, $C_6H_2Me(NH_2)(NO_2)(NO_2)$ [1 : 2 : 3 : 5].
Ethyl dinitro-orthocresol, $C_6H_2Me(OEt)(NO_2)(NO_2)$ [1 : 2 : 3 : 5].
Dinitro-orthocresol (m. p. 85°), $C_6H_2Me(OH)(NO_2)(NO_2)$ [1 : 2 : 3 : 5].
Mononitrobenzyl dinitro-orthocresol, $C_6H_2Me(OC_7H_6NO_2)(NO_2)(NO_2)$ [1 : 2 : 3 : 5].
Ethyl mononitro-orthocresol (liquid), $C_6H_3Me(OEt)(NO_2)$ [1 : 2 : 3].
Ethyl mononitro-orthocresol (m. p. 71°), $C_6H_3Me(OEt)(NO_2)$ [1 : 2 : 5].

The author states that when the same process of removing the amido-group is applied in the case of other dinitrotoluidines, different dinitrotoluenes are obtained. A dinitrotoluidine obtained by Herff, by further nitration of orthonitroparatoluidine, yields a dinitrotoluene. When the dinitrotoluidine, prepared by Tiemann (*Ber.*, **3**, 218), and melting at 168°, is treated with nitrous acid fumes in nitric acid, it yields a dinitrotoluene which crystallises from alcohol in glittering needles, melting at 60—61°. It is probably $C_6H_3Me(NO_2)(NO_2)$ [1 : 2 : 6].

Paranitrobenzylnitrate, $C_6H_4NO_2.CH_2.NO_3$.—When benzylparacresol is acted on with nitric acid, there is formed, in addition to dinitroparacresol, a compound which closely resembles the body termed by Beilstein and Kuhlberg, dinitrobenzyl alcohol. The author finds that it yields paranitrobenzoic acid on oxidation, and that it is paranitrobenzyl nitrate. He has further prepared the latter body by acting on paranitrobenzyl chloride dissolved in alcohol, with silver nitrate. The crystals obtained from an alcoholic solution melt at 70—71°. J. I. W.

Ethyl-amido-cresols. By W. Staedel (*Annalen*, **217**, 217—222). —*Ethyl metamido-orthocresol*, $C_6H_3Me(OEt)NH_2$ [1 : 2 : 5], is prepared by reducing ethyl metanitro-orthocresol (m. p. 71°) with tin and hydrochloric acid, neutralising the mixture with alkali when the reaction is complete, and finally distilling off the free base with steam. It forms a dark yellow oil, which is only sparingly soluble in water.

Ethyl-acetoamido-orthocresol, $C_6H_3Me(OEt),NH\overline{Ac}$, is formed when the above base is treated with an excess of acetic anhydride. It crystallises from water, ether, and benzene.

Ethyl-amidometacresol is prepared by reducing ethyl nitrometacresol (m. p. 54°). After precipitating the tin with hydric sulphide, the hydrochloride is obtained in dark-coloured crystals. The free base is best isolated by distillation with steam. Its salts crystallise well. The aceto-compound is readily obtained.

Ethyl-metamidoparacresol. — Ethyl metanitroparacresol is easily reduced by tin and hydrochloric acid. The hydrochloride forms needle-shaped crystals. The free base is obtained in the form of white glittering crystals, melting at 40—41°. Ethyl aceto-meta-amidoparacresol, $C_6H_2Me(OEt).NH\overline{Ac}$, melts at 106·5°.

Ethyl-diamidoparacresol, $C_6H_2Me(NH_2)(OEt).NH_2$ [1 : 3 : 4 : 5], is formed when ethyl dinitroparacresol (m. p. 75°) is added to a warm mixture of tin and hydrochloric acid. On cooling, the hydrochloride crystallises out in fine white silky needles. On adding an alkali to its solution, the free base is precipitated as a nearly colourless oil.

The following table gives the properties of the salts of the above compounds :—

	Ortho-series.	Meta-series.	Para-series.
Free base	Liquid.	Liquid.	White needle-shaped crystals (m. p. 40—41°).
Hydrochloride	$C_9H_{13}NO,HCl$ + $1\frac{1}{2}H_2O$, silky plates.	Broad glittering plates.	$C_9H_{13}NO,HCl$ + $1\frac{1}{2}H_2O$, fine silky needles.
Hydrobromide	—	—	Long white needles.
Sulphate	$(C_9H_{13}NO)_2H_2,SO_4$, needles.	Quadratic plates.	$(C_9H_{13}NO)_2H_2SO_4$ + $2H_2O$, fine needles.
Nitrate	$C_9H_{13}NO,HNO_3$, slender needles.	—	Glittering plates.
Oxalate	$(C_9H_{13}NO)_2C_2O_4H_2$, silvery plates.	$(C_9H_{13}NO)_2C_2O_4H_2$, red plates.	—
Platinochloride	$(C_9H_{13}NO)_2H_2PtCl_6$, yellow crystals.	—	Golden-yellow needles.
Aceto-compound	Rhombic plates from water; large tables from ether (m. p. 108°).	White needles from water (m. p. 114°).	White glittering plates from water (m. p. 106·5°).

J. I. W.

Nitro- and Amido-derivatives of Azobenzene. By J. V. Janovsky (*Monatsh. Chem.*, **4**, 276—283).—By the direct nitration of azobenzeneparasulphonic acid, two mono-nitro-acids are obtained, of which the more soluble (metanitro-) acid has already been described (Abstr., 1882, 831). The less soluble acid is obtained as follows:—100 grams of azobenzeneparasulphonic acid is placed in 500—550° grams nitric acid (sp. gr. 1·4), and heated at 115° until completely dissolved. When the violent reaction is over, the liquid is cooled to 8—10°, and the crystals separated from the resulting magma by aid of a filter-pump; the mother-liquor, after standing for some hours, deposits a further quantity of the paranitro-acid, whilst the more soluble meta-acid remains in solution.

Paranitroazobenzeneparasulphonic acid, $C_6H_4(NO_2).N_2.C_6H_4.SO_3H = [4 : 4']$, crystallises with 3 mols. H_2O in broad golden-orange needles having acute terminal faces; 3·1 parts of the acid dissolve in 100 parts water at 10°, the solution having an orange-yellow colour; a hot saturated solution gelatinises when cooled to about 30°. The *potassium* salt, $C_{12}H_8(NO_2)N_2.SO_3K$, crystallises in orange-red, rhombic tables, 100 parts of water dissolve 0·161 part of the salt at 17°, and 1·76 parts at 82°. The *sodium* salt, $C_{12}H_8(NO_2)N_2.SO_3Na + 2H_2O$, forms pale-yellow monoclinic tables. The *barium* salt,

$$[C_{12}H_8(NO_2)N_2SO_3]_2Ba,$$

crystallises in pale reddish-yellow scales, consisting of concentric groups of microscopic prisms; it is very sparingly soluble in water. The lead and silver salts crystallise in concentric groups of minute needles, explode readily on heating, and are both anhydrous.

Paramidoazobenzeneparasulphonic acid, $C_6H_4(NH_2).N_2.C_6H_4.SO_3H = [4 : 4']$, is prepared by reduction of the nitro-acid with stannous chloride and hydrochloric acid; it crystallises in pale-yellow interlaced, microscopic needles; 100 parts of water dissolve 0·104 part of the acid at 15°, and 0·39 at 97°, the solution having a dirty yellow colour. The *potassium* salt, $C_{12}H_8(NH_2)N_2.SO_3K$, crystallises in golden-yellow stellate crystals, sparingly soluble in cold, readily soluble in hot water; the *sodium* salt forms long needles; the *barium* salt, $[C_{12}H_8(NH_2)N_2SO_3]_2Ba + 4H_2O$, forms bronze-coloured rhombic crystals showing the combination $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $\breve{P}\infty$; 100 parts water at 15° dissolve 0·104 of the salt. The silver salt precipitates in long needles, and readily decomposes. On complete reduction of either the nitro- or amido-acid with tin and hydrochloric acid, sulphanilic acid and paraphenylenediamine hydrochloride are obtained, showing that the nitro- and amido-groups must be in the para-position.

A. J. G.

Azylines. By E. Lippmann and F. Fleissner (*Monatsh. Chem.*, **4**, 284—308).—Further investigations have convinced the authors that the formula $R_2N.C_6H_3\!:\!N.N\!:\!C_6H_3.NR_2$ assigned by them to the azylines (Abstr., 1883, 55) is incorrect, and that these bodies must be represented by a formula containing two hydrogen-atoms more, and therefore belonging to the azobenzenes. The following additional details are given:—

Dimethylanilineazyline, $C_{16}H_{20}N_4 = Me_2N.C_6H_4.N\!:\!C_6H_4\!:\!NMe_2$, not $C_{16}H_{18}N_4$ as previously given. The *platinochloride*, $C_{16}H_{20}N_4,H_2PtCl_6$, forms a dichroic crystalline powder, red by transmitted, green by reflected light.

Diethylanilineazyline, $C_{20}H_{28}N_4$, crystals monosymmetric; $a : b : c = 1 : 0·7108 : 0·9493$. Observed faces: 100; 110; 101; $\bar{5}01$; 321; $\bar{3}21$; 427; 010. Sp. gr. 1·107 (approx.) at 15°. The *platinochloride*, $C_{20}H_{28}N_4,H_2PtCl_6$, forms small, brownish-red, trimetric tables of copper-green lustre. The *ferrocyanide*, $C_{20}H_{28}N_4,H_4FeCy_6$, crystallises in brown rhombohedral plates. *Dipropylanilineazyline picrate*,

$$C_{24}H_{36}N_4,[C_6H_3(NO_2)_3O_3],$$

forms orange-red crystals insoluble in water. *Diamylanilineazyline picrate*, $C_{32}H_{54}N_4[C_6H_3(NO_2)_3O_3]_2$, forms small citron-yellow crystals, sparingly soluble in alcohol and water. The periodides of the azylines are precipitated on mixing alcoholic solutions of the azylines and iodine; they possess a metallic lustre, are dichroic, insoluble in water, and are completely decomposed by alkalis, mercuric oxide, and silver nitrate. *Diethylanilineazyline periodide*, $4C_{10}H_{14}N_2 + 3I_2$, forms microscopic crystals, apparently trimetric. *Dipropylanilineazyline periodide*, $4C_{12}H_{18}N_2 + 3I_2$, crystallises in brilliant violet needles. *Dibutylanilineazyline periodide*, $4C_{14}H_{22}N_2 + 3I_2$, forms dark crystals of bluish lustre. *Diamylanilineazyline periodide*, $4C_{16}H_{26}N_2,3I_2$, forms black crystals of violet lustre.

By the action of nitrous acid on dimethylanilineazyline, paranitrodimethylaniline is obtained; from diethylanilineazyline the previously unknown *nitrodiethylaniline* was obtained in similar manner, and was prepared, for comparison, by the oxidation of nitrosodiethylaniline. It has the formula $C_6H_4(NO_2).NEt_2$, melts at 76°, crystallises in sulphur-yellow needles showing a pale blue fluorescence, is sparingly soluble in light petroleum, readily in hot alcohol. The crystals are monosymmetric, $a : b : c$ = 1·0342 : 1 : 0·8245. Observed faces: 100; 001; 110; $10\bar{1}$; 010. It is more strongly basic than dimethylaniline, and yields a platinochloride, $[NO_2(C_6H_4).NEt_2]_2,H_2PtCl_6$, crystallising in thin asymmetric prisms.

Diethylanilineazyline when treated with hydrochloric acid and stannous chloride yields *diethylparaphenylenediamine*, $C_6H_4(NH_2).NEt_2$, a colourless oil, which turns brown on exposure to air, and boils at 260—262°; the same substance was obtained by the action of stannous chloride on nitrosodiethylaniline. The acid platinochloride, $2(NH_2.C_6H_4.NEt_2,HCl)_2,H_2PtCl_6$, crystallises in thin yellowish-brown tables.

By the action of ethyl iodide on diethylanilineazyline, and treatment of the resulting hydriodide with potash, *tetraethylphenylenediamine*, $C_6H_4(NEt_2)_2$, is obtained; it melts at 52°, boils at 280° (uncorr.), is very sparingly soluble in alcohol, ether, chloroform, benzene, and light petroleum, but can be crystallised from water. The colourless crystals are monosymmetrical with clinoquadratic habit. $a : b : c$ = 0·99 : 1 : 1·833. Observed faces: 001; 100; 010; 201; 011. The platinochloride, $C_6H_4(NEt_2)_2,H_2PtCl_6$, forms clear yellow tetragonal crystals. Observed faces: 001; 100; 110. The double chloride, $C_6H_4(NEt_2)_2(HCl)_2,HgCl_2$, forms reddish-white monosymmetric crystals. $a : b : c$ = 0·8754 : 1 : 0·5655. Observed faces: 100; 110; 101; $\bar{1}01$; 011. The periodide, $2C_6H_4(NEt_2)_2 + 3I_2$, crystallises in black opaque forms, sparingly soluble in alcohol. The base was also prepared by the action of ethyl iodide on diethylphenylenediamine, and when so obtained showed identity in properties with that obtained from the azyline.

Methyl iodide and diethylanilineazyline yield a crystalline hydriodide, $C_6H_4(NMeI)_2(NEt_2)$, which could not be obtained pure.

Dimethylanilineazyline, heated with ethyl iodide, and subsequently treated with potash, gives a base boiling at 275°.

Dipropylanilineazyline and ethyl iodide yield an iodide crystallising in small needles, and yielding on treatment with potash an oil boiling at 295—300°. From the foregoing results it appears that the nitrogen in these bodies occupies the para-position, the diethyl-compound having the constitution $Et_2N.C_6H_4.N_2.C_6H_4.NEt_2 = [4 : 4']$.

A. J. G.

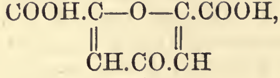
Pyrenequinone. By G. GOLDSCHMIEDT (*Monatsh. Chem.*, **4**, 309—324).—By oxidation of pyrene with chromic acid Gräbe obtained a compound, $C_{16}H_8O_2$, which he regarded as pyrenequinone (this Journal, 1871, 691); this result was disputed by Hintz (*Inaug. Dissert.*, Strasburg, 1878), who stated that he obtained by this reaction two compounds, the one, $C_{12}H_6O_2$, crystallising in red interlaced needles, insoluble in sodium carbonate; the other, $C_{15}H_{16}O_4$, forming short, thick, yellow needles, soluble in sodium carbonate. The author has therefore re-investigated the question, and although closely following the methods described by Hintz, entirely fails to confirm his results. The red crystals are impure pyrenequinone, and the yellow product was obtained only in very small quantity, could not be obtained well crystallised, and on analysis showed about 3 per cent. less carbon than is required by Hintz's formula.

Pyrenequinone, $C_{16}H_8O_2$, forms a network of slender needles of yellow to red colour, according to thickness, and cannot be fused without decomposition. By careful heating in a vacuum it can be sublimed, the greater part, however, suffering decomposition. It is sparingly soluble in alcohol, ether, benzene, light petroleum, chloroform, and acetone, the only good solvent being hot glacial acetic acid. By heating it with zinc-dust or soda-lime, pyrene is obtained. The products of the fusion of pyrenequinone with potash are still under investigation. *Dibromopyrenequinone*, $C_{16}H_6Br_2O_2$, is prepared by heating a solution of pyrenequinone in glacial acetic acid with bromine, and separates as a granulo-crystalline precipitate of a chocolate-brown colour when purified; it is very sparingly soluble in the ordinary solvents. On evaporation the mother-liquors from this substance yield *tribromopyrenequinone*, $C_{16}H_5Br_3O_2$, as a fine red, indistinctly crystalline powder.

Pyrenequinone when boiled with dilute nitric acid (1 part HNO_3, 2 parts water), yields citron-yellow microscopic crystals of a compound whose analytical results agree best with the formula $C_{14}H_5(NO_2)O_4$. By employing nitric acid diluted with acetic acid, there was obtained in addition a substance crystallising in red needles of the formula $C_{14}H_6(NO_2)_2$ (?).

Pyrenequinol, $C_{14}H_6(OH)_2$, is obtained by boiling pyrenequinone with zinc-dust and dilute ammonia; it is a yellow crystalline body, soluble in absolute alcohol, the solution having a strong dark blue fluorescence, and being precipitated by water. It readily absorbs oxygen from the air, and is reconverted into pyrenequinone. *Diacetylpyrenequinol*, $C_{14}H_8O_2\overline{Ac}_2$, obtained by heating pyrenequinol for two hours with acetic anhydride and sodium acetate, is a pale yellow, crystalline powder melting at 166—167°, sparingly soluble in benzene, alcohol, and ether. A. J. G.

Chelidonic Acid. (Preliminary Notices.) By A. LIEBEN and L. HAITINGER (*Monatsh. Chem.*, **4**, 273—275 and 339—340).—Chelidonic acid, when heated to boiling with solutions of the alkalis or alkaline earths, is completely resolved into acetone and oxalic acid, according to the equation $C_7H_4O_6 + 3H_2O = 2C_2H_2O_4 + C_3H_6O$. The acid appears to be dibasic, the neutral tribasic salts of Lerch and the basic salts of Lietzenmeyer being in reality salts of an acid derived from chelidonic acid by addition of the elements of water, and distinguished from it by giving yellow precipitates with lead and silver salts, and a yellowish-red coloration with ferric chloride; whilst chelidonic acid gives white precipitates with lead and silver salts, and a brown coloration with ferric chloride only after long standing. The above-mentioned yellow lead salt has the composition $Pb_2C_7H_2O_7 + H_2O$. By treatment with zinc and acetic acid, chelidonic acid yields a crystalline acid melting at 140°. The authors suggest the expression



$$\begin{array}{l}\mathrm{COOH.C{-}O{-}C.COOH}\\ \qquad\;\;\|\qquad\;\;\|\\ \qquad\;\mathrm{CH.CO.CH}\end{array}$$

as possibly representing the constitution of chelidonic acid.

By the action of ammonia on chelidonic acid, Lietzenmeyer obtained an acid of the formula $C_7H_7NO_6$, termed by the authors *ammonchelidonic acid.* Treated with bromine in presence of water it yields a tribasic crystalline dibromo-acid, which gives a purple coloration with ferric chloride; it probably contains only two carboxyl-groups. The author considers it probable that the nitrogen-atom in ammonchelidonic acid is exclusively in union with carbon.

Ammonchelidonic acid when heated with water at 195°, or by dry distillation, is completely resolved into carbonic anhydride, water, and *hydroxypyridine*, C_5H_5NO; this separates from aqueous solution in fine efflorescent crystals containing water of crystallisation, has a neutral reaction, but yields a hydrochloride and platinochloride: when distilled with zinc-dust it yields pyridine.

Dibromhydroxypyridine, C_5H_3BrNO, is obtained by the action of bromine on hydroxypyridine, or by heating the brominated chelidonic acid. It is crystalline, sparingly soluble in water, insoluble in dilute acids, readily soluble in alkalis, from which solutions it is precipitated unaltered on addition of acids. It dissolves in concentrated hydrochloric acid, and yields with platinic chloride the crystalline *platinochloride* $(C_5H_3Br_2O)_2,H_2PtCl_6$. An ammoniacal solution gives with silver nitrate a heavy, crystalline, sparingly soluble silver compound. It is very probably identical with the dibromhydroxypyridine which Hofmann obtained by the action of bromine on piperidine (Abstr., 1879, 733). A. J. G.

Preparation of Methyl- and Ethyl-derivatives of Hydroxyquinolinetetrahydride, Methoxyquinolinetetrahydride, and Ethoxyquinolinetetrahydride. (*Dingl. polyt. J.*, **248**, 172.)—Fischer and Bedall have shown that hydroxyquinoline and methoxyquinoline prepared from quinolinesulphonic acid can be converted into tetrahydro-compounds by treatment with zinc and hydrochloric acid. Hydroxyquinoline and hydroxyquinolinetetrahydride yield azo colouring matters with bases.

Fischer has found that by the action of the iodides or bromides of the alcohol radicles on the tetrahydro-compounds, the latter are transformed into methyl-, ethyl-, &c., derivatives. By the action of diazo salts on these bases yellowish-red and brown colouring matters can be obtained. Of more importance, however, especially in the case of α-hydroxyhydromethylquinoline, is the fact that they have strongly antipyretic properties, and can replace quinine. D. B.

Action of Hydrochloric Acid on Xanthine. By E. SCHMIDT (*Annalen*, **217**, 308—312).—The decomposition of xanthine by hydrochloric acid is perfectly analogous to that of caffeïne and theobromine, the products consisting of ammonia, glycocine, carbonic anhydride, and formic acid, $C_5H_4N_4O_2 + 6H_2O = 3NH_3 + C_2H_5NO_2 + 2CO_2 + CH_2O_2$. A partial decomposition takes place at 180°, but to decompose the xanthine completely the heating must be carried on for some hours at 220—230°. Xanthine is but very slightly attacked by long-continued boiling with a saturated solution of barium hydroxide. A. K. M.

Theobromine. By E. Schmidt and H. Pressler (*Annalen*, **217**, 287—306).—To prepare theobromine, the authors mix cacao which has been freed from oil by pressure, with half its weight of calcium hydroxide, and boil repeatedly with 80 per cent. alcohol. After recrystallising the residue obtained from the evaporation of the alcohol, the theobromine forms a white crystalline powder. It is anhydrous, and sublimes at about 290° without melting. Its salts are obtained by dissolving the base in concentrated acids, and resemble those of caffeïne in their instability, being decomposed by contact with water or alcohol. The *hydrobromide*, $C_7H_8N_4O_2,HBr + H_2O$, forms colourless transparent platy crystals, which lose their water at 100°, together with a part of the hydrobromic acid. The *hydrochloride*, $C_7H_8N_4O_2,HCl + H_2O$, crystallises in colourless rosette-like groups of needles, which lose both water and hydrochloric acid at 100°. The *platinochloride*, $(C_7H_8N_4O_2)_2,H_2PtCl_6 + 4H_2O$, has been described by Glasson. According to the authors, it sometimes contains $4H_2O$ and sometimes $5H_2O$. The *aurochloride*, $C_7H_8N_4O_2,HAuCl_4$, forms yellow tufts of needles. The *sulphate* has been obtained in small colourless crystals, but of varying composition. The *nitrate*, $C_7H_8N_4O_2,HNO_3$, has been described by Glasson. The *acetate*, $C_7H_8N_4O_2,C_2H_4O_2$, forms a white voluminous precipitate, which gradually loses its acid by exposure to the air. In its behaviour to methyl iodide, theobromine differs markedly from caffeïne (p. 873), for on heating the mixture either alone or in solution in alcohol or in chloroform, no combination of the theobromine with the methyl iodide takes place, whilst if a mixture of theobromine, alcoholic solution of potash, and methyl iodide in equivalent quantities is heated at 100° in sealed tubes, caffeïne is produced, identical with the natural bases: $C_7H_8N_4O_2 + KOH + MeI = C_7H_7MeN_4O_2 + KI + H_2O$. On heating theobromine with hydrochloric acid at 240—250°, it suffers decomposition similar to that of caffeïne, yielding ammonia, methylamine, sarcosine, carbonic anhydride and formic acid. The same products are also formed on boiling theobromine with solution of barium hydroxide, and attempts to obtain an intermediate product, *theobromidine* (corresponding with caffeïdine) have as yet been unsuccessful. The bromine-derivative, $C_7H_7BrN_4O_2$, obtained by the direct action of bromine, agrees with the compound described by Fischer. When theobromine is boiled with five parts of concentrated nitric acid in an upright retort until the greater part of the liquid has been volatilised, and the residue then evaporated on a water-bath, amalic acid is obtained. On boiling the latter with concentrated nitric acid a further decomposition takes place, with evolution of carbonic anhydride and formation of methylparabanic acid and methylamine. Maly and Hinteregger (Abstr., 1881, 747) have shown that, besides these products, ammonia is also produced when the oxidation is effected by means of chromic mixture. Caffeïne is decomposed by nitric acid in the same way as theobromine, dimethylparabanic acid, methylamine, and carbonic anhydride being formed, and in this case also no ammonia.

A. K. M.

Occurrence of Caffeïne in Cacao. By E. SCHMIDT (*Annalen*, **217**, 306—308).—In preparing theobromine from cacao (see p. 872), the last mother-liquors yielded a small quantity of a body crystallising in long needles, which the author has identified as caffeïne. In quantitative estimations the two bases may be separated from each other by means of cold benzene. A. K. M.

Action of Hydrochloric Acid on Caffeïne. By E. SCHMIDT (*Annalen*, **217**, 270—287).—It was thought possible that theobromine might be formed by this reaction with elimination of a methyl-group. No reaction, however, takes place below about 240°, the caffeïne then decomposing, with formation of carbonic anhydride, ammonium chloride, methylamine hydrochloride, sarcosine hydrochloride, and traces of formic acid, $C_8H_{10}N_4O_2 + 6H_2O = 2CO_2 + 2MeNH_2 + NH_3 + CH_2O_2 + C_3H_7NO_2$. The reaction is effected in sealed tubes, the temperature being maintained at 240—250° for 6—12 hours; above 260° the product becomes partially carbonised. The caffeïne employed was the pure product obtained from tea. The methylamine hydrochloride is separated and purified by means of its platinochloride, which crystallises partly in lustrous yellow plates and partly in orange-red rosette-like groups. The sarcosine was identified by means of its copper salt, $(C_3H_6NO_2)_2Cu,2H_2O$, sarcosine obtained by the action of barium hydroxide on caffeïne yielding a perfectly similar salt. These results show that caffeïne yields the same products by the action either of hydrochloric acid or of barium hydroxide, except that in the former case the intermediate product, caffeïdine, is not produced. Theobromine is decomposed by hydrochloric acid, with formation of the same products as in the case of caffeïne, but the proportion of ammonia to methylamine is in this case two molecules of the former to one of the latter, showing that the additional methyl-group in the caffeïne must be united with a nitrogen-atom. The fact that only one of the four nitrogen-atoms in caffeïne can be eliminated as ammonia is in accordance with the formula given by Fischer (*Annalen*, **215**, 314), and Medicus (*ibid.*, **175**, 250), but is not explained by Strecker's formula (*ibid.*, **118**, 171).

The author has also very carefully compared artificial caffeïne as prepared by Strecker (*loc. cit.*) with natural caffeïne obtained from tea. His results confirm those previously obtained by Strecker, a comparison of the following salts proving that artificial and natural caffeïne are identical. The *hydrochloride*, $C_8H_{10}N_4O_2,HCl,2H_2O$, forms colourless monoclinic crystals, which give off hydrochloric acid and water by exposure to air, leaving pure caffeïne, the same change taking place rapidly at 100°, or by the action of water or alcohol. The *platinochloride*, $(C_8H_{10}N_4O_2)_2,H_2PtCl_6$, crystallises in small rosette-like groups of needles, and contains variable amounts of water. *Caffeïne aurochloride*, $C_8H_{10}N_4O_2,HAuCl_4,2H_2O$, forms lustrous gold-coloured plates. *Caffeïne methiodide*, $C_8H_{10}N_4O_2,MeI,H_2O$, is formed when caffeïne is heated for some hours at 130° with an excess of methyl iodide in sealed tubes, and may be purified by washing with cold alcohol and crystallising from water, in which it is moderately

soluble, although but sparingly so in alcohol, and almost insoluble in ether.
A. K. M.

Metalbumin and Paralbumin: a Contribution to the Chemistry of Encysted Fluids. By O. HAMMARSTEN (*Zeitschr. Physiol. Chem.*, 6, 194—226).—Our methods of examination for paralbumin and metalbumin in pathological fluids are incomplete and unsatisfactory, yielding results which have not yet proved of value in diagnosis. Owing to the physical nature of the fluid contents of cystic tumours, frequently tenacious, ropy, scarcely possible of filtration, and brown-coloured, as in ovarian cysts, the investigation is beset with peculiar difficulties. The author's observations were conducted on the fluid contents of some 40 ovarian cysts, which were placed at his disposal during the past year. They are to be regarded as a preliminary contribution to the elucidation of the subject.

Metalbumin.—This name was given by Scherer in 1852 to a proteid substance which he had discovered in the fluid of an ovarian cyst. In 1864, Eichwald, in his monograph on the "Colloïd Degeneration of the Ovaries," ascribed metalbumin a place between serum-albumin and peptone, being, like paralbumin, a transition stage between the two, but more nearly allied to peptone. Metalbumin is not, as stated by Méhn (*Arch. Générales de Med.*, 2, 1869), precipitable by magnesium sulphate, whilst paralbumin under certain circumstances may be. The author describes processes for the separation of metalbumin and paralbumin, which are preferable to those of Plósz, inasmuch as by employing fractional precipitation by alcohol they are obtained free from albumin. Analysis in the case of metalbumin yielded these results:—

	C.	H.	N.	S.	O.	Ash.
I.	49·44	7·11	10·30	—	—	—
	49·45	6·91	10·26	—	—	1·1
II.	50·0	6·84	10·27	1·25	31·54	1·4

He considers metalbumin more closely related to mucin than to albumin, and that the name *metalbumin* being misleading, that of *pseudomucin* might be provisionally bestowed upon it.

In his treatise on "Colloïd Degeneration of the Ovaries," Virchow pointed out that when the colloïd tumour becomes cystic a softening of the colloïd substance is effected. Recollecting that he also showed that the alkaline solution of the colloïd substance is no longer precipitable by acetic acid, the presumption is great that Scherer's metalbumin is only a changed and liquefied colloïd.

Paralbumin.—This was also discovered by Scherer in ovarian fluid. It corresponds with metalbumin in many of its reactions, but differs chiefly in this, that in boiling, as also after the addition of certain reagents, which fail to throw down metalbumin, but only make the solution opalescent or milky, paralbumin is precipitated. It is probable that paralbumin is a mixture of pseudomucin with varying quantities of albumin. The author prepared it by addition of albumin to metalbumin (pseudomucin), and analysis confirmed the same view, affording varying results, as follows:—

	C.	H.	N.	S.
1.	50·20	6·79	11·22	—
2.	50·94	6·92	12·00	1·75
3.	51·80	6·93	12·84	1·66
4.	—	—	13·46	1·80
5.	52·34	7·19	14·52	—

According to the author's experience, his observations are in accordance with those of Hoppe-Seyler, that paralbumin is only a mixture of a mucoïd substance, *pseudomucin*, with varying proportions of albumin, chiefly serum-albumin. So far as he has found, ovarian fluids contain no specific albumins—the so-called metalbumin and paralbumin—but only very small quantities of peptone, varying amounts of globulin and serum-albumin, besides a never-failing constituent in the form of a substance allied to mucin, which he has provisionally termed, as above stated, *pseudomucin*. It is to this substance that ovarian fluids owe their peculiar property: when it is found almost free from adherent albumin, then we have Scherer's metalbumin; on the other hand, when the proportion of albumin is greater, the reactions are those of Scherer's paralbumin.

D. P.

Physiological Chemistry.

Action of Calcium, Barium, and Potassium Salts on Muscle. By T. L. Brunton and T. Cash (*Proc. Roy. Soc.*, **35**, 63).—It has been observed by Ringer that calcium salts prolong, but that the subsequent addition of potash diminishes the contraction of the frog's heart. The authors in the present note show that the action of calcium and potassium salts on voluntary muscles is similar to that which they exert on the gastrocnemius. Barium salts produce a curve of contraction resembling in its form and modifications that produced by veratria, and similarly restored to the normal state by potash. The authors propose to develop the relations existing between groups of elements as regards their physiological action in accordance with Mendelejeff's classification.

V. H. V.

Secretion by the Kidney fed with Defibrinated Blood. By M. Abeles (*Monatsh. Chem.*, **4**, 325—336).—In these experiments the kidney was excised from a recently killed dog which had been fed with defibrinated arterial blood, diluted with one-third of its volume of a solution containing 0·6 per cent. of sodium chloride and $\frac{1}{20000}$ of sodium hydroxide; small quantities of urea, sugar, or glycocine being added in various experiments. The mixture was heated to 35—40° before use. The general result was to show that when the kidney is fed with the diluted blood alone, no secretion flows from the ureter, whilst the addition of urea, sugar, &c., to the blood, leads to the secretion of a liquid in which such crystalloïd substances are present in relatively larger quantity than in the blood employed.

A. J. G.

Formation of Uric Acid in the Animal Economy. By A. B. Garrod (*Proc. Roy. Soc.*, **35**, 63—65).—The author has determined the solubility of uric acid and its more important salts at the temperature of the healthy human body, and has investigated the action of ammonium and sodium urates on their chlorides and phosphates, when mixed with each other in various proportions. Observations were also made on the composition of urinary excretions of the lower animals, whereby it was shown that in the semi-solid urines of birds, reptiles, and invertebrata, the urate is in the form of spherule aggregates, consisting of a number of smaller spherules, united with or contained in colloïd cells.

The author lays stress on the varying amounts of uric acid excreted by different animals in relation to the elimination of nitrogenous substances, and the excessively large excretion of uric acid by birds, reptiles, and invertebrata as compared with the weight of their bodies. Thus a bird throws out relatively to its weight a thousand times more uric acid than a man.

It is also shown that whereas in the kidneys uric acid exists as an ammonium salt, in the blood and different tissues it exists as a sodium salt.

The results of the investigation show that uric acid is not, as hitherto supposed, formed in the animal body during the metabolism of its various organs and tissues, then thrown into blood, and after filtration through the kidneys eliminated from the system; but that it is absolutely formed in the renal organs by the action of peculiar cells, in which it probably exists as the urate of a compound ammonium, readily decomposed into uric acid and ammonia. As such it is secreted, by it the ammonium is replaced, and sodium or other metal when its secretion is obtained by mechanical means or by disease. At times it is deposited as a crystalline sodium salt in the cartilaginous and fibrous tissues. Experiments were also made on the decomposition of uric acid by hippurates and benzoates. Glycine, glucose, and glycerol have no such effect. V. H. V.

Formation and Decomposition of Tyrosine in the Body. By H. Blendermann (*Zeitschr. Physiol. Chem.*, **6**, 234—262).—Tyrosine is a product of the decomposition of albuminoïds, from which, as well as from allied substances, it may be formed by the action of acids or alkalis at a boiling temperature, and also by the influence of certain ferments, especially the trypsin of the pancreas. The constant association of tyrosine in such decompositions of albumin makes it *à priori* probable that it is also formed in the animal body on the breaking up of proteïds. This fact has already been established by Kühne and others. The proportion of proteïd which is thus changed into leucine and tyrosine to that which is absorbed from the alimentary canal as peptone is variable and dependent on several conditions, particularly upon the rapidity of the absorption process, and the circumstances more or less favourable to an abundant development of putrefactive ferments. The question as to whether tyrosine is to be regarded as a normal product of tissue-change in healthy organs is an open one. Virchow long ago referred its presence to cadaveric changes; Naunyn, Neukomer, and others had found it in pus, and lately Leyden discovered it in the sputum of a girl suffering from hæmoptysis. Tyrosine has been abundantly found in pancreatic juice; but according to Kühne, not in the *fresh* secretion. Huber found it in normal organs, especially in fresh spermatic fluid; and he meets Virchow's statement by the results of experiments which show that on free access of air, cadaveric decomposition of albumin yields neither leucine nor tyrosine. Radziejwsky's researches are, however, opposed to these views of Huber's. Hoppe-Seyler has expressed himself of all investigators most decidedly against the occurrence of tyrosine in the normal organism during life. According to him, it is a pathological product of cell-albumin, and occurs when too limited quantities of oxygen are conveyed to the tissues. Thus formed, it may under certain conditions pass away in the urine. Tyrosine is found in the organs in different diseases, almost always together with leucine, and often in considerable quantities. Frerichs has found it in the liver and in the bile, in smallpox and typhus fever; Frerichs and Städeler in acute atrophy of the liver; Scherer in the liver of a drunkard dying of typhus; Huber in the spleen, liver, and kidneys of leukæmia; and Sotnischewsky in the lungs in pneumonia. In cases of phosphorus poisoning, tyrosine has been found in the liver, kidneys, and blood by various investigators. Pouchet asserts that it is further present in traces in healthy urine, and numerous observations accord it, with or without associated leucine, a place in the urine in various disorders. In the urine of acute yellow atrophy of the liver, tyrosine with leucine would appear to be constantly present; but less frequently in the urine in cases of phosphorus poisoning, although all observers agree as to its presence in the liver and other organs. In other diseases tyrosine is rarely present in the urine. Anderson has, however, asserted the contrary. Several observations have quite recently been made regarding the fate of tyrosine in the system. Schultzen and Nencki found increased secretion of urine after administering tyrosine to dogs, and conjectured that this substance might be a transition stage in the formation of urea from the physiological destruction of tissue in man. Brieger found that after giving tyrosine, the excretion of phenolsulphuric acid was enormously increased. The researches of Baumann have established the presence of certain aromatic bodies in the normal urine of man and other animals, which, according to his investigations and those of Brieger and Weyl, are derived from the breaking up of albumin or of tyrosine.

The relations of these aromatic bodies to tyrosine may be readily shown. The now established formula of the latter is

$$C_6H_4(OH).C_2H_3(NH_2).COOH$$

(amido-hydroparacoumaric acid). From it by putrefaction are formed hydroparacoumaric acid, $C_6H_4(OH).(CH_2)_2COOH$; parahydroxyphenylacetic acid, $C_6H_4(OH).CH_2.COOH$; paracresol, $C_6H_4Me.OH$;

and phenol, $C_6H_5.OH$. The occurrence of phenol in the urine had been observed by Städeler, Lieben, and others; but its origin was referred to certain of the vegetable constituents of food, previously to Baumann showing that it was likewise present in the urine of flesh-fed dogs, and that it is a constant putrefactive product of albumin. Brieger also showed that phenol with other aromatic bodies is a constant constituent of fæcal matters. One must, with Baumann and Brieger, regard albumin as the only source of phenol and paracresol in these cases. In harmony with this view are the numerous observations of Brieger in the occurrence of phenol in various diseases; also those of Salkowsky, including an increased excretion of phenol after ligature of the gut. The author also found the same increase in a case of severe intermittent fever. Weyl first proved that phenol and paracresol are formed by the putrefaction not only of albumin, but likewise of pure tyrosine. Baumann obtained hydroparacoumaric acid and parahydroxyphenylacetic acid from the putrefaction of pure tyrosine, the last-named acid being also obtained by E. and H. Salkowsky from putrid albumin. Both of these acids were further decomposed by septic ferments, and yielded paracresol and phenol.

The experiments on the putrefaction of albumin and tyrosine thus cited afford simple and clear views of the relations of the substances occurring in urine to tyrosine. Experiments regarding the excretion of phenolsulphonic acid, and also of the aromatic hydroxy-acids in artificial digestion of tyrosine have not yet been made, save the important observation of Brieger to the effect that in man the administration of tyrosine is followed by an increased excretion of phenol. In the author's experiments an attempt has been made to determine the fate of tyrosine in the system. The formation of yet another substance from tyrosine was also held in view, hydroxymandelic acid, which hitherto has only once been found by Schultzen and Riess, and which undoubtedly stands in close relation to tyrosine, having the formula $C_8H_8O_4$. Baumann did not succeed in finding it among the products of the putrefaction of tyrosine. Tyrosine was introduced into the system in these experiments in two ways; either formed in the system itself by phosphorus poisoning, or administered by the mouth.

I. *Phosphorus Poisoning.—a. In Man.*—In several cases of phosphorus poisoning admitted to the Charité Hospital, the examination of the urine for tyrosine yielded negative results. Two, however, gave positive evidence of its presence. One of them, a child, had poisoned herself with lucifer matches, and died on the seventh day, when the urine was at once examined. Tyrosine crystals were obtained, yielding all the characteristic reactions, and likewise aromatic hydroxy-acids in large amount (580 c.c. urine yielded 0·2475 gram, m. p. 167—168° C.). The second case was of a coachman who had swallowed some prepared rat poison by mistake for cheese. Death likewise followed on the seventh day, when the urine, on examination, yielded tyrosine; its identity was established by a combustion. Leucine was also found. No tyrosine had been detected on the sixth day. This sudden change between the sixth and seventh days was accompanied by an increase of phenolsulphonates and diminution of the sulphates, an increase which the author ascribes to probable increased excretion of phenol and paracresol.

b. In the Dog.—The results of two experiments were entirely negative in regard to the presence of tyrosine. On the other hand, there was an increase of aromatic hydroxy-acids and of phenol. The increase of the hydroxy-acids would nevertheless point to the formation of tyrosine, probably from destruction of the tissue of glandular organs.

II. *Administration of Tyrosine in the food.*—*c.* In the several series of experiments carried out upon dogs, men, and rabbits, the author found the following bodies in the urine, which may be regarded as products of its transformation:—

1. Phenols in large quantities (man, rabbit).
2. Normal hydroxy-acids in increased quantity (dog, rabbit).
3. Tyrosine hydantoïn (rabbit).
4. Hydroxyhydroparacoumaric acid (rabbit).

Those named in 3 and 4 appear only in the urine of animals when saturated, so to speak, with tyrosine; so that it is readily explicable why these should be absent from normal urine. Under 2, the absence of hydroxy-acids in man is remarkable. An interesting accordance is observable between the results of administration of tyrosine and of phosphorus poisoning in the dog, in both instances there being increased formation of normal hydroxy-acids and absence of more than mere traces at most of phenol. The author concludes his paper with notes on the detection of tyrosine in the urine. This has hitherto depended upon its separation by the Frerichs-Städeler method. The reactions for the identification of tyrosine are especially those of Hoffman (red coloration with Millon's test) and of Piria-Städeler, in which the sulpho-acid of tyrosine is formed, which, in neutral solution, gives a blue colour with ferric chloride. This latter test can only be made with pure tyrosine, and the former gives similar reactions with other bodies present in normal urine, such as phenols and hydroxy-acids. Other unknown constituents of urine also give reactions with Millon's test.

From these considerations he regards Anderson's observations referred to at the outset of this paper with distrust. He has further to this end examined the urine of patients in the Charité Hospital under the care of Ehrlich and Brieger, including two consumptives, a case of pneumonia, of acute articular rheumatism, hydatid of the liver and carcinoma of the liver, without in any case finding tyrosine, much less leucine, in the usual way, although Millon's test, as in the case of normal urine, gave reaction. Hoppe-Seyler has also failed to detect tyrosine in a long series of severe cases of typhus fever and other diseases. D. P.

Chemistry of Vegetable Physiology and Agriculture.

Easily Oxidisable Constituents of Plants. By J. REINKE (*Zeitschr. Physiol. Chem.*, 6, 263—279).—It is a well-known fact that the juices of many plants become discoloured on exposure to the air. So, too, sections of stems and roots of leaves and fleshy fruits which acquire a brown colour on exposure. Little has been ascertained in regard to the physiology of these changes. They obviously depend upon the oxidation of certain constituents; this is seen, for instance, on exposing grated potatoes to the air, when the uppermost layer assumes a brown colour, which by frequent turning over of the mass may be communicated throughout. The same is seen in the case of the expressed juice of the potato. Putrefaction or fermentation, and reducing agents, such as sulphurous or hydrosulphuric acid, decolorise these fluids. The juice of the white sugar-beet is even more sensitive, becoming on exposure to the air immediately of a dirty wine-red colour, then violet, brown, and finally almost black. These facts indicate the presence in plants of easily oxidisable bodies, and inasmuch as the products of their oxidation do not occur within the uninjured cells, it follows that there is either no free oxygen in the latter, or that with these oxidisable substances other reducing substances are concomitant, hindering their oxidation, or again, that in the protoplasm oxidation affords other uncoloured products. Upon which of these three factors the colourless state of the protoplasm and cell-juice of living plants depends is not yet decided.

In the study of oxidation processes in the living plant-cell, an important question presents itself, as to whether substances occur in the cell which at ordinary temperatures unite with atmospheric oxygen without the essential co-operation in this process of the living protoplasm. Difficult as the problem is, the isolation and determination of constitution of these easily oxidisable substances forms an indispensable preliminary step. It may be conjectured that they belong to the aromatic series. In this connection the numerous hydroxybenzene derivatives claim attention, of which many are known to be easily oxidisable. Pyrogallol in alkaline solutions greedily absorbs oxygen and becomes decomposed into carbonic anhydride, acetic acid, and a brown body of unknown nature. The dihydroxybenzenes (catechol, resorcinol, and quinol) are easily oxidisable bodies, and their methyl derivative orcinol is coloured red by the air. As regards derivatives of the anthraquinone series, there is the change of indigo-white into indigo-blue, and the behaviour of *Boletus luridus*, the colourless section of which becomes at once blue on exposure to the air. Lastly, there is a series of complex plant-constituents, undoubtedly benzene derivatives, although their constitution has not yet been ascertained, which exhibit many analogies to the discoloration of plant juices. Of these Brazilin may be named, the colourless aqueous solution of which becomes first yellow, then reddish-yellow in the air.

The author, in his endeavours to isolate the easily oxidisable constituents of the sugar-beet and potato to which the discoloration of their respective fluids is attributable, succeeded in the first instance in isolating from the beet-root a chromogen which on exposure to the air acquired a red colour. This substance he has accordingly designated *Rhodogen*. The product of its oxidation he terms *beet-red*, and he notes certain remarkable analogies between the absorption-bands of this substance and of the colouring matter of *Anchusa tinctoria*, alkanet-red, the spectrum of each showing three bands occupying identical positions. These investigations have therefore so far afforded proof of the existence in the colourless cells of the sugar-beet of an easily oxidisable colourless body, capable of isolation, which by itself, without the aid of the living plasma of the plant, can split up the oxygen molecule, forming a coloured substance.

The isolation of the chromogen of the potato has not succeeded so satisfactorily. The presence of vanillin in the juice appeared to be shown by the strong odour of vanilla. Vanillin has been detected by Scheibler in raw beet-sugar. A substance resembling catechol, but not identical with it, was also separated. It would seem to be the same body discovered by Gorup-Besanez in the leaves of *Ampelopsis hederacea*. It is undoubtedly an acid, and amongst the known aromatic acids most closely corresponds in its reactions with hydrocaffeic acid. In conclusion, the author suggests the hypothesis that these easily oxidisable bodies belong, in their physiological relations, to the retrogressive series, perhaps originating from the breaking up of albumin, or formed by the synthesis of the products of such decomposition, and that in these features they are allied to the process of respiration. D. P.

Studies on Ripe Grapes. By C. AMTHON (*Zeitschr. Physiol. Chem.*, **6**, 227—233).—In a paper on the analysis of wines by Amthor and Musculus, which appeared in the *Zeitzchr. Anal. Chem.* for 1882, it was pointed out that extraordinarily high proportions of extract and phosphoric acid were present in wines prepared from unripe grapes. The must of these wines, however, not being then at the author's disposal, this investigation has been made in supplement to the former, and the must, seeds, and wine resulting after completed fermentation of purple grapes at three successive stages, viz., first stage of ripening, of approaching maturity, and of full maturity, have been severally examined. The results may be summarised as follows:—

1. At the beginning of the process of ripening, the grape must becomes poorer in mineral ash, containing, for example, 28·3 per cent. less on the 4th of September than on the 10th day of August.

2. The phosphoric acid of the must becomes less in the same proportion, 29·7 per cent. less on September 4th than on August 10th.

3. After fermentation of the must at the early stage of ripening, the wine is also poorer in extract; 33·2 per cent. of extract less on September 4th than on August 10th.

4. During fermentation phosphoric acid is consumed by the yeast formation, and the more so in proportion to the sugar which is present, the loss being at early stages 14·7 per cent. (August 10),

21·6 per cent. (August 22), but after full maturity 47·5 per cent. (September 4).

5. The amount of ash-constituents in the seeds or grapestones, and likewise of phosphoric acid, gradually increases with the process of ripening.

6. The ratio of phosphoric acid (P_2O_5) to ash in the must is at all three stages nearly constant, 1 : 9·5.

7. The ratio of P_2O_5 to the ash of the stones is also constant at all stages, 1 : 3·5.

The author concludes that inasmuch as these constants remain unaffected in spite of the increase of ash and P_2O_5 during the ripening of the stones on the one hand, and of their decrease during this process in the must, a certain proportion of the mineral constituents of the grape-juice which is unaccounted for in either must or stones, must pass into the stems. Also a part of the bases in combination with the phosphoric acid, chiefly potash, must become free and go over to another acid. As the tartaric acid of the grape is chiefly changed to potassium tartrate, this must be the destiny of part of the potassium. But the whole of the potassium is not present, as Neubauer assumes, to be employed in neutralising the free tartaric acid during ripening; but free tartaric acid is present partly in order to unite with the potassium which had been previously combined with phosphoric acid, the latter being taken up by the grape stones or kernels.

D. P.

Influence of Manuring on the Composition of Potatoes. By VIBRANS (*Dingl. polyt. J.*, **248**, 179).—In order to determine the influence of nitrogenous manures on the percentage of starch in potatoes, Vibrans cultivated good sandy loam soil with so-called "alcohol potatoes." It was found that with sodium nitrate a larger yield of potatoes was obtained than without the use of manure. From the composition of the potatoes, however, it was shown that the larger the amount of nitrate used, the smaller was the quantity of solid matter and starch contained in the potatoes, so that it must be concluded that nitrogenous manures act injuriously on their constitution.

D. B.

Analytical Chemistry.

Estimation of Iron and Steel. (*Dingl. polyt. J.*, **248**, 213—216.)—For determining the total carbon in pig-iron and steel, Starr treats 3 grams of steel or 1 gram of iron with 50 c.c. of a dilute neutral solution of cupric chloride placed in a small beaker, and agitates the mixture so as to separate the copper in a spongy form. When the reaction is ended, 50—75 c.c. of a concentrated solution of cupric chloride, and 10 c.c. concentrated hydrochloric acid are added, and the whole is heated on a water-bath until the copper has been dissolved, and the liquid is finally passed through an asbestos filter. The separated carbon is washed with hot water, then with alcohol, after which the contents of the funnel are transferred to a combustion tube and burnt in a current of oxygen, the carbonic anhydride evolved being absorbed by means of soda-lime.

Eggertz has made a series of estimations of carbon in iron, both by the iodine method and colorimetrically, and finds that the results obtained by the two methods agree very closely with one another.

According to Woodcock, the hardness of steel depends on the conversion of the carbon into a form resembling the diamond. Cementation steel, as obtained from the furnace, is, in spite of the increased amount of carbon, as soft as the wrought iron used in its preparation. If it be then heated and cooled suddenly, it becomes hard, its fractured surface showing numerous crystals resembling diamonds. Woodcock assumes that at a red heat the molecules expand, with partial separation of carbon, which is not re-absorbed when cooled suddenly, but separates by the aid of a small amount of hydrogen in the form of diamonds. When, however, the cooling is effected gradually, no crystallisation, and consequently no hardening, occurs.

According to Goetz, the estimation of manganese in iron is effected colorimetrically at the Cleveland iron works, Ohio. Ledebur mentions that this process is recommendable only for iron containing not more than 2 per cent. manganese.

For determining silicon in iron and steel, Drown and Shimer dissolve the metal in the form of filings in hydrochloric acid, evaporate to dryness, treat the residue with dilute sulphuric acid, filter, wash with hydrochloric acid and hot water, dry, ignite, and weigh. For determining the sulphur in iron and steel, Craig recommends to dissolve the sample in hydrochloric acid, and absorb the gas evolved in an ammoniacal solution of hydrogen peroxide, the sulphuric acid formed being precipitated with barium sulphate. Rocholl states that the presence of copper interferes with the reaction, as a portion of the sulphur is retained by the same. D. B.

Determination and Investigation of Drinking Water. (*Dingl. polyt. J.*, **248**, 37—39.)—According to Mallet (*Chem. News*, **46**, 63), the injurious effects produced by drinking polluted water do not depend on the chemical constitution of the organic matter, but on the presence and action of living organisms. In the determination of the organic matter by combustion according to the directions of Frankland, there is a loss of carbon and gain of nitrogen, varying in amount with the dilution of the solutions. The loss of carbon is due to the volatilisation of butyric acid and other volatile substances during the evaporation of the water with sulphurous acid; the gain of nitrogen is occasioned by absorption of ammonia from the surrounding atmosphere during evaporation. In conducting the albuminoïd ammonia process in accordance with Wanklyn's instructions, there is a loss, resulting from the fact that on boiling with alkaline permanganate, part of the nitrogen is volatilised as amines, and escapes detection by the Nessler reagent. Concordant results are said to be obtained by Tidy's method, using the acidified permanganate at the ordinary temperature.

Mallet recommends extending the time during which the permanganate is allowed to act in the Tidy process to 12—24 hours, determinations being made at intervals of three to six hours, in order to trace the progress of the oxidation. According to Stapleton (*Chem. News*, **46**, 284) the preparation of the alkaline permanganate solution is effected by dissolving caustic potash in water containing calcium carbonate, in order to remove all nitrogenous matter present. The clear solution is then mixed with potassium permanganate dissolved in distilled water and heated to boiling, to remove further traces of ammonia.

For estimating ammonia in potable waters by distillation, Tichborne uses an arrangement of bulbs which he connects with the receiver, and fills with distilled water. Any accidental contamination with atmospheric ammonia is thereby avoided.

For the determination of nitrites in water, Davy (*Chem. News*, **46**, 1) recommends the use of an aqueous solution of gallic acid, decolorised by boiling with animal charcoal, filtering, and treating whilst hot with dilute sulphuric acid. This solution gives with water containing nitrous acid a brown coloration, the depth of the colour produced being in direct proportion to the amount of nitrite reacting on the gallic acid, so that it affords a ready means for the quantitative determination of the nitrites. If ferric oxide is present, it must be removed by precipitation with ammonia.

For the volumetric determination of the carbonates of calcium and magnesium in water free from calcium sulphate, Houzeau (*Compt. rend.*, **95**, 1064) treats 100 c.c. with a solution of cochineal, and adds a solution of oxalic acid until the mixture assumes a permanent yellow colour. The quantity of oxalic acid used is in proportion to the total amount of carbonates. The precipitate of calcium oxalate is filtered off and titrated with potassium permanganate. The difference of the two determinations gives the quantity of magnesia present. D. B.

Detection of Anhydrous Glucose mixed with Refined Cane-sugar. By P. Casamajor (*Chem. News*, **47**, 252—253).—If ordinary glucose is mixed with the cane-sugar, and the adulterated sugar is moistened and stirred with water, the glucose will appear as chalky white specks in the translucent mass of wet sugar; if, however, crystalline glucose is present it cannot be detected in this manner, as it also becomes translucent when moistened. Washing the suspected sugar with a saturated solution of glucose in methyl alcohol is not an efficient method, some of the glucose being dissolved. The optical saccharometer may be used to determine if starch glucose is present in a sugar, for by observing the deviation immediately after getting the solution ready for the saccharometer, and repeating the observations at sufficiently wide intervals of time, the presence of dextrose in any notable quantities will be indicated by a decrease in the deviation. From experimental results the author points out that dextrose does not prevent good results being obtained by inversion, provided that the observations both before and after the inversion are made when the deviation power of the dextrose is constant. The author recommends the following as a simple and efficient test for the presence of either anhydrous or hydrated glucose. Equal quantities of the suspected sugar and of unadulterated refined sugar are respectively put into two beakers, moistened with water, stirred to get them uniformly wet, and the beakers are then placed in warm water; in about ten minutes the pure sugar will appear more moist than when cold, whilst the other sugar if it contain sufficient glucose, will have sunk into a pasty sticky mass. On cooling, the pure sugar will become drier again, whilst the impure sample will remain sticky. Immersion in warm water is not necessary, but it makes the effect immediate and more marked. This test is founded on the property which cane-sugar has of forming viscid compounds with many substances, among which are anhydrous and hydrated dextrose. Molasses is an example of these compounds. As long as a mixture of cane-sugar and dextrose is dry, it looks all right, but as soon as sufficient water is added, the substances which form the molasses can combine, and enough viscous syrup is formed to produce the permanently pasty mass described above. The sugar-maker knows this, and is always careful to dry his sugar before mixing with glucose. In fact adulterated sugars always come into commerce drier than refined sugars of the same grade, which are always sold moist. Fehling's solution is also a useful indicator for detecting glucose; an ordinary refined sugar will rarely show more than 5 per cent. of glucose, so that any considerable excess over this quantity may be looked upon as adulteration. D. A. L.

Detection and Estimation of Phenols and Hydroxy-acids in the Urine. By E. BAUMANN (*Zeitschr. Physiol. Chem.*, **6**, 183—194).—A summary of the several methods employed by the author in his previously published researches on this subject, which have proved best adapted for the separation and estimation of the several urinary constituents in question. D. P.

Detection of Albumin in Urine. By A. B. HASLAM (*Chem. News*, **47**, 239—240).—The suspected urine is mixed with a few drops of sodium chloride solution, and then some iron chloride is carefully poured on so as to form a layer; the appearance of a whitish cone shows the presence of albumin. If phosphates are present the urine must be rendered acid with acetic acid before applying the test. This test is much more delicate than the old nitric acid test.

D. A. L.

Detection of Rice-meal in Buckwheat Flour. (*Dingl. polyt. J.*, **248**, 219.)—On warming 1 gram of meal with 2 c.c. of strong caustic potash solution until the mixture assumes a pasty consistence, rice-meal gives a yellow colour which turns white when hydrochloric acid is added, whilst the paste formed with buckwheat flour has a dark green colour and turns red with hydrochloric acid. On treating rice-meal with alcoholic hydrochloric acid, the liquid remains colourless, whereas it assumes a brownish colour with buckwheat flour. D. B.

Technical Chemistry.

Contributions to the Knowledge of Sewer Gases. By F. Fischer (*Dingl. polyt. J.*, **247**, 501—504).—It is known that the antagonists to the sewer system maintain that through the gases in the sewers, epidemic diseases, viz., cholera, typhus, diphtheria, scarlatina, &c., are propagated, without, however, attempting to prove their assertions by comparative tests of the gases. The author has made a series of investigations on the gases from the sewer in the Gustav-Adolfstrasse in Hanover. He found that during 14 months the pressure of the air in the sewer only in one instance exceeded that of a water-column 9 mm. in height, whilst the maximum external pressure towards the sewer amounted to 10 mm., so that a water-column 20 to 25 mm. high would have prevented the entrance of sewer gases into the houses. The variations of pressure are considerably lessened when sewers are provided with ventilators. With regard to the composition of the gases, the author found $CO_2 = 0·9$ to $1·8$ per cent., $O = 19·3$, NH_3 and H_2S = traces. By comparing these results with the analyses of the gases from other towns (see Renk, *Kanalgase*, p. 13), illustrated by the following table, it will be seen that the sewer gases from towns worked by the carriage system are often more contaminated with noxious impurities than the gases from towns containing properly constructed sewers:—

Sewers in	CO_2. Per cent.	O. Per cent.	NH_3. Mgrms. per lb.	H_2S. Per cent.
London, according to Letheby	0·532	—	much	traces
London, according to Miller	0·106—0·307	20·7	—	—
Paddington, according to Russell	0·51	—	small amount	—
Boston, according to Nichols	0·082—0·24	—	—	—
Munich, according to Beetz	0·217—0·443	—	7—168	—
Paris, according to Glauboy	2·3—3·4	17·4	—	1·25
Paris, according to Levy	—	—	0·09	—
Hanover, according to Fischer (winter) ...	0·9—1·8	19·3	traces	0 to traces
Hanover, according to Fischer (summer)...	2·1—3·53	16·9—18·2	traces to 50	traces

Whilst doubting whether the spreading of diseases is at all effected by the sewer gases, the author maintains that the contents of sewers are at least no more injurious than those of cesspools; moreover, the gases ascending from dry closets must be the most harmful.

D. B.

Working of Sulphuric Acid Chambers. By H. PEMBERTON, JUN. (*Chem. News*, **47**, 266—267).—The author has made observations extending over several years, and on chambers which have been doubled in number and capacity during the time. From numerical data gathered in these observations, he finds that when the chambers are working well, the percentage of nitre used multiplied into the capacity in cubic feet per pound sulphur burnt, gives a nearly constant product—about 280; thus a chamber of 280 cubic feet capacity per pound sulphur will require 1 per cent. nitre, one with 140 cubic feet 2 per cent., one with 14 cubic feet 20 per cent., and so on. Therefore the chamber capacity in cubic feet, multiplied by the per cent. nitre used, and divided by the number of pounds of sulphur burnt daily, should give near about 280 (or better still 300) if the chambers are working well, and any number much lower than this would indicate a low yield of acid. The nitric acid introduced into the Glover tower is taken into account in these remarks. These results are from the author's experience with this set of chambers only. D. A. L.

Notes on the Soda Industry. By A. SCHEURER-KESTNER (*Bull. Soc. Chim.* [2], **19**, 409—423).—I. *Loss of Sodium in the Le Blanc Process.*—Eleven years ago the author established that the loss of sodium experienced in the Le Blanc process is proportional to the quantity of chalk employed. It is thus to the interest of the manufacturer to avoid excess of chalk, but at the same time to use a quantity sufficient to ensure perfect whiteness of the finished product. The author put forward the hypothesis that the loss is occasioned by the formation of a sparingly soluble calcium-sodium carbonate; this view has been confirmed by the researches of Jurisch, Watson Smith, and Liddle and Reidemeister. The latter has found in the lixiviating vats crystals of the composition of gay-lussite, $Na_2CO_3,CaCO_3,5H_2O$, a compound insoluble in sodium carbonate and hydrate, mixed in the proportion in which they occur in the crude lye; it dissolves slowly in water, the crystals becoming opaque from the ready dissolution of the sodium carbonate.

Reidemeister has further shown that gay-lussite is formed not only in the lixiviating vats, but also in the anhydrous state in the soda pans during fusion; it probably also occurs in the residues, and the deposit of the caustification process, but its state of division prevents its detection and isolation.

II. *Presence of Vanadium, Fluorine, and Phosphorus in Crude Soda-lyes.*—In 1864 Rammelsberg detected the presence of vanadium and of sodium phosphate, $Na_3PO_4,10H_2O$, in crude soda-lyes; Baumgarten, a short time after, found fluorine existing as a double sodium phosphate and fluoride, $NaF_2Na_2PO_4,18H_2O$. From the red mother-liquors in the manufacture of the carbonate and hydroxide, Rammelsberg separated crystals, either white, or red from the presence of iron, which proved on analysis to be identical with Baumgarten's compound; they also contained about 1·2 per cent. of vanadic acid. It is probable that the chalk and coal furnish the vanadium and phosphorus; the origin of the fluorine is quite uncertain.

III. *Loss of Sodium in Caustification.*—The author has previously shown that the loss of sodium in caustification arises from the same cause as the loss of sodium in the Le Blanc process, *i.e.*, the formation of a double sodium calcium carbonate. Analyses by Jurisch (*Chem. Indust.*, 1880, 377) would lead to the conclusion that this loss is less the greater the excess of lime; but this statement is in direct contradiction to experience. According to Jurisch, the density of the liquor for caustification should not exceed 14° Baumé; the author, however, points out that under ordinary atmospheric pressure it is impossible to caustify denser liquors than these, for the reaction became incomplete owing to a commencement of a reverse chemical change. The author also criticises Jurisch's statements as regards the amount of combustible substance required for the evaporation of caustic soda of various densities.

In the remainder of the paper no new chemical facts are detailed; the author quotes, and offers some critical remarks upon Weldon's statements as regards the extraction of ammonia from coal, the use of pyrites from Rio Tinto for the manufacture of sulphuric acid, and the total production of sodium carbonate from the Le Blanc and the ammonia processes throughout the world. V. H. V.

Analyses of Bauxite. By L. MAYER and O. WAGNER (*Dingl. polyt. J.*, **248**, 213).—The samples of bauxite, Nos. 1 to 8, were taken from Feistritz in the Wocheïn, No. 9 from Pitten near Wiener-Neustadt. The latter, though resembling bauxite in physical properties, is in reality clay-ironstone :—

Sample.	Hygroscopic moisture.	Water (combined).	Al_2O_3.	Fe_2O_3.	SiO_2.	Mn_2O_3.	CaO.	MgO.	P_2O_5.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
1	2·33	13·86	29·80	3·67	44·76	—	2·75	0·84	1·47
2	1·03	27·85	43·22	14·39	10·43	—	1·61	—	1·13
3	0·84	27·61	38·38	18·29	12·32	—	1·66	—	0·79
4	0·79	26·80	40·60	22·70	6·66	—	2·10	—	0·35
5	1·30	27·70	50·38	11·68	8·34	traces	traces	traces	0·61
6	1·34	23·12	33·86	25·69	12·41	2·42	traces	—	0·53
7	1·31	23·81	46·18	22·05	4·82	—	0·89	—	0·66
8	0·95	20·83	62·10	6·11	5·06	2·01	3·20	traces	traces
9	1·17	4·75	21·80	3·75	60·10	—	6 06	2·49	traces

Bauxite No. 1 had a white colour, Nos. 2 to 5 were pale yellow, and Nos. 6 to 9 red. D. B.

Clay and Earthenware Goods. (*Dingl. polyt. J.*, **248**, 167—171.)—Some specially selected specimens of best American clays were investigated by Bischof. According to Cock, State Geologist, New Brunswick, they had the following composition :—

No. of sample.	1.	2.	3.	4.	5.	6.
Al_2O_3	41·10	40·72	40·09	39·14	38·81	38·34
SiO_2	38·66	34·10	43·93	44·20	44·14	42·90
Sand	3·10	6·50	0·60	0·20	0·80	1·50
MgO	—	0·39	—	—	0·11	—
CaO	—	—	—	—	trace	—
Fe_2O_3	0·74	2·49	0·88	0·45	1·14	0·86
K_2O	0·46	1·91	0·20	0·25	0·17	0·44
Loss by ignition	13·55	12·35	13·80	14·05	12·97	13·50
Hygroscopic water	1·00	1·35	0·50	0·90	1·23	1·10
TiO_2	1·20	—	—	1·05	1·30	1·20

No. of sample.	7.	8A.	8B.	9A.	9B.
Al_2O_3	38·24	37·02	21·83	36·35	38·38
SiO_2	43·90	42·95	67·33	40·10	45·45
Sand	1·10	3·85		0·40	0·77
MgO	0·11	—	0·14	0·13	0·07
CaO	trace	—	0·19	—	0·13
Fe_2O_3	0·96	0·88	1·13	0·15	0·18
K_2O	0·15	0·20	1·14	0·14	0·22
Loss by ignition	14·10	12·60	7·11	22·60	15·00
Hygroscopic water	0·70	0·80	—	—	—
TiO_2	1·30	1·70	1·14	—	—

No. 1. Sayre and Fischer's No. 1. Fire clay. Brownish-grey. Refractoriness (R.) above 50 per cent.

No. 2. Hokessin, Delaware. Washed kaolin clay. White with brownish tint. R. approaching 60 per cent.

No. 3. Evens Mine, Howard County, Missouri. Crude clay. Light brown, hard, and firm. R. above 50 per cent.

No. 4. E. F. and P. M. Roberts, selected fire-clay. Brownish. R. above 50 per cent.

No. 5. H. Cutter: ware clay. Bluish-grey. R. above 50 per cent.

No. 6. Geo. Such: washed clay. Brownish-green. R. above 30 per cent.

No. 7. H. Butter: fire-clay. Bluish-grey, very hard. R. above 50 per cent.

No. 8. Hawe's flint clay. Johnstown, Penn. Bluish-grey. R. partly under 20 per cent., and not much more than 10 per cent.

No. 9. Huron: porcelain clay. Lawrence County. White, with yellow spots. R. above 60 per cent.

By subjecting these clays to the melting heat of platinum, Bischof found that, with the exception of No. 8, all retained their form, exceeding therefore the standard of 50 per cent. in refractoriness. The character of clay No. 8 did not coincide with the American analysis (8A). Bishof therefore analysed samples 8 and 9 (8B and 9B), and his results differed widely from the numbers given by Cock. It is questionable, therefore, whether the remaining analyses are altogether correct.

Seger has made an extensive series of experiments on glazes. He finds that quantitatively the glaze is out of all proportion as compared with the clay mass, so that its properties are affected to a great extent by the composition of the clay substance forming the under layer. The extreme limits of the composition of the various glazes employed are for common earthenware, and the fine French Faience $RO,1{\cdot}5SiO_2$ to $RO,3SiO_2$. For the harder German and English materials the limits may be expressed by the formulæ $RO,0{\cdot}1Al_2O_3,2{\cdot}5SiO_2$ to $RO,0{\cdot}4Al_2O_3,4{\cdot}5SiO_2$, whilst for porcelain glazes the formulæ

$$RO,0{\cdot}5Al_2O_3,5SiO_2 \text{ to } RO,1{\cdot}25Al_2O_3,12SiO_2,$$

may be assumed. The main difficulty experienced in the preparation of a faultless composition of glaze and clay substance lies in the differences of expansion by heat.

In order to obtain coloured glazes, the material is treated with coloured metallic oxides, or the colourless fluxes used in the preparation of the glazes are replaced by equivalent quantities of coloured metallic oxides. D. B.

Process for Preparing Dichromates. (*Dingl. polyt. J.*, **248**, 90.)—According to Pontius, the melt obtained by treating chrome-iron ore with lime and potash is lixiviated with the mother-liquor of preceding operations, which contains sufficient potassium carbonate to convert the calcium chromate in the melt into the potassium salt.

This liquor is then treated with carbonic anhydride in closed iron vessels at a pressure of several atmospheres, potassium dichromate and bicarbonate being formed: $2K_2CrO_4 + 2CO_2 + H_2O = K_2Cr_2O_7 + 2HKCO_3$. The sparingly soluble dichromate is allowed to settle and separated from the mother-liquor. The latter is then used for lixiviating further melts of chrome-iron ore. The melt can be treated also with warm water in closed agitators, carbonic anhydride being pumped in. Thus the normal potassium chromate produced is converted into the dichromate, with simultaneous formation of potassium carbonate, whilst the normal calcium chromate is changed into the dichromate, which in the nascent state is transformed together with the potassium carbonate into calcium carbonate and potassium dichromate. The latter is separated in the usual manner. Sodium and calcium dichromates may be obtained in a similar way. Magnesium dichromate is produced from the calcium salt by adding the corresponding amount of magnesium hydroxide or carbonate, and treating the mixture with carbonic anhydride. D. B.

Scale of Hardness of Metals. (*Dingl. polyt. J.*, **248**, 41.)—Gollner has determined the hardness of the principal metals which are technically useful, made in the following manner. The various test pieces were provided with a polished surface, and a hardened pin of cylindrical form, and drawn out to a conical point, was moved to and fro an equal number of times, the pressure and distance being the same in all trials. The action of the pin on the polished surface was then observed.

The following table gives the succession of metals arranged according to their hardness: Refined lead, pure tin, slag lead, soft copper, refined copper (cast), soft bronze (85 Cu, 10 Sn and 5 Zn), cast-iron (tempered), wrought-iron (fibrous), cast-iron (granular and light grey), cast-iron (re-cast with 10 per cent. malleable iron in the reverberatory furnace), soft ingot iron (0·15 per cent. C), ingot steel (not hardened, 0·45 per cent. C), ingot steel (not hardened, 0·96 per cent. C), crucible steel (hardened, blue), crucible steel (hardened, violet to orange-yellow), crucible steel (hardened, straw-yellow), hard bronze (83 Cu + 17 Zn), and crucible steel (chilled). D. B.

Extraction of Lead from Ores occurring in the Upper Hartz. (*Dingl. polyt. J.*, **248**, 124—128.)—These ores are treated at the Altenau works. If the percentage of lead is small, the ores are associated with comparatively large quantities of quartz and zinc blende, and cannot be treated by the precipitation method usually adopted in the Upper Hartz.

Clausbruch has successfully introduced the following process. The ore to be treated, containing 54 to 55 per cent. lead, 0·08 silver, 0·9 copper, 7 to 8 zinc, and 14 to 18 silicic acid, is roasted in reverberatory furnaces with single hearth and provided with 15 working doors on each side, of which 13 are used for working the ore, the remainder communicating with the pit and the fire-place. The hearth is 19 m. long and 3 m. wide, and the crown of the arch is located 0·5 m. above the bottom of the hearth, which has a rise of 10 cm. from the fire bridge to the flue. Between the flue and the chimney a system of condensing chambers is arranged. The fire-bridge and hearth pit are cooled by air-flues. The smelting of the roasted ore is effected in pit furnaces having two tuyeres, the back of the furnace being surrounded by a cold water-jacket, which protects it from the corrosive action of the basic charge. The furnace, which is admirably adapted for smelting these ores, is described in detail, as also the working of the same and the fluxes most profitably used. It may be mentioned that this process effects a saving of 6·51 marks per five tons of material operated on, whilst 98·5 per cent. of the total lead introduced into the furnace comes out in the form of furnace lead without the use of a blast. Owing to the regular division, and the delivery of the furnace gases at a considerable height, the injurious action of the fumes on the surrounding forests is lessened to a great extent, a circumstance which is of extreme importance to the smelting industry in the Hartz. D. B.

Process for Preparing Litharge and Red Lead. (*Dingl. polyt. J.*, **248**, 220.)—According to Lewis, the fumes from lead smelting furnaces are mixed with carbonate or caustic soda and roasted or boiled. The whole is then allowed to settle, washed to free it from sodium sulphate, and smelted to form either litharge or red lead. If the fumes contain zinc, the latter must first be dissolved out with sulphuric acid. D. B.

Spontaneous Combustion of Coal. (*Dingl. polyt. J.*, **247**, 506). While Durand explains the spontaneous ignition of coal in the pit by the presence of pyrites which, becoming heated, gives rise to combustion, Fayol maintains that the first and main cause of spontaneous inflammability is the absorption of oxygen by the coal, accelerated by fine division and high temperature. The ignition of fuel in the form of dust occurs at the following temperatures: Lignite, 150°; Cannel coal, 200°; coking coal, 250°, and anthracite, 300° and over. It is shown that coal absorbs oxygen and becomes heated more readily than pyrites, and that the addition of the latter to coal does not aid the ignition of coal-dust. D. B.

Italian Red Wines. (*Dingl. polyt. J.*, **248**, 219.)—Three kinds of red wines from the Chianta Valley in Tuscany, known as "Chianti wines," were analysed by Kayser, viz., Stra Vecchio of 1878 (A), Vecchio of 1880 (B), and Vino Nuovo of 1881 (C). 100 c.c. contained—

	A.	B.	C.
Alcohol	9·5 c.c.	11·6 c.c.	11·7 c.c.
Extract	2·15 g.	2·52 g.	2·50 g.
Mineral ingredients	0·21	0·21	0·24
Acidity, calculated on tartaric acid	0·532	0·600	0·63
Pyroracemic acid	0·024	0·027	0·029
Tartaric acid	—	—	—
Sulphuric acid	0·014	0·013	0·014
Phosphoric acid	0·028	0·030	0·031
Lime	0·007	0·008	0·008
Magnesia	0·022	0·020	0·022
Potash	0·087	0·084	0·090
Sugar	0·105	0·240	0·200
Glycerol	1·000	1·200	1·400

The absence of tartaric acid, which appears to be replaced by pyroracemic acid, is remarkable. D. B.

Contribution to the Problem of Frothy Fermentation. By F. Pampe (*Dingl. polyt. J.*, **248**, 76—83 and 128—133).—Several efforts have recently been made to solve the question of the frothing which occurs in the fermentation of potato mash, and to suggest a ready means of preventing the same. In 1879 an extensive investigation was conducted by the German Society of Distillers; the results, however, were not very satisfactory. It was recommended to change the mashing material, to add oat malt, and treat the mash with steamed maize at a high pressure, but the reason of the frothing was not explained. The author has studied this subject very minutely, and the result of his experiments may be summed up as follows:—

When the frothing occurs, the cohesion of the fermented liquid is considerably less than is the case when the normal conditions of fermentation exist. The main reason of this lies in the peculiar form in which the nitrogenous compounds are present, also in the amount of the latter. This peculiarity may be due to the fact that the nitrogenous compounds were contained in the raw material in such a form as to diminish the cohesive power, and served, therefore, as direct yeast nutriment (asparagine and other amides). By the steaming process the nitrogenous compounds are transformed so as to be no longer suitable as direct nutrients. When potatoes are steamed imperfectly, which takes place when they are frozen, frothy fermentation at once sets in, as this transformation has not occurred. In addition to this, the nitrogenous compounds are brought into the diffusible condition by special ferments. In most cases, however, the frothing is due to the circumstance that the constitution of the yeast is not in relation to the remaining conditions in the distillery; either the formation of yeast is too large, and sugar is unnecessarily consumed for the production of yeast-cells, or it is too small, in which case sugar remains in the mash in an unfermented state. D. B.

Process for Preparing Orcinol. By A. WINTHER (*Dingl. polyt. J.*, **248**, 133—135).—Orcinol (*Ger. Pat.*, 20713, Oct., 1881) can be produced from those derivatives of toluene containing substituted groups in the meta-position, which are convertible into hydroxyl-groups. For the preparation of orcinol from metadinitrotoluene, the latter is first transformed into metanitrotoluidine by means of alcoholic ammonium sulphide, precipitation by water, solution in hydrochloric acid, and reprecipitation by ammonia. The metanitrometatoluidine is then dissolved in a warm mixture of equal volumes of sulphuric acid and water, and cooled down, when the sulphate crystallises out. A solution of potassium nitrite is now added until all the sulphate has been redissolved. The solution of the diazo-compound thus obtained is diluted with water and heated, metanitrometacresol being formed, which by crystallisation from the separated oil, as well as from the ethereal extract by water, is obtained in the pure form. It is reduced by tin and hydrochloric acid, and the metamidometacresol is converted into the dihydroxy-compound by means of the diazo-reaction. From the solution the orcinol is obtained by evaporation or by extraction with ether. D. B.

Adulterated Soaps. (*Dingl. polyt. J.*, **248**, 92.)—A firm in New Isenberg has recently introduced into commerce, at a profit of from 300 to 1200 per cent., a heavily weighted palm-oil soap, which dries up to a small residue. A soap of English make has been recently imported into Germany under the name of "Sinclair's cold water soap," at a cost of 80 marks per 100 kilos. It is described as equal in efficiency to thrice its weight of ordinary soap. Borcheot has analysed this soap, and finds that it consists of about 70 parts tallow, 30 parts bleached palm oil, and 25 resin, boiled together, then mixed with 3 to 5 parts Venice turpentine. Two days after about 8 per cent. sodium silicate is added. Other analyses showed 1 per cent. talc instead of sodium silicate. The soap known as "Army blue mottled soap" consists of palm and cocoanut oils, coloured with ultramarine, and heavily loaded with lyes. D. B.

Use of Soap in Dyeing. By LAUBER and A. STEINHEIL (*Dingl. polyt. J.*, **247**, 507—508).—For the preparation of soap, the following process is successfully being worked at the Zawiercier works:—360 litres of water and 69 kilos. of ley at 36° B. are boiled, and 140 kilos. of oleic acid added, with constant agitation, until a uniform mixture has been obtained. 3120 litres of water are then added, and the whole is well stirred until a clear soap solution has been obtained. Using the above proportions, the oleic acid was in some cases found to be in excess, and more soda had to be used. In *Bull. de Mulhouse*, 1882, 142, Scheurer has published an interesting article on oleic acid soap and its influence as a clearing agent on colours. A soap used for clearing purposes should produce a perfectly white ground, on which the colour then appears much more brilliant, and should not attack the colour. On comparing the different soaps of commerce from this point of view, Scheurer had to give the preference to Marseilles soap. He was further able to prove that the so-called alkaline soaps obtained with oleic acid simply contain free oleic acid and alkali, because the saponification has not been completed, owing to insufficient boiling. Oleic acid soaps are always more alkaline than others, a circumstance which is due to the fact that owing to the strong affinity of oleic acid, the saponification is effected in less time than in the case of soaps from other fatty acids. Consequently these oleic acid soaps were not treated sufficiently long to effect a perfect union of the acid and soda. This combination may be hastened by an increase of temperature or pressure. D. B.

Mordants used for Fixing Artificial Colouring Matters. (*Dingl. polyt. J.*, **248**, 39.)—Köchlin (*Bull. de Mulhouse*, 1882, 266) discusses the application of various mordants for fixing artificial colouring matters, with the following results:—

Phloxine gives bad results with aluminium acetate, a bright cherry-red colour with a mixture of aluminium and magnesium acetate, a pink with calcium and aluminium acetates, and an amaranth-red with chromium and magnesium acetates.

Ponceau 3. Bright red with a mixture of aluminium and magnesium acetate, red resembling garancine with chromium and magnesium acetates.

Primrose. Pink with blue shade, resisting soaps when fixed with chromium acetate.

Magenta. The best result is obtained with chromium acetate.

Safranine. The same.

Eosine. Dark red colour with chromium acetate, not permanent if fixed with aluminium acetate.

Picric acid. Yellow with a mixture of aluminium and magnesium acetate, does not stand soaping; no result with aluminium or chromium acetates.

Orange No. 2 is fixed by chromium and magnesium acetates; chromium acetate *per se* gives a brown colour, magnesium acetate *per se* does not fix the colour.

Phosphine gives with aluminium acetate a buff colour, not attacked by hot soap baths.

Blue 5 B gives a deep blue with chromium acetate, a lighter colour with magnesium and chromium acetates, resisting soaps.

Methylene blue. Dark colour with chromium acetate; stands soaping if fixed by magnesium and aluminium acetates.

Indigo carmine requires aluminium acetate, but is not permanent.

Malachite green. The finest shades are obtained with a mixture of aluminium and magnesium acetate.

Coeruleïn, Violet Poirrier, and Orseille. With chromium acetate.

Roccellin. Aluminium acetate or a mixture of chromium and magnesium acetates gives a brick-red colour, which is attacked by soaps.

Dinitronaphthol does not dye.

Bismarck brown gives a stable colour with chromium acetate.

Grey coupier and induline require chromium acetate, or the latter, mixed with magnesium acetate. D. B.

Novelties in Dyeing and Calico-printing. (*Dingl. polyt. J.*, **248**, 83—86.)—Scheurer (*Bull. de Mulhouse*, 1882, 42) fixes colouring matters by reducing potassium chromate with sodium thiosulphate or sulphite. The following is the strongest colour which it is possible to prepare; it is, however, not durable, and can be thickened only with difficulty:—200 grams normal potassium chromate, 380 sodium thiosulphate, and 420 starch paste. To fix the colour it is treated with a mixture of 50 grams normal potassium chromate, 95 sodium thiosulphate, 755 thickening, then printed, steamed, and washed. Schäfer (*ibid.*, 43) draws attention to a peculiar incident which occurred at Dollfus, Mieg, and Co.'s works in oxidising by the hanging process. The goods dyed with garancin exhibited streaks and coloured spots after hanging, showing they had undergone an accidental mordanting operation. This peculiarity is attributed to the soot collected on the roofs of the dye house, which was blown through the spaces between the tiles by the wind.

Köchlin (*ibid.*, 63) mentions that when aniline-black is developed at a temperature above 70°, it does not grow darker, irrespective of the mordant used as oxidising agent, provided however that the amount of the latter and the time during which the temperature is maintained are sufficient. All goods developed in the cold undergo a subsequent darkening.

Lauth recommends to complete the dyeing with aniline-black by passing the fabric through hot solutions of salts of chromium, copper, iron, mercury *per se* or in conjunction with chlorates, ferrocyanides, or chromates. Schmidt (*ibid.*, 97) produces chrome yellow or orange by steaming. Barium chromate is readily decomposed by lead nitrate when the mixture is heated; a steam colour may therefore be obtained from a thickened mixture of lead nitrate and barium chromate, prepared by precipitating normal potassium chromate with barium chloride. Although the conversion is imperfect, and the colour not intimately fixed, it is possible, owing to the fact that one of the reagents exists in an insoluble form in the dye, to obtain a good yellow which strongly resists soaping, by employing concentrated colours of perfect smoothness and homogeneity, *e.g.*, 250 grams gum tragacanth (200 grams per litre), 250 lead nitrate, 550 barium chromate (50 per cent.), and 50 water. To prepare chrome-orange, Schmidt adds to lead nitrate a certain quantity of lead acetate. The following receipt is given for chrome-orange:—500 grams gum tragacanth (200 grams per litre), 500 lead nitrate, 750 lead acetate, and 1400 barium chromate (50 per cent.). By reducing the quantity of lead acetate, yellower shades are produced.

Köchlin uses finely-divided coal fixed with albumin for calico-printing, in place of lampblack. D. B.

Utilisation of Battery Residues. (*Dingl. polyt. J.*, **248**, 89.)—The residues from the batteries used in the telegraph department of the German Empire are sold annually by public tender. The purchaser takes possession of the residues at fixed prices without guarantee as to the percentage of metals (zinc, lead, and copper) contained in residues. Experience has shown that the proportion between the amounts of copper and zinc recoverable from the residues is within narrow limits. Previous to the delivery, which takes place twice a year, the residues are washed in river or rain-water, to remove all salts mixed therewith. The sale is said to realise 22 per cent. of the total expenditure of battery materials. D. B.

Preparation of Terra Cotta Lumber. (*Dingl. polyt. J.*, **248**, 179.)—Gillman mixes 1 part pure clay with 1 to 3 parts sawdust and the requisite amount of water, presses the mass into large blocks, dries the latter and burns it for two days. The blocks are then cut with circular saws into the desired forms. Terra cotta lumber is incombustible; resists acids and atmospheric influences; is a bad conductor of heat, sound, and electricity; has only half the weight of bricks, can be sawn, cut, and planed; and combines intimately with lime, gypsum, &c. D. B.

Polychrome Varnish for White Metal. (*Dingl. polyt. J.*, **248**, 220.)—According to Puscher, 30 grams of crystallised cupric acetate are ground to a fine powder and kept in thin layers in a warm place until the water of crystallisation and a large proportion of the acetic acid have been volatilised. The light brown powder is then mixed with 100 grams of gum copal, and heated to 75°. This mixture is painted on white metal and the colour developed by heating in a drying box. In consequence of the reduction of the dissolved cupric oxide to cuprous oxide, green, yellow, orange, or reddish colours can be produced, according to the temperature and time of heating. D. B.

Process for Preparing Printing Ink. (*Dingl. polyt. J.*, **248**, 92.)—Schmidt Brothers recommend manganese dioxide instead of lampblack for the preparation of printing and marking ink. Waste paper which has been printed with this ink is said to be suitable for the manufacture of white paper. D. B.

General and Physical Chemistry.

Electro-dynamic Interference of Alternating Currents. By A. OBERBECK (*Compt. rend.*, **96**, 1498—1499).—A claim for priority.

Distortion of Polarised Electrodes. By GOUY (*Compt. rend.*, **96**, 1495—1497).—When a narrow band of thin gold foil varnished on one side is used as the positive electrode in the electrolysis of a solution of copper sulphate, the negative electrode being of copper, the positive electrode becomes polarised, and the gold foil is distorted and becomes concave on the unvarnished side. Similar phenomena are observed with a narrow riband of gold coiled into a helix. If the current is broken, the electrode returns to its former position. The distortion commences immediately the current is completed, and attains its maximum in less than a second. The introduction of a great resistance into the circuit slightly retards the polarisation and distortion. If the gold is previously covered with a film of copper, there is no distortion until all the copper has dissolved away. Similar distortion is observed with electrodes of other metals in other solutions. It is particularly well marked in the electrolysis of manganese nitrate, and if the circuit is broken and the two electrodes are put into communication with each other, the curved electrode returns to its original position, and then curves in the opposite direction. In this case there is a deposit of manganese dioxide on the positive electrode.

If a metal is deposited on an electrode, or if a deposit is dissolved away, the electrode experiences a displacement which is doubtless due to the mechanical action of the deposit. C. H. B.

Pyroelectricity of Quartz. By C. FRIEDEL and J. CURIE (*Compt. rend.*, **96**, 1262—1269, and 1390—1395).—These papers are mainly a *résumé* of results previously obtained (*Bull. Soc. Min.*, 1879, **31**), and a criticism of Hankel's papers (this vol., 412, 540). The authors have repeated Hankel's experiments, and have been unable to recognise the vortical distribution of electrical tension on the faces of the crystals, and they find that the rhombic axes instead of being neutral points, are electrified positively. They also find that when a crystal is surrounded with metallic filings, and heated in a metallic case, the metallic filings cool more rapidly than the crystal, and exercise a cooling effect on the latter, which consequently cools irregularly; the outer layer of the crystal being cooled most rapidly, contracts and exerts pressure on the interior, which is at a higher temperature than the mean temperature of the crystal, and also on the uncovered faces, which are compressed laterally, and consequently expand in a direction at right angles to the compression, *i.e.*, in the direction of the lateral axis of the prism. The positive electricity developed on the rhombic faces, and the negative electricity developed on the opposite faces, as observed by Hankel, are due to expansion along the axes of hemimorphism, produced by the pressure resulting from irregular cooling. The production of internal tensions under these conditions is proved by heating a cylinder of glass in the same way, and examining it with polarised light. When a quartz crystal is heated and then allowed to cool gradually and regularly by exposure to air, there is no development of electricity. The authors' results agree with those of Röntgen. C. H. B.

Specific Heats of Gases at High Temperatures. By VIEILLE (*Compt. rend.*, **96**, 1358—1361).—The temperature calculated from the maximum pressure developed in closed vessels by the explosion of cyanogen and oxygen in the proportions necessary to form carbonic oxide, constitutes an inferior limit of the temperature of combustion. A small quantity of the carbonic oxide is decomposed into carbon and carbonic anhydride, and another small quantity reduces the water vapour present in the gases. Analysis of the products, however, shows how far these changes have taken place, and enables a maximum limit of temperature to be calculated. The quotient of the inferior and superior limits of temperature gives a superior limit for the specific heats at constant volume of the gases nitrogen, hydrogen, oxygen, and carbonic oxide. By the explosion of mixtures of cyanogen and oxygen in the proportions necessary to form carbonic oxide, with varying quantities of nitrogen, the author has obtained the following maximum values for the mean molecular heats of hydrogen, oxygen, nitrogen, and carbonic oxide:—

Temperature.	Molecular heat.
Ordinary	4·8
3100°	6·30
3600	7·30
4400	8·10

These values are based on the assumption that the laws of expansion and compressibility hold good at the high temperatures.

C. H. B.

Critical Point of Gases. By J. JAMIN (*Compt. rend.*, **96**, 1448—1452).—The author defines the critical point as *the temperature at which a liquid and its saturated vapour have the same density* (comp. Abstr., 1862, 267). In the experiments of Cagniard-Latour the disappearance of the meniscus at the critical point is due to the fact that the liquid and its vapour have acquired the same density in consequence of the compression of the vapour and the expansion of the liquid. There is no interruption of the general law of evaporation. The liquid remains at its boiling point and point of maximum vapour-tension, but is invisible because it mixes with and floats in its own vapour, both having the same density. As the temperature rises, the vapour-tension increases until the whole of the liquid is volatilised, and after this point, but only after this point, the vapour ceases to be saturated, and passes into the state of gas. Since there is no change of volume at the critical point, the vapour has no latent heat. In other words, at the critical point the liquid does not differ from its vapour in tension, density, heat of constitution, appearance, nor in any other property by which they can be distinguished. The same explanation holds good in the case of Andrew's experiments.

In one of Cailletet's experiments a mixture of 1 vol. air with 5 vols. carbonic anhydride, was compressed until the carbonic anhydride liquefied, but on increasing the pressure to 150—200 atmospheres, the liquid entirely disappeared. According to the author's view, the volume of the liquefied carbonic anhydride undergoes little or no further diminution, but the volume of the air diminishes continually, and its density consequently increases until it becomes equal to that of the liquid, and at this point the meniscus disappears. If this view be correct, the substitution of hydrogen or some other light gas for air should render a higher pressure necessary to cause the disappearance of the meniscus. At the author's suggestion Cailletet has made experiments with mixtures of 5 vols. carbonic anhydride with 1 vol. air and 1 vol. hydrogen respectively, and the following table gives the pressures required to bring about the disappearance of the meniscus at different temperatures:—

Temperature....	15°	16°	17°	18°	19°	20°	21°	
Carbonic anhydride and air..	135	130	125	120	114	108	102	atmos.
Carbonic anhydride and hydrogen	245	236	227	218	208	199	190	„

Temperature	22°	23°	24°	25°	
Carbonic anhydride and air	96	90	85	79	atmos.
„ „ „ hydrogen ..	181	172	163	153	„

These results are in accord with the author's theory. Cailletet has shown that when carbonic anhydride is mixed with a considerable proportion of air, or a similar gas, its liquefaction is retarded or is even rendered impossible. This, however, is due to the fact that at high pressures the volume of the air diminishes more rapidly than that of the carbonic anhydride, so that when the latter has reached the tension at which it liquefies, its density is equal to or even lower than that of the admixed air, and the gas appears not to liquefy, whereas the liquid has only lost its property of collecting at the bottom of the vessel.

It would appear that if the pressure is continually increased, the carbonic anhydride will continue to liquefy, and its density will vary but little, but the density of the admixed air or other gas will continually increase, and will at last become greater than that of the liquid, which will then collect at the top of the tube instead of at the bottom. C. H. B.

Modification of V. Meyer's Vapour-density Apparatus. By H. Schwarz (*Ber.*, **16**, 1051—1056).—The author employs a combustion furnace containing a deep iron trough fitted with a lid. An ordinary wide combustion tube closed at one end is placed in the furnace, filled with nitrogen and connected with the apparatus for collecting the displaced gas. For the latter purpose the apparatus used in the estimation of nitrogen is employed (*Ber.*, **13**, 771). When the temperature has become constant, the weighed substance is introduced in a boat into the front cold part of the tube, the cork replaced and the front end of the furnace raised 20—30 c.m. The boat is then made to slide down the tube, the furnace being supported in the inclined position. Bubbles of gas begin to collect in a few seconds and cease suddenly when the volatilisation is complete; the displaced gas is then measured in the usual way (*loc. cit.*). A. K. M.

Air-baths. By L. Meyer (*Ber.*, **16**, 1087—1092).—A description of some improvements introduced by the author. A. K. M.

Inorganic Chemistry.

Action of Nascent Hydrogen on Oxygen Gas. By M. Traube (*Ber.*, **16**, 1201—1208).—A reply to Hoppe-Seyler (*Ber.*, **16**, 117). The author maintains that his experiments (Abstr., 1882, 795; 1883, 150, 282) prove (1) that palladium-hydrogen does not give off nascent hydrogen; (2) nascent hydrogen does not render oxygen active; (3) living tissues do not evolve hydrogen; (4) the action of palladium-hydrogen depends on the formation of hydrogen peroxide, which acts partly directly, and also in conjunction with metallic palladium, as an oxidising agent.

The author points out that the use of potassium iodide and starch as a test for nitrous acid is a source of error, as in many cases the liberation of iodine is due to hydrogen peroxide, and not to nitrous acid.

W. C. W.

Decomposition of Water by Metalloïds. By C. Cross and A. Higgin (*Ber.*, **16**, 1195—1199).—When water containing flowers of sulphur is distilled, sulphur, insoluble in carbon bisulphide, is found in the distillate, but if air is excluded from the apparatus, a clear distillate is obtained. The distillate becomes turbid, and deposits sulphur on exposure to the air. It gives a white precipitate with lead acetate, soluble in acetic acid, and with mercurous nitrate a yellow precipitate, which soon blackens. It bleaches potassium permanganate. Hence it appears that lower sulphur-acids are formed by the action of water on sulphur. Below 95° no action takes place. The solubility of arsenious sulphide in boiling water is probably due to the formation of an oxysulphide of arsenic, as such a compound is produced by boiling arsenious oxide and sulphide in water.

W. C. W.

Pyrosulphuric Chloride. By D. Konowalow (*Ber.*, **16**, 1127—1130).—Pure pyrosulphuric chloride, prepared by the action of sulphuric anhydride on chloride of sulphur, boils at 153°. The presence of chlorosulphonic acid lowers the temperature at which the substance boils. This fact probably accounts for the lower temperatures, viz., 140·5° and 146°, observed by Ogier (*Compt. rend.*, **94**, 217), and by Heumann (this vol., 710).

The density of the vapour of pyrosulphuric chloride is normal between 180 and 210°. In conducting the vapour-density determination, every precaution must be taken to avoid the presence of moisture, otherwise the pyrosulphuric chloride decomposes, and false results are obtained. W. C. W.

Phosphorus Sesquisulphide. By ISAMBERT (*Compt. rend.*, **96**, 1499—1502).—Sulphur and phosphorus do not combine together when dissolved in carbon bisulphide, and dry sulphur does not unite with melted phosphorus at 100°, but at 130° sudden and explosive combination takes place. The best method of preparing the sesquisulphide is to place 313 grams of carefully dried ordinary phosphorus in a tubulated retort through which a current of carbonic anhydride is passing, then add 24 grams of coarsely powdered sulphur, and heat carefully in a water-bath with repeated agitation until the mixture is completely fused. Now add, through the tube through which the carbonic anhydride passes, 110 grams of fine sand, which has previously been placed in a tubulated flask traversed by the gas. Agitate vigorously in order to mix the sand intimately with the fused mixture, and then heat somewhat strongly over a flame, continuing the passage of the carbonic anhydride. If the materials are intimately mixed, combination takes place gradually, and the phosphorus sulphide is afterwards separated from the sand by distillation.

Phosphorus sesquisulphide is a yellow crystalline solid, which when pure melts at 167° to a somewhat darker liquid. It ignites at about 100°, and burns slowly, with formation of phosphoric and sulphurous anhydrides. Nitric acid and aqua regia attack it but gradually, even when heated, and chlorine in presence of water converts it into phosphoric and sulphuric anhydrides. The sp. gr. of the sesquisulphide at 11° is 2·00, and it boils regularly at about 380°. Its vapour-density, determined by Meier's method, is 7·90 (calc. 7·62), and its heat of formation, determined by the action of iodine on the sulphide in presence of carbon bisulphide, is $P_2 + S_3 = + 18{\cdot}4$ cals. Since the heat developed by the conversion of ordinary phosphorus into red phosphorus is about 20 cals., it follows that red phosphorus and sulphur ought not to combine together directly. Red phosphorus and sulphur, however, combine at 180°; the tension of transformation of red phosphorus must therefore be sufficiently high at this point to convert the red phosphorus into ordinary phosphorus at the moment of combination. C. H. B.

Analogy between the Allotropic Modifications of Phosphorus and Arsenic. By R. ENGEL (*Compt. rend.*, **96**, 1314—1315).—The author has previously shown that when arsenic is liberated from its compounds at a temperature below 300° it forms *amorphous arsenic*, an allotropic modification which differs from ordinary crystallised arsenic in its specific gravity and point of sublimation. It is usually stated that arsenic sublimes at 180°, but the author finds that crystallised arsenic does not sublime below 360°, either in a vacuum or in an inert gas, whilst the amorphous variety begins to sublime at 260° in a vacuum, and at 280—310° in an inert gas. The sublimation of amorphous arsenic is at first very rapid, but after some hours it ceases, and a residue of crystallised arsenic of sp. gr. 5·7 is left. It follows, therefore, that amorphous arsenic is converted into the crystallised variety at about 310° if the heating is continued sufficiently long. Crystallised arsenic corresponds with red phosphorus, whilst amorphous arsenic corresponds with ordinary phosphorus. The sp. gr. of crystallised arsenic is higher than that of the amorphous variety, just as the sp. gr. of red phosphorus is higher than that of the ordinary variety; and just as ordinary phosphorus sublimes at a temperature below that at which it is converted into the red variety, so amorphous arsenic sublimes at a temperature below that at which it becomes crystalline. Amorphous phosphorus and crystallised arsenic respectively do not, however, sublime at these particular temperatures. The vapour of red phosphorus yields the yellow variety when condensed at a temperature below the point of transformation, and in like manner crystallised arsenic yields the amorphous form when its vapour is condensed below 300°. Moreover, it is possible to obtain red phosphorus in crystals, and these crystals are isomorphous with the crystals of arsenic. C. H. B.

Potassium Carbonate. By F. A. FLÜCKIGER (*Ber.*, **16**, 1143—1144).—An earthenware vessel used as a receptacle for crude potash, having been washed out and exposed to the sun, became covered with an incrustation of white needle-shaped crystals, which had the composition $K_2CO_3,KHCO_3,5H_2O$. Attempts to prepare this salt artificially were unsuccessful. W. C. W.

Silver Nitrate and Ammonia. By A. REYCHLER (*Ber.*, **16**, 990—994).—Two compounds of silver nitrate with ammonia are known, viz., $AgNO_3,3NH_3$ and $AgNO_3,2NH_3$. A strongly acid solution of silver nitrate is not precipitated by ammonia, whilst from a neutral or nearly neutral solution the silver is partially thrown down as hydrated oxide. To redissolve the precipitate, slightly more ammonia must be used than is required by the proportion $AgNO_3 + 2NH_3$. If sufficient ammonia is added to produce only a slight precipitate, and the latter is then separated by filtration, the further addition of ammonia produces no precipitate. On adding ammonia in quantity sufficient to produce the maximum precipitate, and evaporating the filtrate on a water-bath, a brown deposit (AgO ?) is formed, and silver is precipitated in the form of a mirror, whilst the concentrated solution crystallises on cooling to a mass of lustrous needles; these, after washing with alcohol and ether, should be dried at a low temperature. The product, *silver ammonium nitrate*, $NH_3Ag.NO_3$, blackens by exposure to light, and is only partially soluble in water, moderately in alcohol, very sparingly in ether. On dialysing a concentrated solution of silver ammonium nitrate into water, white needles are obtained on the lower side of the dialyser, which after being washed with alcohol and ether, and dried at a low temperature, contain 77 per cent. silver, which approximately corresponds with silver ammonium hydroxide. Silver ammonium nitrate forms a crystalline compound with aldehyde, $CH_3.CH(OH).NHAg$, very readily soluble in water, moderately in alcohol, and almost insoluble in ether. It blackens by exposure to light and is decomposed below 100°. On adding aldehyde to a solution of silver nitrate and ammonia containing 1 mol. of the former to 2 mols. of the latter, it yields Liebermann and Goldschmidt's ethylidenimide silver nitrate. A. K. M.

Double Salts of Lead. By G. ANDRÉ (*Compt. rend.*, **96**, 1502—1504).—If litharge is added gradually to a hot solution of ammonium chloride in its own weight of water and heated at about 100° for some hours, the liquid on cooling deposits crystals of the composition $PbCl_2,6NH_4Cl,H_2O$. This compound is decomposed by water with formation of an amorphous oxychloride, $PbCl_2,PbO,H_2O$, and a solution which, after concentration, deposits small brilliant micaceous lamellæ of the composition $2PbCl_2,NH_4Cl,6H_2O$.

If a small quantity of the compound $PbCl_2,6NH_4Cl,H_2O$ is heated with about 50 c.c. of water in a sealed tube at about 200° for five hours, white needles of the oxychloride $PbCl_2,PbO,H_2O$ are obtained. If some of the mother-liquor from $PbCl_2,6NH_4Cl,H_2O$ is added to an excess of water and the mixture heated in a sealed tube at 200° for about five hours, small slender brilliant needles of the oxychloride $2PbCl_2,PbO,2H_2O$ are deposited. When the salt $4PbCl_2,22NH_4Cl,7H_2O$ previously described is heated with water in a similar manner, lead chloride separates out in slender needles, but no oxychloride is formed. It would appear, therefore, that the double chlorides obtained by the action of litharge on a solution of ammonium chloride contain a small quantity of oxychloride, which is easily separated by water, and crystallises under pressure. This oxychloride is probably formed in accordance with the equation $2PbO + 2NH_4Cl = 2NH_3 + PbCl_2,PbO,H_2O$.

When lead bromide is added to an aqueous solution of ammonium bromide until it ceases to be dissolved, the liquid deposits crystalline nodules of the composition $7PbBr_2,12NH_4Br,7H_2O$, which rapidly alter when exposed to air. The mother-liquor, after evaporation, deposits small lamellæ of the composition $2PbBr_2,14NH_4Br,3H_2O$, much more stable when exposed to air. By digesting litharge with ammonium bromide solution, a crystalline crust of the composition $PbBr_2,6NH_4Br,H_2O$, is obtained. It is decomposed by water with formation of an amorphous oxybromide, $2PbBr_2,2PbO,3H_2O$. By treating the double salt $PbBr_2,6NH_4Br,H_2O$, or its mother-liquor in the same manner as the chlorine compounds, the oxybromide $PbBr_2,PbO,H_2O$ is obtained in slender needles. It would appear that the double bromides obtained by the action of litharge on ammonium bromide solution contain some oxybromide; but the compounds obtained from lead bromide and ammonium bromide yield only lead bromide and no oxybromide when heated with water in sealed tubes.

C. H. B.

Basic Double Salts. By H. KLINGER (*Ber.*, **16**, 997—999).—The author has made experiments with the view to obtain basic lead cadmium nitrates from cadmium oxide and lead nitrate, and from cadmium nitrate and lead oxide, and to compare the products. In both cases insoluble basic salts are formed together with *basic lead nitrate*, NO_3PbOH, the latter crystallising in white needles. When hydrated lead oxide is added to a hot solution of cadmium nitrate and the basic lead salt allowed to crystallise out, the mother-liquor sometimes yields a second salt, *basic cadmium nitrate*, NO_3CdOH,H_2O, crystallising in iridescent plates. The latter is also obtained by the action of heat on cadmium nitrate, or by dissolving hydrated cadmium oxide in hot cadmium nitrate solution. When mercuric oxide is added to a boiling solution of calcium chloride and the solution filtered, colourless, lustrous plates of *basic mercury calcium chloride*, $CaCl_2,2HgO,4H_2O$, separate, which lose their water at 175—178°. It is decomposed by water with formation of calcium chloride, a small quantity of mercuric chloride, and an insoluble red amorphous body containing mercury, calcium, and chlorine. Hydrochloric acid dissolves it with difficulty. A basic lead calcium salt has also been obtained. A. K. M.

Formation of Sulphides by Pressure. By W. SPRING (*Ber.*, **16**, 999—1004).—This is a continuation of the author's experiments on the production of compounds by pressure (this vol., p. 650). A mixture of a metal with sulphur is subjected to a pressure of 6500 atmospheres, the block so obtained powdered, and the operation repeated until a uniform mass is obtained. In this way the following sulphides have been produced:—*Magnesium sulphide*, *zinc sulphide* (in appearance resembling the natural blende), *ferrous sulphide*, *cadmium sulphide*, *bismuth sulphide*, *lead sulphide*, *silver sulphide*, *copper sulphide*, *stannic sulphide*, and *antimony sulphide*. Only a partial combination could be effected between sulphur and aluminium, the product yielding with hydrochloric acid an abundant evolution of hydrogen sulphide. Sulphur and red phosphorus do not combine under the influence of pressure, neither do sulphur and carbon. A. K. M.

Colloïdal Copper Sulphide. By W. SPRING (*Ber.*, **16**, 1142—1143).—If copper sulphide, prepared by passing sulphuretted hydrogen through a dilute solution of copper sulphate in ammonia, is washed by decantation with water containing sulphuretted hydrogen, until the precipitate is perfectly free from ammoniacal salts, the copper sulphide dissolves, forming a dark brown solution. The solution may be boiled without decomposition, but the addition of small quantities of metallic salts causes the sulphide to precipitate. On evaporating the solution on a water-bath, the copper sulphide remains as a dark resinous mass. If the copper sulphide is dried *in vacuo*, it loses its property of dissolving in water. Pure dry copper sulphide has a dark green colour. Under a pressure of 6500 atmospheres, it forms a dark blue compact mass, possessing metallic lustre.

Antimony, arsenic, and stannic sulphides, antimony oxide, stannic oxide, and manganese peroxide, all resemble copper sulphide in their behaviour with pure water. W. C. W.

Iridium Potassium Sulphate. By L. DE BOISBAUDRAN (*Compt. rend.*, **96**, 1406—1409).—The green iridium potassium sulphate, which separates out from solutions of the product obtained by fusing an iridium compound with hydrogen potassium sulphate at a dull red heat (next abstract), has the composition $Ir_2 3SO_4, 3K_2SO_4$. It dissolves in water or dilute sulphuric acid, but is insoluble in a saturated solution of potassium sulphate and in dilute alcohol. When deposited slowly from concentrated solutions, it forms small transparent crystals, which have no action on polarised light, and are apparently octahedra, flattened parallel with one of the faces. An acid solution of the salt is not altered by boiling; but if the solution is nearly neutral and especially if it contains a certain proportion of potassium sulphate, the green colour rapidly changes to a very pale rose tint, and potassium hydroxide or ammonia now precipitates the iridium in the form of an oxide, which dissolves in dilute sulphuric acid, forming a deep violet solution. With ammonia, the precipitation is incomplete, and therefore it is preferable to use potash when testing for iridium (*loc. cit.*). An excess of potash added to the green solution in the cold changes the colour to pale blue, without any immediate precipitation; but on heating it, a rich violet colour is quickly developed, and the iridium rapidly separates out as a blue-violet oxide, soluble in dilute sulphuric acid; sometimes the colour produced by potash is violet-grey, and the precipitate is also violet-grey, but it yields the same rich violet solution with dilute sulphuric acid.

The green salt is not altered by dilute hydrochloric acid, nor by hydrochloric acid and iodine, but hot dilute nitric acid changes the colour to a somewhat feeble blue-violet. Aqua regia decomposes the salt completely with formation of iridium tetrachloride, and the sulphuric acid can be precipitated by barium chloride. If barium chloride is added to a solution of the original salt, the precipitated barium sulphate has a deep green colour, and retains a considerable quantity of iridium, which is not removed even by aqua regia.

A solution of the green salt in dilute sulphuric acid acquires a pale blue-violet colour, when heated with potassium permanganate. If hydrochloric acid is previously added, the colour produced is very deep green. A hydrochloric acid solution of the salt also acquires a deep green colour when heated with potassium chlorate. Sulphurous anhydride has no action on a hot acid solution of the salt.

C. H. B.

Reactions of Iridium. By L. DE BOISBAUDRAN (*Compt. rend.*, **96**, 1336—1339).—A. The iridium salt is fused with hydrogen potassium sulphate at a dull red heat in a gold crucible for some minutes, either directly or after it has been evaporated with excess of sulphuric acid, until white fumes are given off; if the proportion of iridium is not too great, the residue dissolves completely in hot water, forming a solution which is usually green, but is sometimes blue or violet. Concentrated solutions on cooling deposit a deep green crystalline powder containing iridium, potassium, and sulphuric acid. This salt dissolves in water or dilute sulphuric acid, but is precipitated by potassium sulphate. Without removing the precipitate, the liquid is nearly neutralised with potash or ammonia, when potassium sulphate is precipitated and carries down the greater part of the iridium, which gives it a green colour. The precipitate is collected on a filter, washed once or twice with potassium sulphate solution, and the filtrate and washings mixed and boiled for 15 to 30 minutes, when the iridium is converted into a compound which yields a precipitate with potash or ammonia, especially on boiling. This precipitate dissolves in dilute sulphuric acid, forming a deep violet solution which appears rose-coloured when very dilute. The same precipitate is obtained by dissolving the iridiferous potassium sulphate in hot water slightly acidified with sulphuric acid, boiling the solution, and then adding potash or ammonia. If the boiling liquid is only very slightly acid, the greater part of the precipitate separates out before adding the alkali, and is then much less soluble in dilute sulphuric acid. If the amount of iridium is very minute, the iridiferous potassium sulphate is not treated separately, but the liquid is boiled after partial neutralisation. When the alkaline filtrate has a faint rose colour it is evaporated to dryness, heated with sulphuric acid, and treated as above. By this method 0·025 mgrm. of iridium can be detected in 50 grams of hydrogen potassium sulphate.

In order to separate traces of iron, the solution is neutralised with ammonia, digested with excess of ammonium sulphide at a gentle heat for some time, filtered, and the filtrate evaporated almost to dryness. On boiling the residue with aqua regia, ammonium salts are destroyed, sulphur separates out, and the iridium tetrachloride is recognised by its colour, or is examined by the following methods:—

B. The iridium salt is heated with a slight excess of sulphuric acid in order to expel any chlorine, allowed to cool slightly, and ammonium nitrate added in successive small quantities. The heating is then continued, and more nitrate is added, when a deep blue colour is produced if only 0·001 mgrm. of iridium is present. If the heating is stopped whilst some nitrate remains undecomposed, the blue substance dissolves in water without change. Sometimes the substance has a rich emerald-green tint, but if it is moistened with a little sulphuric acid after cooling, and then again gently heated, the green colour changes to blue. Foreign metals interfere more or less with this test, but it succeeds well in presence of gold, ruthenium, platinum, or rhodium. The blue colour is of course modified by colour due to any of the other metals: in presence of gold, for example, it is changed to green.

C. If ammonium nitrate and chloride are added to the cold sulphuric acid solution of the iridium salt, and the mixture then heated, a rose-red colour is produced; this is destroyed by excess of ammonium salts, but reappears on adding sulphuric acid and heating gently. If the heating is discontinued before all the ammonium salts are decomposed, the residue, when treated with water after cooling, leaves a rose-red powder, soluble in pure water, but insoluble in a solution of ammonium hydrogen sulphate. The aqueous solution of the heated mass appears to contain ammonium iridiochloride. This reaction is obtained with 0·001 mgrm. of iridium.

By combining method A with the reactions B and C, it is easy to detect with certainty 0·01 mgrm. of iridium mixed with two million times its weight of potassium hydrogen sulphate. C. H. B.

Organic Chemistry.

Carbon Thiobromides. By C. Hell and F. Urech (*Ber.*, **16**, 1147—1149).—By the action of bromine on carbotrithiohexbromide in presence of water, 2 atoms of sulphur are oxidised to sulphuric acid, and the third atom escapes in the form of carbon oxysulphide. When the compound CS_2Br_4 is diluted with ether and mixed with alcohol, carbotrithiohexbromide is produced. This body is decomposed by alcohol at 120°. With phenol and cresol, the hexbromide forms red liquids which lose their colour on the addition of an acid.

W. C. W.

Formation of a new Colouring Matter by the Action of Heat on Carbotrithiohexbromide. By C. Hell and F. Urech (*Ber.*, **16**, 1144—1147).—*Carbotrithiohexbromide*, $C_2S_3Br_6$, melts at 125° and decomposes at 180°, whilst free bromine, bromide of sulphur, and the compound CS_2Br_4 distil over. If the act of distillation is interrupted when the contents of the retort thicken, carbon tetrabromide may be extracted from the residue by ether. A blue compound of the composition $C_9Br_4S_4,2H_2O$ now remains, which is very slightly soluble in alcohol, ether, and glacial acetic acid. It dissolves, however, in strong sulphuric acid or in phenol, forming a blue solution which is changed to brownish-red by the action of zinc-dust. It is reprecipitated as a blue powder from the sulphuric acid solution, on dilution with water, and from the phenol solution by the addition of ether.

The authors consider that the blue substance is an aromatic compound, and that it owes its colouring power to the presence of the group-S—S. W. C. W.

Dicyandiamide, I. By E. Bamberger (*Ber.*, **16**, 1074—1078).—Water has no action on dicyandiamide below 150°, but when the latter is heated with about 12 parts of water for 15—20 hours at a temperature of 160—170° in sealed tubes, ammonia is liberated, whilst the glass becomes coated with a crystalline powder. On acidulating the ammoniacal filtrate with acetic acid a voluminous precipitate is obtained which, after being purified and dried over sulphuric acid in a vacuum, has the composition represented by the formula $C_3N_4H_4O_2$. The formation of *dicyandiamidocarboxylic acid* may be represented by the equations: $C_2N_4H_4 + 4H_2O = 2CO_2 + 4NH_3$ and $2C_2N_4H_4 + 2CO_2 + 4NH_3 = 2C_3N_4H_4O_2.NH_3 + 2NH_3$.

The free acid is an amorphous chalk-like powder which does not melt when heated, and at elevated temperatures gives off white fumes condensing to a crystalline sublimate (dicyandiamide?), whilst cyanic acid volatilises. It is insoluble in the ordinary solvents, and dissolves but very sparingly in boiling water, from which it separates on cooling in the form of a heavy powder consisting of microscopic aggregates of lustrous prisms. On warming the ammonium salt, the ammonia is liberated, and the acid obtained in needles. When heated with water a few degrees above the temperature of its formation, it is decomposed with formation of ammonia and carbonic anhydride. The *ammonium* salt is obtained in the form of slender lustrous prisms, when a boiling solution of the acid in ammonia is allowed to cool; it decomposes on exposure to the air, ammonia being given off. The *barium* salt, $(C_3N_4H_3O_2)_2Ba + 2H_2O$, crystallises in groups of silky prisms; its aqueous solution is decomposed by boiling. The compound, $C_3N_4H_3AgO_2,AgNO_3$, separates in white flocks on adding ammoniacal silver solution to a slightly ammoniacal solution of the acid. On adding acetate of lead to a boiling solution of the barium salt, a double *lead dicyandiamidocarboxylate* and *acetate*,

$$C_3N_4H_3O_2,PbO\overline{Ac},$$

is precipitated as a heavy crystalline powder. When a solution of the acid in boiling hydrochloric acid is allowed to cool, crystals of the *hydrochloride*, $C_3N_4H_4O_2,HCl$, are obtained.

Dicyandiamidocarboxylic acid can be prepared synthetically by heating dicyandiamide with ammonium carbonate solution for 6—8 hours at 120°, and decomposing the ammonium salt thus formed with acetic acid. A. K. M.

Formation of Amyl Alcohol in Alcoholic Fermentation. By J. A. Le Bel (*Compt. rend.*, **96**, 1368—1370).—By careful fractionation of large quantities, the author has been able to separate several cubic centimetres of amyl alcohol, mixed in all probability with higher alcohols, from wine, beer, and fermented solutions of sugar. C. H. B.

Allylamine Derivatives. By C. Liebermann and C. Paal (*Ber.*, **16**, 523—534).—The authors have endeavoured to convert ethyl allylamine and its derivatives into piperidine. By the action of concentrated sulphuric acid they hoped to introduce a molecule of water into the compound base, as has been done by Oppenheim (*Annalen*, Suppl., **6**, 367) in the case of allyl chloride. By the subsequent extraction of a molecule of water, a hydrogen-atom being taken from the ethyl group, piperidine would be left. The authors have only succeeded in performing the first part of the operation. They have arrived at no definite conclusion regarding the second phase of the reaction. They have, however, observed a curious property of the allyl platinammonium chlorides. They have prepared the ethyl-, propyl-, and amyl-allylamine bases by the action of the iodides or bromides of the respective alcohol radicals in the usual manner; in addition to the secondary bases, tertiary compounds are generally formed. The separation of the mixture requires repeated distillation, in the course of which small quantities of glittering plates separate out, but afterwards disappear or conglomerate. The authors have not made any exact examination of their composition. The bases are all colourless liquids of an odour resembling that of allylamine. Their solubility in water decreases with the increasing complexity of the alcohol radical in combination. Their solutions in hydrochloric acid decolorise bromine-water, and on adding an alkali even very dilute solutions become milky from the separation of a yellow oily base. This reaction has been made use of as a test for the presence of unattacked allyl groups.

Monethylallylamine, $C_3H_5.NHEt$, boils at 84—86°.

Ethylallylamine platinochloride, $(C_3H_5NHEt)_2,H_2PtCl_6$, crystallises from water in orange-coloured well-formed crystals melting at 154—156°. The acid oxalate forms colourless plates sparingly soluble in alcohol.

Diethylallylamine, $C_3H_5.NEt_2$, is stated by Rinne to boil at 100—103°. The authors find its boiling point to be 110—113°. Its platinochloride melts at 128—130°.

Monopropylallylamine, $C_3H_5.NHPr$, boils at 110—114°. Its sp. gr. at 18° is 0·7708. The platinochloride forms orange-coloured crystals.

Dipropylallylamine, $C_3H_5.NPr_2$, boils between 145° and 150°. Its platinochloride crystallises from water in fine glittering orange-red rhombic crystals. When the mother-liquor is allowed to evaporate in the air, lemon-coloured crystals of a new platinum salt are obtained. The compound can be readily prepared by boiling an aqueous solution of the ordinary salt. When the liquor becomes concentrated an oily precipitate forms. After diluting and boiling, the solution is allowed to cool slowly, yellow needles of the composition $C_3H_5NPr_2,HPtCl_3$ (m. p. 152—153°) then separating out. All the above platinum salts yield analogous compounds.

Monethylallylamine platinichloride, $C_3H_5NHEt,HPtCl_3$, forms anhydrous lemon-coloured crystals melting at 220°.

Diethylallylamine platinichloride, $C_3H_5NEt_2,HPtCl_3$, forms groups of chamois-coloured needles melting at 189°.

Allylamine platinichloride, $C_3H_5.NH_2,HPtCl_3$, crystallises in ochre-coloured needles.

The platinochlorides of pyridine and quinoline are not altered by boiling with water.

Isoamylallylamine, $C_3H_5\,NH.C_5H_{11}$, boils at 148—153°. Its sp. gr. at 18° is 0·7777. The allylamine bases were all subjected to the action of concentrated sulphuric acid at 130—140°. In addition to quantities of the unattacked base, allylamine was always found accompanied by a new base boiling considerably higher than the original one. The platinochlorides are very soluble in water and alcohol, and difficult to crystallise. The bases contain oxygen, and when dissolved in hydrochloric acid do not decolorise hydrobromic acid, showing that the allyl group is saturated.

Hydroxypropylamine, $(C_3H_6.OH).NHPr$, prepared by the action of sulphuric acid on propylallylamine, boils at 174—177°. Its sp. gr. at

18° is 0·9018. At the ordinary temperature it is a colourless liquid; but at lower temperatures it forms slender needles which melt at 30°.

Hydroxypropylpropylamine platinochloride,

$$[(C_3H_6.OH)NHPr]_2,H_2PtCl_4 + 2H_2O,$$

crystallises from water in efflorescent warty masses.

Hydroxypropyldipropylamine, $(C_3H_6.OH)NPr_2$. The platinochloride has the composition $[(C_3H_6.OH)NPr_2]_2,H_2PtCl_6$.

Hydroxypropylethylamine, $(C_3H_6.OH)NHEt$, boils at about 160°. The platinochloride, $[(C_3H_6.OH)NHEt]_2,H_2PtCl_6 + 2H_2O$, is very soluble.

Hydroxypropyldiethylamine platinochloride,

$$[(C_3H_6.OH)NEt_2]_2,H_2PtCl_6,$$

is also a very soluble salt.

Hydroxypropylamylamine, $(C_3H_6.OH)NH.C_5H_{11}$, boils at about 200°. In a freezing mixture it solidifies to needles resembling asbestos, which melt a few degrees above 0°. It is insoluble in water.

The authors have ascertained that the oxy-bases on further treatment with concentrated H_2SO_4, undergo a change, and propose to pursue the investigation thereof. J. I. W.

Imines. By A. LADENBURG (*Ber.*, **16**, 1149—1152).—*Pentamethylenediamine*, $C_5H_{10}(NH_2)_2$, is produced by the action of zinc and hydrochloric acid on an ethereal solution of trimethylene dicyanide. An isomeride of piperidine is also formed by this reaction. Soda is added to the product, and the free base distilled over in a current of steam; in order to get rid of ammonia, the distillate is neutralised with hydrochloric acid, and the diamine is precipitated by the addition of a solution of iodine in potassium iodide. The precipitate is then washed free from ammoniacal salts, and converted into the hydrochloride by treatment with silver and silver chloride. The hydrochloride crystallises in prisms which are slightly hygroscopic. The platinochloride, $C_5H_{10}(NH_2)_2,H_2PtCl_6$, is deposited from a hot aqueous solution in golden prisms. The base is not easily decomposed by strong hydrochloric acid, even at 160°. By the action of soda solution at 260°, it splits up into ammonia and a base of the same composition as piperidine. The identity of this compound with piperidine, however, has not yet been established.

The isomeride of piperidine mentioned above, forms a platinochloride crystallising in yellow glistening plates. It is less soluble than piperidine platinochloride. The aurochloride is more soluble than the corresponding piperidine compound. W. C. W.

Oxaline and Glyoxalines. By O. WALLACH (*Ber.*, **16**, 534—547).—Having shown in a previous research that oxalmethyline is a derivative of glyoxaline (Abstr., 1882, 821), the author has now studied the properties of oxalethyline for the special purpose of determining the composition of the base from which it is derived.

Ethylglyoxaline, $(C_3H_3N)NEt$, prepared by the action of ethyl bromide on glyoxaline dissolved in alcohol, is a clear liquid boiling at 209—210°, sp. gr. 0·999. It is miscible with water. Its platinochloride, $(C_5H_8N_2)_2,H_2PtCl_6$, crystallises from water. It combines with methyl iodide, forming a salt which crystallises in large deliquescent prisms melting at 74—75°; this forms with cadmium iodide a double salt which is very insoluble in water, but crystallises from dilute alcohol in small plates melting at 151—152°, and having the composition $(C_3H_3N : NEtMeI)_2,CdI_2$. The methiodide salt, when shaken with silver chloride, is converted into the corresponding chloride which forms salts with platinum chloride and zinc chloride. The former, $(C_3H_3N : NEtMeCl)_2,PtCl_4$, crystallises well, and melts at 194—195°. The latter, $(C_3H_3N : NEtMeCl)_2,ZnCl_2$, forms transparent soluble crystals melting at 157—159°.

When ethylglyoxaline methiodide is distilled with potash, no higher boiling base is obtained; but a violent reaction takes place, and a primary amine distils over.

The compound $C_3H_3N : NEtMeI$ crystallises in deliquescent prisms. Its derivatives, $(C_3H_3N : NEtMeI)_2,CdI_2$, $(C_3H_3N : NEtMeCl)_2,PtCl_4$, $(C_3H_3N : NEtMeCl)_2,ZnCl_2$, resemble those of ethylglyoxaline, but possess somewhat lower melting points. The compound

$$C_3H_3N : NEtMeI$$

differs greatly from the corresponding salts of oxalethyline,

$$C_3H_2MeN : NEtHI.$$

When methylglyoxaline is treated with bromine in a solution of dilute sulphuric acid, it yields a tribromomethylglyoxaline; it forms white crystals melting at 88—89°. Ethylglyoxaline, when treated in a similar manner, yields a tribromo substitution-product melting at 61—62°. Oxalethyline forms dibromoxalethylene. Chloroxalethylene contains only one hydrogen-atom replaceable by bromine. The author considers from the above facts that oxalethyline is methylethylglyoxaline, $C_3H_2MeN.NEt$. He considers that Radziszewsky's formula for glyoxaline, considering it to be a tertiary base, is altogether indefensible, since his experiments and those of Wyss have shown that it is a secondary base, in which 1 atom of hydrogen is easily replaceable by hydrocarbon radicals. The direct substitution is exemplified by the formation of benzylglyoxaline on gently heating glyoxaline with benzyl chloride; it forms crystals melting at 70—71°, and boils at 310°. When glyoxaline is boiled with aniline hydrochloride, ammonia is evolved. The fact that the boiling point of glyoxaline is *lowered* about 70° by the introduction of a methyl group, affords further evidence of its secondary nature.

The author finds that by passing the substituted glyoxalines through a short tube, heated to redness, they are converted into isomeric compounds. Hydrocyanic acid is produced as a bye-product. *Paramethylglyoxaline*, so formed, is identical with paroxaline-methyline. Its platinochloride crystallises in long needles. *Parethylglyoxaline*, $C_5H_8N_2$, melts at 76—77°. When heated with propyl bromide at 120°, it forms oxalpropyline (b. p. 229—234°). *Parapropylglyoxaline* is not so easily prepared as its homologues.

When oxalethyline is passed through a red-hot tube it yields a small quantity of a higher boiling base resembling paroxalmethyline.

J. I. W.

Synthesis of Ketonic Acids (II).—By C. A. Bischoff (*Ber.*, **16**, 1044—1046).—*Ethyl benzomalonate* is obtained by the action of benzoic chloride on ethyl sodomalonate. By the action of acetophenone bromide on ethyl sodomalonate, *ethyl β-benzoisosuccinate* is produced, and yields on saponification *β-benzoisosuccinic acid*, $CH_2\overline{Bz}.CH(COOH)_2$, melting at 114°. *Ethyl orthonitrobenzomalonate*, $NO_2.C_6H_4.CO.CH(COOEt)_2$, is obtained by the action of nitrobenzoic chloride on ethyl sodomalonate suspended in ether or light petroleum; it melts at 92°, decomposing at 100°. *Ethyl acetylenetetracarboxylate* is produced when the sodium compound of ethyl malonate is suspended in ether and ethereal solution of iodine added. In the same way *ethyl butonhexacarboxylate* (m. p. 56°) is obtained from the sodium compound of ethyl ethenyltricarboxylate,

$$2[CNa(COOEt)_2.CH_2.COOEt] + I_2 = 2NaI + \\ COOEt.CH_2.C(COOEt)_2.C(COOEt)_2.CH_2.COOEt.$$

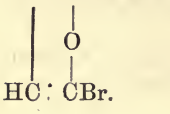
A. K. M.

Correction. By R. Andreasch (*Ber.*, **16**, 1185—1186).—The statement that Guareschi (*Ber.*, **12**, 682) found that potassium ethylenedisulphonate contains 2 mols. H_2O is a misprint. Guareschi's observation agrees with the author's, viz., the salt is anhydrous. Barium ethylidenedisulphonate contains $3\frac{1}{2}$, not $2\frac{1}{2}$, mols. H_2O.

W. C. W.

Substituted Pyromucic Acids. By H. B. Hill (*Ber.*, **16**, 1130—1132).—On the addition of bromine to a solution of pyromucic acid in glacial acetic acid monobromopyromucic acid is formed, together with carbonic and hydrobromic acids and other bye-products. The monobromopyromucic acid (m. p. 183°) is identical with the compound described by Tönnies (*Ber.*, **11**, 1088) and by Schiff and Tassinari (*Gazzetta*, **8**, 297). If bromine-vapour is passed into a vessel containing the acid suspended in 30 times its volume of water, the acid is decomposed into fumaric, carbonic, and hydrobromic acids, $C_5H_3BrO_3 + 2Br_2 + 3H_2O = C_4H_4O_4 + CO_2 + 5HBr$. Dibromosuccinic and isodibromosuccinic acids are formed in small quantities. If liquid bromine is used instead of bromine-vapour in the preceding experiment, a larger yield of these acids is obtained. Dibromofurfuranetetrabromide, $C_4H_2Br_6O$, is also produced. $C_5H_3BrO_3 + 3Br_2 = C_4H_2Br_6O + CO_2 + HBr$. It crystallises in colourless prisms (m. p. 110°), soluble in alcohol, chloroform, ether, carbon bisulphide, and light petroleum, but insoluble in water. Silky needles of tetrabromofurfurane (m. p. 63°) are obtained by the action of alcoholic potash on dibromofurfurane tetrabromide.

The formation of fumaric acid when monobromopyromucic acid is treated with bromine-water or hot dilute sulphuric acid, indicates that the constitutional formula of monobromopyromucic acid is



W. C. W.

Occurrence of a New Acid in Beet-juice. By E. O. LIPPMANN (*Ber.*, **16**, 1078—1081).—Besides citric, aconitic, tricarballylic, and malonic acids, the author has isolated a tribasic acid of the formula $C_6H_8O_8$. It is very readily soluble in water, alcohol, and ether. The alkali salts are amorphous, and very readily soluble. The *barium* salt, $(C_6H_5O_8)_2Ba_3 + 5H_2O$, is insoluble in water and in alcohol. The *calcium* salt has the formula $(C_6H_5O_8)_2Ca_3 + 10H_2O$. Pawolleck (*Annalen*, **178**, 155) obtained an acid (hydroxycitric acid) of the same formula by boiling chlorocitric acid with water or alkalis; this acid agrees in its properties with that obtained from beet-juice, the calcium salt, however, containing, according to Pawolleck, 9 mols. H_2O. The author assumes the two to be identical.

A. K. M.

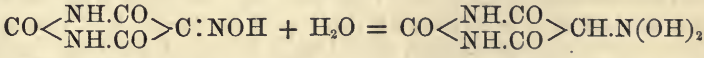
Metallic Derivatives of Amides: Method of distinguishing between Monamides and Diamides. By H. GAL (*Compt. rend.*, **96**, 1315—1317; compare this vol., 653).—Acetamide and butyramide act on an ethereal solution of zinc ethyl at the ordinary temperature with evolution of ethane and formation of zinc acetamide or zinc butyramide, as the case may be. These metallic derivatives are white powders insoluble in ether, and decomposed by water with regeneration of the amide and formation of zinc oxide. Benzamide behaves in a precisely similar manner.

Urea acts on zinc ethyl in the cold, with formation of *zinc carbamide*, CON_2H_2Zn, probably analogous to Liebig's silver carbamide. Oxamide has no action on zinc ethyl in the cold, but on heating the mixture, *zinc oxamide*, $C_2O_4N_2H_2Zn$, is formed.

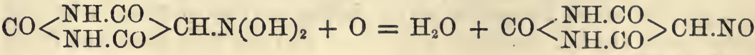
It follows that the action of zinc ethyl on a non-saturated monamine produces a compound with the general formula 2 (amide) $-H_2+Zn$, which is decomposed by water, in accordance with the equation $[2\ (\text{amide}) - H_2 + Zn] + 2H_2O = ZnH_2O_2 + 2\ (\text{amide})$. With diamides, the formula of the product is amide $-H_2 + Zn$. With monamides 2 mols. of the amide take part in the reaction, whilst with diamides only 1 mol. is required. The action of zinc ethyl may therefore be used for distinguishing between monamides and diamides.

C. H. B.

Violuric Acid. By M. CERESOLE (*Ber.*, **16**, 1133—1135).—Violuric acid can be prepared synthetically by the action of hydroxylamine hydrochloride on alloxan. Strong hydrochloric acid decomposes violuric acid with formation of hydroxylamine. Violuric acid is the only isonitroso-compound which is not decomposed by oxidation, but is converted into the corresponding nitro-derivative, viz., dilituric acid.



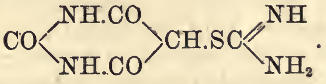
$$CO<\genfrac{}{}{0pt}{}{NH.CO}{NH.CO}>C{:}NOH + H_2O = CO<\genfrac{}{}{0pt}{}{NH.CO}{NH.CO}>CH.N(OH)_2.$$



$$CO<\genfrac{}{}{0pt}{}{NH.CO}{NH.CO}>CH.N(OH)_2 + O = H_2O + CO<\genfrac{}{}{0pt}{}{NH.CO}{NH.CO}>CH.NO_2.$$

W. C. W.

Action of Dibromobarbituric Acid on Thiocarbamide and Thiocyanates. By W. TRZCINSKI (*Ber.*, **16**, 1057—1061).—When aqueous or alcoholic solutions of dibromobarbituric acid and thiocarbamide are mixed, a white granular precipitate is obtained identical with Nencki's thiopseudouric acid, $C_5H_6N_4SO_3$ (*Ber.*, **4**, 722); it is insoluble in water, alcohol, and ammonia, but dissolves readily in the fixed alkalis; it crystallises from concentrated hydrobromic acid in slender concentrically grouped needles: $C_4O_3N_2H_2Br_2 + CSN_2H_4 = C_5O_3N_4H_6S + Br_2$. On adding an alcoholic solution of potassium thiocyanate in slight excess to a cold alcoholic solution of dibromobarbituric acid, a white precipitate is produced, which, after being washed with alcohol, dried and recrystallised from hot water, has the formula $C_4O_3N_2H_2SCNK$, *i.e., potassium thiocyanobarbiturate.* The *ammonium salt* is obtained when ammonium thiocyanate is used, both salts being nearly insoluble in alcohol, and crystallising from aqueous solutions in colourless rhombic anhydrous plates: $C_4O_3N_2H_2Br_2 + CNSK = C_4O_3N_2H_2(SCN)K + Br_2$. Potassium and ammonium thiocyanobarbiturates are precipitated by lead and silver salts with formation of sparingly soluble salts, which are decomposed on boiling. Free thiocyanobarbituric acid has not been isolated, the precipitate obtained on adding hydrochloric acid to its salts decomposing when gently heated with water into thiodialuric, hydrocyanic, and thiocyanic acids, and a body insoluble in acids and alkalis. On warming its salts with dilute potash solution, ammonia, carbonic anhydride, and thiodialuric acid are produced. Thiodialuric acid dissolves in nitric acid to a pink solution, and on warming this a violent reaction takes place with formation of nitrobarbituric acid. From the fact that thiodialuric acid can be obtained from the salts of thiocyanobarbituric acid, $\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}>\mathrm{CH.SCN}$, and from thiopseudouric acid by saponification, the author assigns to the latter the constitution—



$$\mathrm{CO}<\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}>\mathrm{CH.SC}\begin{matrix}\mathrm{=NH}\\ \mathrm{-NH_2}\end{matrix}.$$

A. K. M.

Alkyl-Nitrous Acids. By G. CHANCEL (*Compt. rend.*, **96**, 1466—1470).—The author has previously shown that alkyl-nitrous acids are produced by the action of nitric acid on ketones (Abstr., 1882, 710). He has now extended his researches to the action of nitric acid on ethyl acetoacetate and its mono-derivatives.—5 to 10 c.c. of the acetoacetate are gently heated in a flask with a long neck, and nitric acid of sp. gr. 1·35 is added gradually until the action commences, when the flask is removed from the source of heat, and more nitric acid gradually added until its volume is equal to that of the acetoacetate. When the evolution of nitrogen oxides slackens, the liquid is poured into water, washed once or twice with this liquid by decantation, dissolved in twice its volume of alcohol, mixed with excess of alcoholic potash and agitated, when a crystalline precipitate is thrown down, which is washed with alcohol and then with ether, and finally crystallised from boiling water.

Ethyl acetomethacetate yields *potassium ethyl-nitrite*, $CMe(NO_2)_2K$, which forms bulky deep yellow prismatic crystals. They become deep red when exposed to light, but regain their original colour in the dark. Like the picrates, this compound detonates violently when heated or struck. It is only slightly soluble in cold water, but dissolves readily in boiling water.

Ethyl acetoethacetate yields *potassium propyl-nitrite*,

$$CH_2Me.C(NO_2)_2K,$$

which forms prismatic crystals of a somewhat deeper yellow than the ethyl nitrite. When heated on platinum foil it detonates at 140—145°, but if heated in a tube it explodes at 106°. If heated at 100° for eight or 10 hours, it loses 42 per cent. in weight, and leaves a white residue which does not detonate. If perfectly dry, it may be kept in a closed vessel for any length of time without undergoing change. If moist, it gradually gives off nitric oxide and leaves a white crystalline residue.

Ethylacetopropylacetate is obtained by the action of normal iodopropane on a mixture of ethyl acetoacetate and sodium ethylate in alcoholic solution. It boils at 212° under a pressure of 750 mm., and its sp. gr. at 0° compared with water at 4° is 0·9795. Its sp. gr. at other temperatures up to 40° is obtained by means of the formula $D = 0{\cdot}9795 - 0{\cdot}000914t$. When treated with nitric acid, it yields *potassium butyl-nitrite*, $CH_2Me.CH_2.C(NO_2)_2K$, a yellow compound which crystallises, according to the strength of the solution, either in plates, or in long needles which unite into lamellæ on drying. It deflagrates when heated, and dissolves in 40·3 parts of water at 0°, and in 12·2 parts at 40°. *Silver butyl-nitrite*, $C_4H_7(NO_2)_2Ag$, is obtained by adding silver nitrate to a boiling solution of the potassium salt: it forms deep yellow lamellæ. *Butyl-nitrous acid*, obtained by decomposing the potassium salt with dilute sulphuric acid, is a colourless liquid insoluble in water; sp. gr. at 15° compared with water at 0° = 1·205. It boils at about 197°, with partial decomposition.

C. H. B.

Action of Ethyldichloramine on Aromatic Amines and on Hydrazobenzene. By A. Pierson and K. Heumann (*Ber.*, **16**, 1047—1050).—When ethyldichloramine is gradually added to a solution of paratoluidine in light petroleum, a violent reaction takes place which should be moderated by cooling. Parazotoluene and ethylamine hydrochloride are produced, $2C_7H_7.NH_2 + NEtCl_2 = NH_3EtCl + HCl + C_7H_7.N_2.C_7H_7$. It also reacts violently with aniline, with formation of dichloraniline (m. p. 63—64°) and trichloraniline (m. p. 78—79°), $C_6H_5.NH_2 + NEtCl_2 = C_6H_3Cl_2.NH_2 + NH_2Et$ and $2C_6H_5.NH_2 + 3NEtCl_2 = 2C_6H_2Cl_3.NH_2 + 3NH_2Et$. With hydrazobenzene, it forms azobenzene and ethylamine hydrochloride, $2PhNH.NHPh + NEtCl_2 = NH_3EtCl + HCl + 2PhN:NPh$, and with diphenylhydrazine, $Ph_2N.NH_2$, a reaction takes place which is not yet understood; a substance is obtained crystallising in long white needles, together with a deep violet-red dyestuff.

A. K. M.

Action of Acid Amides on Aromatic Amines. By W. Kelbe. Anilides can be prepared by boiling the theoretical quantities of amide and amine in a flask with a reflux condenser until the evolution of ammonia ceases. The crude product may generally be purified by washing it with ether. In this way the following anilides were obtained:—*Acetanilide* (m. p. 114°) from acetamide and aniline, *propionanilide* (from propionamide and aniline), forms glistening plates (m. p. 105°) very soluble in ether. *Butyranilide* (m. p. 92°) crystallises in cubes. *Valeranilide* from fermentation valerianic acid melts at 115°. *Capronanilide* from fermentation caproic acid is deposited from light petroleum in glistening needles (m. p. 95°), freely soluble in alcohol and ether. *Orthoacetotoluide* melts at 108°, and the *para* compound at 147°. Acetamide and xylidine yield *acetoxylide* (m. p. 127°). *Acetonaphthalide* from acetamide and naphthylamine melts at 157°. *Acetoparanitranilide* (m. p. 207°), *acetoparabromanilide* (m. p. 165·5°), *diacetylphenylenediamine* (m. p. 189°), and *diacetyltoluylenediamine* (m. p. 223°) were also prepared by this method.

W. C. W.

Nitrobenzaldoxime. By S. Gabriel (*Ber.*, **16**, 520—523).—The ortho-, meta-, and para-compounds of nitrobenzaldoxime (isonitrosomethylnitrobenzene) are readily prepared by acting on the corresponding nitrobenzaldehyde with the requisite quantity of alkali solution and hydroxylamine hydrochloride. The author finds that when metanitrobenzaldoxime is boiled with water it is unaltered; if hydrochloric acid be present, metanitrobenzaldehyde and hydroxylamine hydrochloride are formed. If a mixture of alcoholic solutions of metanitrobenzaldehyde and hydroxylamine hydrochloride be allowed to stand for a day, nitrobenzaldoxime is formed. When hydroxylamine and metanitrobenzaldehyde are heated with strong hydrochloric acid to 150—160°, ammonia and metanitrobenzoic acid are obtained. This explains why, after heating the compounds in a sealed tube at 130—140°, they were found unaltered when cold, and also explains the presence of ammonia and nitrobenzoic acid after the tube had been heated above 140°. *The sodium salt* of metanitrobenzaldoxime,

$$NO_2C_6H_4CNONa + 2H_2O,$$

forms long orange-yellow needles which decompose when heated at 140—150°. An aqueous solution gradually decomposes on standing.

When metanitrobenzaldoxime is acted on with phosphorus pentachloride, it yields fine needles melting at 155—177°, which possess the properties of metanitrobenzonitrile, $NO_2.C_6H_4.CN$. J. I. W.

Methylene-blue. By A. Bernthsen (*Ber.*, **16**, 1025—1028).—The author is examining into the nature of this and allied dyes. The base of Laut's violet is said to have the composition $C_{12}H_{10}N_3S$ or $C_{24}H_{20}N_6S_2$, and the base of methylene-blue the formula $C_{16}H_{18}N_4S$ (*Ber.*, **12**, 592 and 2069). The author finds that on precipitating an aqueous solution of commercial methylene-blue with potassium iodide solution and crystallising the precipitate from hot water, bronze-coloured needles are obtained, to which he assigns the formula—

$$C_{16}H_{19}N_3S,HI \text{ (or } C_{32}H_{36}N_6S_2,2HI).$$

By the reduction of methylene-blue, a leuco-base (methylene-white) is obtained crystallising from ether in broad needles; it has a slight yellowish colour, but forms colourless salts. It is moderately stable when dry, but becomes rapidly oxidised when moist. Its composition agrees with the formula $C_{16}H_{21}N_3S$ (or $C_{32}H_{40}N_6S_2$). It yields methyl and acetyl derivatives, the latter forming a white mass which becomes slightly blue by exposure to air. When heated with methyl iodide and methyl alcohol at 100—110°, the compound $C_{16}H_{20}MeN_3S + 2MeI$ is formed, crystallising in yellowish needles which are readily soluble in hot water, sparingly in cold. A. K. M.

Nitro-derivatives of Resorcinol. By P. G. W. Typke (*Ber.*, **16**, 551—557).—The diacetylresorcinol from which the compounds were prepared was obtained by acting on resorcinol with acetic chloride; in a pure state it forms a clear refractive oily liquid having a faint odour resembling that of acetamide. When placed in a mixture of ice and salt it becomes thick. It boils at 278° (uncorr.), with slight decomposition.

Dinitroresorcinol, $C_6H_2(NO_2)_2(OH)_2$, is formed when diacetylresorcinol is very gradually poured into 4—5 times its volume of well cooled fuming nitric acid. It separates out as a nearly white amorphous powder, which is washed with boiling alcohol and then dried at 100°. After boiling it for half an hour with 30 per cent. hydrochloric acid, it is dissolved in a large quantity of boiling water and filtered; on cooling, the new body crystallises out in slender needles (m. p. 212·5°), whilst any trinitroresorcinol which is present remains in solution. The dinitro-body crystallises from ethyl acetate in large yellow prisms with a vitreous lustre. When gently heated, it sublimes in spear-shaped needles. It decomposes carbonates, and forms well crystallised salts with bases. Its solutions colour animal fibre an intense yellow. When a slight excess of silver solution is added to a slightly ammoniacal dilute solution of the nitro-body, the *silver salt*, $C_6H_2(NO_2)_2(OAg)_2$, is obtained as a scarlet precipitate, which on standing changes to copper-coloured needles. On dissolving the nitro-body in an excess of dilute ammonia, the *normal ammonium salt*, $C_6H_2(NO_2)_2(ONH_4)_2$, is obtained in prismatic needles, which appear yellowish-brown by transmitted light and bluish by reflected light. They are sparingly soluble in water.

Hydrogen barium salt, $[C_6H_2(NO_2)_2(OH).O]_2Ba$.—When dinitroresorcinol is added to freshly precipitated barium carbonate suspended in boiling water, the solution on cooling deposits golden-yellow needles melting at 212·5°. The *normal barium salt*, $C_6H_2(NO_2)_2O_2Ba$, is obtained by boiling dinitroresorcinol for a considerable time with the theoretical quantity of barium carbonate suspended in water.

Monobromodinitroresorcinol, $C_6HBr(NO_2)_2(OH)_2$, is obtained by boiling dinitroresorcinol dissolved in glacial acetic acid with an excess of bromine. It crystallises in sulphur-coloured needles melting at 192·5°. With bases it forms a series of well crystallised salts.

Diamidoresorcinol hydrochloride, $C_6H_2(OH)_2(NH_2)_2,2HCl$, is obtained by reducing the dinitro-compound with tin and hydrochloric acid. It forms transparent vitreous needles having a superficial violet-grey colour.

When a current of air is passed through an aqueous ammoniacal solution of diamidoresorcinol hydrochloride, an oxidation-product separates out in glittering scales resembling cuprous oxide. They appear to consist of a di-imidoresorcinol, $(OH)_2C_6H_2(NH)_2$.

The author was unable to detect a mononitroresorcinol in the mother-liquors from the dinitro-compound. J. I. W.

A New Homologue of Resorcinol. By F. Pfaff (*Ber.*, **16**, 1135—1140).—*Mononitroxylenol*, recently described by the author (*Ber.*, **16**, 1136), yields the following derivatives:—

The *methyl ether*, $C_6H_2Me_2(NO_2).OMe$, is deposited from an alcoholic solution in long needles (m. p. 56°), soluble in ether and in hot water. The *potassium-derivative*, $C_6H_2Me_2(NO_2).OK + 2H_2O$, is a red crystalline compound freely soluble in water and alcohol. *Amidoxylenol hydrochloride*, $C_6H_2Me_2(OH).NH_3Cl$, is obtained in lustrous plates when nitroxylenol is treated with tin and hydrochloric acid. It dissolves easily in alcohol, ether, and water. The free base is obtained by decomposing an aqueous solution of the hydrochloride with the theoretical quantity of potassium bicarbonate and treating the mixture with ether. On evaporating the ethereal solution, amidoxylenol remains in glistening crystals (m. p. 161°), which are soluble in alcohol and ether.

Dihydroxyxylene or *xylorcinol*, $C_6H_3Me_2(OH)_2$, is prepared by cautiously adding a solution of sodium nitrite to a well cooled solution of 4 grams of amidoxylenol hydrochloride in dilute sulphuric acid. The mixture is first diluted up to a litre with water containing 120 grams of strong sulphuric acid, and then boiled for 2½ hours in a flask with a reflux condenser. On extracting the liquid with ether, xylorcinol is obtained as a dark-coloured oil, which solidifies (*in vacuo* over sulphuric acid) to a crystalline mass (m. p. 125°). The crystals, which have a bitter taste, dissolve freely in alcohol, ether, and water. Xylorcinol yields a *diacetic-derivative*, $C_6H_2Me_2(O\overline{Ac})_2$, crystallising in transparent prisms (m. p. 45°), soluble in alcohol, ether, and in hot water. When a solution of xylorcinol in glacial acetic acid is warmed with sulphuric acid, a fluorescent condensation-product is formed. The product of the reduction of bromonitranisol is identical with the meta-anisidine prepared from metanitrophenol. W. C. W.

Sulphonic Acids of Paracymene. By A. Claus (*Ber.*, **16**, 1015).—A reply to Spica.

Isoindole. By P. Friedländer and J. Mähly (*Ber.*, **16**, 1023—1025).—By the reduction of ethyl dinitrocinnamate,

$$C_6H_4(NO_2).CH\colon C(NO_2).COOEt,$$

by means of tin and hydrochloric acid in ethereal solution, diamidohydrocinnamic acid is formed, together with a basic substance, $C_8H_8N_2$, which probably belongs to the group of metanitriles. It is obtained by adding alkali to the product and agitating with ether. On evaporating the latter, an oil is obtained which becomes crystalline on standing. It is sparingly soluble in hot water, from which it crystallises in large silky plates, melting at 46°, and distilling unchanged at 312°. It is slightly volatile in steam, and has a faint odour resembling that of aniline. Its vapour-density agrees with the simple formula given. It forms monobasic salts. The *nitrate* is readily soluble in water and in alcohol, and crystallises in large brownish plates. The *hydrochloride* forms small plates, readily soluble in water, and yields a crystalline *platinochloride*, $(C_8H_8N_2)_2,H_2PtCl_6$. The *sulphate* is more sparingly soluble than the free base, and crystallises in long white lustrous needles. It yields an *acetyl-derivative*, crystallising in silky needles and melting at 97°. The probable formula for the base is $NH_2.C_6H_4.C_2H_2N$ (paramido-α- or β-phenylamphinitrile). With dry bromine, it forms an addition-compound, whilst bromine-water added to its solution in hydrochloric acid precipitates a dibromo substitution-derivative. By the action of nitrous acid, a diazo-compound is produced which yields a red hydroxy-body when boiled with water, and with alcohol a colourless oil of characteristic odour, which is probably free amphinitrile. A. K. M.

Action of the Alkyl-derivatives of the Halogen-substituted Fatty Acids on Aniline. (Preliminary Notice.) By C. A. Bischoff (*Ber.*, **16**, 1040—1044).—When aniline (1 mol.) is heated with ethyl chloracetate (1 mol.) to above the boiling point of aniline hydrochloride with an inverted condenser, and the product then distilled, unaltered ethyl chloracetate first passes over, and afterwards hydrochloric acid water and aniline hydrochloride, whilst a reddish coloured oil remains behind, which solidifies to a brittle mass on cooling; its formula is C_8H_9NO, and it is named by the author *dihydro-oxindole.* It dissolves readily in acetone and in hot alcohol, from which it separates in an amorphous condition. It is not attacked when heated with dilute hydrochloric acid or with an alkali. When it is heated to above 360°, a yellow oil distils, depositing crystals of a substance melting at 252—253°, readily soluble in acetone, insoluble in hot alcohol. Dihydro-oxindole is soluble in concentrated sulphuric acid, and on pouring the solution into cold water a flocculent precipitate is obtained, melting at 120° and decomposing at 175—180° with evolution of gas. A body of the same melting point and decomposing at the same temperature is also formed by the action of hydrochloric acid, whilst by the action of nitric acid a substance is obtained decomposing at 100—105°. Alcoholic potash is apparently without action; acetic chloride reacts violently, yielding an insoluble resinous mass and a yellowish oil, which is precipitated on adding soda solution to the liquid portion of the product. By the action of hydriodic acid, a substance is obtained having a powerful odour resembling that of pyridine- and quinoline-derivatives. It forms a hydrochloride, crystallising from alcohol in star-like groups of prisms. A reaction analogous to the above also takes place between aniline and ethyl bromopropionate. A. K. M.

Aromatic Nitroso-compounds. By S. Gabriel (*Ber.*, **16**, 517 523).—Nitrosomethylmetanitrobenzene may be regarded either as metanitrobenzaldoxine (according to Petraczek's nomenclature) or isonitrosomethylmetanitrobenzene (according to Meyer and Ceresole);

since it is formed by the action of hydroxylamine on nitrobenzaldehyde, it belongs to the class of isonitroso-compounds, containing the group—C⁚N.OH. Nitrosomethylorthonitrobenzene must also be considered as an isonitroso-compound on account of its analogous formation from orthonitrobenzaldehyde and hydroxylamine.

Nitroso-oxindole,  $\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CHNO.CN}\\ \mathrm{NH}\end{matrix}\right>$, has previously been obtained by treating paramidoxindole with amyl nitrite, and boiling the resulting paradiazonitroso-oxindole chloride with alcohol. It was prepared by Baeyer from oxindole and nitrous acid. The author finds that the same body is formed when a mixture of 1 mol. of isatin, 1 mol. of hydroxylamine hydrochloride, and ½ mol. of soda is allowed to stand with water and alcohol for several hours: on adding water, orange-yellow needles separate out.

Ethyl orthonitrophenylnitrosoacetate, $\mathrm{NO_2.C_6H_4.CHNO.COOEt}$, has been prepared by heating ethyl paramidorthonitrophenylacetate with amyl nitrite in alcoholic solution (*Ber.*, **14**, 825—830). If it be an isonitroso-compound, its formula must be $\mathrm{NO_2.C_6H_4.CNOH.COOEt}$, which shows that it would probably be formed by the action of hydroxylamine on ethyl orthonitrophenylglyoxylate,

$$\mathrm{NO_2.C_6H_4.CO.COOEt}.$$

The author has prepared ethyl phenylisonitrosoacetate,

$$\mathrm{Ph.CNOH.COOEt},$$

by acting on ethyl phenylglyoxylate (b. p. 257°) with hydroxylamine hydrochloride. It forms colourless needles, which have a vitreous lustre, and melt at 112—113°. When the ethyl salt of orthonitrophenylglyoxylic acid is treated with hydroxylamine in the same manner, ethyl orthonitrophenylisonitroso-acetate is obtained in long colourless needles, melting at 163—163·5°. It is sparingly soluble in weak ammonia, more readily in concentrated. It dissolves freely in potash solution, to which it imparts a yellow colour. J. I. W.

Isobenzil. By H. Klinger (*Ber.*, **16**, 994—997).—The author has repeated Brigel's experiments (*Annalen*, **135**, 172) on the formation of isobenzil by the action of sodium-amalgam on an ethereal solution of benzoic chloride, and has finally succeeded in obtaining this body. The benzoic chloride (1 part) is added gradually to the sodium-amalgam (5—6 parts), which is just covered with ether, and after the spontaneous action has ceased, the whole is heated for 2—3 days on a water-bath. The liquid portion is then decanted, and the solid residue washed with ether. The solution is agitated with soda, evaporated, and the residue steam-distilled to get rid of benzoic acid and benzyl alcohol; it is then treated with soda solution, the residue dissolved in ether, alcohol added, and the filtrate evaporated. On repeating this process, again dissolving the syrupy liquid in ether and then adding alcohol, lustrous scales of isobenzil gradually separate. The mother-liquor contains ordinary benzil, besides benzoic acid and anhydride. Isobenzil separates from alcohol in lustrous scales and needles, and from ether in compact crystals, melting at 155—156°.

It gives the benzil reaction with alcoholic potash. By the action of bromine on its solution in carbon bisulphide, benzil (m. p. 94—95°) and benzoic bromide are produced: $(C_7H_5O)_4 + Br_2 = C_{14}H_{10}O_2 + 2C_6H_5.COBr$. A. K. M.

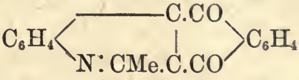
Oxidation of Pentachloronaphthalene. By A. Claus and H. Lippe (*Ber.*, **16**, 1016—1019).—Pentachloronaphthalene is best prepared by heating an intimate mixture of α-dichloronaphthaquinone (1 part) and phosphorus pentachloride (2 parts) in sealed tubes, the temperature being slowly raised to 250°, and maintained at 200—250° for four or five hours. The product is treated with water and dilute alkali, and recrystallised from alcohol and ether. The authors find that the trichloronaphthaquinone obtained by Claus and Spruck (Abstr., 1882, 1211), by boiling pentachloronaphthalene with nitric acid is nothing more than a secondary product due to the presence of α-dichloronaphthaquinone as an impurity in the pentachloronaphthalene, and that it is not connected with the formation of tetrachlorophthalic acid. When pentachloronaphthalene is heated with nitric acid (sp. gr. 1·5) in sealed tubes at 110—120° for ten hours, tetrachloronaphthaquinone is formed, together with some tetrachlorophthalic acid, the production of the former as intermediate between pentachloronaphthalene and tetrachlorophthalic acid, proving that the formation of the tetrachlorophthalic acid is due to a primary reaction, and also that the fifth chlorine-atom in pentachloronaphthalene occupies the α-position in the second ring. Tetrachloronaphthaquinone crystallises from alcohol in long lustrous yellow needles, melting at 160°, and subliming without decomposition. It combines with the alkalis, forming dark red-coloured salts, moderately soluble in water; they are decomposed by dilute acids, with separation of yellow needles of trichlorhydroxynaphthaquinone. With ammonia, aniline, and toluidine, it forms amido-derivatives, crystallising in lustrous copper-coloured needles. When heated with phosphorus pentachloride at 200° in sealed tubes, *heptachloronaphthalene* is produced, subliming in small colourless needles which melt at 154°. A. K. M.

Fluorene Derivatives. By J. Holm (*Ber.*, **16**, 1081—1082).—With the view to ascertain whether in the bromine and chlorine substitution derivatives of fluorene, hydrogen-atoms are substituted in both phenylene groups or in the methylene group, the author is examining the effect of oxidation on these derivatives. By the oxidation of dibromofluorene (m. p. 166°), he obtains *dibromodiphenyleneketone*, $C_{12}H_6Br_2CO$, in two modifications, according to the conditions of the experiment. When the dibromofluorene is dissolved in glacial acetic acid and oxidised with the calculated quantity of chromic anhydride, dibromodiphenyleneketone is formed, crystallising in long yellow needles, readily soluble in ether and in benzene, and melting at 142·5°. If a slight excess of chromic anhydride is used, the second modification is produced, melting at 197°; it forms yellow needles, readily soluble in alcohol, ether, and warm benzene. Both varieties yield the original α-dibromofluorene (m. p. 166°) when reduced with hydriodic acid and phosphorus. By the action of melted potash on β-dibromofluoreneketone (m. p. 197°), *dibromophenylbenzoic acid*, $C_{12}H_7Br_2.COOH$, is produced, readily soluble in alcohol, ether, and benzene, and crystallising in white needles, melting at 212°; the *barium salt*, $(C_{12}H_7Br_2.COO)_2Ba$, is insoluble in water, alcohol, and ether. Tribromofluorene gives the same β-dibromodiphenyleneketone, melting at 197°, showing that the third bromine-atom is in the methylene group.

Trichlorofluorene, $C_{13}H_7Cl_3$, is obtained by passing chlorine into a solution of fluorene in carbon bisulphide. It forms white scales, melting at 147°, and sparingly soluble in alcohol and in ether.

A. K. M.

Coal-tar Quinoline. By E. Jacobsen and C. L. Reimer (*Ber.*, **16**, 1082—1087).—The authors have mentioned the formation of a yellow dye obtained by the action of phthalic anhydride on coal-tar quinoline (*Ber.*, **16**, 513), which was supposed to be identical with Traub's quinophthalene obtained from quinoline which had been prepared from cinchonine (*Ber.*, **16**, 878). They prepare it by heating the commercial quinoline, boiling at 235—240° (2 parts) with phthalic anhydride (1 part) and zinc chloride (1 part) for 4—5 hours at 200°; the product is dissolved in concentrated sulphuric acid at 100°, and the solution poured into water, when the dye separates and can be purified by crystallisation, first from glacial acetic acid and then from alcohol. It forms slender gold-coloured needles, melting at 234—235°, and subliming at higher temperatures. It is insoluble in water, very sparingly in ether, but more readily in boiling alcohol and in glacial acetic acid. It dyes silk and cotton, and resists the action of light, acids, and alkalis; it has no basic properties, water separating it unchanged from its solution in sulphuric acid. The numbers obtained on analysis agree better with the formula $C_{18}H_{11}NO_2$ than with $C_{17}H_9NO_2$, and this led the authors to the supposition that the formation of this dye might be due to the presence of methylquinoline, and that it is not derived from the quinoline itself. They prove that this is the case by showing that after the whole of the methylquinoline has been converted into the dye, the unattacked quinoline no longer gives the reaction, and also that the yellow dye is decomposed by heating with hydrochloric acid into phthalic acid and quinaldine (methylquinoline), and that it can be re-made from the latter, according to the equation $C_{10}H_9N + C_8H_4O_3 = C_{18}H_{11}NO_2 + H_2O$.

Its constitution is probably  $C_6H_4\left\langle\begin{array}{l}\overline{\qquad\qquad}\text{C.CO}\\ \qquad\qquad\;|\\ \text{N:CMe.C.CO}\end{array}\right\rangle C_6H_4$, *i.e.*, quinaldine, in which two hydrogen-atoms of the pyridine nucleus are replaced by the phthalic radical. Homologues of quinoline containing methyl groups in the benzene nucleus only do not react with phthalic acid, whilst homologues of quinaldine behave in the same way as the latter substance.

The red dye previously obtained by Jacobsen by the action of benzotrichloride on coal-tar quinoline can neither be obtained from pure quinoline nor from pure quinaldine, its formation being apparently dependent upon a mixture of the two.

A. K. M.

Quarternary Base derived from Hydroxyquinoline. By A. Wurtz (*Compt. rend.*, **96**, 1269—1271).—Orthhydroxyquinoline (m. p. 75°) is heated with three times its weight of ethylene chlorhydrin in a sealed tube in a water-bath for ten days. The product is distilled in a vacuum in order to expel excess of the chlorhydrin, and the residue is dissolved in absolute alcohol; this solution is then mixed with a large quantity of ether, when an abundant precipitate of a crystalline hydrochloride is gradually deposited. This hydrochloride is dissolved in water and precipitated with platinum tetrachloride, the precipitate decomposed by hydrogen sulphide, the platinum sulphide filtered off, and the filtrate evaporated to dryness on the water-bath. The residue is dissolved in water, decomposed by excess of moist silver oxide, and the liquid agitated with ether, which removes hydroxyquinoline. The red and strongly alkaline aqueous solution is now acidified with hydrochloric acid and precipitated with platinum tetrachloride, when a yellow, crystalline, very slightly soluble precipitate of *hydroxyethylhydroxyquinoline platinochloride*,

$$(C_{11}H_{12}NO_2Cl)_2PtCl_4,$$

is obtained. The free base is obtained by decomposing the platinochloride with hydrogen sulphide. The hydrochloride,

$$C_9H_6(OH)NCl.C_2H_4.OH,$$

forms yellow anhydrous crystals. With gold chloride it yields an unstable crystalline yellow aurochloride, and with mercuric chloride a double chloride crystallising in yellowish lamellæ.

In the preparation of the new base, part of the hydroxyquinoline acts on the ethylene chlorhydrin, liberating ethylene oxide, which combines with the excess of chlorhydrin. The formation of hydroxyquinoline hydrochloride by the displacement of the ethylene oxide considerably diminishes the yield of the quarternary hydrochloride.

C. H. B.

Pyridinemonosulphonic Acid. By O. Fischer and C. Riemerschmid (*Ber.*, **16**, 1183—1185).—*Pyridinesulphonic acid* (*Ber.*, **15**, 62) crystallises in pale yellow needles or plates, which dissolve freely in water, but are only sparingly soluble in alcohol and insoluble in ether. Most of the salts of this acid are crystalline and soluble in water, *e.g.*, the salts of ammonium, sodium, nickel, cobalt, copper, zinc, and silver The barium sulphonate $(C_5H_4N.SO_3)_2Ba + 4H_2O$, loses its water of crystallisation at 120°. The mercurous salt is sparingly soluble. The SO_3 group in pyridinemonosulphonic acid is easily eliminated by reducing agents or by bromine.

β-Pyridine dibromide, $C_5H_3Br_2N$, may be prepared by adding bromine to a boiling aqueous solution of pyridinesulphonic acid; the mixture is rendered alkaline and distilled in a current of steam, when long needle-shaped crystals of the dibromide (m. p. 164°) collect in the distillate. The crystals dissolve easily in alcohol, ether, wood spirit, and benzene, but are only sparingly soluble in water or soda solution. The platinochloride forms reddish-yellow needles

$$(C_5H_3Br_2N)_2,H_2PtCl_6 + 2H_2O,$$

sparingly soluble in water.

W. C. W.

Xanthine and Hypoxanthine. By A. KOSSEL (*Zeitschr. Physiol. Chem.*, **6**, 422—431).—The author has already in previous papers in this Journal shown that xanthine and hypoxanthine are formed by the action of dilute acids and water at 100° on nucleïns, a group of bodies whose representatives are found everywhere in the active cells of plants and animals, and which may therefore be regarded as necessary constituents of the developmentally active living tissue. It was therefore concluded that these products of decomposition of nucleïns have a more universal distribution, and that in the organs which are known to be the place of their formation, they are produced in larger amount than has hitherto been assumed. The present paper relating to some researches in regard to xanthine is in supplement to former communications upon the investigation and quantitative determination of hypoxanthine in a series of animal and vegetable structures.

D. P.

Solubility of Strychnine in Acids. By HANRIOT and BLAREZ (*Compt. rend.*, **96**, 1504—1506).—Strychnine dissolves with difficulty in acids, the solubility being greater the more dilute the acid. When a concentrated solution of a strychnine salt is slightly acidified, a precipitate is formed which is most abundant when the acid added is the same as that contained in the strychnine salt. If the solution is dilute, the precipitate forms less readily, and its formation is accelerated by agitation. The precipitate dissolves in an excess of acid, forming a solution which yields a precipitate when diluted, and it also redissolves if the solution is neutralised with ammonia. The precipitate formed by adding sulphuric acid to a solution of neutral strychnine sulphate consists of slender needles of the acid sulphate, $C_{22}H_{22}N_2O_2,H_2SO_4$, the mother liquid retaining 1·13 parts of salt per 1000. The addition of hydrochloric acid to a solution of strychnine hydrochloride, precipitates the neutral chloride,

$$2(C_{22}H_{22}N_2O_2,HCl),3H_2O,$$

in needles, the mother-liquor retaining 4·13 parts of salt per 1000. Since acid strychnine sulphate is very soluble in water, the formation of the precipitate is not due to the formation of an acid salt, but rather to the insolubility of strychnine salts in slightly acid liquids. It is necessary to bear these facts in mind in testing for strychnine. The amido- and nitro-derivatives behave in a similar manner.

C. H. B.

Putrefaction Alkaloïds. By L. BRIEGER (*Ber.*, **16**, 1186—1191). —In the first stages of putrefaction of albuminoïds, poisonous compounds are produced which resemble curare in their physiological action: they disappear again after the putrefaction has gone on for 8 to 10 days. To extract the poisonous bases from flesh, the following process is employed: Finely chopped horse flesh is stirred up with water and exposed to putrefactive fermentation for 5 or 6 days. The mixture is then boiled and filtered, and lead acetate is added to the filtrate. The lead salt is decomposed by sulphuretted hydrogen, and the filtrate after concentration is extracted with amyl alcohol.

Oxy-acids are removed by acidifying with sulphuric acid and extracting with ether. The sulphuric acid is precipitated by baryta, and the excess of baryta by carbonic acid. The alkaloid is then precipitated by the addition of mercuric chloride. The precipitate decomposed by sulphuretted hydrogen, and the filtrate concentrated: inorganic bodies first crystallise out; but on concentrating the mother-liquor, a compound is deposited in needle-shaped crystals of the composition $C_5H_{14}N_2H_2Cl_2$. This substance is soluble in water and spirits of wine, but is insoluble in ether, absolute alcohol, benzene and chloroform. The crystalline platinochloride is very soluble in water, but is precipitated by alcohol. The pure hydrochloride is slightly poisonous, but the impure salt has a more powerful action. This substance could not be prepared from fibrin or albumin, but only from flesh. On treating the hydrochloride with moist silver oxide, an unstable gelatinous mass is obtained, which resembles seminal fluid in odour. On distillation with soda, a mixture of *di-* and *tri-methylamine* is formed.

The filtrate from the mercuric chloride precipitate mentioned above contains a poisonous base, which forms a platinochloride of the composition $(C_5H_{11}N)_2,H_2PtCl_6$. A small dose of the hydrochloride produces a rapid flow of the saliva, strong secretions from the nose, and constant flow of watery liquids from the intestines, and finally convulsions. W. C. W.

Basic Products of Putrefaction. By E. and H. SALKOWSKI (*Ber.*, **16**, 1191—1195).—The authors have continued their research on the putrefaction of flesh and fibrin (*Ber.*, **12**, 648), and find that two bases are produced. The non-volatile portion of the product is concentrated, rendered alkaline by the addition of sodium carbonate, and treated with alcohol. The alcoholic extract is evaporated, acidified with dilute sulphuric acid, and extracted with ether. A base remains in the sulphuric acid but has not yet been investigated. The oily liquid which remains on evaporating the ethereal solution is dissolved in sodium carbonate solution, and after precipitating the higher acids of the acetic series with barium chloride, the filtrate is acidified with hydrochloric acid and extracted with ether. The residue left on evaporating this extract is purified by solution in absolute alcohol and conversion into the platinochloride; this forms orange-coloured crystals soluble in hot water. The crystalline hydrochloride is very soluble in water and in alcohol. The aurochloride forms dark yellow monoclinic crystals, which melt below 100°. The free base obtained by the action of silver oxide on an aqueous solution of the hydrochloride, is a white crystalline powder (m. p. 156°) having a peculiar odour. It is freely soluble in water, insoluble in ether, and only sparingly soluble in alcohol. It does not appear to have a poisonous effect on animals.

The analysis of the free base, hydrochloride, and gold salt, agree with the formulæ $C_5H_{11}NO_2$, $C_5H_{11}NO_2,HCl$, and

$$C_5H_{11}NO_2,HCl,AuCl_3 + H_2O$$

respectively, but the analysis of the platinochloride corresponds with the formula $(C_7H_{15}NO_2)_2,H_2PtCl_6$.

This seems to indicate that the crystalline substance is a mixture of homologous bases. W. C. W.

Zymase of Human Milk. By A. Béchamp (*Compt. rend.*, **96**, 1508—1509).—Human milk contains a zymase which possesses a much higher rotatory power than the galactozymase from cow's milk, and liquefies starch and converts it into sugar as readily as diastase. To extract this zymase in a somewhat impure condition, the milk is slightly acidified with acetic acid, and mixed with at least three times its volume of alcohol of 95 per cent.; the bulky precipitate is washed with dilute alcohol to remove sugar, treated with ether to extract fat, digested with water for some hours, and the liquid filtered. The filtrate possesses in a high degree the power of liquefying starch and converting it into sugar. The zymase was obtained from several quantities of milk drawn successively, and is therefore a product of the function of the milk gland, and is not formed by the alteration of milk stagnated in this gland. C. H. B.

Peptone. By A. Poehl (*Ber.*, **16**, 1152—1170).—Peptone prepared from blood serum and fibrin, is identical in its properties with peptone from egg albumin. It is thrown down from neutral solutions by alcohol in the form of a white precipitate. Dried at 100° it forms a slightly yellow brittle mass, soluble in cold water. The solution is not changed by boiling. Peptone is not precipitated by the addition of potassium ferrocyanide and acetic acid; but is completely precipitated from moderately concentrated neutral solutions by neutral salts. Tannin produces a brown flocculent precipitate in neutral or slightly acid solutions, but not in alkaline solutions. Millon's reagent produces in neutral or slightly acid solutions a brown precipitate, which turns red on warming. By the putrefaction of peptone, *ptomopeptone* is produced; it differs from peptone in that it has no action on polarised light, is not precipitated by basic lead acetate, and is decomposed by potash with formation of trimethylamine, and by sodium hypobromite with evolution of nitrogen. Peptone can generally be detected in the urine of fever patients. Animal tissue (*e.g.*, of the lungs and kidney) converts blood serum and fibrin into peptone at a temperature of 35°: papaïn, the leaves of *Carica papaya*, and other vegetable tissues, have the same property. The artificial formation of peptone only takes place in the presence of a small quantity of free acid. Peptone is gradually transformed into albumin by the action of dehydrating agents, such as alcohol and neutral alkali salts. In the first stage of the reaction it exhibits the properties of Meissner's β-peptone, and is precipitated by acetic acid and potassium ferrocyanide. In the next stage it is precipitated by nitric acid (Meissner's α-peptone). After the action has continued some time, the product is no longer soluble in cold water (Meissner's metapeptone); and in the last stage the product gives with neutral salts a precipitate which dissolves in hot water, but separates again on cooling. (Meissner's *parapeptone*, *propeptone* of Schmidt-Mülheim, *hemialbuminose* of Kühne.)

Ptomopeptone does not exhibit these changes when treated with dehydrating agents.

The specific rotation of peptone is $[\alpha]_D = -14\cdot479°$ when $q = 0$ (q is the percentage of water in the solution) and $[\alpha]_D = -63\cdot779°$ when $q = 100°$, *i.e.*, for an infinitely dilute solution. The specific refraction of peptone $\frac{n-1}{d} = 0\cdot4212$ when $q = 0$, and $0\cdot3316$ when $q = 100$. No change in specific gravity, rotary power or index of refraction takes place in the conversion of albumin into peptone, hence the author regards the change of albumin into peptone as merely a transformation into a more soluble modification. W. C. W.

Physiological Chemistry.

Behaviour of Elastin in Peptic Digestion. By J. HORBACZEWSKI (*Zeitschr. Physiol. Chem.*, **6**, 330—345).—Little has heretofore been known on this subject, the view obtaining in most of the text-books being that elastic tissue is not acted on by the digestive fluids.

Recently, however, J. Etzinger has made the observation that the ligamentum nucliæ of the ox is in the course of ten days almost completely dissolved by pepsin and 0·3 per cent. solution of hydrochloric acid.

The author's experiments, conducted also with elastic tissue, prepared from the ligamentum nucliæ (cervical vertebral ligament) of the ox comports itself similarly to albumin in peptic digestion, and yields similar products in the reaction. The elastin obtained in the end by repeated purification of the tissue employed, details of which are given by the author, was found to be absolutely free from sulphur, and to yield on ultimate analysis the following percentage results :—

C 54·32; H 6·99; N 16·75; Ash 0·51.

The products of digestion are two substances, which are separable one from another. One of these, to which the name of *hemillactine* is given by the author, is precipitable from its aqueous solution by acetic acid and potassium ferrocyanide, also by freshly precipitated plumbic hydroxide and ferric acetate, and behaves somewhat like the hemialbumin of Salkowski, or the propeptone of Schmidt-Mülheim. The other exhibits properties similar to those of albumin peptone, and is not precipitated by potassium ferrocyanide and acetic acid. It is named *elastin peptone* by the author. As regards ultimate analysis very little difference is perceptible between hemielastin and elastin, as the following results concerning the former show :—C 54·22; H 7·02; N 16·84; ash, 0·48 per cent.

Elastin peptone yielded the following percentage composition:—

C 53·57; H 8·075; N 16·20.

Other details of the properties and reactions of these respective substances are given in the paper.

By simple heating with water at 100° in a closed vessel for about 20 hours, elastin is changed into elastin peptone. Schultze had previously described the process with superheated steam as essential for this transformation.

In regard to the physiology of digestion, it is therefore now shown that elastin is digestible, and doubtless capable of absorption; although not holding any prominent position among the constituents of nutritive substances, it nevertheless must be included with those, and in the form of sarcolemma, neurilemma, and the muscular sheaths, apart from its occurrence in larger amount in the ligaments and walls of vessels, is widely distributed, and a digestible constituent of animal food. The author had an unusual opportunity of testing the digestibility of elastin in the case of a patient under the care of Albert, in the Surgical Clinique, Vienna, who had a gastric fistula. A small bag of closely woven silk, containing 1 gram of elastin powder, was introduced into the stomach through the fistula, and its digestion watched. In 24 hours two-thirds of the elastin had disappeared, some swollen pulpy elastin remaining behind. This was diluted with water and filtered. The clear solution showed the reactions of hemielastin.

D. P.

Vegetarianism from a Physiological Standpoint. By T. Cramer (*Zeitschr. Physiol. Chem.*, 6, 346—385).—The author concludes a historical and physiological consideration of this subject, with the following summary:—

1. The dietary of vegetarianism affords to the system both absolutely as regards total nutriment and the relative proportions of its constituents, sufficient food for the maintenance of bodily and intellectual functions.

2. This dietary is, however, adequate for the maintenance of life, only inasmuch as the vegetable portion is supplemented by animal albumin, in the form of milk and eggs.

3. This dietary, assuming that care be taken not to overburthen the alimentary system, is too costly for the nourishment of large bodies of men, as in workhouses, barracks, and prisons, where the cheapest possible modes of feeding can be employed. It is besides an eminently impracticable method of alimentation, as for the same cost a much larger quantity of mixed and profitable food can be procured.

4. Then there arises the question, how will an organism so nourished comport itself towards disease? Experience and observation in regard to prisoners and others living under otherwise equally favourable hygienic conditions, all point to the conclusion that on vegetarian diet the system has less power of resisting the attacks of disease.

D. P.

Comparative Investigations of Intestinal Gases. By H. Tappeiner (*Zeitschr. Physiol. Chem.*, 6, 432—479).—Investigations into the nature of the intestinal gases have hitherto been limited in number. Besides the recently published analysis of these gases in herbivorous animals by the author (*Ber.*, 1881), Planer had examined those of the dog and of man; Ruge the gases of the colon in man; and C. B. Hofmann of the dog and rabbit. Considerable differences appear, especially in regard to the occurrence of CH_4; Ruge states that in man this gas is formed only after exclusively leguminous or flesh diet, and is absent in a pure milk diet; neither Planer, Ruge, nor Hofmann found it in the case of the dog, even after feeding with leguminous food; and Hofmann obtained a like result in the rabbit. No explanation of these differences has so far been given, the want of which affects the question as to the substances from which, in the process of intestinal change, CH_4 is formed.

The author carried on a series of experiments in regard to this question in a variety of animals and under different conditions of nutrition. His results show that CH_4 occurs in the intestine of the herbivora and of omnivorous animals, but not of carnivorous. In the former it is found in every instance, save after milk diet. Apart from the stomach, it is formed only in the colon, never in the small intestine, with the exception of ruminating animals, in which its formation begins in the ileum.

The abundant formation of CH_4, after feeding with legumina and cabbage, can scarcely have any other source than the cellulose or mixture of tissues collectively termed woody fibre. But of what substance, therefore, CH_4 in the large intestine is formed by fermentation cannot with certainty be affirmed, but the probable sources are albumin and cellulose. D. P.

Sugar from the Lungs and Saliva of Phthisical Patients. By A. G. POUCHET (*Compt. rend.*, **96**, 1506—1507).—The saliva, or, better, an aqueous decoction of the lungs, is acidified with acetic acid, boiled, the coagulated albuminoïd matters filtered off, and the filtrate exactly neutralised with baryta-water. Barium acetate is added until a precipitate ceases to form; the precipitate filtered off; the filtrate mixed with neutral lead acetate; boiled, and again filtered. The filtrate is mixed with a large excess of ammonia, and allowed to stand 48 hours in the cold, when it deposits a bulky dirty grey precipitate consisting of a lead compound of the sugar mixed with a considerable quantity of a compound of lead with peptone. This precipitate is washed with cold water, suspended in water, treated with sulphuretted hydrogen at 100°, and filtered through porous earthenware. The filtrate is mixed with tannin to remove gelatin and peptones; agitated with animal charcoal; again filtered, the filtrate concentrated in a vacuum, and precipitated with alcohol. The precipitate is dissolved in a small quantity of water, and purified by repeated precipitation with alcohol. The sugar thus obtained is an almost white amorphous substance which becomes brown on drying, even in a vacuum and in the dark. Its solution in boiling alcohol of 25 per cent. deposits brilliant crystalline scales on cooling. The aqueous solution, evaporated in a vacuum, yields a syrup which will not crystallise, but which, when completely dried, forms somewhat regular elongated rectangular scales resembling crystals. The sugar is hygroscopic and very soluble in water, forming a perfectly limpid solution, but it is insoluble in strong alcohol, ether, and hydrocarbons. Its composition is $C_{12}H_{20}O_{10}$ when dried in a vacuum, and $C_{12}H_{18}O_9$ when dried at 120°.

If the aqueous solution of the sugar is mixed with neutral lead acetate, and alcohol added, a greyish-white precipitate is formed which, when dried at 120°, has the composition $C_{12}H_{14}PbO_9$. A concentrated boiling aqueous solution yields, with basic lead acetate, a heavy grey precipitate very slightly soluble in boiling water. It is a mixture of $C_{12}H_{14}Pb_2O_9$ and $C_{12}H_{12}Pb_3O_9$ in equivalent proportions. An alcoholic solution of basic lead acetate, added to a boiling solution of the sugar in alcohol of 25 per cent., produces a gelatinous precipitate of the compound $C_{12}H_{10}Pb_4O_9$. Aqueous solutions of the sugar yield no precipitate with zinc acetate, but on careful addition of ammonia a flocculent precipitate is formed which dissolves in boiling water and is deposited in microscopic needles on cooling. After drying in a vacuum, this precipitate has the composition $C_{12}H_{12}Zn_3O_9.8Zn(OH)_2$; it loses $4H_2O$ at 120°. These metallic derivatives are closely analogous to those formed by various sugars and dextrins. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Diastatic Ferment of Bacteria. By J. WORTMANN (*Zeitschr. Physiol. Chem.*, 6, 287—329).—Recent investigations have conclusively established the universal occurrence of diastatic ferments in different parts of plants, and have thrown a new light on the processes of nutrition and fermentation.

According to earlier observations, the presence of diastase in the plant was limited to germinating wheat or barley, and knowledge in regard of its wider diffusion has been advanced by the recent works of Gorup-Besanez, Will, Kranch, and especially Baranetzky. The researches of Musculus, E. Schulze, O'Sullivan, and others, have afforded an insight into the quantitative relations and the modifying external factors of temperature and acidity concerned in the action of diastase in the transformation of starch into glucose.

Having in view the action of bacteria as causes of putrefaction or fermentation in which the destruction of the putrescible or fermentescible body is accomplished by the appropriation for the purpose of nutrition by the bacteria of constituent nitrogen or carbon, the question may be asked—can bacteria also obtain their carbon from starch, just as by the researches of Pasteur and Cohn they have been proved to be capable of obtaining it, not only from sugar but from ammonium tartrate? Are bacteria, by the secretion of a starch-transforming ferment analogous to diastase, or in any other but not clearly defined way, capable of transforming starch into soluble, diffusible, and nutrient combinations? Notwithstanding the numerous investigations into the chemical and physiological relations of bacteria, very little has been made out in regard to their action on starch—a circumstance from which it may be presumed that the solution of starch by bacteria can be effected only in certain instances. In his work, "Ueber die niederen Pilze," Naegeli refers to the secretion by these organisms of a special energetic ferment capable of changing milk-sugar into fermentescible sugar, starch and cellulose into glucose, and of dissolving coagulated albumin and other albuminates, and Sachsse alludes to the circumstance of starch solution undergoing no change so long as it is protected from the influence of organic germs by which otherwise it quickly undergoes transformation.

Some experiments, made by the author in the summer of 1881 with milky juices, led him to believe that certain appearances of corrosion exhibited by the starch granules present must be due to the action of bacteria. The result of further precise experiments, undertaken to decide this point, led to the conclusion that bacteria are capable of drawing their supply of carbon from starch, and that the appearances of solution or corrosion exhibited by the solid starch granules are identical with those caused by the action of diastase or saliva.

The method used by the author was as follows:—To about 20 or 25 c.c. a mixture of inorganic salts (sodium chloride, magnesium sulphate, potassium nitrate, and acid ammonium phosphate) in equal proportions was added to the extent of 1 per cent. The same quantity of solid wheat-starch was then added, and the liquid then inoculated with one or two drops of a strongly bacterial solution, shaken, corked, and allowed to remain in a room at a temperature of 18—22°. [*Bacterium termo* was the predominating organism in the inoculating fluids employed.] In from 5—7 days, the first signs of commencing corrosion of the starch grains become visible, the larger grains being the earliest attacked, and much later, when these have almost completely disappeared, the lesser granules are attacked.

In a second series of experiments soluble starch was substituted for the solid form, the progress of the reaction being watched by the aid of iodine. Samples taken from time to time exhibited at first the blue colour, then violet or dark red, passing to wine-red, and, finally, when the starch had disappeared, underwent no change.

As Baranetzky has shown, the starch granules of different kinds are acted on with very unequal rapidity by the diastatic ferments of plant juices, the strongest ferment of all—malt diastase—being well known to have no perceptible influence, even after long exposure, on solid potato-starch granules, whilst wheat and buckwheat are dissolved with facility.

Experiments were made with a view to ascertain whether the action of bacteria on starch was analogous; in these, wheat-starch grains are shown to be by far the most readily attacked by bacteria—in several instances having even completely disappeared before other sorts of starch were attacked. Differences were also noticed in regard to the times when palm-starch, canna-starch, turmeric-starch, and iris-starch were attacked, their degree of resistance being in the order given. Potato-starch alone resisted attack. When wheat-starch in the solid state was mixed with starch solution or with starch-paste, the solution became entirely (and the paste in greater part) changed before the solid granules were attacked.

With regard to this unequal power of resistance shown by different kinds of starch, the author concludes from his further observations, that the difference of rapidity with which a given kind is attacked and dissolved by a ferment is inversely proportional to its density, provided always that the granules in question are entire and uninjured by cracks or fissures. In the same way are explained the differences in point of time in which granules of the same kind are sometimes observed to undergo change accordingly as these are intact or otherwise.

The cause of potato-starch or of bean-starch, and, even under certain conditions, wheaten starch resisting attack, in spite of the abundant presence of bacteria, is apparently to be sought for in the fact that other more easily accessible sources of carbon nutriment were also present, certain albuminoïd constituents of the potato slices or of the beans employed affording this more readily than the starch granules, just as in the experiments, above cited, with wheaten starch solution, and solid wheaten starch: the former was preferentially attacked; only after all, or at least the chief portion of the albuminoïds present, had been used up was the starch in these cases attacked.

Experiments were also made with the same results in which, after Cohn, ammonium tartrate was employed along with starch as a nutrient medium for the bacteria, with the result that so long as even a trace of this salt was present with the starch, the latter was not attacked by bacteria in the slightest degree, but, on its disappearance, appearances of solution became at once visible in the starch granules. Another point was also established in the course of these experiments, that if air is excluded, no appearances of corrosion or solution of the starch granules are manifested.

Other researches were made to answer the problem as to whether the nature of this action of bacteria on starch was such that an unformed ferment analogous to diastase was secreted by those organisms to which the corrosive appearances may be ascribed, these being, as already stated, precisely similar to the resulting action of diastase itself.

That the starch in the process became changed in part to glucose was easily ascertained by testing with Fehling's solution, and a detailed series of experiments, made with a view to eliminating if possible the ferment itself, yielded evidence showing that bacteria possess the remarkable property of producing a starch-transforming ferment only when no source of carbon other than starch is at their disposal, and this ferment is incapable of changing albumin into peptone, just as in the case of diastase. It is well known that the pepsin of gastric juice acts only in an acid medium. The plant juices which possess a diastatic property exhibit likewise a more or less acid reaction, so that as Baranetzky assumes, the co-operation of an acid in the case of diastase is a necessary condition of its activity. The solutions in which starch in one or another form was submitted to the action of bacteria were always slightly acid, due to the presence of acid ammonium phosphate, and when the solutions were purposely made neutral, the process of starch transformations went on more slowly. Detmer some time since has shown that addition of small quantities of citric acid to a solution containing diastase, hastens its action on starch. The author's observations are in harmony with this, but in addition show that the process of starch transformation by bacteria is capable of going on in the absence of acid, and that the bacteria do not yield any acid in the process. The results of the author's researches may be briefly recapitulated.

1. Bacteria are capable of acting on starch, whether in the solid state, as paste, or in solution, in a manner analogous to diastase.
2. As in the case of diastase, different kinds of starch are attacked by bacteria with different degrees of rapidity.
3. The action of bacteria on starch is manifested only in the absence of other sources of carbon nutriment, and when access of air is not prevented.
4. The action of bacteria on starch is effected by a ferment secreted by them, and which, like diastase, is soluble in water, but precipitable by alcohol.
5. This ferment acts precisely as diastase in changing starch into a sugar capable of reducing cupric oxide, but not possessed of peptonising properties.
6. The ferment itself is also capable of acting on starch in the absence of oxygen.
7. The ferment is secreted by the bacteria also in neutral solution of starch, and exerts its influence under these conditions.
8. This influence is expedited in slightly acid solutions.

The author concludes his paper with speculations as to the conditions under which bacteria are capable of generating this amylolytic (diastatic) ferment, instead of the ordinary peptonising one.

D. P.

Cultivation of the Cacao Tree. By BOUSSINGAULT (*Compt. rend.*, **96**, 1395—1399).—The cacao tree requires a rich deep moist soil, in shaded localities, close to the sea or to rivers. The tree flowers when about thirty months old, and the fruit is ripe about four months after the fall of the flowers. The weight of the fruit varies from 300—500 grams, and after picking they are exposed to the sun during the day, and placed under sheds at night. Active fermentation soon sets in, but if allowed to proceed too far is injurious. The cacao is decorticated by careful roasting, which also develops an aroma, due to a minute quantity of a volatile oil. Examination of Trinidad cacao showed the presence of butter, starch, theobromine, asparagine, albumin, gum yielding mucic acid, tartaric acid free and combined, soluble cellulose, ash, and indeterminate substances. Decorticated cacao, slightly roasted and separated from the seeds, forms the basis of chocolate, which, when genuine, consists only of cacao and sugar. The superiority of chocolate over tea, coffee, maté, &c., is due to the fact that in addition to theobromine it contains in a small bulk a large quantity of food materials, and indeed approximates in composition to milk. C. H. B.

Analytical Chemistry.

Use of Hydrogen Peroxide in Analytical Chemistry. By A. Classen and O. Bauer (*Ber.*, **16**, 1061—1074).—When hydrogen peroxide is added to a solution of ammonium or sodium sulphide, and the liquid boiled, the whole of the sulphur is converted into sulphuric acid. This reaction furnishes a method for the quantitative estimation of hydrogen sulphide, either as gas or in solution, and of the sulphur in metallic sulphides, the sulphuric acid obtained on oxidation being precipitated in the usual way as barium sulphate. The method applies also to the estimation of sulphurous acid and sulphites. To estimate hydrochloric acid in a solution containing hydrogen sulphide, ammoniacal hydrogen peroxide is added, and the solution boiled until no more oxygen is evolved; silver nitrate and nitric acid are then added, according to the usual method. In estimating hydriodic and hydrobromic acids in the presence of hydrogen sulphide, the method is the same, except that sodium carbonate takes the place of the ammonia. Arsenious sulphide in ammoniacal solution is oxidised by the same reagent to arsenic acid and sulphuric acid, the former of which can be precipitated as ammonium magnesium arsenate, and weighed as pyroarsenate, and the latter as barium sulphate. Antimonious sulphide is also completely oxidised by hydrogen peroxide, whilst in the case of the pentasulphide only a partial oxidation can be effected. A more convenient method of analysing sulphides decomposable by hydrochloric acid is to pass the evolved hydrogen sulphide into the alkaline hydrogen peroxide, a current of carbonic anhydride being driven through the apparatus, then acidulating the solution with hydrochloric acid, boiling to decompose the excess of peroxide, and precipitating with barium chloride. The sulphides of antimony, tin, cadmium, and iron can be treated in this way. The oxidation and estimation of sulphites is carried out in the same way as in the case of the sulphides. A. K. M.

Distillation of Wine. By S. Kiticsan (*Ber.*, **16**, 1179—1183).—The author having repeated Liebermann's experiments (*Ber.*, **15**, 154, 438, 2554) on the distillation of wine, finds that the distillate contains ammonia and formic acid, and that the precipitate produced on addition of silver nitrate contains organic silver salts; Wartha's method (*Ber.*, **15**, 437) for detecting sulphurous acid in wines is therefore untrustworthy. Old wines contain from 0·0057—0·034 per cent. of ammonia. W. C. W.

Estimation of Carbon Bisulphide in Thiocarbonates. By A. Müntz (*Compt. rend.*, **96**, 1430—1433).—30 c.c. of the thiocarbonate (*i.e.*, 42 grams, since the sp. gr. of the commercial product is 1·4) is introduced into a flask of 500 c.c. capacity, and mixed with 100 c.c. of water and 100 c.c. of a saturated solution of zinc sulphate, and the flask closed with a caoutchouc stopper, through which passes a long tube bent at right angles and drawn out to a point at the far end, the upper part being surrounded by a condenser. The tube dips into a narrow cylinder of 60 c.c. capacity, graduated in 0·1 c.c. This cylinder contains about 30 c.c. of ordinary petroleum, the volume of which is accurately read off, and the tube is arranged so that its extremity is immersed to about two-thirds the total depth of the petroleum. The flask is agitated, and when the evolution of gas slackens, the liquid is very carefully heated, the temperature being gradually raised to ebullition, and the boiling being continued until 10—12 c.c. of water has condensed in the graduated cylinder. The carbon bisulphide which is given off dissolves in the petroleum without contraction. At the close of the operation, the total volume of the liquid in the cylinder is read off, the volume of the condensed water subtracted, and 0·2 c.c. added to the increase in the volume of the petroleum, in order to correct for the small quantity left adhering to the tube. The corrected increase in volume multiplied by 1·27 (sp. gr. of carbon bisulphide) gives the weight of carbon bisulphide in the 30 c.c. of thiocarbonate. If the petroleum at the lower part of the cylinder dissolves so much carbon bisulphide that it becomes heavier than water, and sinks below the condensed water, the total volume of the liquids is read off, the cylinder closed with the thumb, and gently inclined so as to mix the separated layers of petroleum, and the volume again read off after standing about 15 minutes. Copper sulphate, lead acetate mixed with acetic acid, and recently precipitated lead sulphate may be used instead of zinc sulphate. The method gives good results. C. H. B.

Occurrence and Estimation of Free Tartaric Acid in Wine. By A. Claus (*Ber.*, **16**, 1019—1022).—The author has previously pointed out that the presence of small quantities of tartaric acid in wine is no proof of adulteration. From the examination of a number of pure but poor wines, he finds a percentage varying from 0·01 to 0·05. Weigelt (*Ber.*, **16**, 812) also finds about the same amount, viz., 0·01—0·059 per cent. This is easily accounted for by the fact that the grapes employed in the manufacture of the wine are not all ripe, the unripe ones containing the free acid.

To estimate the free tartaric acid, the wine is evaporated to dryness, and the residue heated in an air-bath at 110°. It is then extracted with alcohol, and the acid precipitated by means of potassium acetate. If a known quantity of tartaric acid is added to a wine free from acid and an analysis is then made, the results obtained will vary according to the composition of the wine; the tartaric acid added decomposing the salts of other acids, part of which are volatilised during the evaporation, and thus a low result will be obtained. From the amount of tartaric acid which in this way becomes *latent*, the author suggests the possibility of devising a method for estimating the value of a wine. A. K. M.

Examination of Fats. By K. Zulkowsky (*Ber.*, **16**, 1140—1142).—Gröger's modification (*Dingl. polyt. J.*, 1882, **244**, 303, and **246**, 286) of Hausamann's method (*ibid.*, **240**, 62) of testing fats depends on the fact that fatty acids are at once saponified by alcoholic potash, whereas neutral fats are only saponified on boiling.

Phenolphthaleïn is added to an alcoholic solution of the fat, and standard alcoholic potash dropped in until the red coloration disappears. Excess of standard potash is then added, the mixture boiled for half an hour, and the excess of alkali determined volumetrically. In this way the amount of fatty acids and of neutral fats is ascertained.

The author points out that the quantity of fat saponified by a litre of the normal alkali, gives a clue to the nature of the fat, and would for example distinguish between artificial and natural butter.

The amount of glycerol in fats can be estimated in this way, each c.c. of normal alkali required to saponify the neutral fat corresponding with 0·030667 gram of glycerol.

If the fat is dry and pure, then the weight of neutral fat $F - G$ $[G = (0·012667v)]$ = the amount of fatty acids, when v = the c.c. of standard potash used.

The molecular weight of the fatty acid can also be ascertained. W. C. W.

Technical Chemistry.

Modifications of Silver Bromide and Chloride. By H. W. Vogel (*Ber.*, **16**, 1170—1179).—After referring to the researches of Stas (*Ann. Chim. Phys.*, 1874, 2, 3), Monckhoven, Eder (*Theorie und Praxis der Gelatinemulsion*, 1 Aufl., 9) and Abney (*Proc. Roy. Soc.*, 1881, No. 217), the author states that only two modifications of silver bromide exist, viz., one precipitated from aqueous, and a second from alcoholic solutions. The former is most sensitive to the blue rays of the solar spectrum (wave-length 450); the latter has its maximum of sensibility in the indigo between 438 and 440.

The formation of these two modifications is neither influenced by the presence of gelatin or collodion, nor by the temperature at which the precipitation takes place. The nature of the silver bromide does not depend on whether an excess of silver salt or of alkaline bromide is used in the precipitation; neither does treatment with ammonia change the particular modification produced. The variety sensitive to indigo rays is only produced in solutions containing alcohol of at least 96 per cent. It cannot be brought into a finely divided state by shaking with gelatin solution, but this is easily effected if collodion is used. The variety sensitive to blue rays on the other hand is easily obtained in a finely divided state in gelatin, but not in collodion. For photographic purposes, the silver bromide is always precipitated in presence of gelatin solution or collodion, in order that it may be obtained in a very finely divided state.

The modification sensitive to blue rays is more difficult to reduce to the metallic state than the indigo modification. Collodion plates are therefore much more rapidly acted on by the "chemical developer"—ammonium pyrogallate—than gelatin plates. Collodion silver bromide plates are more easily acted on by sensitisers than the gelatin plates. The variety of silver bromide sensitive to blue rays is 15 times more sensitive to chemical than to physical developers; the other modification is only three times more sensitive to chemical developers. If any excess of bromide is used in preparing the silver bromide, and the precipitate is heated for some hours in water, the sensitiveness of the first modification increases, but the variety sensitive to indigo rays is not affected by this treatment. The finely divided silver bromide sensitive to blue rays has a tendency to adhere together, forming a compact mass, which is less soluble in sodium thiosulphate than ordinary silver bromide. Although the indigo modification is more easily reduced than the blue variety, the latter is more sensitive to the action of light.

Silver chloride gelatin emulsion is most sensitive to ultra-violet rays of light between Fraunhofer's lines H″ and H′, the maximum of sensitiveness of silver chloride collodion emulsion lies between G and H, about wave-length 410. W. C. W.

Scientific Basis of Antisepsis and Origin of Septic Poison. By P. ZWEIFEL (*Zeitschr. Physiol. Chem.*, **6**, 388—421).—The practical application by Lister of the principles of antisepsis in surgery, in aiming at the destruction during operation, and the subsequent exclusion during recovery by appropriate dressings, of pathogenic organisms or germs believed to enter from the air and external surroundings, has been successful in preventing the occurrence of putrefaction in wounds. Hence it has been conjectured that the healthy body itself must be free from these causes of putrefaction if the above results are due to the protection of the wound from their access from without; otherwise if existing already in the organism, what benefit is likely to arise from such efforts designed to ward off bacteria from superficial parts?

The earliest experiments concerning the presence of putrefactive germs in the normal and healthy organism are those of Billroth and Tiegel, in which the various portions of the body experimented upon were rapidly removed after the animal had been bled to death by excision with a knife previously heated to redness, and at once imbedded in paraffin. The results were apparently affirmative.

The author repeated the methods of these investigators, and showed that it was impossible to avoid sources of error, there being an unavoidable if only momentary exposure to air to begin with, in the act of removing the organ from the body to the paraffin, and those viscera which chiefly, without exception, became putrid, were the pancreas, liver, and spleen, precisely those to which previous access of germs from the intestinal canal was most likely to have taken place.

Burdon Sanderson obtained like results. Similar objections as to exposure to the air for periods however brief, attach to the method by which at a later period Nencki and Giacosa sought to establish the occurrence of bacteria in healthy tissues, in which the organs investigated were at once upon removal plunged into bell-jars filled with mercury previously heated until mercurial vapours were given off, and then covered over with a thin stratum of carbolic acid solution. After the immersion of the organ, the whole apparatus was then transferred to the culture oven, and kept at a constant temperature of 38—40°. All possible precautions were employed by the above-named experimenters to prevent the access of germs by means of the instruments and other parts of the apparatus.

It is evident that only under rigidly absolute conditions of air exclusion can the question of the pre-existence of such germs in healthy tissues be decided. This is certainly inconceivable as regards solid structures which cannot be subjected to experiments without some degree of exposure to the air, and it is only in the case of the blood which admits of being drawn directly from the artery or vein, and at once transferred to the previously disinfected mercury, that these conditions can be met. Blood was accordingly employed by the author in his crucial series of experiments, being drawn from the vessel under antiseptic precautions. Thus drawn and maintained at constant temperatures under mercury, no signs of putrefaction blood appeared.

The author repeated the experiment with the heart, an organ admitting of almost instantaneous removal from the body, but in every instance putrefaction occurred.

Microscopic examination of the blood thus preserved from contact with air, revealed the constant presence of various coccus forms in lively movement, confirming earlier observations in this direction, especially those of Hensen.

To decide whether the difference in results between the two sets of experiments with blood and with the heart was due to the influence of air and its germs, another series was made in which air was designedly introduced by means of a small glass syringe into the blood under the bell-jar: no putrefaction took place, but when the blood was first received in a saucer, and then taken up into a syringe and brought under mercury, all the signs of putrefaction and evolution of gases occurred. Seeing that the blood to which air had been added underwent no change, whilst the heart, muscle, and other solid organs, after short contact with air in removal became putrid, it became apparent that the blood is not adapted as a medium for the development of bacterial germs. But this could presumably depend only on the larger proportion of oxygen in the blood, which otherwise is analogous to the solid tissues, and extremely putrescible under conditions of warmth and moisture.

Experiments were instituted to determine this point as to the influence of oxygen, in which the oxygen was removed from its solution in the blood by means of hydrogen gas; and in the other the solid organs were exposed in an atmosphere of pure oxygen. The results were remarkable. The blood thus deprived of its oxygen underwent putrefactive changes, whilst the heart and other organs remained unchanged. Venous blood reacted in the same way as arterial.

Experiments were made to determine the infectious quality of the blood which had been withdrawn under antiseptic precautions, and maintained for days under mercury at a temperature of 38—40° C. If the presence of oxygen hinders the advent of septic changes, blood, which with its oxyhæmoglobin has been preserved at 40°, will not be septic. On the other hand, the mere withdrawal of its oxygen and the conditions of experiment remaining unchanged, will make it of septic quality.

The blood in these experiments was injected into the peritoneal cavity of rabbits. Blood, from which the oxygen had been removed by displacement with hydrogen alone, showed septic qualities, the animals dying of septicæmia. The author refers to the circumstance that in place of fever, a lowering of the temperature was observed; but recalls the fact that peritoneal septicæmia may run its course without elevation of temperature.

Similar results were obtained in experiments in which Potain's apparatus replaced hydrogen, thus removing any objection as to a possible noxious influence of this gas. The whole series of experiments establish the fact that blood from which the oxygen has been removed and for eight days maintained at a temperature of 40°, becomes of virulent quality through the development of something analogous to the septic poison. The blood, it is to be noted, had no positively putrid smell, but was either quite odourless or faintly mawkish, resembling that of a slaughter-house. As *Septicæmia* is derived from *septicos*, putrid, this term is not an accurate one for the blood poison, which for the present may be designated "*Anoxygenhœmia.*"

The author infers from these results that blood from which oxygen is expelled, and which has been kept at a blood heat for eight days, becomes, even when it has been derived from a perfectly healthy animal, virulent, the poison thus generated being the septic poison or nearly allied thereto, and that the change is effected without the concomitant presence of atmospheric germs. This poison would appear to have not a fermentative, but a chemical effect, as it kills only in a certain somewhat large dose, strong animals being able to resist and recover from it. The withdrawal of oxygen is the essential point, and this, with a large amount of blood (taken by the author from the carotid artery), preservation for eight days, and a temperature of 38—40°, are the conditions of success.

Whether or not two different sorts of organisms exist in normal blood, of which one cannot undergo development in presence of much oxygen, but only exhibits its properties in the absence of this gas, is a crucial point of this problem.

Pasteur has already described, as the result of experiments conducted with Joubert and Chamberland, that the septic bacteria can develop only when oxygen is excluded, as in a vacuum or in carbonic acid. Kaufmann, Grossmann, and Mayerhausen have found that the rod bacteria were killed by the introduction of pure oxygen. In the present instance, however, healthy blood has acquired septic properties upon withdrawal of oxygen. As to whether in the treatment with oxygen other morphological elements thrive than in the opposite condition, this is denied by the author. The formation of the virus is apparently independent of micrococci and a result of purely chemical influences. D. P.

Hardening of Soft Calcareous Rocks by means of Fluosilicates of Insoluble Bases. By L. KESSLER (*Compt. rend.*, **96**, 1317—1319).—The ordinary method of hardening calcareous stone by means of alkaline silicates has many disadvantages, mainly owing to the fact that it leaves the stone impregnated with soluble alkaline salts. The author proposes to treat the stone with a solution of a fluosilicate of some metal which forms an insoluble oxide, such as magnesium, aluminium, zinc, or lead. Carbonic anhydride is given off, and calcium fluoride, silica, and alumina, or the carbonate of lead or zinc, or magnesium fluoride, are formed, all these compounds being more insoluble than the stone itself. No soluble salts are introduced into the stone, and stones treated in this manner do not suffer from the action of frost. In order to give a smooth surface to rough stones, some of the powdered stone is made into a paste with water, applied to the surface of the stone, and, after drying, treated with the fluosilicate solution. The paste soon becomes as hard as the stone itself, and by mixing the paste with various insoluble colouring matters, many different effects can be produced. If some coloured fluosilicate, such as copper fluosilicate, is used, the stone is coloured for a considerable depth, and usually various markings are produced, owing to the unequal absorption of the colouring matter by different parts of the stone, which is not homogeneous. C. H. B.

Treatment of the Washings from Wool. By DELATTRE (*Compt. rend.*, **96**, 1480—1483).—The crude potassium carbonate obtained from the suint which is extracted from wool by systematic washing has the average composition, $K_2CO_3 = 80$; $K_2SO_4 = 6$; $KCl = 4$; $Na_2CO_3 = 3$; insoluble, 5; loss, 2 = 100. After the removal of the suint, the wool is washed systematically, and the washings are allowed to run into deep narrow cisterns, where they deposit a heavy sand, which makes an excellent manure. The liquid is then run into a larger cistern, at the entrance to which it meets with a jet of hydrochloric acid or acid ferric chloride, which liberates a large quantity of fatty acids. These rise to the surface and are skimmed off, and the acid liquid is run into a tub provided with a mechanical agitator, treated with milk of lime, and run into another cistern where the calcareous matter is deposited, the clear liquid being allowed to run away into the river. The calcareous deposit constitutes a very rich vegetable soil, or may be used for making bricks. The fatty acids are compressed at a moderate temperature, and yield an oil which furnishes a good illuminating gas, and a solid cake containing a considerable proportion of fragments of wool and nitrogenous substances. This method is profitably applied to the wash-water from 6,000,000 kilos. of wool per annum. C. H. B.

Mineral Combustibles. By BOUSSINGAULT (*Compt. rend.*, **96**, 1452—1456).—The following table shows the composition of a number of combustible substances from South America and other localities :—

	1	2	3	4	5	6	7
Carbon	86·82	82·85	85·29	77·84	82·7	71·89	80·96
Hydrogen	13·16	13·09	8·24	8·93	10·8	6·51	5·13
Oxygen	0·00	4·06	6·22	11·54	6·5	21·57	12·50
Nitrogen	0·02	0·00	0·25	1·70	0·0	0·03	1·41

	8	9	10	11	12	13	14
Carbon	87·05	87·81	93·05	92·25	94·83	97·6	97·87
Hydrogen	5·00	3·88	3·35	2·27	1·27	0·7	0·37
Oxygen	6·56	7·67	3·43	4·94	3·16	1·7	1·70
Nitrogen	1·39	0·64	0·17	0·54	0·74	—	0·06

1 and 2 are analyses of *bitumen* from the fire pits of Ho-Tsing in the province of Szu-Tchuan, China. This bitumen is dark green by reflected light, brown by transmitted light. It is liquid at ordinary temperatures, but when cooled deposits a crystalline granular mass of *naphthalene.* Column 1 gives the analysis of the portion remaining liquid. Column 2 the analysis of the semi-solid portion. 3. *Egyptian asphalt*, which left an ash consisting of ferric oxide. 4. *Bitumen of Judea*, found floating on the Dead Sea. 5. *Fossil resin*, resembling amber in appearance, from the auriferous alluvium at Giron, near Bucaramanga, New Granada. 6. *Fossil resin* from the auriferous alluvium of Antioquia, New Granada. 7. *Coal* from Canoas, plateau of Bogota; height, 2800 m. It occurs in grit connected with neocomian limestone. 8. *Fibrous coal* from Antioquia. 9. "*Fusain*" from Blanzi. 10. "*Fusain*" from Montrambert, Loire. Fusain is a variety of coal, resembling wood-charcoal in appearance. Some stalks, the interior of which is composed of fusain, are covered with a bark which has been converted into coal. It is apparently the fossil form of wood which was dried by exposure to air before becoming embedded, and which has not undergone the same changes as vegetable *débris* which decomposes in swamps. 11. *Anthracite* from Chili. 12. *Anthracite* from Muso, New Granada. It occurs in masses in the schists in the emerald mines. It is hard, brilliant, and takes a very high polish; sp. gr. 1·689. 13. *Anthracite* supposed to come from Brazil. 14. *Graphite* from Kaison. C. H. B.

Investigation on Boiler Fires. By F. FISCHER (*Dingl. polyt. J.*, **248**, 73—76).—The author has recently examined the flue gases from a boiler furnace, the evaporation trials being made by Kobus. On the 22nd February, 1883, an experiment was made, which lasted from 9·30 A.M. to 6 P.M. Forty gas analyses and 40 determinations of temperature at intervals of 10 minutes, gave as a mean $CO_2 = 5{\cdot}96$ per cent., $O = 14{\cdot}55$, $N = 79{\cdot}49$, and temperature 221° in the gases carried away. The temperature of the admitted air was 37°. To lessen the influx of air, the back of the furnace was covered with stones. The second trial was made on the 27th February, from 10 A.M. to 6 P.M. The temperature in the boiler-house was 30°. From an average of 41 determinations of the gases carried off, $CO_2 = 9{\cdot}50$, $O = 9{\cdot}90$, $N = 80{\cdot}6$; temperature 196°. The coal used had the following composition:—

C.	H.	O.	N.	S (volatile).	H_2O.	Ash.
80·18	5·29	8·10	0·61	0·52	1·08	4·22 (0·11 S)

corresponding to a fuel value of—

$$\frac{8100 \times 80{\cdot}18 + 34220 \times (5{\cdot}29 - \frac{8{\cdot}1}{8}) + 2500 \times 0{\cdot}52}{100} = 7973,$$

calculated on water at 0° as combustion product. The hydrogen in 1 kilo. coal produces, by combustion, 0·476 kilo. water plus the hygroscopic water, making a total of 0·487 kilo., so that by taking water-vapour at 100° as combustion product, 310 or (as the temperature of the coal is 30°) 295 must be deducted, leaving, say, 7680 as fuel value. The loss of heat, due to the high temperature of the flue gases was equal to the following (sulphurous anhydride being disregarded):—

	1 kilo. coal gives.		Loss of heat.	
	I.	II.	I.	II.
CO_2	1·487 c.m.	1·487 c.m.	120	105
O	3·630	1·549	208	80
N	19·833	12·616	1118	642
Steam	0·487 k.	0·487 k.	28	22
+ Atmospheric moisture	0·570	0·401	50	32
			1524	881

So that on the first day 20 per cent., and on the second day 11 per cent. of the fuelvalue was lost. In order to arrive at accurate data for judging as to the most economical mode of firing, the author thinks as a rule five or six analyses of the smoke gases suffice to form an opinion; if, however, the analyses show wide differences, it is best to determine the carbonic anhydride and oxygen, say, every five minutes during one hour. D. B.

Process for Preparing Weatherproof Wall Paintings. (*Dingl. polyt. J.*, **248**, 92).—According to Keim, the ground colour is prepared from a mixture of slaked lime, sand, and water, which, after drying, is polished with rough sandstone and saturated with potash-water glass. The ground on which the painting is produced consists of a mixture of 4 parts quartzy sand, 3·5 marly sand, 0·5 infusorial earth, 1 caustic lime, and the requisite amount of distilled water. After drying, the painting-ground is saturated with hydrofluosilicic acid and again dried, when it is ready for use. The picture is washed with a hot solution of potash water-glass, dried, treated with a solution of ammonium carbonate, and washed. D. B.

New Substance obtained from some of the Commoner Species of Marine Algæ; Algin. By E. C. C. Stanford (*Chem. News*, **47**, 254—257, and 267—269).—The main object of the present paper is to introduce a new seaweed industry, the present uses for this substance being very limited, and in some cases a great loss of useful material occurs in the preparation of the products for commercial purposes. In the process recommended by the author, the sea-weed is first macerated with cold water by washing in a number of vats in turn, by which means about one-third of the weight of the sea-weed is removed. The weed is now bleached with chlorinated lime-water, treated with acid, and washed. To extract the algin, it is acted on with one-tenth of its weight of sodium carbonate for 24 hours in the cold, and is then carefully heated, filtered, and evaporated: the residue on the filter is cellulose, and can be used in the manufacture of paper. The result of this treatment of *laminaria* is the separation of the sea-weed into the following parts:—Moisture, 20; extracted by water, 30; extracted by acid, 5; extracted by sodium carbonate (*algin*), 35; and cellulose, 10 per cent.

When evaporated to dryness the *aqueous extract* forms a viscid mass, consisting of the salts mixed with a saccharine matter resembling mannite in appearance; this precipitates Fehling's solution to the extent of 15 per cent. glucose; it does not ferment, and would hence be very useful, but as yet there is no process for separating it from the salts. The whole mass is therefore carbonised and treated in the usual manner for separating the iodine and salts. Analysis of mixed samples of the salts yielded the following results:—

	Laminaria vesiculosus.	*Fucus stenophylla.*
Calcium sulphate	1·69	4·33
Potassium sulphate	11·29	23·62
Potassium chloride	19·90	13·71
Sodium chloride	60·96	58·20
Magnesium chloride	4·35	—
Sodium carbonate	0·53	—
Sodium iodide	1·26	0·12
	99·98	99·98

From experiments, it is demonstrated that the extraction is practically complete after four macerations.

The *sodium carbonate extract* is evaporated, and the residue (the *algin* combined with soda) when dry resembles gum in appearance, but can be obtained in thin transparent flexible sheets. The solution is slightly alkaline; any great excess of sodium carbonate apparently destroys the algin, whilst excess of acid gelatinises it so that a solution of only 2 per cent. becomes semi-solid when acidified. A solution can be neutralised without the algin being precipitated. The solution gives the following reactions with various reagents. Dilute mineral acids generally coagulate it. Boracic acid, however, has no effect; and it is not affected by acetic, formic, citric, tartaric, or benzoic acids. Barium, calcium, strontium, copper, zinc, aluminium, tin, antimony, cobalt, and nickel salts all precipitate it. Ferric chloride gives a dark brown coagulum; mercurous nitrate forms a white precipitate, but mercuric chloride and silver nitrate have no effect. Both basic and normal lead acetates give white precipitates. It is unaffected by magnesium salts; by potassium silicate, dichromate, ferrocyanide, and permanganate; and by sodium borate, tungstate, stannate, and succinate; and by tannin. Concentrated sulphuric acid dissolves it; concentrated nitric oxidises it, oxalic acid being amongst the products. From these reactions, it will be seen that it differs from all similar substances: thus, from albumin by not being coagulated when heated, and by not precipitating silver nitrate; from gelose, by being soluble in dilute alkalis, but insoluble in boiling water, gelose is just the reverse; from gelatin, by giving no reaction with tannin; from starch, by not reacting with iodine; from dextrin, &c., by being insoluble in dilute alcohol and dilute mineral acids. The purest form of algin is the precipitate produced by a mineral acid. It dries to a hard horny substance.

The composition of this substance is still obscure, for although the compounds with calcium, aluminium, barium, and lead have been investigated, no uniform results have been obtained. The sodium carbonate appears to be unaltered in its compound with algin; the carbonic acid is, however, only given off by treating with excess of hydrochloric acid, and heating. When a solution of algin is precipitated by acid, re-dissolved in alkali, and this treatment repeated, decomposition seems to go on continually. The author then suggests various uses for algin, founded on the properties above described; mixed with starch it could be used as a stiffener for fabrics, or alone as a dressing material, or as a mordant. It would also form a useful food. It can be used to prevent boiler incrustations, for fining wines and spirits, for insulating electrical appliances, &c. It can also be used to replace horn for the manufacture of various moulded articles.

D. A. L.

General and Physical Chemistry.

Electric Researches. By G. QUINCKE (*Ann. Phys. Chem.*, **19**, 705—782).—*Dielectric Constants of Insulating Liquids.*—Faraday conceived that in every point of an insulating dielectric there is a strain in the direction of and a stress normal to the lines of force. If P be the difference of potential, and a the distance between two condensing plates, k the dielectric constant of the intervening medium, then, according to Clerk Maxwell, the strain parallel to is equal to the strain normal to the lines, both being expressed by the equation (1) $p = \frac{k_1 P^2}{8\pi a^2}$. According to Helmholtz, these values vary with the nature of the insulating substance.

If a condensing plate of area O be placed in a liquid of dielectric constant k, then the quantity of electricity collected upon $Q = CP = k\frac{OP}{4\pi a}$, where C is the capacity of the condenser. The constant, k, of equation (2) is, according to Maxwell and Helmholtz, equal to the constant, k_1, of equation (1), and according to Maxwell equal to the square of the refractive index for a wave of infinite wave-length. Helmholtz supposes that two quantities of electricity, E and E′, attract one another with the same force as two quantities, $E\sqrt{k}$ and $E_1\sqrt{k}$, when separated by a dielectric medium of constant k.

The values of k for different liquids have recently been made the subject of various investigations at the hands of Silow, Werner Siemens, Gordon, and Hopkinson. The author has determined for a number of liquids the constants k_1 and k according as the stress acts parallel or normal to the lines of force.

1. In order to determine the dielectric constant k_p for a strain parallel to the lines of force, the author used a form of induction balance enclosed in a glass vessel filled with air or the liquid to be examined; the condensing plates were connected with a Thomson's screw electrometer. The plates were charged by a Holz' machine or a Ruhmkorff's coil. Great care was taken in the introduction of the liquids within the glass vessel in order to avoid contact with dust and absorption of water. The various parts of the apparatus are described at length in the original memoir. The value for k_p found for the strain within the liquid corresponds to k_1 of equation (1).

2. At the same time the dielectric constant k was determined by the ordinary method of measurement of the capacity of a condenser (*vide* equation 2), formed by the plates of the electric balance when immersed in air or an insulating liquid.

3. The electric stress k_s normal to the lines of force was estimated by the pressure exerted on an air bubble with the insulating liquid in which the condenser was immersed. On the lower plates of the condenser a vertical metal tube was soldered; this was connected with a

glass tube, on which was fused a **U**-shaped manometer half filled with a mixture of carbon bisulphide and ether of sp. gr. 1·2720. Through this arrangement the bubble of pure dry air was introduced. The difference of level in the two limbs of the manometer depends on the height of the liquid in which the condenser is immersed, and the capillary pressure of the air bubble. On connecting the plates with a Leyden battery, the electric stress of the liquid acts on that of the air bubble, causing it to contract: this produces a fall in level of the outer branch of the manometer, which is proportional to the difference of potential of the plates. This difference in level was measured by a cathetometer microscope, described at length in the memoir. The value for k_s can thus be deduced from equation (1).

The values found for k_1, k_p, and k_s, and the refractive index n_D of some of the liquids examined, are given in the table below.

Liquid.	Refractive index.	Dielectric constants.		
		k.	k_p	k_s.
Ether	1·360	3·364	4·851	4·672
5 vol. ether + 1 vol. carbon bisulphide	1·4044	2·871	4·136	4·392
1 vol. ether + 1 vol. carbon bisulphide	0·9966	2·458	3·539	3·392
1 vol. ether + 3 vols. carbon bisulphide	1·5677	2·396	3·132	0·061
Carbon bisulphide	1·6386	2·217	2·669	2·743
Benzene (from benzoic acid)	1·505	2·05	2·325	2·375
Rape-seed oil	1·4743	2·443	2·385	3·296
Turpentine	1·4695	1·94	2·259	2·356
Petroleum	1·4482	1·705	2·138	2·149

Maxwell's theory that values for k_1, k_p, and k_s, and that of the square of the index of refraction, are equal, is not confirmed. In most cases k_p and k_s are approximately equal, and, with the exception of rape-seed oil, are always greater than k. If a volume v_1 of a liquid of dielectric constant k_1, and v_2 of a liquid of dielectric constant k_2, be mixed, the mixture has approximately a dielectric constant $k = \frac{k_1v_1 + k_2v_2}{v_1 + v_2}$. The observed values and those calculated from this equation are given for various mixtures of carbon bisulphide with ether and turpentine. Further determinations of k by Siemens' method are given, the values of which are only approximately equal to those given above, the discrepancy being explained by differences in the conditions of the experiment. They prove, however, the inaccuracy of Maxwell's law.

Electric Double Refraction (comp. Kerr, Abstr., 1880, 599—601).—The author formerly propounded the view that insulating substances display the phenomenon of double refraction when subjected at various parts to unequal electric forces; but the hypothesis is untenable, for Kerr has shown that carbon bisulphide between two parallel metallic plates becomes doubly refractive when the plates are charged as the coatings of a Leyden jar. Kerr has also proved that in the case of carbon bisulphide the difference of phase in the rays of light polarised parallel and normal to the lines of force is proportional to the square of the difference of potential and inversely proportional to the square of the distance of the plates.

The author has critically examined the phenomenon of double refraction induced in various liquids, in an apparatus named an "electric liquid condenser," which is described at length. This apparatus consists in the main of a German glass tube containing two concentric nickel plates, the annular space between which is filled with the liquid the electro-optic properties of which are to be determined; these plates are connected with a Thomson's screw electrometer, and can be charged by a Holz' machine or a battery of Leyden jars. If such an electric condenser is introduced between two parallel or crossed Nicol's prisms whose plane of polarisation is inclined at an angle of 45° to the lines of electric force, then the layer of liquid enclosed between the metallic plates, through which the polarised light passes, displays the same polarisation colours as a crystal whose optical axis is parallel to the lines of force. In most cases, the amount of birefringent action was measured by a Babinet's compensator. Among the liquids examined in the above apparatus were carbon bisulphide and ether, either alone or mixed in various proportions; pure, heavy, and light benzenes; sulphur dissolved in carbon bisulphide; turpentine either alone or mixed with carbon bisulphide; and rape-seed oil. The determination of B, the birefringent action, follows from Kerr's law (*vide supra*), expressible by the equation $\delta = B\frac{P_2}{a_2}\frac{l}{100}$, in which δ is the difference of phase of the rays of light polarised at right angles to one another, P the difference of potential, l the length of column of liquid relatively to 100 cm., and a the distance in cm. between the plates. If cylinders are used instead of plates, then the expression $R \log \frac{R_2}{R_1}$ must be used instead of a, R_2 and R_1 being the respective lengths of the radii of the cylinders, and R their difference. For the same liquid, the value of B is constant for different values of P, δ, l, and a, and can be characterised as the *electric double refraction* for the liquid in question. In the table below are given the mean values of $B\,10^6$ for some of the liquids examined, nickel plates being used.

Liquid.	Values for $B\,10^6$.	Liquid.	Values for $B\,10^6$.
Carbon bisulphide........	32·798	Rape-seed oil	− 2·273
3 vols. carbon bisulphide + 1 vol. ether............	27·252	Ether	− 6·4
1 vol. carbon bisulphide + 5 vols. ether	4·422	Turpentine	0·109
Pure benzene............	3·842		

From the table above, it will be seen that petroleum and turpentine display practically no birefringent action. In the case of mixtures of liquids the electric double refraction cannot be deduced from an equation $B = \frac{v_1B_1 + v_2B_2}{v_1 + v_2}$, in which v_1 v_2 are the volumes of liquid in the mixture, and B_1 B_2 their electric double refractions respectively.

The author calls attention to a peculiar phenomenon observed when the electric forces within the liquid are subjected to periodic fluctuations by alteration of difference of potential in the charging apparatus. Simultaneously with the necessary contraction or total disappearance of the dark stripes in the Babinet's apparatus, several bubbles rise from the insulating liquid, and a musical note is heard, whose tone decreases with the lowering of potential. The notes resemble those obtained from a Dolbear's telephone.

Change of Refractive Index of Liquids by Electric Forces.—With the aid of the liquid condenser apparatus described above, the author has made a series of observations on the effect of electric forces on the refractive index of liquids when charged as the glass of a Leyden jar. An interference apparatus was used, which the author has constructed for the examination of the influence of hydrostatic pressure on the refractive index of liquids. The following are the principal facts noticed in the course of the experiments :—

1. With the same liquid, sometimes an increase and at other times a decrease of refractive index is caused by electric forces, which can be alternated either frequently or only once. This phenomenon probably arises from a change of hydrostatic pressure within the liquid caused by a vortex motion of the electric forces.

2. By the prolonged action of the forces, a decrease of refractive index is noticed, corresponding to a rise in temperature of 0·0001° to 0·1°, which is increased by a greater difference of potential between the electrodes and a greater viscosity of the liquid. This is apparently due to a rise in temperature caused by a friction of the particles within the liquid.

3. The electric current seems to pass intermittently and not continuously between the metallic plates. V. H. V.

Theory of Galvanic Circuits. By A. Witkowski (*Ann. Phys. Chem.*, **19**, 844—849).—According to Sir William Thomson, the sum of the heat evolved from the resistance in an entire circuit is equivalent to the heat evolved in the same time by the chemical changes produced within the circuit. On the other hand, Edlund (Abstr., p. 767) supposes that the amount of heat produced is equal to the amount consumed by the E.M.F. within the circuit, without reference to the concomitant chemical changes. In the present paper the author seeks to reconcile these opposing theories. Imagine a circuit whose temperature does not differ from its environment, and whose potential energy is known from the mass of material, composition of solution, and structure of its solid portion. Let a perfectly constant current pass through the circuit when closed, and its temperature be kept constant by the abstraction of heat from some parts and its addition to others. On opening the circuit and testing the potential energy, it will be found to be diminished by a quantity equal to the heat conducted away to the environment. It may be expressed in the following equation: $i^2R = ki + \Sigma\lambda_2 i - \Sigma\lambda f i + k'$, in which i^2R is the heat evolved by the resistance, $\Sigma\lambda_2 i$, $\Sigma\lambda f i$ the sums of heat absorbed by the contact surface within and that conducted away by surfaces from without, ki the difference of chemical potential energy proportional to the intensity of the current, and k' a change of energy independent of the intensity. Taking the latter as 0, then $E = k + \Sigma\lambda_2 - \Sigma\lambda f$, in which E is the E.M.F. Adopting Thomson's view, the equation becomes $E = k$, or the E.M.F. is equal to the difference of potential energy for unit of time and current. Edlund's hypothesis can also be expressed by the same equation if we write $\lambda = \mu - v$, in which $\mu_2 v$ represents the quantity of heat evolved by chemical action; the equation becomes of the form $E = \Sigma\mu_2 - \Sigma\mu f$, or the E.M.F. is equal to the quantity of heat absorbed in the circuit.

According to this latter hypothesis the chemical action within the battery is of itself of no intrinsic importance, but merely serves to heat the contact surface causing the E.M.F.; a thermoelectric pile is then merely another form of a battery, the E.M.F. being caused by the chemical processes occurring with the gas flame, which serves to heat the junction. From the above, it is evident that as regards the estimation of E.M.F. both Thomson's and Edlund's hypotheses lead to practically the same result. V. H. V.

Difference of Positive and Negative Discharge. By H. HELLMANN (*Ann. Phys. Chem.*, **19**, 816—818).—Goldstein for some time past has investigated the question whether the difference of appearance between the so-called positive and negative discharge is dependent entirely on the external conditions of the discharge, and not on the nature of electricity. The author has succeeded with a Crookes's tube, filled with air, in obtaining simultaneously from both electrodes a discharge of the same form and arranged in alternating striæ. The red aureole and the concave striæ appeared at both electrodes; in the middle of the tube were two striæ opposed near to one another. The striæ from the negative pole were farther distant from one another, of a redder colour, and more curved than those from the positive pole. The nearer the positive electrode and the greater the oscillation of the commutator, the more marked were the negative striæ. If the induction apparatus ceased to work, the positive striæ disappeared first, while the negative striæ became clearer, and finally disappeared.
V. H. V.

Researches on the Glow Discharge. By H. HERZ (*Ann. Phys. Chem.*, **19**, 782—816).—The author has investigated several questions as regards the phenomenon of the glow discharge in rarefied gases; the source of electricity used was a battery of 1000 secondary Planté's elements, arranged in series of fives. By the aid of this battery and various forms of apparatus, which are described at length in the original memoir, the author shows (i) that the electric discharge in rarefied gases is not, as Gassiot supposed, necessarily a discontinuous phenomenon; but under certain conditions, *i.e.*, by the use of a battery of sufficiently low resistance, it has all the properties of continuity. (ii.) The luminous rays from the kathode are a concomitant phenomenon of the discharge, but this cause is not identical with that of the current; these rays have practically no electrostatic or electrodynamic properties. (iii.) The illumination of the gases by the glow discharge does not arise from a phosphoresence induced directly from the current, but only from the kathode rays. These rays are electrically indifferent; they resemble rays of light most nearly, and their inflection on the approach of a magnet may be considered to be analogous to the phenomenon of plane polarisation of light. V. H. V.

Observations on Thermo- and Actino-electricity of Quartz. By W. HANKEL (*Ann. Phys. Chem.*, **19**, 811—844).—The author, after enumerating the various results obtained in the course of his investigations on the phenomenon of pyro-, actino-, and piezo-electricity of quartz crystals (this vol., 412, 540), proceeds to discuss the points of difference between his results and those of Friedel and Curie (this vol., p. 897). The latter have observed that pressure or cooling,—approach of the molecules,—and release of pressure or warming,—separation of the molecules,—call forth the same kind of electricity at the ends of the crystallographic axes. The results of the author are, however, in direct opposition to this simple rule, and the discrepancy is attributed by Friedel and Curie to an irregular cooling of the crystal. Secondly, the latter do not consider actino-electricity to be a particular phenomenon, but merely to be caused by an irregular heating of the crystal. In the present paper the author describes various forms of experiments made both to confirm his previous results, and to prove that the position of the poles is reversed according as the crystal is left or right handed. He has also extended his experiments on actino-electricity, which is shown to differ from pyro-electricity in that, *firstly*, the former causes a polarity of crystallographic axes precisely the reverse of that which would be produced by the latter, were the ray of light merely a source of heat. *Secondly*, actino-electricity reaches its maximum about 40″ after the commencement of the radiation, and disappears at about the same interval of time after the withdrawal of the radiating body; whilst the pyro-electric difference of potential is slowly evolved by heating or cooling the crystal. *Thirdly*, it is proved that the actino-electricity is not produced by unequal heating of the crystal. But if the radiation be long continued, then from the warming of the mass of the crystal pyro-electricity is produced, causing ultimately an opposite polarity in the axes. Experiments are also quoted to show that actino-electricity is a reversible phenomenon, for the approach of a cold body near a crystal causes an opposite polarity to that produced by a warm body. If Y be the maximum potential produced by a radiation of given intensity, and y the time in seconds from the commencement of the radiation, then $\mathrm{A}y/dt = a\,(\mathrm{Y}-y)$, where a is a constant. By integration, when $t = 0, y = 0$ the formula becomes $y = \mathrm{Y} - \mathrm{Y}e^{-at}$; on removal of the source of radiation, when $t = 0$, $y = \mathrm{Y}$, then $y = \mathrm{Y}e^{-at}$. Experiments are quoted to prove the accordance of the values calculated from these formulæ with those obtained directly by experiment. The author has been unable to detect the phenomenon of actino-electricity in other hemimorphous and symmetrical crystals, with the one exception of cinnabar, which, like quartz, is hemimorphous in its secondary axes, and in the direction of its principal axes rotates the plane of polarisation. In conclusion, the author gives a list of substances, crystallising in perfectly symmetrical forms, which display the phenomenon of pyro-electricity. Regular System. *Fluorspar.* Tetragonal System. *Idocrase*, *Apophyllite*, and *Mellite.* Hexagonal System. *Calcspar*, *Beryl*, *Brucite*, *Apatite*, *Pyromorphite*, *Mimetesite*, *Phenacite*, *Pennine*, and *Dioptase.* Rhombic System. *Topaz*, *Heavy Spar*, *Celestine*, *Aragonite*, *Strontianite*, *Cerussite*, *Phrenite*, and *Natrolite.* Monoclinic System. *Gypsum*, *Diopside*, *Orthoclase*, *Scolecite*, *Datolite*, *Euclase*, and *Titanite.* Triclinic System. *Albite*, *Pericline*, and *Axinite.* The author has been unable to detect the phenomenon of piezo-electricity in perfectly symmetrical crystals. V. H. V.

Determination of Vapour-density. By P. PAWLEWSKI (*Ber.*, **16**, 1293—1297).—In this modification of Dumas's method, a cylindrical flask of only 20—30 c.c. is used; it is drawn out to a thick-walled tube 10—12 cm. long and 1 mm. internal diameter; the tube is bent at 2—3 cm. from the flask, and is thickened to a conical form at the extremity. A small glass tube is provided 10—12 mm. long and 5—7 mm. broad, closed at one end, and containing a piece of thick caoutchouc tubing; this, when placed over the conical end of the neck of the flask, makes a perfectly air-tight joint and obviates the necessity of sealing the tube. In cases where many determinations have to be made, to avoid trouble in cleaning and drying, it is better to employ a flask having in addition an upright tube 8 cm. long and $1\frac{1}{2}$—2 mm. internal diameter, widened at the top, and closed by an accurately fitting stopper. The determination is made as usual, but the small size of the flask makes a medium-sized beaker a sufficient bath. By constantly employing the same apparatus, the calculations can be much simplified. A. J. G.

Relation between the Tension and Temperature of Saturated Vapours. By A. JAROLIMEK (*Monatsh. Chem.*, **4**, 193—202).—The author, in continuation of his researches on this subject already noticed (p. 417 of this volume), now gives for all vapours the formula

$$t = a + bp^{0{\cdot}25} + \frac{c}{p}.$$

The constants are :—

	a.	*b.*	*c.*
Water-vapour................	8	97	− 5
Carbon dioxide	−154·5	63	+13·5
Mercury	175	190·5	− 8
Alcohol	− 8·2	90	− 3·5

	a.	b.
Ether	−72·5	108
Acetone	−56	112·5
Chloroform	−58·5	118·5
Carbon bisulphide	−73·5	120
Carbon tetrachloride	−53·3	130

For the last five liquids, *c* may be neglected. H. W.

Congelation of Aqueous Solutions of Organic Bodies. By F. M. Raoult (*Ann. Chim. Phys.* [3], **28**, 133—144).—By delicate apparatus, the author has accurately determined the lowering of the freezing point produced by dissolving organic compounds in water. The lowering corresponding with a solution containing 1 part of the substance to 100 of water he calls the *coefficient of lowering*, and this multiplied by the molecular weight, the *molecular lowering*. The *molecular lowering* is sensibly constant for all organic compounds, and may be calculated for any compound, as $C_pH_qN_rO_s$, by the formula—

$$\frac{15p + 15q + 30r + 30s}{p + q + r + s}.$$

In other words, the *molecular lowering* is the mean of the empirically calculated *atomic lowering* of the elements of the compound, which is the same for all organic bodies, having the value 15 for carbon and hydrogen, and 30 for nitrogen and oxygen.

These results have important practical applications in testing the purity or strength of a liquid, and, above all, the law is available for fixing the choice of a molecular formula in the many cases where the determination of the vapour-density is impracticable. R. R.

Inorganic Chemistry.

Liquefaction of Nitrogen and of Carbonic Oxide. By S. v. Wroblewski and K. Olszewski (*Monatsh. Chem.*, **4**, 415—416).—The authors have liquefied these gases by the method previously applied by them to the liquefaction of oxygen (see p. 781). Their liquefaction takes place under conditions exactly similar to those required in the case of oxygen, but is much more difficult. Neither of them assumes the liquid state at − 136° under a pressure of about 150 atmospheres; but if the gas be then suddenly relieved from pressure, a brisk effervescence of liquid is seen in the nitrogen tube, like that of liquid carbon dioxide when the tube containing it is plunged into hot water. With carbon monoxide the effervescence is not so strong. If however the expansion be made not too quickly, and the pressure not allowed to fall below 50 atmospheres, both nitrogen and carbon monoxide liquefy completely, the liquid exhibiting a distinct meniscus and volatilising very quickly. These gases cannot however be thus retained in the liquid state for more than a few seconds: to retain them in that state for a longer time would require a temperature lower than any that the authors were able to obtain.

Nitrogen and carbon monoxide in the liquid state are colourless and transparent. H. W.

Bleaching Powder and Analogous Compounds. By G. LUNGE and P. NAEF (*Annalen*, **219**, 129—161).—As Kraut has recently taken up the subject of the constitution of bleaching powder, directing a polemical paper against the investigations of Lunge and Schaeppi (Abstr., 1880, 789), the authors have repeated their former experiments, and those of Kraut, with a view of establishing the correctness of the formula Cl.Ca.OCl first proposed by Odling. In their former paper great stress was laid on the complete and ready expulsion of all the chlorine in bleaching powder by carbonic anhydride in the presence of a little moisture, as militating against the presence of free calcium chloride. Kraut has shown that calcium chloride, when treated with a mixture of hypochlorous anhydride and carbonic anhydride, forms calcium carbonate thus: $CaCl_2 + Cl_2O + CO_2 = CaCO_3 + 2Cl_2$, and concludes from this that calcium chloride is present as such in bleaching powder. But the authors point out that this reaction can equally be explained by the intermediate formation of bleaching powder and its subsequent decomposition thus: $CaCl.OH + HOCl = H_2O + CaCl.OCl$ and $CaCl.OCl + CO_2 = CaCO_3 + Cl_2$. To prove the correctness of their interpretation, a series of experiments were conducted in which pure hypochlorous anhydride was passed over pure calcium hydroxychloride, CaCl.OH; and the chloride in every case the resultant material always contains a considerable proportion of bleaching powder (mixed with unaltered chloride and traces of chlorate), which can be subsequently decomposed by carbonic anhydride. Kraut's experiments are therefore inconclusive.

Secondly, Kraut having established that when lithium hydroxide is heated with chlorine, only half of it is attacked with formation of LiCl + LiOCl, draws the conclusion that as the lithium hydroxide is an integral part of the resultant compound, so calcium hydroxide is an integral part of bleaching powder. The authors however show that 80 per cent. of lithium hydroxide can be converted into the mixture LiCl + LiOCl, which is far less stable than bleaching powder in presence of excess of chlorine, in that it gives off oxygen, the presence of which could be recognised. On the other hand, the mixture LiCl + LiOCl is far more stable than bleaching powder towards carbonic anhydride; at low temperatures it is practically unaltered, whilst at higher temperatures the mixture is converted partly into the chloride and chlorate, and is partly decomposed into the chloride and oxygen. The gas given off is not chlorine, but hypochlorous anhydride. As the properties of the so-called chloride of lithia differ so markedly from those of bleaching powder, a different constitution must be assigned to each. Arguments drawn from the behaviour of the one compound have no bearing on the constitution of the other.

The analogous compounds of barium and strontium were also examined; that of barium is very unstable, whilst that of strontium is readily prepared, and resembles bleaching powder in its decomposition by carbonic anhydride. V. H. V.

Spectral Researches on Scandium, Ytterbium, Erbium, and Thulium. By T. THALÉN (*Chem. News*, **47**, 217).—The emission spectra were obtained with the use of two Leyden jars. The spectrum of scandium contains a great number of lines. Tables of wave-lengths for the first three metals are given. The absorption-bands distinguishing thulium from erbium are broad and intense, their centres having the wave-lengths $\lambda = 6840$ and $= 4650$. The emission spectrum given by thulium consists of two bands, the above $\lambda = 6840$, and another $= 4760$. There is no trace of a bright line corresponding with the dark band 4650, but such a bright line is given by salts of erbium, hence it is doubtful if the absorption-band 4650 belongs to thulium. H. B.

Position of Thallium in the Chemical System, and its Presence in Sylvin. By J. SCHRAMM (*Annalen*, **219**, 374—384).—Elements resembling one another in their chemical and physical properties, and belonging to the same natural group, are generally associated with one another in nature. The element thallium is assigned by some to the alkali, but by others to the lead-group. It has however been found associated with the alkali-metals in specimens of lepidolite, mica, alum, carnallite, and the mother-liquors of the Nauheim salt springs. The author has examined with the spectroscope specimens of carnallite and sylvin from Kalusz, and found the presence of thallium in both minerals. As thallium is so often associated with the alkali-metals, and its chloride and potassium chloride crystallise together, it is exceedingly probable that thallium is to be classified with these metals, a view which receives great support from the many points of resemblance of their compounds. The author reviews these points, and the less distinctly marked points of difference. The compounds in which thallium functions as a triad are not so stable as those in which thallium acts as a monad; many of them are decomposed by water like potassium tri-iodide, whilst the greater stability of thallium trichloride is probably connected with the more sparing solubility of the monochloride. The trisulphides of thallium and potassium are analogous compounds. The relation of thallium to the alkalis is the same as that of lead to the alkali-metals, or of bismuth to the nitrogen-group. The author regards the presence of thallium sulphide in pyrites not as indicating the association of thallium with the heavy metals, but as a relic of the presence of the alkaline sulphides. V. H. V.

Preliminary Notice. By F. WILM (*Ber.*, **16**, 1298—1301).—In the course of the author's investigations on the estimation of the metals in native platinum, he has come across a peculiar substance whose nature still remains obscure. A solution of native platinum after filtration from osmium-iridium was treated with excess of barium carbonate in the cold, the precipitate dissolved in hydrochloric acid, heated and saturated with hydrogen sulphide. The precipitate was reduced in hydrogen, extracted first with nitric acid and then with aqua regia, and the insoluble residue treated according to Wohler's method with sodium chloride and chlorine. The portion still remaining insoluble was fused with sodium carbonate and extracted with water, when a snow-white indistinctly crystalline powder was left, which by its extraordinary indifference to reagents has so far baffled all the author's attempts at its further investigation.

A. J. G.

Mineralogical Chemistry.

Minerals from Upper Silesia. By KOSMANN (*Jahrb. f. Min.*, 1883, **2**, 15—16).—This paper treats at some length of the minerals occurring in the ore-deposits of the "Muschelkalk" of Upper Silesia, more especially in the so-called blende bed, which is a thick bed of sulphuretted ores from which the upper deposits of oxidised ores have originated. The minerals described are: Blende, cerussite, zinc spar, zinc silicate, and manganese ores. Manganite, psilomelane, and manganese ochre are found at Beuthen. Heavy spar is very rarely met with. In conclusion, the author mentions the discovery of a bed of asphalt in the deep workings of the Friedrich's mine.

B. H. B.

Hieratite, a new Mineral Species. By A. COSSA (*Jahrb. f. Min.*, 1883, **2**, 11).—This mineral was found among the products of the volcanic activity of the Island of Vulcano, and derives its name from Hiera, the ancient name of that island. Grey stalactitic concretions, enclosing small octohedral crystals, were found near the apertures of the fumaroles. 3 kilos. gave 200 grams of these crystals, which were isolated by dissolving the mass in hot water. They crystallise in the regular system, and have the composition $2KF,SiF_4$. The mineral is mixed selenium sulphide, realgar, potassium, cæsium, and rubidium alum, sodium sulphate, sassoline, and compounds of arsenic, iron, thallium, zinc, tin, lead, bismuth, and copper. Until now, tin, zinc, and bismuth have never been found as volcanic exhalations.

B. H. B.

The so-called Liebigite from Joachimsthal. By A. SCHRAUF (*Jahrb. f. Min.*, 1883, **2**, 26).—The mineral forms crusts on the decomposed uranium ores of Joachimsthal. The crystals are microscopically small or imperfectly developed. The forms observed were: $\infty\breve{P}\infty$, ∞P, $\infty\breve{P}3$, $2\bar{P}\infty$, $2P$, $2\breve{P}3$. The analysis gave:—

CaO.	UrO_2.	CO_2.	H_2O.	Total.
16·42	36·29	22·95	23·72	99·38

corresponding with the formula—

$$2CaCO_3 + Ur(CO_3)_2 + 10H_2O.$$

The author gives this mineral the name of "Uranothallite," and proposes to reserve the name Liebigite for the compound poor in lime, analysed by Smith in 1848. B. H. B.

Rhodizite. By A. Damour (*Jahrb. f. Min.*, 1883, **2**, 5).—Rhodizite, discovered by Rose, is a white mineral crystallising in the form $\infty O \,.\, \frac{O}{2}$; it occurs in small crystals on the red tourmaline of Sarapulsk and Schaitansk, in the Ural Mountains. By the blowpipe reactions, this rare substance was thought to consist chiefly of calcium borate. A complete analysis has now been made for the first time by the author with material collected by G. Rose himself. A considerable amount of alumina was found, whilst the calcium plays only a subordinate part. The results obtained are given under I:—

	B_2O_3.	Al_2O_3.	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Volatile constituents.	Total.
I.	33·93	41·40	12·00	1·62	0·74	0·82	1·93	2·96	95·40
II.	41·49	41·40	12·00	1·62	0·74	0·82	1·93	—	100·00

The loss of 4·6 and the 2·96 per cent. volatile constituents are regarded as boric acid. The analysis then takes the form shown under II, and from this the empirical formula, $R_2O,2Al_2O_3,3B_2O_3$, is deduced. B. H. B.

Danburite from Switzerland. By A. Schrauf and others (*Jahrb. f. Min.*, 1883, **2**, 11—15).—The crystals of this mineral are found at Scopi in a fissure filled with chlorite. They are transparent, colourless, and as hard as quartz. The sp. gr. is 2·986. The pyramid, $2\breve{P}4$, is a very characteristic form of the Swiss crystals. The chemical analysis gave the following results. An analysis (*d*) of the American variety from Danbury, Connecticut, is added for the sake of comparison:—

	a.	*b.*	*c.*	*d.*
Analyst.	E. Ludwig.	Schrauf.	Bodewig.	Smith and Brush.
SiO_2	48·52	48·92	48·66	48·15
B_2O_3	28·77	(26·88)	28·09	27·15
Al_2O_3	—	1·87	0·08	0·30
Fe_2O_3	—		0·23	
Mn_2O_3	—	—	—	0·56
CaO	23·03	21·97	22·90	22·37
MgO	0·30	—	—	0·40
Loss on ignition.	—	0·36	—	0·50
Total	100·62	100·00	99·96	99·43

From these analyses the formula, $Si_2B_2CaO_8$, is deduced.

B. H. B.

Minerals, mainly Zeolites, occurring in the Basalt of Table Mountain, Colorado. By C. W. Cross and W. F. Hillebrand (*Amer. J. Sci.*, 1882, **23**, 452, **24**, 129).—In the following description of the minerals occurring in the basalt of Table Mountain, near

Golden, Colorado, the order followed is that in which the minerals have been deposited:—

1. *Chabazite.*—This mineral seems to be the oldest of the zeolites with the exception of a peculiar stratified deposit. It is also preceded in some places by yellow calcite. A second generation of chabazite came after thomsonite and analcime, but the crystals are few and minute.

2. *Thomsonite.*—As in the case of chabazite, a second generation of thomsonite was deposited towards the close of the zeolite formation. Chemical analyses were made with material of the older as well as of the more recent growth. In each case they gave an excess of silica, and the authors believe that the results obtained indicate a greater variation in the composition of thomsonite than is allowable under the generally accepted formula.

3. *Analcime.*—A second generation of analcime was also observed upon the apophyllite. All the analcime examined was doubly refractive, but so irregularly that it cannot be used in confirmation of the observations of Ben-Saude (Abstr., 1882, 285).

4. *Apophyllite.*—This mineral occurs in well-developed crystals of the combination $\infty P \infty$, P, while 0P is quite subordinate or entirely wanting. In chemical composition the apophyllite is quite normal. The presence of Fe_2O_3 is owing to minute particles of limonite which could not be completely removed. A pseudomorph, resembling albine, has originated by an increase of SiO_2, Al_2O_3 and H_2O. The alteration proceeds from without, and the result is a white substance with a pearly lustre, and finely foliated parallel to the basal plane of the apophyllite. There is no calcite in the product.

5. *Calcite.*—Calcium carbonate has had three periods of deposition in the basaltic cavities—two as calcite and one as arragonite.

6. *Mesolite.*—This appears in masses composed of exceedingly delicate needles, the crystal form of which could not be determined even under the microscope at a high power. The chemical analysis gave the following results, which correspond exactly to a composition of 2 mols. of scolecite and one of natrolite:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
46·13	26·88	8·77	6·19	12·16	100·13

7. In many of the cavities of Table Mountain a reddish-yellow sandstone-like mineral occurs. In this mass small fissures may sometimes be observed, some of which are partially filled with minute white crystals, easily recognisable under the microscope as laumontite and stilbite. Chemical analyses of the yellow granular mass gave the following results; care being taken to exclude all red spherules:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
55·37	17·64	0·79	8·52	0·17	1·42	16·27	100·18

This composition is such as would result from a mixture of stilbite and laumontite.

The reddish spherules gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	H_2O.	Total.
40·51	29·21	0·78	12·42	4·30	12·79	100.04

These figures agree with the analysis of thomsonite.

B. H. B.

Beryl from Craveggia in Piedmont. By G. Spezia (*Jahrb. f. Min.*, 1883, **2**, 10).—This beryl occurs in loose blocks of a coarsely granular pegmatite rock. These blocks were probably derived from a gneiss in the neighbourhood, and contain tourmaline and manganese-garnet in addition to the beryl. The latter is generally found in the quartz, and never in the felspar. The analysis gave the following results:—

SiO_2.	Al_2O_3.	BeO.	Fe_2O_3.	MgO.	CaO.	Loss on ignition.	Total.
65·12	19·65	11·49	0·67	0·48	trace	1·95	99·36

B. H. B.

Garnet and Amphibole Rocks of the Bastogne Region. By A. Renard (*Jahrb. f. Min.*, 1883, **2**, 68—71).—The metamorphic rocks of Bastogne, belonging to what Dumont called the metamorphic belt of Paliseul, were submitted by the author to a searching microscopical and chemical examination.

The rock described by Dumont as quartzite containing garnet is a hard black rock containing brownish-yellow crystals of garnet, 1 to 2 mm. large, in a ground-mass saturated with carbonaceous matter. The sp. gr. is 2·751. The rock is composed of 4·8 graphite, 1·51 apatite, 1·02 titanite, 4·14 garnet, 20·85 paragonite and muscovite, 30·62 quartz, and 1·32 water. The analysis of the rock gave the following results:—

SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
55·82	0·42	0·69	19·67	0·96	4·18	0·61	8·42

MgO.	K_2O.	Na_2O.	H_2O.	C.	Total.
2·21	0·39	1·42	2·29	4·80	101·88

The analysis of the inclosed garnets gave:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
37·58	20·45	3·21	15·53	14·72	10·03	0·68	102·20

Dumont's quartzite and eurite with actinolite and hornblende may be distinguished from the rock described above by its lighter colour. A typical specimen of this rock from Ourt gave the following analytical results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	Total.
69·34	12·07	1·88	4·74	7·70	2·96	0·40	1·57	100·66

The rock was composed of 46·73 hornblende, 52·36 quartz, and 1·57 water.

Dumont's phyllite containing garnet is distinguished from the rocks described by its evidently stratified nature and bluish-black colour. The enclosed garnets are translucent and of a brownish-yellow colour. Dumont's classification of these rocks is abandoned, as garnet and amphibole mostly occur together. Felspar, which the term "eurite" demands, has not been observed, and the percentage of silica in the quartzite is not high enough to render that name suitable.

In conclusion, an analysis is given (I) of a mineral from the quartz veins of Libramont, called Bastonite by Dumont. The author regards this as a variety of phlogopite. The sp. gr. is 2·928. An analysis (II) is also given of the ottrelite from Lierneux, the sp. gr. of which was 3·266.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	36·91	20·04	20·01	3·73	trace	0·95	7·96	3·07
II.	40·55	30·80	3·82	12·46	6·51	1·29	0·45	—

	Na_2O.	H_2O.	Total.
I.	0·22	6·98	99·87
II.	—	(4·12)	100·00

B. H. B.

Diabase from Weilburg. By W. Will and K. Albrecht (*Ber.*, **16**, 1323—1327).—This diabase is dark greyish-green in colour; the ground-mass appearing uniform even when examined with a lens. It contains roundish dark-green masses of chloritic substances, and numerous concretions of calcspar which in places give the stone an amygdaloïd appearance; single crystals of iron pyrites also occur. Microscopic examination of the ground-mass showed it to be a crystalline mixture of triclinic felspar, magnetite, ilmenite, and fine needles of apatite, the whole being interpenetrated with green chloritic mass. Analysis of the stone gave:—

SiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.
50·26	1·46	11·61	13·53	5·45	3·59

Na_2O.	K_2O.	TiO_2.	P_2O_5.	CO_2.	Cl.	H_2O.
5·34	1·57	0·50	1·14	1·10	0·40	3·38

Sp. gr., 2·796. Loss on ignition, 4·40 per cent.

A. J. G.

Notes on the Occurrence of certain Minerals in Amelia Co., Virginia. By W. F. Fontaine (*Amer. J. Sci.* [3], **25**, 330—339).—The minerals in question occur in so-called veins of gigantic granite, which are not fissure veins but ruptured portions of the country rock—micaceous gneiss and mica schist, into which the components of the granite have been introduced, most probably by solution in hot water. The essential minerals of these deposits, mica, felspar, and quartz, have crystallised pretty constantly in the same order of succession, viz., mica first and quartz last. The mica has been worked during the last few years, and at the outcrop it has been removed in prehistoric times; the mica is mostly muscovite, and is sometimes bent, showing movements in the vein. The felspar is mostly orthoclase, but albite also occurs, and in such a manner as to clearly show that it is a secondary product after the formation of the mass of granitic materials; labradorite and amazon stone also occur. Very large opaque beryls are found, as are also smaller transparent ones; they seem to have crystallised at the same time as the felspar and after the mica. Fluorite is only found in crystalline masses. Columbite occurs quite frequently, and often in crystals of groups weighing up to six pounds; a variety occurs containing considerably more manganese than iron, and with the ratio of niobic to tantalic acid 1 : 1. Garnet—spessarite—is common; one variety is intimately mixed with helvite, which is the last mineral deposited; the spessarite gave on analysis :—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.
36·34	12·63	4·57	44·20	1·49	0·47 = 99·70

Orthite occurs in long thin-bladed crystals, sometimes 15 inches long; the ends are imperfect, and most of the crystals have suffered partial decomposition. Microlite occurs between the interstices in tangled masses of quartz, felspar, and mica. It was formed after the mica but before the felspar. The crystals are all of good size, and very large aggregates are sometimes found; the form is that of a modified octohedron. Monazite is found only in a couple of localities; it does not occur in isolated crystals, but in large aggregates. It is very much more prone to change than microlite. Helvite is only found in one locality, in the interstices of spessarite. No crystalline forms have been observed, and a great deal of the mineral has undergone alteration. Galena, stilbite, pyrochlore, manganese-tantalite (?), apatite, tourmaline, and fluocerite (?) occur but rarely. H. B.

The Gneiss of Beura. By G. Spezia (*Jahrb. f. Min.*, 1883, 2, 17—18).—At Beura, in the Ossola valley, gneiss is quarried to a considerable extent. The rock occurs in several varieties, and contains a number of minerals, either disseminated through it or crystallised out in fissures and geodes. These minerals are: quartz, tourmaline, chlorite, orthoclase, mica, staurolite, cyanite, laumontite, calcite, fluorspar, titaniferous iron ore, limonite, iron pyrites, magnetic pyrites, marcasite, stilbite, titanite, apatite, and anatase. Quartz is the most frequent. Hornblende has not been met with. All the minerals mentioned occur in fissures or geodes, only yellow tourmaline, cyanite, and staurolite are disseminated through the rock. B. H. B.

Minerals in the Sodalite Syenite of South Greenland. By J. Lorenzen (*Jahrb. f. Min.*, 1883, 2, 18—21).—The nepheline syenite containing sodalite, which occur on both sides of the Tunugdliarfik and Kangerdluarsuk fjords in the Julianehaab district, South Greenland, is very rich in accessory constituents. The rock is composed of a greenish-white felspar, probably orthoclase, arfvedsonite, aegirine, sodalite, nepheline, eudialite, lievrite, calcite, several zeolites, especially analcime and natrolite, lithium mica, dinigmatite, and steenstrupine. The first four of these minerals predominate.

Analyses were made of most of these minerals; the results obtained in the analysis of steenstrupine were as follows :—

SiO_2.	TaO_2.	Al_2O_3.	Fe_2O_3.	ThO.	MnO.	CeO.	LaO.	CaO.
27·95	0·97	2·41	9·71	7·09	4·20	10·66	17·04	3·09

K_2O.	H_2O.	Total.
7·98	7·28	98·38.

Sp. gr. = 3·38. Hardness, 4. The mineral has a brown colour and a white streak. Ainigmatite belongs to the monoclinic system; the usual combination being ∞P, $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, with a pyramid and two clinodomes. It has a black colour and a hardness of 5·5. It may be distinguished from arfvedsonite by its red streak, and sp. gr. 3·80.

B. H. B.

Organic Chemistry.

Compounds of Hydrogen Sulphide with Ethers. By De Forcrand (*Ann. Chim. Phys.* [3], **28**, 1—67).—Some properties of the compound of hydrogen sulphide and water formed at a low temperature or high pressure, are first described. The tensions of dissociation at various temperatures from 0·5° to 28·5° are given, a *critical point* being found at about 29°. The composition assigned to this compound by the author is $H_2S + 12H_2O$. He then proceeds to detail the preparation, and the most important properties of a large number of compounds similarly formed by hydrogen sulphide with the simple chlorides, bromides, and iodides of radicals of the fatty series, or with their chlorinated, brominated, or iodated derivatives. These compounds have all well-defined crystalline forms belonging to the cubic system, and all correspond with the general formula—

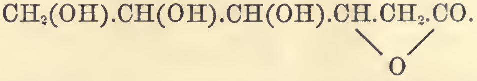
$$R + 2H_2S + 23H_2O.$$

Their dissociation-tensions are constant for the same temperature, as is also the composition of the vapours evolved, and the tension increases regularly with the temperature. The heat of formation of these compounds is considerable, but it is mainly due to the change in the physical state of the water entering into their composition. The heat of formation of the ethyl bromide compound (37·08 cal.) is about the same as that of the chloroform compound (37·5 cal.). The author has also examined a few analogues of these compounds in which hydrogen sulphide is replaced by hydrogen selenide, and he finds the closest resemblance in their properties. R. R.

Bromodinitromethane. By J. Kachler and F. V. Spitzer (*Ber.*, **16**, 1311—1312).—By the distillation of α-dibromocamphor (m. p. 61°) with nitric acid and treatment of the product of the reaction with alcoholic potash, a yellow crystalline precipitate of potassium bromodinitromethane, $CBr(NO_2)_2K$, is obtained, whilst on diluting and heating the alcoholic mother-liquors, carbon tetrabromide distils.

Losanitsh has stated (Abstr., 1882, 950) that the potassium salt of this composition yields on treatment with acids dibromodinitromethane; the authors, on the contrary, find the oil so obtained to give numbers intermediate between those required for mono- and di-bromonitromethane, and as, on gentle heating, carbon tetrabromide sublimes, it is in all probability a mixture of the latter with monobromodinitromethane. A. J. G.

Saccharone and Saccharin. By H. Kiliani (*Annalen*, **218**, 361—374).—Scheibler (Abstr., 1881, 149) showed the formula of saccharin to be $C_6H_{10}O_5$, and suggested the constitution



$$CH_2(OH).CH(OH).CH(OH).\underbrace{CH.CH_2.CO}_{O}$$

The author obtained acetic acid and glycollic acid by the oxidation of saccharin with silver oxide (Abstr., 1882, 820), and from this result he assumed it to contain the groups CH_3 and $CH_2.OH$. By the oxidation of saccharin with concentrated nitric acid, saccharone, $C_6H_8O_6$, is produced, containing carboxyl, COOH, in the place of $CH_2.OH$; this compound is slightly lævorotatory, and forms large crystals of the formula $C_6H_8O_6,H_2O$; it yields two classes of salts, *e.g.*, *sodium saccharone*, $C_6H_7O_6Na$, and *sodium saccharonate*, $C_6H_8O_7Na_2$, the former of which is obtained by mixing saccharone solution with the calculated quantity of sodium carbonate and evaporating, when rhombic crystals are obtained, sometimes anhydrous, and sometimes containing 1 mol. H_2O. Sodium saccharonate is obtained by boiling an aqueous solution of saccharone with the calculated quantity of sodium carbonate, and evaporating. *Ammonium saccharone*, $C_6H_7O_6.NH_4$, is obtained by neutralising a cold solution of saccharone with ammonia, and allowing it to evaporate spontaneously, whilst *ammonium saccharonate*,

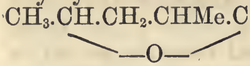
$$C_6H_8O_7(NH_4)_2,$$

is prepared by boiling saccharone with an excess of ammonia. *Calcium saccharonate*, $C_6H_8O_7Ca$, and *silver saccharonate*, $C_6H_8O_7Ag_2$, have also been prepared, the former by boiling saccharone with lime-water, and the latter by precipitating an alkaline saccharonate with silver nitrate. Copper compounds are also obtained by boiling a solution of saccharone with copper carbonate. By the long-continued boiling (21 hours) of a mixture of saccharone with hydriodic acid and amorphous phosphorus, an acid, $C_6H_{10}O_4$, is formed, which the author identifies as α-methylglutaric acid,

$$COOH.CH_2.CH_2.CHMe.COOH,$$

described by Wislicenus and Limpach (*Annalen*, **192**, 134). If the heating is carried on for a much shorter period, an acid of the formula $C_6H_8O_4$ is produced. From the formation of α-methylglutaric acid, the author assigns to saccharonic acid the constitution

$$COOH.CH(OH).CH(OH).CMe(OH).COOH,$$

whilst for saccharone, which is the lactone obtained by the abstraction of 1 mol. water, two formulæ are evidently possible. In the same way hydriodic acid acts on saccharin, yielding α-methylvalerolactone,  $\underbrace{CH_3.CH.CH_2.CHMe.CO}_{\text{—O—}}$, proving that saccharic acid has the constitution, $CH_2(OH).CH(OH).CH(OH).CMe(OH).COOH$.

A. K. M.

Condensation-products of Aldehydes and their Derivatives. By A. Lieben and S. Zeisel (*Third Memoir*). **Constitution of Butyl Chloral.** (*Monatsh. Chem.*, **4**, 531—539).—In a previous paper (p. 570 of this volume) the authors have endeavoured to explain the manner in which condensation accompanied by elimination of water takes place between two molecules of the same or of different aldehydes; and in the present communication they examine the condensation of an aldehyde with a monohalogenated aldehyde, viz., that of acetaldehyde with its monochlorinated derivative, which may be expected to give rise to a monochlorocrotonaldehyde, represented by one of the following formulæ:—

I. $CH_3.CH:CCl.CHO$. II. $CH_2Cl.CH:CH.CHO$.

Either of these compounds would be converted, by addition of chlorine, into a butyric chloral, $C_4H_5Cl_3O$, isomeric or identical with that already known.

To obtain such a compound, monochloraldehyde in the form of the crystallised hydrate, $C_2H_3ClO,\frac{1}{2}H_2O$, was heated in a sealed tube with an equivalent quantity of aldehyde, a drop of strong hydrochloric acid being added as condensing agent, and the heating continued for several days. On distilling the contents with steam, there passed over, first an oil, then water, and lastly the hydrate of monochloraldehyde, whilst crotonaldehyde and higher-boiling substances remained in solution. The residue consisted of a black unctuous substance, which hardened on cooling to a pitch-like mass, surmounted by a yellow, somewhat turbid liquid, exhibiting a strong green fluorescence. The oil obtained from the distillate, which was somewhat heavier than water, was dried over calcium chloride and distilled in a current of carbonic anhydride; it then passed over between 150° and 160°, but could not be obtained of constant boiling point. It is a colourless liquid, becoming thicker on keeping, and having an odour like that of crotonaldehyde, but more pungent. It gave by analysis 37·83 per cent. chlorine, whereas monochlorocrotonaldehyde requires 33·97 per cent. Nevertheless the body in question appears to consist mainly of chlorocrotonaldehyde, inasmuch as it is capable of uniting with chlorine, and forming a crystalline hydrate of trichlorobutyraldehyde or butyric chloral, $C_4H_5Cl_3O$. The crystals of this hydrate are orthorhombic, exhibiting the combination $0P . P\breve{\infty} . P$. Axes $a : b : c = 0·6486 : 1 : 1·1939$.

According to the formulæ above cited for monochlorocrotonaldehyde, butyric chloral must be represented by one of the two following:—

I. $CH_3.CHCl.CCl_2.CHO$. II. $CH_2Cl.CHCl.CHCl.CHO$, both of which differ from the formula hitherto assigned to it, viz., $CCl_3.CH_2.CH_2.CHO$. To decide between the formulæ I and II, it is necessary to ascertain whether butyric chloral contains an entire methyl-group, and with this view the authors prepared dichloropropylene, $C_3H_4Cl_2$ (b. p. 77°), by boiling the hydrate of butyric chloral with sodium carbonate, and heating it with chromic acid mixture in a sealed tube for 48 hours at 100°, and then for 24 hours at 130°. By this treatment the dichloropropylene was converted into acetic acid, showing that it contains an entire methyl-group, and must therefore be represented either by the formula $CH_3.CH\colon CCl_2$, or by

$$CH_3.CCl\colon CHCl.$$

Hence also it follows that butyric chloral must be represented by $CH_3.CHCl.CCl_2.CHO$, and this determines also the constitution of the numerous derivatives of butyric chloral, *e.g.*, trichlorobutyl alcohol, trichlorobutyric acid, trichlorangelactic acid, &c.

The formation of butyric chloral by the action of chlorine on aldehyde or paraldehyde may be explained in two ways: 1. The aldehyde is converted into crotonaldehyde, then into monochlorocrotonaldehyde, which, by the further action of the chlorine, is transformed into butyric chloral. 2. The aldehyde is first converted by the chlorine into monochloraldehyde, which, almost as soon as it is formed, condenses with the acetaldehyde, under the influence of the hydrochloric acid evolved at the same time, into monochlorocrotonaldehyde, and thereby gives rise to the production of butyric chloral in the manner above explained. The second view is supported by the consideration that crotonaldehyde has not yet been found amongst the products of the action of chlorine on acetaldehyde, and that in presence of water, chloral is formed from aldehyde, a fact which points to the previous formation of monochloraldehyde.

The constitution of butyric chloral above established shows that the monochloraldehyde obtained by condensation must have the formula $CH_3.CH\colon CCl.CHO$, and that accordingly, in the process of condensation, the oxygen of the acetaldehyde must have acted on the hydrogen-atom of the monochloraldehyde nearest to the chlorine; and consequently that in this case, as in that of propaldehyde, the methylene-group is more readily attacked by the aldehydic oxygen than the methyl-group. H. W.

$\alpha\gamma$-Dichlorocrotonaldehyde, a Condensation-product of Monochloraldehyde.—By K. NATTERER (*Monatsh. Chem.*, 4, 539—553).—When hydrated monochloraldehyde is heated for 15 hours at 100° with a drop of strong sulphuric acid, a heavy dark-coloured oil passes over, together with a supernatant watery liquid, still containing chloraldehyde. This layer is removed, and the oily liquid when cold is washed with water (after which treatment it consists of condensation-products, and a small quantity of polymerised monochloraldehyde), and then distilled under reduced pressure, whereupon resinous products are left behind, and monochloraldehyde collects in the receiver (into which a little water may be advantageously introduced to dissolve it), together with the more volatile condensation-products formed by dissociation of the polymeride, and a certain quantity of the polymeride itself.

The oily liquid obtained as above, after renewed washing with water to remove any attached monochloraldehyde, is dried in a stream of carbonic anhydride, and then subjected to fractional distillation in the same gas. In this way a fraction is obtained boiling at 86—87°, together with a small quantity of a viscid oil boiling at 130—150°.

The liquid boiling at 86—87° is mobile, strongly refractive, colourless when recently distilled, but soon turns yellow. It becomes much thicker at $-30°$; solidifies to a vitreous mass at the temperature of a mixture of carbonic anhydride and snow; has a very pungent odour; is nearly insoluble in water; and distils, with partial decomposition, under ordinary pressure. It gives by analysis numbers agreeing nearly with the formula $C_4H_4Cl_2O$, which is that of dichlorocrotonaldehyde, formed according to the equation $2C_2H_3ClO - H_2O = C_4H_4Cl_2O$. All its reactions are in accordance with the constitutional formula $CH_2Cl.CH \vdots CCl.CHO$. Its aldehydic nature is shown by its power of reducing ammoniacal silver solution; by the red coloration and separation of resin consequent on boiling it with potash; by its power of absorbing oxygen, with formation of an acid; and of forming a crystalline compound with sodium hydrogen sulphite.

Dichlorocrotonaldehyde is reduced by acetic acid and iron filings to normal butyraldehyde, normal butyl alcohol, and crotonaldehyde, the latter convertible by treatment with bromine and water into butenylglycerol, $C_4H_7(OH)_3$.

By energetic oxidation with nitric acid, the aldehyde is converted into hydrochloric, chloracetic, and oxalic acids: $CH_2Cl.CH \vdots CCl.CHO + 2O_2 + H_2O = HCl + CH_2Cl.COOH + C_2H_2O_4$. The hydrochloric and nitric acids yield free chlorine, which converts part of the chloracetic acid into chloropicrin.

$\alpha\gamma$-Dichlorocrotonaldehyde forms with acid sodium sulphite the compound $CH_2Cl.CH \vdots CCl.CH(OH)(SO_3Na) + 3$ or $4H_2O$, and on heating this compound with solution of sodium carbonate, carbonic anhydride is given off, and a residue is left containing chloride and sulphate of sodium, and the sodium salt of an aldehyde-sulphonic acid.

$\alpha\gamma$-Dichlorocrotonaldehyde unites directly with bromine, forming $\alpha\gamma$-dichlor-$\alpha\beta$-dibromobutyraldehyde, $CH_2Cl.CHBr.CClBr.CHO$, which, when agitated with a strong solution of sodium hydrogen sulphite, unites therewith, forming a crystalline very slightly soluble compound. On agitating the bromine addition-compound with an equal volume of water, it solidifies to a white compact crystalline mass, which may be purified by trituration with water, draining, and once recrystallising from ether, and then consists of the hydrate $C_4H_4Cl_2Br_2O,H_2O$. This compound is permanent in the air, has a faint melon-like odour, dissolves sparingly in water, readily in alcohol, and melts at about 72° to a turbid liquid, the turbidity increasing on further heating (up to 85°), diminishing again on cooling, and disappearing at about 70°, whilst the clear liquid solidifies after some time at the temperature of the room. This behaviour shows that the hydrate is resolved into its components even at ordinary temperatures.

When the aqueous solution of the bromine addition-product is mixed with solution of potash or of sodium carbonate, a heavy oil smelling like petroleum is immediately deposited, with simultaneous production of sodium bromide and formate. It is highly probable that the bromine addition-product reacts with aqueous alkalis and their carbonates in the same manner as chloral or bromal, forming a bromopropylene or bromallylene, with separation of the CO-group and of hydrogen bromide.

On slowly passing gaseous hydrogen chloride through $\alpha\gamma$-dichlorocrotonaldehyde at 0° for 12 hours, then leaving the liquid to itself for two days, and expelling the uncombined chlorine with a stream of carbonic anhydride, a residue is left consisting of trichlorobutyraldehyde, isomeric with butyric chloral, and smelling very much like the latter, but having a more viscid consistence. It solidifies to a vitreous mass at $-78°$; does not give off HCl on standing; oxidises but very slowly on exposure to the air; is sparingly soluble in water, and does not form a hydrate. It unites with sodium hydrogen sulphite, and is very easily converted by fuming nitric acid into the corresponding trichlorobutyric acid, $CH_2Cl.CHCl.CCl_2.COOH$, which forms fine crystals. H. W.

Methyl β-Butyl Ketone and its Derivatives. By J. Wislicenus (*Annalen*, **219**, 307—321).—The author has prepared from ethylic ethomethacetoacetate, ethyl β-butyl ketone, and converted it into the corresponding secondary alcohol and pinacone. The products formed by the action of nascent hydrogen,—zinc and acetic acid,—on the iodide from the secondary alcohol, are also studied.

Methyl β-butyl ketone, Me.CO : CHMeEt, is formed by the action of potash on ethyl ethomethacetoacetate: $CH_3.CO.CMeEt_2.COOEt + 2KOH = CH_3.CO.CHMeEt + K_2CO_3 + EtOH$. It is a light mobile oil, smelling like peppermint, boiling at 118°, and having a density of 0·8181. This is converted by the action of sodium and water partly into the corresponding secondary alcohol, and partly into the pinacone. The former, *methyl β-butyl carbinol*, CHMe(OH).CHMeEt, is a thick oil resembling stale peppermint in its odour, boiling at 134°, and having a density of 0·8307; the latter, *methyl β-butyl pinacone*,

$$CHMeEt.CMe(OH).CMe(OH)CH.MeEt,$$

is a colourless pasty mass melting at 248—250°; it yields on heating with dilute sulphuric acid (1 : 4) probably a mixture of two pinacolines.

The author calls attention to the difficulty experienced in converting methyl β-methyl iodide into β-hexane; in this respect the iodide differs most markedly from the hexyl, heptyl, and octyl iodides already known. On subjecting to fractional distillation the crude product of the action of zinc and acetic acid on the iodide, mixtures of methyldiethylmethane, a hexylene, and a dihexylene, and methyl diethyl carbinol, together with subsidiary products, were obtained. The hexane, *methyldiethylmethane*, purified from the olefine by repeated treatment of the mixture of the hydrocarbons with sulphuric or hydriodic acid, is a liquid having a pleasant odour of peppermint, boiling at 64°, and of sp. gr. 6765. The product formed by the addition of hydriodic acid to the hexylene is a tertiary or methyl diethyl iodide, readily converted by water into methyl ethyl carbinol, boiling at 122°. From the above it is evident that the first product of the reaction of zinc and acetic acid on methyl β-butyl iodide is methyldiethylmethane,

$$2(\mathrm{CH_3.CHI.CHMeEt}) + 2\mathrm{Zn} + 2\overline{\mathrm{Ac}}\mathrm{OH} = \mathrm{ZnI_2} + \mathrm{Zn(O\overline{Ac})_2} + 2(\mathrm{CH_3.CH_2.CHMeEt}),$$

together with its derived hexylene or α-methylethylpropylene, thus: $2(\mathrm{CHMeI.CHMeEt}) + \mathrm{Zn} = \mathrm{ZnI_2} + \mathrm{CHMe\!:\!CMeEt} + \mathrm{CHMeEt_2} + \mathrm{H_2}$. Some portion of the olefine is polymerised at the moment of its formation, while another portion combines with the water present to form diethyl methyl carbinol, thus: $\mathrm{CHMe\!:\!CMeEt} + \mathrm{H_2O} = \mathrm{CMeEt_2.OH}$. The ready conversion of the olefine into the iodide and the saponification of the latter by water, show that it has the constitution of a tertiary-secondary olefine. V. H. V.

Specific Volumes of the Alkyl Salts of Fatty Acids. By E. Elsässer (*Annalen*, **218**, 302—338).—The author has made a number of experiments in continuation of Kopp's work, and repeated his determinations. Determinations of the boiling points and of the specific gravities of the pure substances experimented with have also been made:—

Boiling Points at 760 mm.

	Formate.	Acetate.	Propionate.	Butyrate.	Isobutyrate.	Valerate.
Methyl ...	32·3°	57·5°	79·9°	102·3°	92·3°	116·7°
Ethyl	54·4	77·1	98·3	119·9	110·1	134·3
Propyl ...	81·0	100·8	122·2	142·7	133·9	155·9
Isobutyl ..	97·9	116·3	136·8	156·9	146·6	168·7
Amyl	123·3	—	160·2	178·6	168·8	—

Specific Gravities at Boiling Points.

	Formate.	Acetate.	Propionate.	Butyrate.	Isobutyrate.	Valerate.
Methyl ...	0·95196	0·88086	0·83680	0·80261	0·80397	0·77518
Ethyl	0·86667	0·82673	0·79868	0·76940	0·77725	0·74764
Propyl ...	0·82146	0·79439	0·77201	0·74569	0·74647	0·72740
Isobutyl ..	0·78287	0·77080	0·74424	0·71630	0·73281	0·70549
Amyl	0·77027	—	0·73646	0·71148	0·70662	—

Specific Volumes.

	Formate.	Acetate.	Propionate.	Butyrate.	Isobutyrate.	Valerate.
Methyl ...	62·84	83·77	104·86	126·75	126·54	149·60
Ethyl	85·14	106·15	127·37	150·37	148·86	173·44
Propyl ...	106·83	128·06	149·87	173·89	173·71	197·47
Isobutyl ..	129·95	150·10	174·23	200·53	196·01	223·40
Amyl.....	150·21	—	195·04	221·52	223·04	—

A. K. M.

Monohalogen Derivatives of Crotonic Acids. By R. FRIEDRICH (*Annalen*, **219**, 322—374).—The researches of Fittig and Erlenmeyer have shown that the products of the decomposition by water of the mono- and di-halogen derivatives of the acids of the acetic series vary according to the relative position of the halogen-atoms and the carboxyl-group. In the case of the α-acids, the halogen element is replaced by a hydroxyl- or ethoxyl-group; but the β-acids are decomposed with formation of an acid of the oleïc acid series and separation of the haloïd acid. The author has carried on a series of experiments on the action of alkalis on the monohalogen derivatives of isomeric and substituted crotonic acids, in order to determine which of the two above-mentioned reactions takes place. These researches have revealed the existence of a new series of ethoxy-acids, isologous with ethoxyacetic acid, and have shown that the chlorocrotonic acids obtained simultaneously from ethyl acetoacetate are probably physical isomerides. The influence of the concentration of the solution and the nature of the solvent are also studied. The following acids were used in the research: β-chlorisocrotonic acid (m. p. 39·5°), β-chlorocrotonic acid (m. p. 94·5°), α-chlorocrotonic acid (m. p. 97·5°), and α-methyl-β-chlorocrotonic acid.

β-Chlorisocrotonic acid is converted by sodium ethylate or alcoholic potash into *β-ethoxycrotonic acid*, $C_6H_{10}O_3$, which crystallises in monoclinic prisms melting at 137°, soluble in alcohol and ether, insoluble in water. Its potassium salt crystallises in long needles, an aqueous solution of which gives precipitates with solutions of the chloride as of metals of the iron-group. The ethyl salt crystallises in rhombic tables melting at 30°. Ethoxycrotonic acid is decomposed by dilute sulphuric acid into carbonic anhydride, acetone, and alcohol, thus: $C_6H_{10}O_3 + H_2O = C_3H_6O + C_2H_6O + CO_2$ (this reaction is perfectly general), and by concentrated potash into potassium acetate and alcohol,

$$C_6H_9O_3K + KOH + H_2O = 2(CH_3.COOK) + C_2H_5OH.$$

Concentrated aqueous solution of potash converts β-chlorisocrotonic acid into acetone and carbonic anhydride. A more dilute solution yields a tetrolic acid melting at 94·6°: as this latter on oxidation with permanganate solution gives acetic acid, it contains a methyl-group, and has the composition CMe⋮C.COOH.

(ii.) When *β-chlorocrotonic acid* is treated with concentrated alcoholic or dilute aqueous solution of potash, it yields products identical with those from the iso-acid.

(iii.) *α-Chlorocrotonic acid* is attacked neither by sodium ethylate nor by dilute alkali; by concentrated solutions, it is decomposed into carbonic anhydride, acetic, and oxalic acids, and a higher carboxylic acid, probably of the formula $C_4H_6O_3$.

(iv.) *α-Methyl-β-chlorocrotonic acid* is converted by alcoholic potash into methyl-β-ethoxycrotonic acid, which crystallises in prisms melting at 132°. Concentrated aqueous solutions of potash decompose α-methyl-β-chlorocrotonic acid into ethyl methyl ketone and carbonic anhydride; dilute potash is without action.

The identity of the ethoxycrotonic and tetrolic acid obtained from β normal and isocrotonic acids, proves either that the latter is converted even by very dilute alkali into the former or less stable acid (a view which the author regards as untenable), or these acids are physical isomerides. By long-continued heating the author succeeded in partially converting the β-chloro-acid (m. p. 94·5°) into its isomeride melting at 59·5°.

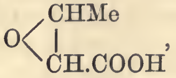
Attention is drawn to the decomposition of the ethoxy-acids by water according to the equation $CMe(OX)\colon CY.COOH + HOH = Me.CO.CYH_2 + XOH + CO_2$, a reaction which is analogous to the decomposition of that of isocrotyl ether.

The author draws a comparison between the action of alkalis on the acetoacetates and on the crotonic acids; with dilute alkalis, the former yield acids, the latter ketones; conversely, with concentrated alkalis the former give ketones, the latter acids. This difference may be attributed to the presence of a double bond in the crotonic acids.

V. H. V.

Derivatives of the Isomeric Crotonic Acids. By P. MELIKOFF (*Ber.*, **16**, 1268—1271).—By the addition of hypochlorous acid to isocrotonic acid, and treatment with zinc carbonate, two zinc salts of chlorhydroxybutyric acids are obtained, one crystalline and the other gummy. The crystalline salt forms rhombic tables of the formula $(C_4H_6ClO_3)_2Zn,2H_2O$, sparingly soluble in cold water. The free acid, $C_4H_7ClO_3$, from this salt crystallises in long needle-shaped prisms, melts at 82°, and is readily soluble in water, alcohol, and ether. The calcium salt, $(C_4H_6ClO_3)_2Ca,4H_2O$, consists of granular aggregates of microscopic crystals, is readily soluble in cold water, and effloresces slowly in air. By the action of alcoholic potash on the acid, potassium chloride and *butylglycidic acid* are formed: this latter acid is very unstable, and does not yield any characteristic salts; it unites with hydrochloric acid to form the chlorhydroxybutyric acid melting at 82°.

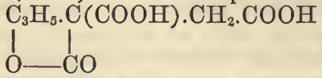
The addition-product of α-crotonic acid and hypochlorous acid has been already studied by Erlenmeyer and Müller (Abstr., 1882, 598); the author's results, however, differ somewhat from theirs. The *chlorhydroxybutyric acid*, $C_4H_7ClO_3$, obtained in this way, crystallises in stellate groups of needles, is readily soluble in water, deliquesces in air, and melts at 62—63° (Erlenmeyer and Müller give 53—56°). The zinc salt, $(C_4H_6ClO_3)_2Zn$, crystallises in groups of tables, and is very soluble in water; the calcium salt, $(C_4H_6ClO_3)_2Ca$, forms an amorphous white powder, readily soluble in water. By the action of alcoholic potash on this acid, *oxypropylenecarboxylic acid,*



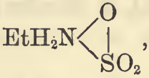
isomeric with butylglycidic acid, is obtained. It crystallises in rhombic prisms, melts at 84°, and is readily soluble in water, alcohol, and ether. The potassium salt, $C_4H_5KO_3,\frac{1}{2}H_2O$, crystallises in transparent granules; the silver salt, $C_4H_5AgO_3$, is a white crystalline powder, sparingly soluble in cold water. Hydrochloric acid converts the acid into a chlorhydroxybutyric acid, $C_2H_2MeCl(OH).COOH$, which crystallises in large prisms or in thin transparent tables, melts at 85°, and is reconverted into propyleneoxycarboxylic acid by treatment with alcoholic potash. The zinc salt separates from hot aqueous solution in rhombic prisms containing 2 mols. of water of crystallisation. A. J. G.

New Acid of the Series $C_nH_{2n-4}O_6$. By A. BAUER (*Monatsh. Chem.*, **4**, 341—344).—Some years ago the author, in conjunction with Gröger, obtained a new acid of this series by the action of potassium cyanide and potassium hydroxide on monochlorosuberic acid, and the present paper is devoted to a further examination of this acid. It is crystalline, moderately soluble in water, and decomposes when heated even at 100°, the decomposition apparently consisting in the reproduction of suberic acid, with separation of carbonic anhydride. The solution of its ammonium salt gives with barium salts a white precipitate; with cupric salts, a bulky mountain-green precipitate; with silver nitrate, a white precipitate not much affected by heat or light; with magnesium sulphate and with mercuric chloride, white precipitates after some time; with manganous sulphate, a pale-red precipitate after a while; and with ferric chloride at once a very bulky light-brown precipitate.

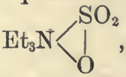
The analysis of the acid and of its silver salt led to the formula $C_9H_{14}O_6$ or $C_{18}H_{28}O_{12}$, which has been confirmed by that of the lead salt, $C_{18}H_{22}Pb_3O_{12}$, and of the ferric salt, $C_9H_{11}Fe'''O_6$. H. W.

Dicarbocaprolactonic Acid. By E. HJELT (*Ber.*, **16**, 1258—1259).—Allylethenyltricarboxylic acid is dissolved in fuming hydrobromic acid and the solution placed over caustic potash, when, after a time, crystals of an isomeric acid separate. The new acid, *dicarbocaprolactonic acid,* is bibasic, and crystallises in triclinic forms, which, however, closely resemble the rhombic pyramids of sulphur. It is soluble in water, sparingly soluble in ether, and melts at 152—153°. The *barium* salt, $C_8H_8O_6Ba$, is a white amorphous powder, readily soluble in water; the *silver* salt, $C_8H_8O_6Ag_2$, is obtained as a pulverulent precipitate on adding a silver salt to a hot ammoniacal solution of the acid. On boiling the acid with baryta-water, a flocculent precipitate of the barium salt of the *hydroxy-acid* is obtained. On fusion, the lactonic acid is resolved into carbonic anhydride and carbocaprolactonic acid (this vol., 656). Dicarbocaprolactonic acid is represented by the formula  $\begin{array}{l}C_3H_5.C(COOH).CH_2.COOH \\ \,|\qquad\;| \\ O\text{——}CO\end{array}$, and is the first instance of a dibasic lactonic acid. A. J. G.

Alkylsulphamic Acids. By F. BEILSTEIN and E. WIEGAND (*Ber.*, **16**, 1264—1268).—In the hope of synthesising taurine or isotaurine, the authors investigated the action of sulphuric anhydride on ethylamine, but obtained instead the isomeric ethylsulphamic acid. Other bases of the fatty series behave in a similar manner with sulphuric anhydride, and thus differ entirely from those of the aromatic series.

Ethylsulphamic Acid, $NHEt.SO_3H$.—Sulphuric anhydride and ethylamine, both in the state of vapour, were passed into a cooled flask, and the product exposed for some time to a moist atmosphere; then diluted with water and boiled with barium carbonate, when, on concentrating the filtrate, barium ethylsulphamate crystallises. At times, however, although the working was the same, a thick neutral syrup was obtained, which contained no barium, and was probably an anhydride,  $EtH_2N{<}\begin{array}{l}O\\ |\\ SO_2\end{array}$, or amide, $SO_2(NHEt)_2$; boiling with baryta-water resolved it into barium ethylsulphonate, and a small amount of ethylamine. The *free acid*, prepared by the action of hydrogen sulphide on the lead salt, crystallises in needles, is soluble in water, alcohol, and ether, and is not decomposed by boiling with water. The *calcium* salt, $(NHEt.SO_3)_2Ca,2H_2O$, forms moderately large, brilliant prisms, is soluble in ether, readily soluble in alcohol and water; the *barium* salt, $(C_2H_6NSO_3)_2Ba,\frac{1}{2}H_2O$, crystallises in lustrous cholesterin-like plates, and is readily soluble in water; 1 part of the anhydrous salt dissolves in 74·2 parts of alcohol (90 per cent.) at 18°. The lead salt forms needles readily soluble in water and alcohol.

Diethylamine and sulphuric anhydride unite with great energy; the product, when treated with water and barium carbonate, yields a brown syrup, which, on being boiled with baryta-water, is resolved into diethylamine and *barium diethylsulphamate*, $(NEt_2.SO_3)_2Ba,2H_2O$, readily soluble in water and alcohol, insoluble in ether. The free acid has already been described by Behrend.

Triethylamine and sulphuric anhydride react with great energy, yielding a thick viscous mass, from which, on dilution with water, brilliant crystals separate, and are purified by solution in acetone. The *Anhydrotriethylsulphamic acid*,  $Et_3N{<}\begin{array}{l}SO_2\\ |\\ O\end{array}$, thus obtained forms colourless tabular crystals, which melt at 91·5°; it is readily soluble in acetone, alcohol, and hot water, sparingly soluble in cold water and ether, and reacts neutral. On boiling with water, it is decomposed into triethylamine and sulphuric acid.

With methylamine and sulphuric anhydride, results are obtained similar to those with ethylamine. A. J. G.

Dialkyldisulphisethionic Acids. By J. ENGELCKE (*Annalen*, **218**, 269—283).—It has been shown by Laube and by Stengel (see last Abstract) that the salts of sulphacetic and sulphobenzoic acids are capable of combining with ethyl sulphate. With a view to ascertain whether the carboxyl-group in the above acids plays an essential part in the reaction, the author has made experiments with isethionic acid and with benzenesulphonic acid. Dry sodium isethionate is well mixed with a slight excess of sulphuric acid, absolute alcohol added, and the whole digested for several days with frequent shaking; the product is then filtered, the excess of alcohol distilled off, and the syrupy liquid is diluted with water and neutralised with barium carbonate in the cold. On evaporating the filtrate at a gentle heat, crystals are obtained consisting of barium isethionate and the double salt, $(C_2H_4OHSO_3)_2Ba,SO_4Et_2$, from which the former can be separated by adding absolute alcohol to the saturated aqueous solution. A more convenient method is to neutralise with sodium carbonate instead of barium carbonate, add alcohol to precipitate the sodium sulphate formed, and then cautiously evaporate the filtrate on a water-bath to complete dryness. On extracting the residue with absolute alcohol and recrystallising, the compound is obtained in a state of purity. *Sodium dimethyldisulphisethionate*,

$$C_2H_4(OH).SO_3Na,SO_4Me_2,$$

forms a white silky mass of monoclinic plates; it is anhydrous, but rapidly deliquesces on exposure to the air. Attempts to prepare the free dimethyldisulphoisethionic acid were unsuccessful. On boiling an aqueous solution of the sodium salt, it is decomposed according to the equation—

$$C_2H_4(OH).SO_3Na,SO_4Me_2 + 2H_2O = C_2H_4(OH).SO_3H + 2MeOH + SO_4NaH.$$

Sodium diethyldisulphisethionate, $C_2H_4(OH).SO_3Na,SO_4Et_2$, resembles the methyl-derivative in its properties, but is less stable.

The author has also made several experiments with the view of obtaining a corresponding double compound from benzenesulphonic acid, but all his attempts were unsuccessful. A. K. M.

Methylsulphonic Acid. By NISHACK (*Annalen*, **218**, 283—288). —The *lithium* salt, $MeSO_3Li,H_2O$, obtained on adding lithium sulphate to a solution of the barium salt and evaporating the filtrate, crystallises in hygroscopic prisms, very readily soluble in water; the *ammonium* salt, $MeSO_3NH_4$, forms small thin hygroscopic scales of a mother-of-pearl lustre; the *strontium* salt, $(MeSO_3)_2Sr,H_2O$, crystallises in concentrically grouped rhombic prisms, which lose their water at 120°; the *calcium* salt, $(MeSO_3)_2Ca$, is anhydrous, and forms groups of rhombic prisms; the *magnesium* salt, $(MeSO_3)_2Mg,10H_2O$, crystallises in clusters of flat rhombic plates, which effloresce in dry air and dissolve very readily in water. *Methylsulphonic chloride*, $MeSO_2Cl$, obtained by the action of phosphorus pentachloride on patassium methylsulphonate, is a colourless liquid having a penetrating odour and boiling at 160°.

Attempts to prepare double compounds of methylsulphonates with methyl and ethyl sulphates proved unsuccessful (see also last Abstr.).

A. K. M.

Constitution of the Double Compounds of the Sulphonates with Alkyl Sulphates: Constitution and Dimorphism of Sulphates. By A. GEUTHER (*Annalen*, **218**, 288—302).—From the results obtained by Laube, Stengel, and Engelcke (p. 972), the author assigns to the double compounds obtained by them the following constitutional formulæ, in which M and R denote respectively metal and alcohol-radicle:—

$$C_6H_4(COOM).SO(OM){<}\substack{O\\O}{>}SO(OR)_2,$$

Dialkyldisulphobenzoate.

$$CH_2(CH_2.OH).SO(OM){<}\substack{O\\O}{>}SO(OR)_2$$

Dialkyldisulphoisethionate.

He explains the fact that the sulphonic acids of the hydrocarbons do not form corresponding compounds, by pointing out that the stability of these compounds becomes greater the greater the amount of oxygen present, and *vice versâ*. He regards these compounds as derivatives of a *disulphuric acid*, $(OH)_2SO{<}\substack{O\\O}{>}SO(OH)_2$, the existence of which would readily explain the constitution of the persulphates $S_2O_8H_3M$ and similar salts, and also the occurrence of dimorphism and of other variable properties exhibited by many sulphates.

A. K. M.

Biguanide. By F. EMICH (*Monatsh. Chem.*, **4**, 408—414).—I. According to Rathke, biguanide, $C_2H_7N_5$, is a biacid base, its normal sulphate having the composition $C_2H_7N_5,H_2SO_4$; but cupric biguanide is mono-acid, its normal sulphate being represented by the formula $(C_2H_6N_5)_2Cu,H_2SO_4$ or $(C_2H_6cuN_5)_2,H_2SO_4$. Emich, however, has shown (see p. 975) that ethylbiguanide is a monacid base, forming two series of salts, normal and acid. Now as it appeared very unlikely that the ethyl-derivative should have a saturating power different from that of biguanide itself, the author was induced to repeat Rathke's experiments (which were made upon very small quantities of material), and he finds that biguanide, like its ethyl-derivative, is a monacid base, its normal and acid sulphates having respectively the formulæ $(C_2H_7N_5)_2,H_2SO_4$ and $C_2H_7N_5,H_2SO_4$.

II. Biguanide is resolved by prolonged boiling with acids or alkalis into carbonic anhydride and ammonia, according to the equation $C_2H_7N_5 + 4H_2O = 2CO_2 + 5NH_3$, the decomposition being analogous to that of guanidine: $CH_5N_3 + 2H_2O = CO_2 + 3NH_3$. The constitution of these two bases may therefore be represented by analogous formulæ, viz.:—

$HN:C(NH_2)_2$	$HN:C(NH_2).NH.C(NH_2):NH$
Guanidine.	Biguanide.

H. W.

Methylguanide and its Compounds. By A. F. Reibenschuh (*Monatsh. Chem.*, 4, 388—394).—The copper-derivative of this base is obtained in the form of sulphate, $(C_3H_8N_5)_2Cu,H_2SO_4 + 2\frac{1}{2}H_2O$, by triturating dicyanodiamide with cupric sulphate, and digesting the resulting powder with a 20 per cent. solution of methylamine, till the whole dissolves to a deep blue liquid, which, when left at rest for several days, deposits the required compound in red needles. A larger quantity may however be obtained, and in a few hours, by heating the blue solution in a sealed tube at 100—110°. For success in the preparation, however, it is essential that the methylamine solution be of the strength above mentioned, as weaker solutions are apt to decompose and deposit cupric oxide. By proceeding as above, the copper sulphate compound is obtained as a network of very slender needles, having the colour of peach-blossom, and extremely hygroscopic.

The copper-base, $(C_3H_8N_5)_2Cu$, may be prepared in the free state by repeatedly agitating cupric oxide with methylamine solution during several days, then shaking up the filtered liquid with pulverised dicyanodiamide, and heating the resulting solution for several hours at 100—110°; but a better yield is obtained by mixing a solution of the sulphate in the smallest possible quantity of dilute sulphuric acid, with a quantity of soda-lye sufficient to redissolve the resulting precipitate, then filtering hot, and recrystallising from hot water. The amaranth-coloured solution on cooling deposits the copper-base in glittering rose-coloured needles, having the composition

$$(C_3H_8N_5)_2Cu,3\frac{1}{2}H_2O,$$

and giving off their water at 110°.

Methylbiguanide, $C_3H_9N_5$, is obtained in the free state by decomposing its sulphate (*infra*) with baryta-water, and may be concentrated in a vacuum over sulphuric acid to a viscid uncrystallisable syrup. It quickly absorbs carbonic anhydride from the air, and forms both normal and acid salts, which dissolve readily in water, and crystallise, with the exception of the extremely deliquescent carbonate, in laminæ or in slender prisms, often aggregated in radio-fibrous hemispherical groups. The *normal sulphate*, $(C_3H_9N_5)_2,H_2SO_4$, prepared by decomposing the above-described copper sulphate compound with hydrogen sulphide, crystallises in spherical groups of short rhomboïdal prisms, permanent in the air, not losing weight at 100°, and melting at 110°. The *acid sulphate*, $C_3H_9N_5,H_2SO_4$, is a crystalline powder more soluble than the normal salt. The *normal* and *acid nitrates* and *hydrochlorides* are obtained by decomposing the corresponding sulphates with nitrate and chloride of barium. The normal hydrochloride crystallises in efflorescent laminæ, extremely soluble in water, and forming a crystalline platinochloride. The *chromate* and *picrate*, obtained by direct combination, crystallise in slender prisms, the former with orange-yellow, the latter with dark yellow colour. H. W.

Ethylbiguanide and its Compounds. By F. Emich (*Monatsh. Chem.*, 4, 395—408).—The author prepares this base by the action of ethylamine on dicyanodiamide, $(CN)_2(NH_2)_2 + EtNH_2 = C_2H_6EtN_5$. Its copper sulphate compound, $(C_4H_{10}N_5)_2Cu,H_2SO_4$, prepared like the corresponding methyl-compound (p. 974), by the action of cupric sulphate on dicyanodiamide dissolved in ethylamine, separates in carmine-red, highly lustrous granules, or in rose-red mostly microscopic needles, containing 1 mol. H_2O, accordingly as the reaction takes place in a hot or cold solution. The crystals of both kinds, especially the latter, are highly hygroscopic, and to render them anhydrous they must be dried for several hours in the exsiccator at 115—120°. This salt is nearly insoluble in pure water, but dissolves more readily in alkaline liquids, with partial separation, however, of the cupric base. Dilute acids, even aqueous carbonic acid, dissolve it readily, with formation of the corresponding salts of copper and ethylbiguanide.

Cupric Ethylbiguanide, $(C_4H_{10}N_5)_2Cu$, is formed synthetically by the action of a solution of cupric hydroxide in ethylamine on dicyanodiamide, but the process is slow, and the compound is more readily obtained by decomposing the sulphate above described with a caustic alkali. It dissolves sparingly in cold, more freely in hot water, forming a pale violet-red strongly alkaline solution, which precipitates many metallic salts, *e.g.*, $MgCl_2$, $ZnCl_2$, $HgCl_2$, also potassium or sodium sulphate, with formation of KOH or NaOH, and the very slightly soluble copper sulphate compound. The solution absorbs carbonic acid from the air, and deposits the carbonate of the copper-base in pale red needles. The copper-base is anhydrous, and bears a temperature of 125° without alteration, but decomposes at 140° with evolution of ammoniacal vapours.

Ethylbiguanide, $C_4H_{11}N_5 = C_2H_6EtN_5$, prepared by decomposing either of its sulphates with baryta-water, forms a white extremely delicate crystalline mass, soluble in alcohol, insoluble in ether, and obtained by concentration of its aqueous solution, as a clear syrup, which often does not solidify till it has been kept for weeks over sulphuric acid. It produces a strong alkaline reaction on moist litmus-paper, expels ammonia from its salts, and rapidly absorbs carbonic acid from the air. When heated in a test-tube, it gives off ammonia and ethylamine with strong effervescence, leaving a yellowish mass resembling mellone, which sublimes at incipient redness, with evolution of fumes smelling like prussic acid, leaving scarcely a trace of charcoal. It forms two series of salts, mono- and bi-acid, most of which are crystalline. The carbonate and oxalate are very soluble. H. W.

Nitration of Benzene-derivatives. By P. SPINDLER (*Ber.*, **16**, 1252—1257).—The author has worked at this subject in the hope of obtaining an answer to the following questions:—

1. Can the same result be obtained by nitration with a more dilute acid continued for a sufficiently long time as with a stronger acid during a shorter interval?

2. What is the explanation that the result is only equal within certain limits in the concentration of the acid?

3. What degree of concentration of the acid is the most favourable?

Benzene, methylbenzene, chlorobenzene, bromobenzene, and ortho-, meta-, and para-benzonitranilide were nitrated, and all gave similar results; the experiments with benzene are quoted in the paper in a series of tables, the main results of which are given below.

Nitration in the Cold.

Nitric acid.	Sp. gr. of acid.	Water.	Benzene.	Percentage of NO_2 found.		
				Duration of reaction.		
				1 day.	10 days.	150 days.
c.c.		c.c.	c.c.			
10	1·527	0	5	39·07	39·31	—
10	1·500	0	5	35·79	35·49 36·13	35·88
10	,,	1	5	35·61	36·66	36·94
10	,,	2	5	35·17	35·61	36·41
10	,,	3	5	32·59	35·21	36·03
10	,,	4	5	28·99	33·09	36·39 35·97
10	,,	5	5	20·78	28·99	35·37
10	,,	6	5	8·25	18·81	30·78
10	,,	7	5	2·89	13·58	25·56
10	,,	8	5	0·84	4·40	15·94
10	,,	9	5	0·00	1·68	6·73
10	,,	10	5	0·51	0·67 0·45	3·15
10	,,	15	5	—	—	0·79
10	,,	20	5	0·39	—	0·14

Nitration at the Temperature of the Water-bath.

Nitric acid.	Sp. gr. of acid.	Water.	Benzene.	Percentage of NO_2 found.		
				Duration of reaction.		
				10 hours.	30 hours.	120 hours.
c.c.		c.c.	c.c.			
10	1·500	0	5	35·82	37·54	—
10	,,	5	5	36·68	—	—
10	,,	10	5	26·33	30·22	—
10	,,	20	5	1·51	5·48	—
10	,,	30	5	—	1·78	—
10	,,	50	5	—	—	0·00
10	,,	100	5	—	—	0·00

The reason of the hindrance to nitration by too great dilution is still unknown; it is not due to the decomposing action of water, as after heating pure nitrobenzene with twice its volume of water for 750 hours at about 100°, for 25 hours at 125°, or for 6—7 hours at 200°, not the slightest trace of an acid reaction could be detected in the water.

A. J. G.

Action of Allyl Chloride on Benzene in Presence of Aluminium Chloride. By P. Wispek and R. Zuber (*Annalen*, **218**, 374—382).—Silva showed that diphenylpropane is formed by this reaction (Abstr., 1880, 260), but the authors thought it possible that, by modifying the conditions of the experiment, allylbenzene might be formed. When the allyl chloride is allowed to react on a mixture of benzene and aluminium chloride, diphenylpropane is obtained, together with traces of a substance boiling at 160°. If the benzene is first warmed with the aluminium chloride in presence of dry hydrochloric acid, and, after cooling, a mixture of equal volumes of benzene and allyl chloride is added drop by drop, a different reaction takes place; on distilling the product, hydrochloric acid and benzene first pass over, then between 130° and 200° a slightly coloured fluorescent liquid, and between 270° and 290° other products, leaving a black resinous residue in the retort. An examination of the fraction 130—200° proves it to consist principally of normal propylbenzene, boiling at 157·5—158·5°.

A. K. M.

Action of Bromine on Aromatic Hydrocarbons. By J. Schramm (*Annalen*, **218**, 383—396).—It has been shown by Radziszewski that bromethylbenzene is decomposed by distillation into styrene and hydrobromic acid (*Ber.*, **6**, 493), and that bromopropylbenzene and bromobutylbenzene also suffer analogous decomposition. The author has experimented with other aromatic hydrocarbons with the view of ascertaining if the above reaction is a general one, and has adopted this method for the preparation of unsaturated hydrocarbons. *Pentylbenzene*, $C_6H_5.C_5H_{11}$, obtained by the action of sodium on benzyl bromide and butyl bromide, is a colourless liquid of agreeable odour, boiling at 200·5—201·5° under a pressure of 743 mm. Its sp. gr. is 0·8602 at 22°. The preparation of *isopentylbenzene* (b. p. 193°) has been described by Fittig and Tollens (*Annalen*, **129**, 369, and **131**, 313). *Hexylbenzene*, $C_6H_5.(CH_2)_3.CHMe_2$, is formed by the action of sodium on a mixture of benzyl bromide and isopentyl bromide; it boils at 212—213°, and has a sp. gr. of 0·8568 at 16°. When bromine-vapour is brought into contact with pentylbenzene heated in an oil-bath at 150—155°, it is readily absorbed, with evolution of hydrobromic acid; and on distilling the monobromo-derivative thus formed, phenylpentylene is obtained, boiling at 210—215°. It combines with bromine to form a dibromide melting at 53—54°, crystallising in needles or scales, readily soluble in ether and alcohol. In the same way *phenylisopentylene*, $C_{11}H_{14}$, can be obtained; it is a colourless liquid, of sp. gr. 0·878 at 16°, boiling at 200·5—201·5°. The dibromide, $C_{11}H_{14}Br_2$, crystallises from alcohol in white silky needles, readily soluble in ether, benzene, and toluene, and melting at 128—129°. Hexylbenzene behaves exactly in the same way as the above hydrocarbons, yielding *phenylhexylene* and the *dibromide* $C_{12}H_{16}Br_2$, the latter forming star-like groups of needles or scales melting at 79—80°.

A. K. M.

Researches on Periodides. By F. W. DAFERT (*Monatsh. Chem.*, **4**, 496—511).—I. PERIODIDES OF TRIALKYLPHENYLIUM IODIDES.—These compounds are obtained by precipitating the solutions of the corresponding moniodides in alcohol or water with a solution of iodine in alcohol or in potassium iodide, as apparently microcrystalline or amorphous, easily decomposible bodies, which may be recrystallised from alcohol, and then form well-defined compounds not much affected by exposure to the air. They may also be prepared by the action of iodine dissolved in alcohol on solutions of the hydroxides, as shown by the following equation:—

$$6(NEt_3Ph.OH) + 3I_2 = NEt_3PhIO_3 + 5NEt_3PhI + 3H_2O,$$

the moniodide thus formed uniting with the excess of iodine to form a periodide. When, however, a solution of iodine in potassium iodide is used, the iodate formed in the first instance appears to react with the compound KI,I_2 in the following manner:—

$$NEt_3Ph.IO_3 + KI,I_2 = KIO_3 + NEt_3PhI,I_2;$$

or the reaction may take place as shown by either of the following equations:—

$$6(NEt_3Ph.OH) + 18I + KI = 6(NEt_3PhI,I_2) + KIO_3 + 3H_2O$$
$$6(NEt_3Ph.OH) + 30I + KI = 6(NEt_3PhI,I_4) + KIO_3 + 3H_2O.$$

These periodides may also be formed from the ammonium iodides in alcoholic solution by addition of potassium ferricyanide, which is thereby reduced to ferrocyanide, with separation of iodine.

The periodides of this group hitherto examined are dichroic bodies, appearing under the microscope as opaque indistinct crystals, sometimes elongated in one or two directions.

The pentiodides are more deeply coloured than the tri-iodides. They melt with partial decomposition, and give off part of their iodine on exposure to the air. The law of variation of their melting points according to the proportion of iodine which they contain, is different from that which holds good in the corresponding tetralkylium periodides, as shown in the following table:—

Tetralkyl-compounds.	m.p.	*Trialkylphenyl-compounds.*	m.p.
NMe_3EtI,I_2	64°	NMe_3PhI,I_2	116°
NMe_3EtI,I_4	68	NMe_3PhI,I_4	87
NEt_4I,I_2	142	NEt_3PhI,I_2	81
NEt_4I,I_4	—	NEt_3PI,I_4	68

The iodine in these compounds, like that of periodides in general, is easily separated by the action of water, caustic potash, mercury, sodium-amalgam, &c. The result is usually complicated by secondary processes, but the primary reaction consists in a separation into free iodine and the moniodide of the base. Thus when trimethylphenylium tri-iodide is heated with water, iodine is separated, and several products are formed, amongst which iodoform may be recognised by its smell, colour, crystalline form, and melting point (119°).

As, however, the moniodide of this base likewise yields iodoform when boiled with water, the occurrence of that substance amongst the decomposition-products of the periodide may be regarded as due to a secondary process, the periodide being resolved in the first instance into NMe_3EtI and I_2.

Trimethylphenylium tri-iodide, NMe_3PhI,I_2, formed by adding the weighed quantity of iodine in aqueous or alcoholic solution, crystallises in light-red laminæ having a coppery lustre, melting at 116°, easily soluble in alcohol, sparingly in ether. The *pentiodide*, NMe_3PhI,I_4, obtained by treating the moniodide with excess of iodine dissolved in alcohol, crystallises in moss-green glittering needles, melting at 87°, easily soluble in alcohol, sparingly in ether.

Triethylphenylium tri-iodide, NEt_3PhI,I_2, is always precipitated from a solution of the moniodide on addition of alcoholic iodine, even when the iodine is in excess. It forms glistening laminæ, melting at 81°, easily soluble in alcohol, less soluble in ether than the preceding periodides. The *pentiodide*, NEt_3PhI,I_4, separates from the mother-liquor of the last compound in large black strongly dichroic laminæ, melting at 68°, easily soluble in alcohol, sparingly in ether.

The higher members of this series also give precipitates with iodine; but they have not yet been examined. *Bromine* throws down from solutions of the moniodides stable precipitates of perhaloïd compounds, containing both bromine and iodine; from solutions of the hydroxides, it precipitates unstable compounds containing bromine, and perhaps consisting of the corresponding perbromides.

II. PERIODIDES OF THE NITROSODIALKYLANILINES.—These bodies, nitrosodiethylaniline for example, form with iodine two series of compounds represented by the formulæ—

$$\underset{\alpha.}{2NR_2C_6H_4(NO),I_3} \qquad \underset{\beta.}{3NR_2C_6H_4(NO),I_2,}$$

R denoting a radicle of the series C_nH_{2n+1}. The α-formula must however be doubled, in accordance with the law of even numbers.

These periodides are prepared by treating the nitrosodialkylanilines with the weighed quantity of iodine dissolved in alcohol, solution of potassium iodide, carbon bisulphide, or chloroform, and may be purified by washing with ether and crystallisation, which latter process is however attended with a certain amount of decomposition. When recrystallised from alcohol, they form well-defined compounds, which exhibit strong dichroism, and give off a very small portion of their iodine on exposure to the air. Their melting points rise as the proportion of iodine diminishes, as may be seen from the following table:—

	Melting point.	Percentage of iodine.
$2NMe_2C_6H_4(NO),I_3$	115·5°	55·9
$2NEt_2C_6H_4(NO),I_3$	118·0	51·7
$3NMe_3C_6H_4(NO),I_2$.........	123·5	36·1
$3NEt_3C_6H_4(NO),I_2$	127·0	32·2

All these bodies are decomposed, with separation of iodine, by water, potash-lye, mercury, sodium-amalgam, and other reagents, secondary decompositions, however, taking place at the same time, the bases which they contain being much more easily attacked than those of the trialkylphenylium periodides.

The following are the characters of some of these periodides:—

$2NMe_2C_6H_4(NO),I_3$. Black crystalline scales having a bluish shimmer, melting at 115·5°, easily soluble in alcohol and chloroform, less readily in ether.—$3NMe_2C_6H_4(NO),I_2$. Brown-red laminæ having a violet shimmer, melting at 123·5°, easily soluble in alcohol, less easily in ether.—$2NEt_2C_6H_4(NO),I_3$. Black laminæ and needles having a bluish shimmer, easily soluble in alcohol, sparingly in ether, crystallising from strong solutions in tufts and in better defined crystals.—$3NEt_2C_6H_4(NO),I_2$. Light copper-red laminæ having a golden lustre, and melting at 127°.

III. Periodides of Pyridine, C_5H_5N,HI,I_4.—On adding iodine dissolved in potassium iodide to a solution of pyridine in sulphuric acid, this compound separates in glittering needles having a splendid emerald-green colour. It is extremely soluble in alcohol, easily in benzene, light petroleum, and chloroform, sparingly in ether, and melts at 89°. Water separates iodine from it. It appears to be converted into dipyridine by sodium-amalgam.

On adding alcoholic iodine to an alcoholic or aqueous solution of pyridine, a red precipitate is formed, which is not identical with the periodide just described. A similar precipitate is formed by a solution of iodine in potassium iodide or in carbon bisulphide.

IV. Second Periodide of Quinoline.—A solution of iodine in potassium iodide added to a solution of quinoline in sulphuric acid forms a precipitate resembling the pyridine compound just described, and different from the periodide of quinoline described by Claus and Istel (*Wien. Akad. Ber.*, **15**, 824). This precipitate is crystalline, has a shimmering aspect, a grass-green colour when moist, dull grey-green after drying. It dissolves with extreme facility in alcohol, easily also in benzene and light petroleum, sparingly in ether. It melts at 67°, and is not decomposed by cold water. On heating the alcoholic solution of this compound with sodium-amalgam rich in sodium, the liquid becomes decolorised, and ether extracts from it a crystalline organic substance melting at 110—115°. On heating this body with water, iodine is separated.

The primary bases, such as aniline, toluidine, &c., the secondary bases, such as diphenylamine, the nitroso-compounds of the latter, the nitro-derivatives of the tertiary bases, and the homologues of acetanilide, treated by either of the methods above described, do not yield any periodides. The azylines, however, yield addition-products similar to the periodides of the nitroso-dialkylanilines.

From the facts hitherto observed, it appears that only tertiary bases and ammonium bases are capable of yielding periodides. Moreover, if a residue capable of greatly weakening the basic character (*e.g.*, NO_2 or C_2H_3O) be added, or if the base itself is sensibly altered by free iodine, as is the case with diethylaniline, the formation of a periodide no longer takes place.

H. W.

Derivatives of Triphenylmethane. By E. RENOUF (*Ber.*, **16**, 1301—1307).—I. *Paraleucaniline and Leucaniline.*—In the preparation of paraleucaniline from paranitrobenzaldehyde and aniline, another base is obtained in very small quantity. It separates from benzene in small crystals containing benzene, is colourless, but turns red on exposure to air. It is distinguished from paraleucaniline by its behaviour with oxidising agents; chloranil oxidises it to a dye of but little tinctorial power, somewhere between magenta and violet in shade. The platinochloride is sparingly soluble, and is decomposed on boiling its solution.

Paraleucaniline sulphate, prepared by the action of cold concentrated sulphuric acid on an alcoholic solution of the leuco-base, crystallises in bundles of needles. A hot solution of the salt oxidises very readily, with separation of rose-coloured crystals. *Paraleucaniline oxalate* forms small, short prisms, readily soluble in water, sparingly soluble in alcohol and ether. *Paraleucaniline platinochloride* crystallises in rosettes of thick, yellow needles, sparingly soluble in water, insoluble in alcohol.

Benzoylparaleucaniline, prepared by heating a solution of paraleucaniline in benzene with excess of benzoic chloride, crystallises in colourless needles, melts at 149°, is moderately soluble in hot alcohol, nearly insoluble in ether and benzene. *Triacetylparaleucaniline*,

$$C_{19}H_{16}N_3\overline{Ac}_3,$$

is obtained by heating the dry leuco-base with excess of acetic anhydride for one hour. It crystallises in pale rose-coloured thin tables, and melts at 177°. On oxidising it with chromic acid in glacial acetic acid solution, and boiling the product with hydrochloric acid, pararosaniline is obtained. *Triacetyl-leucaniline*, $C_{20}H_{18}N_3\overline{Ac}_3$, prepared in a similar manner from leucaniline, forms tufts of pale rose-coloured needles, and melts at 168°: oxidised with chromic acid in glacial acetic acid solution, it yields tetracetylrosaniline. *Tetracetylrosaniline*, $C(C_6H_4.NH\overline{Ac})_2(C_6H_3Me.NH\overline{Ac}).O\overline{Ac}$, prepared by boiling rosaniline for two hours with acetic anhydride, forms an amorphous red powder.

II. *Condensation of Orthonitrobenzaldehyde with Aniline.*—By heating orthonitrobenzaldehyde and aniline sulphate for ten hours on the water-bath, in presence of zinc chloride, a nitroleuco-base is obtained as a yellowish-red, indistinctly crystalline mass. This on reduction with zinc and hydrochloric acid gave the hydrochloride of a new *triamidotriphenylmethane*, $C_{19}H_{19}N_3,3HCl$, crystallising in groups of needles, readily soluble in water, sparingly soluble in alcohol, insoluble in ether. The free base, $C_{19}H_{19}N_3$, forms small pale-brown crystals, and melts at 165°. The platinochloride crystallises in yellow needles, readily soluble in water and alcohol; the oxalate crystallises in groups of small brownish needles, readily soluble in water, more sparingly in alcohol; the sulphate forms very small quadratic tables, is readily soluble in water, very sparingly in alcohol. On oxidising the base with chloranil, only a very faint yellowish-brown coloration is obtained. By heating it with arsenic acid at 150°, a brown dye is formed; heated with excess of acetic anhydride, it yields an acetyl-compound crystallising in needles. As the behaviour of the new triamidotriphenylmethane on oxidation is so different from that of the one obtained from orthonitrobenzaldehyde, a comparative examination of the methiodides of both bodies was made in the expectation that any difference in structure would be manifested by a difference in these derivatives, but the result showed them to be closely related substances.

III. *Condensation of Salicylaldehyde with Aniline.*—Salicylaldehyde, aniline sulphate, and zinc chloride heated for 30—40 hours at 110—120°, yields a compound which, after purification, crystallises from benzene in groups of pale red-yellow needles of the formula $C_{19}H_{18}N_2 + C_6H_6$. The acetyl-compound, obtained by boiling the base with excess of acetic anhydride, forms reddish-white needles.

A. J. G.

Hydroxyazo-compounds. By R. MEYER and H. KREIS (*Ber.*, **16**, 1329—1333).—Benzeneazoresorcinol is readily purified by solution in hot aqueous ammonia; on cooling, the ammonium-compound separates in nearly black scales or plates of greenish lustre. It loses ammonia on exposure to air. By treatment with hydrochloric acid, benzeneazoresorcinol is obtained as a red powder melting at 165°. By reduction with tin and hydrochloric acid, it yields the amidoresorcinol of Weselsky, together with aniline.

By the action of orthonitrophenol in alkaline solution on paradiazobenzenesulphonic acid, the parasulphobenzeneazo-orthonitrophenol of Griess is obtained. Paranitrophenol similarly treated yielded substances which could not be purified, probably belonging to the class of di-azo-compounds. Parasulphobenzene-azoresorcinol yielded with both nitrophenols substances which could not be purified.

A. J. G.

Amarine. By A. CLAUS and K. ELBS (*Ber.*, **16**, 1272—1274).—If the formula for amarine containing one imide-group only recently proposed by Claus (*Ber.*, **15**, 2333) be correct, a silver salt containing but 1 atom of silver should be obtained. On mixing silver nitrate with alcoholic solution of amarine and subsequent addition of concentrated aqueous ammonia, a silver derivative, $C_{21}H_{17}N_2Ag$, separates in the course of a few days. The same compound is obtained even when silver nitrate is employed in large excess. It forms small, brilliant, nearly colourless crystals, insoluble in water, alcohol, and ether; concentrated ammonia dissolves only traces. On slowly heating it, a residue of metallic silver is left, whilst pure lophine sublimes in theoretical amount.

The silver derivative of amarine reacts easily with organic haloïds. Heated with benzyl bromide in sealed vessels at 100° it yields *monobenzylamarine* as a colourless transparent resin, which could not be obtained in the crystalline state; it dissolves in dilute acids, even acetic. Addition of platinic chloride to the hydrochloric solution gives a fine golden-yellow precipitate of *benzylamarine platinochloride*, $[C_{21}H_{17}(C_7H_7)N_2]_2,H_2PtCl_6$, containing also water of crystallisation, which is completely driven off at 120°. On further heating, it softens at 165—167°; melts to a thick yellow liquid at 236°, and decomposes into a black mass at 240°.

Monobenzylamarine is distinguished from the bi-derivatives by the readiness with which its chromate oxidises when boiled in glacial acetic acid solution. A. J. G.

Silicates of the Phenol By A. Martini and A. Weber (*Ber.*, **16**, 1252).—These compounds are prepared by the action of an excess of the respective phenols on silicon tetrachloride.

Tetraphenyl silicate, $Si(OPh)_4$, forms a colourless syrupy liquid, which only solidifies after long cooling.

Tetraparacresyl silicate, $Si(OC_7H_7)_4$, is obtained in fine crystals. Both compounds distil unchanged at a high temperature.

A. J. G.

Constitution of Benzoyl-carbinol. By J. Plöchl and F. Blümlein (*Ber.*, **16**, 1290—1293).—If the formula of benzoyl carbinol is really $Ph.CO.CH_2.OH$,—that usually assigned to it,—it will, on addition of hydrocyanic acid and saponification of the resulting nitrile, yield atroglyceric acid, $CPh(OH)(COOH).CH_2.OH$; but if, on the contrary, it has the constitution CHPh(OH).CHO, it will be converted by such treatment into phenylglyceric acid,

$$CHPh(OH).CH(OH).COOH.$$

The result of the authors' experiments prove the former supposition to be correct, the acid formed being identical with atroglyceric acid.

A. J. G.

Hydroxylation by Direct Oxidation. By R. Meyer (*Annalen*, **219**, 234—307).—In this paper an account is given of experiments of the author and his associates on the hydroxylation by direct oxidation, preliminary notices of which have appeared in the *Berichte* (see Abstrs., 1879, 157, 465, 795; 1880, 165; 1881, 45, 819, &c.).

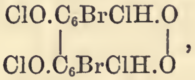
In the introduction, a few general remarks are offered on the subject. Before the author's investigations, it had been observed that triphenylmethane, $CHPh_3$, is converted by oxidation into triphenylcarbinol, $C(OH)Ph_3$ (Hemilian), aniline into quinol, and di- and tri-nitrobenzene into di- and tri-nitrophenol. In the alizarin manufacture, it had been observed that anthraquinonemonosulphonic acid when fused with potash yields alizarin, whilst the corresponding disulphonic acid yields purpurin; these changes, though effected by the air, are usually assisted by the manufacturers by the addition of potassium chlorate. On reviewing these various reactions it is to be observed that all the above compounds contain a CH-group, or *tertiary hydrogen-atom*. The author's investigations have been carried out with a view of proving that the hydroxylation by oxidation, or conversion of H into (OH), is a reaction general to all substances which contain such a tertiary hydrogen-atom. The following are the principal examples given in the paper: oxidation of isobutyric acid, $CHMe_2.COOH$, into hydroxyisobutyric acid, $C(OH)Me_2.COOH$;

cumic, $CHMe_2.C_6H_4.COOH$, into hydroxypropylbenzoic acid, $C(OH)Me_2.C_6H_4.COOH$; cymene-sulphonic, $C_6H_4(SO_3H).CHMe_2$, into oxypropylbenzenesulphonic acid, $C_6H_4(SO_3H).C(OH)Me_2$.

In order to effect these conversions, it is necessary in practice to use a 4 per cent. strongly alkaline permanganate solution; the reaction cannot be effected with an acid substance. V. H. V.

Chloroxy- and Bromoxy-derivatives of Benzene. By R. BENEDIKT (*Monatsh. Chem.*, **4**, 223—236). Third memoir. Compare this Journal, **36**, 717, and **38**, 246.—I. Resorcinol-derivatives.—*Trichlorometadibromoxybenzene*, or *Trichloro-resodibromoxybenzene*, $C_6Cl_3H(\overset{1}{O}Br)(\overset{3}{O}Br)$.*—To prepare this compound, trichlororesorcinol, $C_6Cl_3H(OH)_2$ (obtained by passing chlorine into a solution of resorcinol in glacial acetic acid, and melting at 83°), was suspended in fine powder in a mixture of equal parts of water and hydrochloric acid, and mixed with excess of bromine-water, and the resulting precipitate was twice crystallised from chloroform. It forms small yellowish crystals, decomposing at 130°, with emission of brown vapours. By heating with sodium hydrogen sulphite or with tin and hydrochloric acid, it is reconverted into trichlororesorcinol, showing that both its bromine-atoms are directly attached to oxygen, as represented by the above formula. Heated to 130—140°, it decomposes with evolution of brown vapours containing bromine, but the decomposition is not very definite.

Chlorodibromo-meta-chlorobromoxybenzene, $C_6ClBr_2H(OCl)(OBr)$, is prepared by passing chlorine into a mixture of 500 c.c. water and 500 c.c. hydrochloric acid in which 50 g. tribromoresorcinol is suspended, expelling the excess of chlorine by a stream of air, filtering, pressing the precipitate, and twice crystallising it from chloroform. It forms small yellow crystals, melting without decomposition. Heated to 175° it gives off exactly 1 mol. bromine, but no chlorine, leaving a residue which crystallises on cooling, and when purified by washing with ether and recrystallisation from chloroform, gives by analysis numbers leading to the formula $C_6BrCl_2HO_2$, which when doubled represents *dichloroxydichlorodibromodiphenoquinone*,



$$\begin{array}{l} ClO.C_6BrClH.O \\ \quad\quad\ \ | \quad\quad\quad\ \ | \\ ClO.C_6BrClH.O \end{array},$$

a compound analogous to the product obtained by decomposition of tribromoresorcinol, viz., dibromoxytetrabromodiphenoquinone,

$$(BrO.C_6Br_2H.O)_2,$$

and resembling the latter in all its properties. It begins to turn brown at 180°, and melts with decomposition at a temperature above 200°. Heated with tin and hydrochloric acid, it is converted into a

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* Called in the original paper *Trichlorresorcinbrom*, the other compounds being similarly named. The method of preparing this compound and also the corresponding orcinol derivative was briefly described by Stenhouse and Groves (*Chem. News*, **41**, p. 287).

white bulky mass, which, when crystallised from glacial acetic acid, has the composition of *dichlorodibromotetrahydroxydiphenyl*,

$$(HO)_2C_6BrClH.C_6BrClH(OH)_2;$$

it melts without decomposition at 265°. Dichloroxydichlorobromodiphenoquinone decomposes at 220—230° (just like dibromoxytetrabromodiphenoquinone), giving off, however, not chlorine, as might be expected, but bromine, and being converted into an amorphous mass. The decomposition is by no means definite.

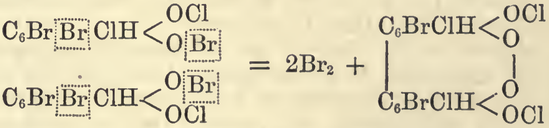
Comparison of the Behaviour of the four known Pentahalogen-resorcinols when Heated.

1. Trichloro-*m*-dichloroxybenzene, $C_6Cl_3H(OCl)(OCl)$, volatilises without decomposition, the chlorine in this compound being much more closely united to the oxygen and carbon, than the bromine in the analogously constituted bromine- and chlorobromine-compounds.

2. Trichloro-*m*-dibromoxybenzene, $C_6Cl_3H(OBr)(OBr)$, in like manner gives off no chlorine, but only bromine, leaving a residue no longer containing any haloxy-groups, and probably consisting chiefly of $C_6Cl_3H:O_2:C_6Cl_3H$. This residue exhibits all the properties of the bodies $C_{12}Br_6H_4O_2$ and $C_{12}Br_6H_2O_4$, obtained respectively by the action of heat on tribromo-bromoxybenzene and on dibromoxytetrabromodiphenoquinone. All these bodies dissolve readily in ether and in alcohol, and none of them have yet been crystallised.

3. Chlorodibromo-*m*-chlorobromoxybenzene, $C_6ClBr_2H(OCl)(OBr)$, gives up exactly 1 mol. bromine, leaving a crystalline residue insoluble in ether, and having half its chlorine directly united to oxygen, so that it has not undergone any change of atomic arrangement. Hence it follows that the compound $C_6ClBr_2H(OCl)(OBr)$, when heated, gives up the bromine-atom attached to the oxygen, and another situated in the benzene-nucleus.

Moreover, since the crystalline residue has been shown to be a diphenyl-derivative (*supra*), its formation and constitution must be represented as follows :—



$$\begin{array}{l} C_6Br\boxed{Br}ClH<^{OCl}_{O\boxed{Br}} \\ C_6Br\boxed{Br}ClH<^{O\boxed{Br}}_{OCl} \end{array} = 2Br_2 + \begin{array}{l} C_6BrClH<^{OCl}_{O} \\ \;| \qquad\qquad\quad | \\ C_6BrClH<^{O}_{OCl} \end{array}$$

4. Tribromo-*m*-dibromoxybenzene is decomposed exactly like the preceding compound.

II. Phenol-derivatives.—*Trichloro-chloroxybenzene*, $C_6Cl_3H_2.OCl$, is produced by passing chlorine into a solution of trichlorophenol in dilute potash-lye: the action is very slow, and requires to be conducted with particular precautions, for which we must refer to the original paper.

This compound crystallises in shining orthorhombic prisms, having the axial ratio $a:b:c = 1:0{\cdot}6059:0{\cdot}5073$. It melts at 119°, and distils without decomposition; it may also be crystallised without decomposition from boiling alcohol. The crystals when drenched with potash-ley assume a fine blue colour without alteration of form. They are completely decomposed when boiled with the alkaline liquid, yielding a large quantity of trichlorophenol, together with brown amorphous bodies. Cold nitric acid does not act upon the compound, but the boiling acid decomposes it with brisk evolution of gas. On heating the compound with sulphuric acid, hydrogen chloride is abundantly evolved, and on pouring the resulting mass into water and distilling with steam, trichlorophenol passes over and chloranil remains behind:

$$3(C_6Cl_3H_2.OCl) + H_2O = 2(C_6Cl_3H_2.OH) + C_6Cl_4O_2 + 2HCl.$$

Trichloro-bromoxybenzene, $C_6Cl_3H_2.OBr$, is obtained by mixing a solution of trichlorophenol in dilute potash-lye with an equal volume of strong hydrochloric acid, then adding an excess of bromine dissolved in the same acid, agitating the liquid repeatedly for some hours, then filtering and crystallising the product from chloroform. The resulting crystals are slightly coloured, and melt at 99°. The compound heated above its melting point gives off bromine, and leaves an amorphous mass. When fused under sulphuric acid, it is converted into bromotrichlorophenol, $C_6HCl_3Br.OH$.

The trichlorophenol used in the preparation of the compounds just described was obtained by passing chlorine into liquefied phenol at 80°, till the product solidified at 30°. Now when this product is heated with dilute potash-lye, it does not dissolve completely, but leaves a fused residue which solidifies on cooling, and when crystallised from alcohol yields long needles of consecutive tetrachlorobenzene [1 : 2 : 3 : 4], melting at 42°. The occurrence of this compound in crude trichlorophenol is in all probability due to a replacement of the hydroxyl-group of the phenol by chlorine; and since the trichlorophenol may also be obtained by chlorination of ordinary dichlorophenol [OH : Cl : Cl = 1 : 2 : 4], there remains for the trichlorophenol only the formula [OH : Cl : Cl : Cl = 1 : 2 : 3 : 4]. There are, however, other considerations which indicate for this compound the formula [1 : 2 : 4 : 6], so that the final decision of the question must be left for further investigation.

Action of Chlorine on Tribromophenol.—When chlorine is passed into tribromophenol suspended in dilute hydrochloric acid, the compound is gradually converted into a granular mass occupying a much smaller volume; and, on crystallising the product from chloroform, small shining crystals are obtained, consisting of two or more isomorphous substances, separable by fractional crystallisation into portions containing various quantities of chlorine and bromine, and consisting of tribromo-bromoxybenzene, $C_6Br_3H_2.OBr$, chlorodibromo-bromoxybenzene, $C_6Br_2ClH_2.OBr$, bromodichloro-bromoxybenzene, $C_6BrCl_2H_2.OBr$, and perhaps other products richer in chlorine. A similar displacement of bromine by chlorine in the benzene nucleus has been already noticed in the action of chlorine on tribromoresorcinol. In the case of tribromophenol, part of the displaced bromine appears to act on hitherto unattacked tribromophenol, converting it into tribromobromoxybenzene. H. W.

Hydroxyquinol, the Third Isomeric Trihydroxybenzene. By L. BARTH and J. SCHREDER (*Monatsh. Chem.*, **4**, 176—181).—The authors have previously shown (*Monatsh.*, **3**, 650) that quinol fused with sodium hydroxide yields, together with condensation-products, an unstable difficultly crystallisable body; and having now obtained this body in larger quantity, they find that it consists of hydroxyquinol, $C_6H_3(OH)_3$.

To prepare hydroxyquinol, quinol is fused with 8 to 10 parts of sodium hydroxide, a little water being added at the commencement, and the heat being quickly raised as soon as this water is evaporated, till the frothing begins to subside: the temperature is then lowered, and the operation discontinued as soon as hydrogen ceases to go off. The cooled mass is then added to dilute sulphuric acid; the filtered solution shaken 10 to 15 times with ether; the ether-solution evaporated; the residual brownish syrup dissolved in water; the filtered solution fractionally precipitated with lead acetate; the precipitates decomposed with hydrogen sulphide; the resulting solutions fractionally shaken up with ether; and the extracts evaporated, redissolved in water, fractionally precipitated with lead acetate, and so on, till at length the lightest-coloured ethereal extracts, after evaporation of the ether, gradually begin to crystallise. Lastly, the crystalline pulps are drained, washed with water or amyl alcohol, and dried between paper, being at the same time protected from light.

Hydroxyquinol softens gradually when heated, and melts completely at 132—133°. It dissolves very readily at ordinary temperatures in water, ether, ethyl acetate, ethyl alcohol, and amyl alcohol, but is nearly insoluble in light petroleum, chloroform, carbon bisulphide, and benzene. The aqueous solution is extremely sensitive to light, becoming dark-coloured even in a vacuum over sulphuric acid, depositing dark-brown flocks, and finally drying up to a black-brown, somewhat greasy mass. This coloration takes place more quickly in the open air, still more readily on adding a drop of alkali. The solution blackens the skin, and gives with dilute aqueous ferric chloride a brownish-green colour, which quickly becomes paler, and changes to dark-blue on addition of a little sodium carbonate, wine-red with a larger quantity. A somewhat large quantity of ferric chloride produces a dark greenish-brown coloration, which does not become paler but turns nearly black, on addition of sodium carbonate. The solution is not altered by ferrous sulphate, but, on adding a small quantity of sodium carbonate, a violet colour is produced, changing to deep blue on addition of a larger quantity. Hydroxyquinol triturated with bromine forms, with evolution of hydrogen bromide, a brown substance which dissolves with dark cherry-red colour in dilute alcohol, and crystallises therefrom in blue-violet granules. When hydroxyquinol is subjected to dry distillation in a stream of hydrogen, part of it goes over unaltered, whilst the rest becomes carbonised, and yields a distillate of quinol.

Constitution of the Three Trihydroxybenzenes.—Quinol having the constitution [OH : OH = 1 : 4], hydroxyquinol must be the unsymmetrical trihydroxybenzene [1 : 2 : 4]; and, as previous experiments by the authors have tended to show that phloroglucol has the symmetrical constitution [1 : 3 : 5], they infer that pyrogallol must be the consecutive modification [1 : 2 : 3]. H. W.

Action of Sulphur on Sodium Phenate. By L. HAITINGER (*Monatsh. Chem.*, **4**, 165—175).—Kolbe has shown that when sodium phenate is heated in a stream of carbonic anhydride, a reaction takes place represented by the equation

$$2(C_6H_5.ONa) + CO_2 = NaO.C_6H_4.COONa + C_6H_5.OH,$$

the products being phenol and disodic salicylate. Sulphur appears to act upon sodium phenate in a similar manner, not however yielding immediately the products indicated by the equation

$$2(C_6H_5.ONa) + S = NaO.C_6H_4.SNa + C_6H_5.OH,$$

namely, phenol and the disodic derivative of hydroxyphenyl mercaptan, $HO.C_6H_4.SH$, but an oxidation-product of the latter, viz., dihydroxyphenyl disulphide, $HO.C_6H_4.S.S.C_6H_4.OH$. To prepare this compound, 2 mols. sodium phenate and 1 of sulphur are mixed in fine powder and heated in a retort for an hour at 180—200°. The mass then liquefies, and a small quantity of phenol distils over. The cooled melt is decomposed by dilute sulphuric acid, and the black oil thereby separated is distilled with steam till the distillate no longer gives a yellow precipitate with lead salts. There then remains a black viscid resin, apparently containing a considerable quantity of sulphobenzide, $(C_6H_5)_2SO_2$.

The first portions of the steam distillate contain a heavy oil, consisting mainly of phenol, and the water passing over therewith quickly becomes turbid on exposure to the air, in consequence of partial oxidation of the dissolved hydroxyphenyl mercaptan. On neutralising the strongly acid distillate with soda and evaporating to a syrup, phenol volatilises, the mercaptan is oxidised by the oxygen of the air, and the liquid deposits, either immediately or after prolonged exposure in flat dishes, a sulphur-yellow crystalline precipitate, which, after washing with cold water and recrystallisation from weak spirit, is found to consist of the primary sodium salt of dihydroxydiphenyl disulphide, $C_{12}H_9O_2S_2Na + 6H_2O$, which gives off the greater part of its crystal-water at 100°, the rest, with slight decomposition, at 140°.

The *primary potassium salt*, $C_{12}H_9S_2O_2K + 5H_2O$, is somewhat more soluble than the sodium salt, gives off 3 mols. water at 100°, and begins to decompose at 120—130°. The *dimethylic ether*, $C_{12}H_8S_2O_2Me_2$, formed by heating the primary sodium salt with sodium hydroxide and methyl iodide, crystallises from alcohol in small thick colourless needles, melting at 119° (corr.).

Free dihydroxyphenyl disulphide, prepared from the sodium salt by agitation with dilute sulphuric acid and ether, is a thick faintly-smelling oil, nearly insoluble in water. Heated above 200°, it begins to boil briskly, but decomposes completely at the same time, giving off torrents of hydrogen sulphide, and yielding a small quantity of a mobile liquid distillate, which after a while deposits a few crystals.

An aqueous solution of the sodium salt of dihydroxyphenyl disulphide gives a black precipitate with silver nitrate, brown with cupric acetate, white with zinc acetate, egg-yellow with lead acetate, all insoluble in dilute acetic acid. All the compounds of dihydroxyphenyl disulphide, when brought in contact in the dry state with strong sulphuric acid, produce a very deep bluish-green coloration.

Hydroxyphenyl mercaptan, $C_6H_6SO = HO.C_6H_4.SH$, is formed by the reducing action of sodium-amalgam, zinc-dust, or ferrous oxide and potash, on the disulphide; in small quantity also by the action of alcoholic potash at the boiling heat, or by fusion with potassium hydroxide. It is best prepared by treating the primary sodium salt of dihydroxydiphenyl disulphide with sodium-amalgam, as long as a brisk evolution of hydrogen takes place, care being taken that the alkaline solution, which rapidly absorbs oxygen, does not remain too long in contact with the air. The reduction being completed, the solution, decanted from the mercury, is acidulated with sulphuric acid, and the precipitated oil is washed, dried, and rectified. The formation of the disodium-derivative of the mercaptan takes place according to the equation—

$$C_{12}H_9S_2O_2Na + 3NaOH + H_2 = 3H_2O + 2(NaO.C_6H_4.SNa).$$

Hydroxyphenyl mercaptan is a strongly refractive liquid, having an extremely powerful odour, and cauterising the skin like phenol. It distils with steam and is moderately soluble in water. Under a pressure of 750·7 mm. it distils without decomposition at 216—217°. At a very low temperature it solidifies to a shining crystalline mass, very much like solid phenol, and melting at + 5° to 6°. Under certain circumstances, however, it does not crystallise even at the temperature of a mixture of solid carbonic anhydride and ether. Its sp. gr. is 1·2373 at 0°; 1·189 at 100°, referred to water at the same temperature.

Hydroxyphenyl mercaptan is a moderately strong acid, reddening litmus, and decomposing carbonates. Its aqueous solution, mixed with a small quantity of ferric chloride, quickly becomes turbid, with faint and transient violet coloration; but if a little sodium carbonate be immediately added, a very deep green colour is produced, which, on addition of caustic potash, changes to an equally intense red. Sometimes also blue and violet tints are developed. With lead salts, hydroxyphenyl mercaptan forms a bulky yellow precipitate, insoluble in dilute acids (distinction from dihydroxydiphenyl sulphide), becoming dense and crystalline on long standing, and then consisting of C_6H_4SOPb. This lead salt (not previously dried) gives on dry distillation a distillate of phenol, together with a small quantity of diphenylene oxide.

Hydroxyphenyl mercaptan forms with silver nitrate a yellow precipitate, soluble in potash, insoluble in ammonia; it also precipitates mercury, copper, zinc, and calcium salts. It is slowly oxidised in the free state by permanganate, chromic acid, &c.; much more quickly and completely in alkaline solution, yielding the corresponding salts of dihydroxydiphenyl disulphide.

Oxidation of the Methylic Ether of Dihydroxylphenyl Disulphide.—A solution of this compound in acetic acid, mixed with excess of chromium trioxide dissolved in glacial acetic acid, yields a sulphonic acid, the potassium salt of which agrees in all its characters with that of anisoilsulphonic or methylphenolsulphonic acid, prepared from orthophenolsulphonic acid. This salt, fused with a large excess of potassium hydroxide, yields a considerable quantity of catechol, whence it may be inferred that hydroxyphenyl mercaptan belongs to the ortho-series [SH : OH = 1 : 2]; and this conclusion is confirmed by the fact that, on triturating the potassium salt of *o*-methylphenolsulphonic acid with phosphorus pentachloride, a product is obtained which, when treated with water, yields orthomethylphenolsulphonic chloride in crystals melting at 55°. This sulphochloride, treated in alcoholic solution with zinc, is converted into the zinc salt of the corresponding sulphinic acid; and on further reducing the latter with zinc and hydrochloric acid, then adding excess of hydrochloric acid, and distilling with steam, an oil passes over, very much like that which is formed by reduction of the dimethyl-derivative of dihydroxyphenyl disulphide. On adding ferric chloride, the aqueous distillate became turbid, the odour disappeared after some time, and the oil was converted into a solid mass, which, after exhaustion with ether and recrystallisation from alcohol, exhibited all the properties of the previously described dimethylic derivative of the dihydroxyphenyl disulphide prepared from sodium phenate and sulphur, especially in melting at 119°. The reactions by which these products are obtained may be represented by the following equations:—

$$C_6H_4(OMe).SO_2Cl + 6H = C_6H_4(OMe).SH + 2H_2O + HCl$$
$$2[C_6H_4(OMe).SH] + Fe_2Cl_6 = [C_6H_4(OMe)S]_2 + 2HCl + Fe_2Cl_4.$$

As the phenolsulphonic acid employed was the ortho-modification, and the occurrence of intramolecular transposition is very improbable, it follows that the dimethyl-derivative of the disulphide obtained as above described belongs to the ortho-series of benzene-derivatives.

H. W.

Similarity of the Boiling Points of the Corresponding Ketones, Ethereal Salts, and Chloranhydrides. By H. SCHRÖDER (*Ber.*, **16**, 1312—1315).—The author draws attention to the fact that the boiling points of corresponding ketones and ethereal salts are always very near to one another, whilst with methyl ketones, methyl salts, and the corresponding chloranhydride, the boiling points are nearly identical. Taking two examples from those given by the author:—

	B.P.	
Ethylmethylketone, $C_2H_5.COMe$	79·5—81°	(Popoff)
Methyl propionate, C_2H_5COOMe	79·9°	(Schumann)
Propionyl chloride, C_2H_5COCl	79·5	(Brühl).
Phenylmethylketone, $C_6H_5.COMe$....	199—200°	(Popoff)
Methyl benzoate, $C_6H_5.COOMe$......	199·2°	(Buff)
Benzoyl chloride, $C_6H_5.COCl$........	198·7	(Buff).

A. J. G.

Aromatic Ketones. By W. STAEDEL (*Annalen*, **218**, 339—361). —To prepare *tetranitrodiphenylmethane*, $C_{13}H_8(NO_2)_4$, diphenylmethane is gradually introduced into nitric acid (sp. gr. 1·53), kept cool by a freezing mixture, and the product, after being left at rest for some time at the ordinary temperature, is gradually heated on a water-bath to about 70°; on then precipitating with water and recrystallising from glacial acetic acid, a pure product is obtained, melting at 172°; it is almost insoluble in benzene, but is moderately soluble in glacial acetic acid. If the diphenylmethane is added rapidly to the nitric acid, and the product then poured into water, Doer's dinitro-derivative is produced, together with a large amount of resin. *Tetranitrobenzophenone*, $C_{13}H_6O(NO_2)_4$, is obtained by the oxidation of tetranitrodiphenylmethane by means of chromic acid in acetic acid solution. It is insoluble in benzene, and very sparingly soluble in hot glacial acetic acid, from which it crystallises in minute plates, melting at 225°, and decomposing above this temperature. By the action of tin and hydrochloric acid on tetranitrodiphenylmethane, *tetramidodiphenylmethane*, $C_{13}H_8(NH_2)_4$, is obtained melting at 161°. It is sparingly soluble in benzene, readily in hot water and in alcohol; its salts are very readily soluble in water. The *hydrochloride* forms slender yellow needles; the *acetate* a white crystalline powder. The author previously showed that two dinitro-products are obtained by the nitration of benzophenone (*Annalen*, **194**, 307), the α-compound melting at 189—190° and the β-derivative at 148—149°, whilst by the nitration of diphenylmethane and subsequent oxidation with chromic acid, a dinitrobenzophenone is obtained, also melting at 189—190°, and supposed to be identical with the α-compound. An examination of the corresponding amido-derivative proves however that they are not identical. By the action of tin and hydrochloric acid on the dinitrobenzophenone from diphenylmethane, *diamidobenzophenone*, $C_{13}H_8O(NH_2)_2$, is obtained, crystallising in white needles melting at 172°. It is insoluble in cold water, sparingly soluble in hot water, and readily in alcohol; it forms a *hydrochloride* crystallising in large thick plates. By the action of zinc-dust and hydrochloric acid, an intermediate substance is obtained, apparently $C_{13}H_{12}N_2O_2$; it crystallises from glacial acetic acid and from aniline in reddish-brown microscopic needles. By the reduction of the high-melting dinitrobenzophenone obtained from benzophenone, diamidobenzophenone is produced, melting at 131°, and crystallising from dilute alcohol in lustrous plates. It forms an *acetate* crystallising in plates which are readily soluble in alcohol, insoluble in water. *β-diamidobenzhydrol*, $C_{13}H_9(OH)(NH_2)_2$, is obtained by the action of sodium-amalgam on diamidobenzophenone, and forms lustrous scales melting at 128—129°. The *hydrochloride* and *sulphate* crystallise in white efflorescent needles; the *nitrate* forms long silky hygroscopic needles, and the *acetate* indistinct crystals, melting at 220°. *α-Dihydroxybenzophenone* is obtained from α-diamidobenzophenone by means of the diazo-reaction, and crystallises from hot water in hair-like needles, melting at 210°. On heating it with an excess of benzoic chloride, and then decomposing the latter with sodium carbonate, the benzoic ether of α-dihydroxybenzophenone is formed, crystallising from alcohol in silky scales melting at 181—182°. *β-dihydroxybenzophenone*, prepared from β-diamidobenzophenone, is more readily soluble in water than the α-compound, and forms star-like aggregates of crystals melting at 161—162°; the *benzoic ether*, $\overline{Bz}O.C_6H_4.CO.C_6H_4.O\overline{Bz}$, resembles the corresponding α-compound in appearance, but is more readily soluble in alcohol, and melts at 101—102°; the *diacetate* forms lustrous scales melting at 89—90°. By the action of melted potash on β-dihydroxybenzophenone, phenol and parahydroxybenzoic acid are produced as was previously shown for α-dihydroxybenzophenone.

A. K. M.

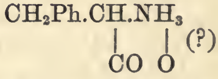
Cinnamic Acid Derivatives. By E. Erlenmeyer and A. Lipp (*Annalen*, **219**, 179—233).—The authors, in the course of their investigation on the synthesis of tyrosine, prepared and examined several derivatives of cinnamic and phenyllactic acids.

Phenyl-α-hydroxypropionitril (phenyl-ethylidene cyanhydrin), $CH_2Ph.CH(OH).CN$, prepared by the direct addition of hydrocyanic acid to phenylethaldehyde, crystallises in small needles (m. p. 57°), easily soluble in alcohol and ether, sparingly soluble in water. It decomposes at 100° with evolution of hydrocyanic acid.

Phenyl-α-amidopropionitril, $CH_2Ph.CH(NH_2).CN$, is obtained together with the imidonitril by heating the hydroxynitrile with alcoholic ammonia, and is separated from the imido-compound by the more sparing solubility of the latter in hydrochloric acid. Its hydrochloride forms glistening prisms belonging to the rhombic system, easily soluble in alcohol.

Phenyl-α-imidopropionitril, $CH_2Ph.CH(CN).NH.CH(CN).CH_2Ph$, crystallises in needles of the monoclinic system, sparingly soluble in cold water, readily soluble in ether. On crystallising out the crude substance (m. p. 86°) from ether, two crops were obtained, the one forming six-sided crystals (m. p. 105°), the other rhombic tables (m. p. 108°). As the authors were unable to convert one modification into the other, and as the melting and solidifying points were unaltered even by repeated recrystallisation, they must be regarded not as physical, but more probably as polymeric isomerides. Similar modifications have been observed in the case of the imidoisovalero- and capro-nitrils (Abstr., 1881, 85).

Phenyl-α-amidopropionic acid (phenylalanine),



$$\begin{array}{l} CH_2Ph.CH.NH_3 \\ \qquad\quad\ \, |\quad\ \ | \\ \qquad\quad CO\ \ O \end{array} \text{(?)},$$

obtained as a hydrochloride by pouring the crude product of the action of ammonia on phenylethylidine cyanhydrin into hydrochloric acid, and boiling the mixture. On dissolving the hydrochloride in water and saturating the solution with ammonia, the free alanine crystallises out in glistening prisms, soluble in alcohol and hot water. When boiled with potash, it evolves no ammonia, thus differing from the phenylamidopropionic acid of Posen. The phenylalanine forms crystalline salts both with acids and bases; the *hydrochloride* crystallises in white prisms, the *platinochloride* in dark golden needles, the *nitrate* in hair-like interlaced needles. The *copper salt*,

$$(C_9H_{10}NO_2)_2Cu,2H_2O,$$

forms small blue prisms, the *silver salt*, white microscopic prisms.

Phenylethylamine, $CH_2Ph.CH_2.NH_2$, is obtained, together with phenyllactimide, by the dry distillation of phenylalanine; the former passes over into the receiver, while the great part of the latter remains in the retort. This compound is identical, as shown by its melting point and the solubility of its platinochloride, with the phenylethylamine obtained by Bernthsen by the action of hydrogen on benzonitrile.

Phenyllactimide, C_9H_9NO, crystallises in fine silky needles (m. p. 290°), easily electrified; it is insoluble in cold water and ether, soluble in acetic acid. The compounds described above differ most markedly in their chemical and physical properties from Posen's compound obtained from cinnamic acid; the former are α-, whilst the latter are β-derivatives.

Parasulphophenylamine, $C_6H_4(SO_3H).CH_2.CH(NH).COOH$, obtained by sulphonating paraphenylalanine, crystallises in small colourless prisms, soluble in hot water, insoluble in ether and alcohol; on melting with alkali, it yields parahydroxybenzoic acid. The *barium salt* of the sulpho-acid crystallises in flat colourless prisms.

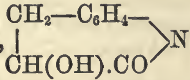
Paranitrophenylalanine, $C_6H_4(NO_2).CH_2.CH(NH_2).COOH$, prepared by the nitration of paraphenylalanine, crystallises in glistening prisms melting at 220°, sparingly soluble in water and alcohol. On oxidation with chromic mixture, it yields paranitrobenzoic acid. It forms crystalline salts with acids and bases; the *hydrochloride*, $C_9H_{10}N_2O_4,HCl$, crystallises in glistening prisms belonging to the rhombic system, soluble in water and alcohol; the *copper salt*, $(C_9H_9N_2O_4)_2Cu,2H_2O$, forms a sparingly soluble crystalline precipitate.

Paramidophenylalanine, $C_6H_4(NH_2).CH_2.CH(NH_2).COOH$, obtained by reduction of the above compound, crystallises in glistening prisms, which are decomposed on heating; when boiled with potash, it does not evolve ammonia. Its *hydrochloride* crystallises in glistening prisms, the *platinochloride* in light golden needles, and the *copper salts* in amethyst-coloured needles. This paramidophenylalanine can also be obtained by the action of nascent hydrogen on ethylparanitrocinnamate, $C_6H_4(NO_2).CH : C(NO_2).COOEt$ (Friedländer).

Parahydroxyphenyllactic acid, $OH.C_6H_4.CH_2.CH(OH).COOH$, is obtained together with tyrosine, in the preparation of the latter from amidophenylalanine, and may be separated from the mother-liquors by the addition of a mineral acid, and taking up the product with ether. It crystallises in white needles melting at 144°, sparingly soluble in cold alcohol and ether. Its *calcium salt* is easily soluble in water and alcohol.

The *nitrate of nitrophenyllactic acid*, $NO_2.C_6H_4.CH_2.CH(NO_2).COOH$, obtained by treating phenyllactic acid with excess of nitric acid, forms a golden pasty mass, easily soluble in ether, sparingly soluble in water. On oxidation with chromic acid mixture it is converted first into paranitrobenzaldehyde, and finally into the corresponding acid.

Hydroxyhydrocarbostyril,



$$\left.\begin{array}{l}CH_2{-}C_6H_4{-}\\ \vert\\ CH(OH).CO\end{array}\right\rangle NH$$

is formed, together with paramidophenyllactic acid, by the reduction of the above compound with tin and hydrochloric acid. It crystallises in white glistening leaflets melting at 198°, sparingly soluble in water and ether, more soluble in dilute alkalis.

Paramidophenyllactic acid, $NH_2.C_6H_4.CH_2.CH(OH).COOH$, crystallises in slender white needles melting at 188°, soluble in water, acids, and bases; the first-named has a strong acid reaction and taste; it does not give Piria's reaction. The authors and others are engaged in a further study of these derivatives. V. H. V.

Synthesis of Tyrosine. By E. Erlenmeyer and A. Lipp (*Annalen*, **219**, 161—178).—At the outset, the authors give a full historical account of the preparation of tyrosine, $C_9H_{10}NO_3$, and of the various attempts made to obtain the natural product by an artificial synthesis. The researches of Barth and Ost have established that tyrosine, when melted with potash, yields parahydroxybenzoic acid; whilst Hüfner has shown that on treatment with hydriodic acid it yields ammonia only; and Staedler has demonstrated the presence of two hydrogen-atoms replaceable by metals. It follows from these facts that tyrosine contains a hydroxyphenyl grouping, $C_6H_4.OH$ (in which the OH is in the para-position), and that the three remaining carbon-atoms are combined in a single side-chain, which must be regarded as an alanine less one atom of hydrogen. A comparison of the chemical properties of the phenylamidopropionic acid (phenylalanine) in which the amido-grouping is in the β-position, with that of tyrosine and the α-amido-acid, renders it probable that tyrosine is an α- and not a β-derivative. Starting with this knowledge the authors prepared paramidophenylalanine, $NH.C_2H_3(C_6H_4.NH_2).COOH$, from phenylethaldehyde, ammonia, hydrocyanic and hydrochloric acid (cf. preceding Abstract); and treated the hydrochloride of the latter compound with nitrous acid in order to replace by Griess' reaction the amido- by the hydroxyl-group, and thus to convert it into *p*-hydroxyphenylalanine, $NH_2.C_2H_3(C_6H_4.OH).COOH$. This substance was found to be identical in all its chemical and physical properties with natural tyrosine; and in the original paper a full comparison is given of the melting point and solubility in hot and cold water of the base, of the hydrochlorides, and the metallic salts of the natural and artificial products.

It follows from this synthesis, that tyrosine has the constitution of an alanine in which one hydrogen-atom of the CH_3-grouping is replaced by the parahydroxyphenyl-residue,

V. H. V.

Phenylglyceric Acid. By A. Lipp (*Ber.*, **16**, 1286—1290).—In the preparation of phenethylaldehyde from phenylchlorlactic acid, an acid was obtained in considerable quantity, and was proved to be identical with the phenylglyceric acid, CHPh(OH).CH(OH).COOH, of Anschütz and Kinnicutt (Abstr., 1879, 644). A. J. G.

Tannins of Oak-bark. By C. Etti (*Monatsh. Chem.*, **4**, 512—530).—The tannin of oak-bark exists in two forms, viz., as a tannic acid, which in the free state has a reddish-white colour, and as an anhydride of that acid, called *phlobaphene*, the colour of which is brown-red. The distinction between these two bodies is familiar to tanners, who designate the anhydride simply as "colouring matter," and reject barks containing a large proportion of it, as it imparts too red a colour to leather dyed with such barks.

The question as to the existence of a glucoside in oak-bark is now decided in the negative, as tannic acid extracted from the bark by ethyl acetate does not yield any such substance. The reactions which were supposed to indicate the presence of a glucoside were really due to lævulin, which, on treating the bark with dilute sulphuric acid, was converted into lævulose.

The tannic acid obtained by agitating an alcoholic extract of the bark with ethyl acetate may be contaminated with two substances, a brownish-green amorphous terpene-resin and phlobaphene. The former may be separated by its ready solubility in ethyl acetate, ethyl oxide, and benzene. The phlobaphene is easily recognised by the brown-red precipitate which it gives with lead acetate.

Quercitannic acid cannot be extracted from the bark in the pure state by ethyl acetate, inasmuch as it decomposes that compound into alcohol and acetic acid almost as easily as sulphuric or hydrochloric acid, and the acetic acid thus set free dehydrates a portion of the tannic acid, producing phlobaphene. Pure quercitannic acid dissolves completely in ethyl acetate, and does not give up any foreign bodies to pure ethyl oxide or to benzene; its solution in very dilute alcohol gives with basic lead acetate a precipitate of pure yellow colour.

Phlobaphene is nearly insoluble in water and in ether, but dissolves readily in alcohol of all strengths. As prepared from the bark, it may be contaminated with terpene-resin and pectin-substances. The former of these bodies may be recognised and separated by treatment with ether or benzene, which dissolve it; the pectin-substances by their insolubility in spirit of 90 per cent. The presence of tannic acid in the phlobaphene may be recognised by the fact that the latter, after being freed from adhering moisture by drying at 110°, gives off a further quantity of water at 130—140°.

Quercitannic acid is represented by the formula $C_{17}H_{16}O_9$. At 130—140°, it gives off water, and is converted into the brown-red anhydride, $C_{34}H_{30}O_{17} = 2C_{17}H_{16}O_9 - H_2O$, identical with the phlobaphene contained in the bark. 1 mol. of this substance boiled with sulphuric or hydrochloric acid gives up 1 mol. water, and is converted into a second anhydride, $C_{34}H_{28}O_{16}$; and by boiling the tannic acid free from anhydrides with either of these anhydrides, a third anhydride, $C_{34}H_{26}O_{15}$, is obtained. These three anhydrides are soluble in alcohol and in caustic alkalis.

Löwe (this Journal, 1881, Abstr., 901), by treating quercitannic acid or phlobaphene with dilute sulphuric acid, or with oxalic acid, has obtained a fourth anhydride, $C_{34}H_{24}O_{14} = 2C_{17}H_{16}O_9 - 4H_2O$, which he designates as *oak-red*. The same name has been applied to the first anhydride by Oser, and to the second by Böttinger.

Another oak-bark examined by the author yielded a tannic acid having the composition $C_{20}H_{20}O_9$, and agreeing with the former in all its properties, excepting in its reaction with ferric chloride, with which it gives a bluish-green colour, quickly changing to deep green, and on addition of sodium carbonate, first to blue and then to red, whereas the quercitannic acid above described, and all its anhydrides, give with ferric chloride a black-blue precipitate. This tannic acid begins to lose water at 124°, melts at 140°, resolidifies on further loss of water, and is converted into a brown-red substance identical in composition with phlobaphene.

The tannic acid, $C_{20}H_{20}O_9$, also yields four anhydrides agreeing in character with those obtained from the acid $C_{17}H_{16}O_9$. These anhydrides are represented by the formulæ $C_{40}H_{38}O_{17}$, $C_{40}H_{36}O_{16}$, $C_{40}H_{34}O_{15}$, and $C_{40}H_{32}O_{14}$. The same tannic acid heated in a sealed tube with hydrochloric acid yielded a gas burning with a green flame, but smaller in quantity than that obtained from the acid $C_{17}H_{16}O_9$. Heated in a tube with dilute sulphuric acid, it gave a red liquid and a large quantity of undissolved anhydrides; and on agitating this liquid with ether, a small quantity of crystals was obtained consisting of gallic acid.

The phlobaphene submitted to dry distillation, yielded pure catechol, free carbon, and an oil insoluble in potash, smelling like the terpenes and containing 72·46 per cent. C and 7·11 H. This oil, oxidised with permanganate, yielded an amorphous resin, whence the author concludes that it is derived, not from the tannin, but from the terpenes mixed with the phlobaphene which was submitted to dry distillation.

For the theoretical considerations relating to the constitution of all the bodies above described, the original paper must be consulted.

H. W.

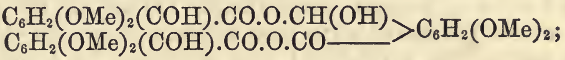
Derivatives of Opianic Acid. By R. WEGSCHEIDER (*Monatsh. Chem.*, **4**, 262—271).—Opianic acid heated for six hours at 180—190° yields a condensation-product, the formation of which may be represented by the equation $3C_{10}H_{10}O_5 - H_2O = C_{30}H_{28}O_{14}$ (not $4C_{10}H_{10}O_5 - H_2O = C_{40}H_{38}O_{19}$, as stated by Matthiessen and Wright). The author's analyses give for this product 58·76 per cent. carbon and 4·48 hydrogen, agreeing better with the formula $C_{30}H_{18}O_{14}$ (which requires 58·82 C and 4·58 H), than with $C_{40}H_{38}O_{19}$ (58·39 C and 4·62 H).

The condensation-product fused with potassium hydroxide and a little water, yielded a thin jelly, from which, after acidulation, ether extracted hemipinic acid. The whole was then thrown into dilute sulphuric acid, whereby a solution was obtained, which, on cooling, yielded white needles of meconin (m. p. 103°). The formation of these two bodies is represented by the equation $2C_{30}H_{28}O_{14} + 2H_2O = 3C_{10}H_{10}O_4 + 3C_{10}H_{10}O_6$; but as Matthiessen and Foster have shown that the same two bodies are formed by heating opianic acid with potash, it appears most probable that the first action of the alkali on the compound $C_{30}H_{28}O_{14}$ is to reconvert it into opianic acid, which is then decomposed in the manner just mentioned.

From the preceding results, it follows that the opianic residues in the body formed by the action of heat on opianic acid are linked together, not by carbon, but by oxygen. The body is in fact a complex anhydride, analogous to those formed from several of the aromatic hydroxy-acids (*e.g.*, the three hydroxybenzoic acids and phloretic acid), which it moreover resembles in its properties. It may accordingly be designated as *Triopianide.* Its mode of formation is, however, somewhat different from that of the anhydrides of the hydroxy-acids, inasmuch as these latter are formed from n molecules of the corresponding acids by abstraction of $n-1$ mol. water, whereas triopianide is formed from 3 mols. opianic acid by abstraction of one (that is to say $n-2$) molecule of water: $C_{30}H_{28}O_{14} = 3C_{10}H_{10}O_5 - H_2O$. To account for its composition, we must suppose that the COH-group—which may be regarded as the anhydride of $CH(OH)_2$—serves as a connecting link between the molecules. Of the two possible formulæ thus constructed, viz.:—

$$C_6H_2(COOH)(OMe)_2.CH[O.CO.C_6H_2(OMe)_2.COH]_2,$$

and



$$\left.\begin{array}{l} C_6H_2(OMe)_2(COH).CO.O.CH(OH) \\ C_6H_2(OMe)_2(COH).CO.O.CO\text{———} \end{array}\right> C_6H_2(OMe)_2;$$

the second can alone be regarded as the true representative of triopianide, inasmuch as this body does not exhibit acid properties, and therefore cannot contain the group COOH.

Action of Bromine.—Triopianide triturated with bromine is converted into a viscid brominated resin, which gives up the greater part of the uncombined bromine on standing, and the rest when pulverised and heated at 100°. On crystallising the residue from alcohol or toluene, a mixture of two bodies is obtained, one of which melts at about 200°, the other at a higher temperature; the former is more soluble than the latter in alcohol, less soluble in toluene. A rough separation of the two having been thus effected, the chief product is boiled with water, which leaves undissolved small quantities of the higher-melting secondary product. The more soluble body, purified by recrystallisation from water, forms tufts or arborescent groups of small white needles melting at 204°. This body is *Brom-opianic acid,* $C_{10}H_9BrO_5$. It dissolves readily in methyl and ethyl alcohols, glacial acetic acid, benzene, and xylene; very sparingly in carbon bisulphide, scarcely at all in light petroleum; moderately in hot, very sparingly in cold water, and separates from all these solutions in anhydrous crystals. It is a decided acid, uniting with ammonia and the oxides of barium, silver, copper, mercury, lead, and nickel, forming salts which are soluble in water, and do not give any characteristic reaction with ferric chloride or lead acetate. A brom-opianic acid apparently identical with that above described was obtained, though not pure, by Prinz (*J. pr. Chem.* [2], **24**, 367) by the action of bromine-water on opianic acid.

The secondary product obtained, as above mentioned, by the action of bromine on triopianide, appears to be a bromine-derivative of that body. After recrystallisation from xylene, it melts at 250—251°, dissolves very readily in chloroform, easily in ethyl acetate and in benzene, with aid of heat also in xylene, glacial acetic acid, and amyl alcohol, sparingly in methyl and ethyl alcohols, very sparingly in light petroleum and boiling water, and is quite insoluble in cold water. It dissolves in boiling potash-lye, and the solution if acidulated after long boiling yields brom-opianic acid.

Triopianide dissolves without alteration in cold strong nitric acid; but on adding it to a lukewarm mixture of strong nitric and sulphuric acids in equal parts, a nitro-product is obtained melting at 248—249°. When, however, the experiment was repeated with larger quantities of material, the action went further, yielding a body which melted at 248—249°, and appeared to consist of nitro-opianic acid. H. W.

Pimelic Acid. By A. Bauer (*Monatsh. Chem.*, **4**, 345—348).—The author in 1878 published, in conjunction with J. Schüler, some observations on pimelic acid obtained by a synthetic process from isopentylene (amylene). The acid thus prepared was crystallised, and on agitation with ether was obtained in conjunction with another acid, supposed to be an isomeric pimelic acid. On boiling the normal ammonium salts of the mixed acids with solution of calcium chloride, the calcium salt of the crystallised acid separates as a sparingly soluble precipitate, and the mother-liquor, when decomposed and shaken up with ether, yields an amorphous acid isomeric with pimelic acid. The calcium salt of this amorphous acid has the composition $C_7H_{10}CaO_3$, and is more soluble in water than that of crystallised pimelic acid.

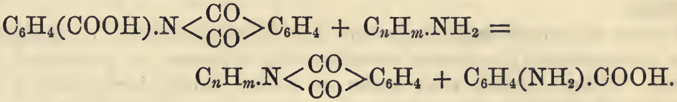
Amorphous pimelic acid has a vitreous aspect; its reactions with metallic salts differ for the most part but slightly from those of the crystallised acid, the only characteristic reaction being that of the ammonium salt with cupric sulphate, whereby no precipitate is formed, even in concentrated solutions, either at ordinary temperatures or on boiling, or after long standing.

By heating pimelic acid in sealed tubes with a quantity of bromine sufficient to convert it into a dibrominated acid, and decomposing the product with moist silver oxide, an acid was obtained having nearly the composition $C_7H_{10}O_5$. H. W.

Metazophenylglyoxylic Acid. By C. M. Thompson (*Ber.*, **16**, 1308—1311).—Metanitrophenylglyoxylamide is saponified with dilute potash, and the resulting potassium metanitrophenylglyoxalate reduced by means of ferrous sulphate and concentrated potash, the ferrous sulphate being added from time to time until the colour of the precipitate has changed to brownish-black; a large excess of hydrochloric acid is then added, and the whole heated to boiling. The yield of the azo-acid is about 50 per cent. of the nitro-amide employed.

Metazophenylglyoxylic acid crystallises with 2 mols. H_2O in light orange-yellow needles, loses its water of crystallisation at 100°, but regains its original weight on a few hours' exposure to air. It is sparingly soluble in cold water, more readily in hot; insoluble in dilute acids, readily soluble in absolute alcohol. It melts at 134·5—135°. The silver salt is an orange-yellow powder, and appears to be slightly soluble in water. The barium salt is obtained as an orange-yellow indistinctly crystalline powder insoluble in water. A. J. G.

Phthalamidobenzoic Acid. By A. PIUTTI (*Ber.*, **16**, 1319—1322).—By the action of aniline on phthalamidobenzoic acid, no anilide is formed, and the reaction is very complex; in some operations, colourless crystallisable bodies of high melting point were obtained, whilst in other cases, and under apparently identical conditions, non-crystalline coloured masses of low melting point were formed. In all cases large quantities of phthalanil and of the original acid were formed. As phthalamidobenzoic acid is known to decompose into phthalanil and carbonic anhydride on heating, it was an open question if the aniline played any other part than that of a solvent during the reaction, but by employing paratoluidine instead of aniline, tolylphthalamide and amidobenzoic acid were formed, and with ammonia phthalimide was formed: hence by analogy the aniline must take part in the reaction. The action of primary monamines on the acid is represented by the equation—



$$\mathrm{C_6H_4(COOH).N}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{C_6H_4} + \mathrm{C}_n\mathrm{H}_m\mathrm{.NH_2} =$$
$$\mathrm{C}_n\mathrm{H}_m\mathrm{.N}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{C_6H_4} + \mathrm{C_6H_4(NH_2).COOH}.$$

By the action of aniline on amidobenzoic acid, amidobenzanilide is formed; it melts at 129° and not at 114° as stated by Engler and Volkhauser (this Journal, 1875, p. 643). On heating with aniline at 200°, it yields a mixture of amidobenzoic anhydrides, of which *amidobenzoïd*, $\mathrm{C_6H_4}{<}\substack{\mathrm{NH.CO}\\ \mathrm{CO.NH}}{>}\mathrm{C_6H_4}$, crystallises in nodules, melts at 225°, and dissolves in alcohol, benzene, chloroform, and ether, and another apparently polymeric compound forms a white amorphous powder, insoluble in ordinary solvents, soluble in concentrated sulphuric acid, from which it is precipitated unchanged on addition of water. By heating amidobenzanilide with phthalic anhydride, *phthalamidobenzanilide*, $\mathrm{C_6H_4(CO.NHPh).N}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{C_6H_4}$, is obtained. It crystallises in small prisms, and melts at 207—209°. A. J. G.

Cymenesulphonic Acids. By E. PATERNÒ (*Ber.*, **16**, 1297).—A reply to A. Claus.

Dialkyldisulphobenzoates. By F. STENGEL (*Annalen*, **218**, 257—269).—These compounds correspond with the diethyldisulphoacetates obtained by Laube. To prepare *barium diethyldisulphobenzoate*, $\mathrm{C_{11}H_{14}O_9S_2Ba} + 3\frac{1}{2}\mathrm{H_2O}$, sulphuric acid is added to sodium sulphobenzoate in quantity sufficient to form hydrogen sodium sulphate and free sulphobenzoic acid, and the mixture after evaporation to dryness, is well shaken with absolute ethyl alcohol: after some days the product is filtered, the excess of alcohol removed by distillation, and the syrupy liquid obtained is diluted with water and neutralised with barium carbonate. The product, which must be regarded as a compound of *barium sulphobenzoate* with *diethyl sulphate*, $\mathrm{C_7H_4O_2(SO_3)Ba,SO_4Et_2,3\frac{1}{2}H_2O}$, crystallises in groups of long colourless needles. When its aqueous solution is heated in sealed tubes at

107°, it decomposes, yielding sulphobenzoic acid, barium sulphate, and alcohol. The *sodium salt*, obtained by decomposing the barium salt with sodium carbonate, is anhydrous, and very readily soluble in water; the *copper salt* forms small blue crystalline scales containing $2\frac{1}{2}$ mols. H_2O; the *lead salt* crystallises with $2\frac{1}{2}$ H_2O in small silky needles.

Barium dimethyldisulphobenzoate, $C_9H_{10}O_9S_2Ba,3\frac{1}{2}H_2O$, is prepared in the same way as the diethyl-compound, and crystallises in colourless monoclinic plates, which lose their water at 100° or when exposed over sulphuric acid. It requires a higher temperature (150°) for the decomposition of its aqueous solution than in the case of the corresponding ethyl-compound. The *copper salt* contains $5H_2O$, and is readily soluble in water; the *sodium salt* is still more readily soluble and anhydrous; the *lead salt* is also anhydrous, and is decomposed readily at the temperature of the water-bath, with separation of lead sulphate.

Barium dipropyldisulphobenzoate, $C_{13}H_{18}O_9S_2Ba,7H_2O$, crystallises in long concentrically grouped needles of a vitreous or mother-of-pearl lustre. When heated with water in sealed tubes, it requires a temperature of 180° for its complete decomposition. It loses its water at 170°, partially decomposing at the same time.

From the mother-liquors of barium diethyl- and dimethyl-disulphobenzoates, the author has obtained isomeric salts forming *anhydrous* granular crystals. A. K. M.

Syntheses with Chloropicrin. By K. Elbs (*Ber.*, **16**, 1274—1277).—By mixing benzene (4—5 mols.) with chloropicrin (1 mol.) in presence of aluminium chloride, triphenylmethane and triphenylcarbinol are obtained, together with a very small amount of diphenylmethane. The nitro-groups are mainly converted into nitrous acid, only a small amount of nitric oxide being formed.

Phenol (3 mols.) and chloropicrin (1 mol.) do not react readily in presence of aluminium chloride, the mixture requiring to be heated for 1—2 days on the water-bath. The main product of the reaction is aurin.

Trinaphthyl carbinol, $(C_{10}H_7)_3C.OH$, the main product of the reaction of naphthalene, chloropicrin, and aluminium chloride, forms a brownish-yellow crystalline powder, softening at 180°, and completely fusing at 278°. It is readily soluble in chloroform, carbon bisulphide, benzene, toluene, and nitrobenzene, sparingly soluble in ether and acetone, and nearly insoluble in alcohol and light petroleum. It could not be obtained quite pure.

Phenanthrene reacts readily with chloropicrin and aluminium chloride. The product, which resembles the above naphthalene-derivative, is under investigation.

Triphenylmethane was brominated according to the method of Schwarz (Abstr., 1881, p. 913), and a solution of the crude bromide was treated with ammonia gas, and, after removal of excess of ammonia, with hydrochloric acid. The hydrochloride of the base obtained in this way crystallises in colourless needles, melts at 244°, is soluble in water, very soluble in alcohol. The free base crystallises in colourless needles, and melts at 105°. The platinochloride crystallises in large orange-yellow needles. The formulæ of these compounds are still under investigation. A. J. G.

α-Naphthonitrilsulphonic Acid. By U. K. DUTT (*Ber.*, **16**, 1250—1251).—The barium salt of this acid, $(CN.C_{10}H_6.SO_3)_2Ba$, was obtained in thin colourless tables by treating with water the product of the action of chlorosulphonic acid on a solution of α-naphthonitril in carbon bisulphide, and neutralising with barium hydrate.

A. J. G.

Pyrene-derivatives. By G. GOLDSCHMIEDT and R. WEGSCHNEIDER (*Monatsh. Chem.*, **4**, 237—261).—*Action of Chlorine on Pyrene.*—When a rapid stream of chlorine is passed at ordinary temperatures through a solution of pyrene in chloroform, hydrogen chloride is abundantly evolved, the liquid becomes warm, and a yellow crystalline substance separates, consisting of a mixture of chloropyrenes, some of which also remain in solution; they may be separated from one another by fractional crystallisation from alcohol, chloroform, and xylene, alcohol being almost exclusively employed to separate the portions boiling below 200°, xylene for those of highest boiling point, and chloroform for the intermediate portions. The separation cannot be effected by sublimation, as partial decomposition takes place at the same time.

By proceeding as above, mono-, di-, tri-, and tetra-chloropyrenes were isolated, and indications were obtained of a second dichloro-compound. An easily fusible resin was also separated in very small quantity. If the passage of the chlorine be continued for three-quarters of an hour, the chief product obtained is tetrachloropyrene, small quantities of the lower products being however enclosed within it, and thereby escaping further chlorination. If the process be continued for a short time only, a considerable quantity of trichloropyrene is formed. To obtain a large yield of monochloropyrene, the passage of the chlorine must not be continued for more than a quarter of an hour. The two dichloropyrenes are always obtained in subordinate quantity only.

1. *Monochloropyrene*, $C_{16}H_9Cl$, forms long, thin, flattened, shining needles, melting at 118—119°, very soluble, even in the cold, in ether, chloroform, carbon bisulphide, benzene, and xylene; also in ethyl acetate (even at low temperatures); in alcohol; also when heated in light petroleum, amyl alcohol, and glacial acetic acid; moderately soluble in cold glacial acetic acid; soluble also in hot methyl alcohol, insoluble in water. From all these solutions, it separates on cooling, or on evaporation, in more or less flattened needles. Strong sulphuric acid dissolves it on warming, with splendid violet-blue fluorescence. When boiled with fuming nitric acid, it turns red and dissolves partially, forming a solution which, on dilution with water, deposits a nitro-compound.

Chloropyrene-picric acid, $C_{16}H_9Cl,C_6H_2(NO_2)_3OH$, formed by mixing an alcoholic solution of monochloropyrene with excess of picric acid dissolved in alcohol, crystallises in needles very easily soluble in hot alcohol, and melts with decomposition at 177—178°. It turns yellow on prolonged exposure to the air, and is readily decomposed by boiling water. Hot alcohol likewise decomposes it, unless an excess of picric acid is present.

2. *α-Dichloropyrene*, $C_{16}H_8Cl_2$, forms flat, sulphur-yellow, shining needles, melting at 154—156°, easily soluble in carbon bisulphide, even at ordinary temperatures; also in ether, chloroform, benzene, xylene, light petroleum, ethyl acetate, and hot glacial acetic acid; moderately soluble in hot, sparingly in cold alcohol, very sparingly in methyl alcohol, insoluble in water. The alcoholic solutions exhibit blue, all the others green fluorescence. From solution in alcohol or glacial acetic acid, the compound crystallises on cooling in needles; also from solution in benzene, or ethyl acetate, on spontaneous evaporation. From ether, it separates on evaporation in slender silky needles, from chloroform, in felted silky needles, from light petroleum and carbon sulphide, in branched groups of needles. Strong sulphuric acid dissolves it, with aid of heat, forming a solution which exhibits a very deep violet-blue fluorescence. It is decomposed by ignition with lime, yielding pyrene.

3. *β-Dichloropyrene* (?).—A fraction melting at 194—196° gave on analysis quantities of chlorine indicating a mixture of dichloropyrene with about 15 per cent. of the trichlorinated compound, and as a similar mixture of tri- with α-di-chloropyrene would melt at a much lower temperature, the substance in question was probably a somewhat impure isomeric dichloropyrene.

4. *Trichloropyrene*, $C_{16}H_7Cl_3$, forms thin soft felted needles, white with a tinge of yellow. It dissolves easily, with aid of heat, in benzene and carbon bisulphide (in the latter with almost equal facility in the cold), somewhat sparingly in chloroform, amyl alcohol, and light petroleum, sparingly in ether, glacial acetic acid, and ethyl acetate, very sparingly in methyl and ethyl alcohols, not at all in water. From all these solutions it crystallises on cooling, in especial abundance from amyl alcohol and xylene, also from glacial acetic acid and benzene, but very sparingly from methyl alcohol, ether, or chloroform, and not at all from carbon bisulphide. Strong sulphuric acid dissolves it sparingly on slight warming, but if a large quantity of sulphuric acid be used, a somewhat deep violet-blue fluorescence is produced. On strong heating, complete solution takes place, but the colour of the liquid becomes darker and the fluorescence indistinct.

5. *Tetrachloropyrene*, $C_{16}H_6Cl_4$, forms long slender flexible needles, having a splendid silky lustre, and a pale yellow colour with a tinge of green. It dissolves readily in hot xylene, with moderate facility in hot benzene, somewhat sparingly in hot amyl alcohol, sparingly in carbon bisulphide, hot ethyl acetate, glacial acetic acid, and chloroform, and in cold benzene and xylene, very sparingly in light petroleum, hot methyl or ethyl alcohol, ethyl oxide, cold glacial acetic acid, and chloroform, and is nearly insoluble in cold methyl, ethyl, or amyl alcohol, ethyl oxide, and ethyl acetate. By strong sulphuric acid it is but very slightly attacked, even near boiling heat, a faint rose colour being produced at the commencement of the action. The solubility of the several chloropyrenes in all the above-mentioned liquids decreases as the proportion of chlorine becomes greater.

Tetrachloropyrene melts at a temperature above 330°. By ignition with quicklime, it yields a small quantity of pyrene.

Action of Concentrated Sulphuric Acid on Pyrene.—Pyrene-disulphonic acid, $C_{16}H_8(SO_3H)_2$, is prepared by heating pyrene (10 g.) on the water-bath with 5 c.c. strong sulphuric acid till it dissolves, then adding $2\frac{1}{2}$ c.c. sulphuric acid, and as soon as a sample is found to dissolve completely in water, pouring the entire product into water. The resulting solution, after filtration, is saturated with lead carbonate; the solution of lead pyrenesulphonate thereby obtained is decomposed with hydrogen sulphide; and the liquid filtered from lead sulphide is evaporated to dryness, whereupon the sulphonic acid remains in the form of a green uncrystallisable pasty residue, dissolving readily in water and forming a yellow solution with green fluorescence. It is insoluble in ether and sparingly soluble in alcohol, the solutions always leaving on evaporation a small quantity of inorganic matter. A fraction purified as completely as possible, lost on drying in the exsiccator, 6·35 per cent., and at 120°, 9·83 per cent. of its weight. ($C_{16}H_{10}S_2O_6,2H_2O$, would require 9·05 per cent.) The *potassium salt*, obtained by neutralisation, gave on analysis numbers agreeing with the formula $C_{16}H_8(SO_3K)_2$. Its aqueous solution leaves on evaporation a salt containing $2\frac{1}{2}$ mols. H_2O, 2 mols. of which are given off in the exsiccator or at 100°, the remainder at 120°. The *barium salt*, obtained by saturation, remains on evaporating its aqueous solution, in sulphur-yellow films having the composition $C_{16}H_8S_2O_6Ba,3\frac{1}{2}H_2O$, and giving off their water at 210°. The *calcium salt*, $C_{16}H_8(SO_3)_2Ca,2H_2O$, gives off half its water over sulphuric acid, the rest at 130°.

Potassium pyrenedisulphonate fused with potash does not yield the corresponding phenol, but, according to the temperature and the proportions used, either pyrene or the monosulphonic acid. The potassium salt of this acid separates from aqueous solution in crystals having the composition $C_{16}H_9SO_3K,H_2O$, and gives off half its water in the exsiccator, the rest at 118°.

Distillation of Potassium Pyrenedisulphonate with Potassium Cyanide or Ferrocyanide.—The conversion of this salt into cyano-derivatives of pyrene is best effected by distilling it at a low red heat, in portions of 6 g. each with 8 g. of an intimate mixture of potassium ferrocyanide and iron filings, whereby an oily distillate is obtained which soon solidifies to a crystalline mass; and on treating this mass with water to remove ammonium salts, and recrystallising it from benzene, alcohol, and light petroleum, two bodies are obtained, one melting at about 150°, the other above 300°. These are best separated by combining them with picric acid and repeatedly crystallising the resulting compounds from alcohol, whereby a sparingly soluble fraction was obtained melting at 222—223° and yielding by decomposition with ammonia a body which melted at 147—149°, and exhibited all the properties of pyrene,—together with an easily soluble fraction which when decomposed by ammonia yielded mono-cyanopyrene. This compound, $C_{12}H_9(CN)$, is nearly white, usually however with a more or less greenish tinge. It dissolves very easily at ordinary temperatures in chloroform and benzene, and at higher temperatures in xylene, easily also in methyl, ethyl, and amyl alcohols, ethyl oxide, carbon bisulphide, glacial acetic acid, ethyl acetate, and light petroleum. From the last-mentioned solvent, and from methyl and amyl alcohols, it crystallises in needles.

Cyanopyrene-picric acid, $2C_{16}H_9(CN),C_6H_2(OH)(NO_2)_3$, is obtained by mixing the alcoholic solutions of 1 part cyanopyrene and more than 2 parts picric acid, and distilling till the liquid forms a nearly saturated solution at boiling heat: it then crystallises on cooling. It is much more easily decomposible than monochlopyrene-picric acid, being decomposed by cold alcohol, partially by cold water, completely by hot water.

Dicyanopyrene, $C_{16}H_8(CN)_2$.—The above-mentioned fraction boiling above 300° is a yellow granular microcrystalline powder, the solutions of which exhibit a bright green fluorescence. It appears to decompose at high temperatures.

Pyrene-carboxylic Acid.—The monocarboxylic acid, $C_{16}H_9.COOH$, is obtained, as potassium salt, by fusing monocyanopyrene in a silver crucible with potassium hydroxide and a little water as long as ammonia continues to be evolved, dissolving the melt in water, and decomposing the solution with sulphuric acid. The carboxylic acid then separates as a very bulky, gelatinous opalescent precipitate, which may be purified by washing with water, solution in sodium carbonate, reprecipitation with sulphuric acid, and recrystallisation from ether-alcohol, with addition of animal charcoal. It is thus obtained in yellowish nodules melting at 267°, subliming, when cautiously heated, in long needles, which have the same melting point, but are partly resolved at a slightly higher temperature into pyrene and carbonic anhydride. The same decomposition is effected almost quantitatively by heating with lime. The acid is not quite insoluble in water, moderately soluble in hot absolute alcohol and in ether. Its *barium salt*, $(C_{17}H_9O_2)_2Ba,2\frac{1}{2}H_2O$, forms a yellowish crystalline powder, which gives off its water at 100°. The *calcium salt*,

$$(C_{17}H_9O_2)Ca,H_2O,$$

is also a microcrystalline powder. The *silver salt* obtained by precipitation is yellowish at first, but quickly decomposes and blackens. When pyrene dicyanide is fused with caustic alkali, the product consists mainly of pyrenemonocarboxylic acid, but a small quantity of the dicarboxylic acid appears also to be formed.

All the above-mentioned pyrene-derivatives (sulphonic acids, cyanides, carboxylic acids) agree in the facility with which they take up hydrogen in exchange for their lateral chains. Thus the disulphonic acid is converted by fusion with potash chiefly into the monosulphonic acid, part of it however being reconverted at a higher temperature into pyrene. The conversion of the monocyanide into the monocarboxylic acid is also attended with reproduction of pyrene. A similar reproduction of a fundamental hydrocarbon has been observed by Goldschmiedt (*Monatsh. Chem.*, **1**, 234) in the saponification of idryl cyanide. H. W.

Reichenbach's Picamar. By P. Pastrovich (*Monatsh. Chem.*, **4**, 182—187); also by G. Niederist (*ibid.*, 487—493).—The results obtained by these two authors as to the constitution of Reichenbach's picamar do not quite agree. Pastrovich assigns to it the formula $C_{10}H_{14}O_3$, and regards it as the monomethyl ether of propyl-pyrogallol, $C_6H_2Pr(OH)_2,OMe$; but Niederist, whose experiments were made on a sample of Reichenbach's original preparation, preserved in the University Laboratory of Vienna, finds that it gives by analysis numbers agreeing with the formula $C_{11}H_{16}O_3$, which is that of dimethylic propyl-pyrogallate, $C_6H_2Pr(OH)(OMe)_2$ [mean of analyses 67·80 per cent. carbon and 8·27 hydrogen; calc. 67·35 C and 8·16 H. Vapour-density by Hofmann's method in aniline-vapour, 6·532; calc. 6·78].

Potassium-picamar, $C_{11}H_{15}O_3K$, prepared by boiling picamar with strong potash-lye, solidifies on cooling to a mass of slender needles, and when purified by pressure between filter-paper and recrystallisation from hot alcohol, forms white nacreous laminæ which acquire only a faint brown colour after prolonged exposure to the air.

Acetyl-picamar, $C_{13}H_{18}O_4 = C_{11}H_{15}\overline{Ac}O_3$, prepared by heating picamar for several hours in a reflux apparatus with excess of acetic anhydride, is insoluble in water, and crystallises from warm alcohol in shining prisms melting at 80—87°, therein agreeing exactly with the acetyl-derivative of Hofmann's dimethylic propylpyrogallate (Niederist).

Monomethylic Propylpyrogallate, $C_{10}H_{14}O_3 = C_6H_2Pr(OH)_2,OMe$, which Pastrovich obtained from beech-tar, and from the portion of birch-bark tar boiling above 270°, is a colourless, oily, strongly refracting liquid, becoming slightly yellowish on prolonged exposure to light. It boils at 290° and has a density of 1·10288 at 15°. Vapour-density 6·41—6·53 (exp.); 6·32 (calc.). By prolonged heating in a sealed tube at 140° with excess of strong hydrochloric acid, it is converted, with separation of methyl chloride, into the compound $C_9H_{12}O_3$, which after purification crystallises in small colourless prisms melting at 80°, and agreeing in composition and properties with the compound which Hofmann obtained in like manner from dimethylic propylpyrogallate (picamar). H. W.

Cœrulignol: Reichenbach's Oxidising Principle. By P. Pastrovich (*Monatsh. Chem.*, **4**, 188—192).—The high-boiling portions of beech-tar oil are characterised by the splendid blue colour which they give with chloride of lime, or in alcoholic solution with baryta-water. The separation of the body to which this colour is due—called by Reichenbach the "oxidising principle"—from the other constituents of the tar-oil, is very difficult, but is best effected by boiling the oil for some time with the weakest acetic acid capable of dissolving it, and pouring the resulting solution into a large quantity of water, whereby the oil is separated, while a nitrogenous body remains in solution. The "blue oil," or Cœrulignol, thus purified, distils between 240° and 241°; it is nearly colourless, has a not unpleasant creosote-like odour and burning aromatic taste; sp. gr. = 1·05645 at 15°. It dissolves very sparingly in cold, more readily in hot water, and in almost any quantity in alcohol, ether, and acetic acid, forming neutral solutions. It is coloured red by strong sulphuric acid, and when mixed with potash-lye, becomes dark-coloured on exposure to the air. With chloride of lime, and in alcoholic solution with baryta-water, it produces the splendid blue colour already mentioned. Its alcoholic solution is coloured green by alcoholic ferric chloride; its aqueous solution gives a fine carmine-colour with aqueous ferric chloride.

Cœrulignol gives by analysis numbers leading to the formula $C_{10}H_{14}O_2$, which is confirmed by the vapour-density (5·69—5·84 by V. Meyer's method; 5·76 by calculation). By prolonged heating in sealed tubes at 140° with excess of strong hydrochloric acid, it is resolved into methyl chloride and a body which when purified by repeated crystallisation from water and finally from benzene, is found to have the composition $C_9H_{12}O_2$,—its formation, represented by the equation $C_{10}H_{14}O_3 + HCl = CH_3Cl + C_9H_{12}O_2$, being exactly analogous to that of the compound $C_9H_{12}O_3$ from methylic propylpyrogallate (p. 1005). The solution of this body is coloured green by ferric chloride, and when mixed with alkalis, gradually acquires a darker colour in contact with the air.

Acetocœrulignol, $C_{12}H_{16}O_3 = C_{10}H_{13}\overline{Ac}O_2$, formed by boiling cœrulignol (3 parts) for two days with 1 part of acetic anhydride, was once obtained in fan-shaped groups of crystals, but mostly as a viscid nearly colourless oil, insoluble in water, freely soluble in alcohol, ether, and acetic acid, boiling with partial decomposition near 265°.

Nitrocœrulignol, $C_{10}H_{13}(NO_2)O_2$, formed by treating cœrulignol with nitric acid of sp. gr. 1·2, separates from water or alcohol in honey-yellow crystals, resembling those of picric acid, and melting at 124°.

The decomposition of cœrulignol by hydrochloric acid, and the formation of its acetyl-derivative, show that it contains the groups OCH_3 and OH, and that it may accordingly be regarded as the methyl-ether of a higher homologue of one of the three dihydroxybenzenes, the compound $C_9H_{12}O_2$ formed from it by the action of hydrochloric acid being this higher homologue itself, which, together with cœrulignol and its acetyl-derivative, may be represented by the formulæ—

$$C_9H_{10}(OH)_2 \qquad C_9H_{10}(OMe)(OH) \qquad C_9H_{10}(OMe)(O\overline{Ac}).$$

To determine from which of the three dihydroxybenzenes cœrulignol is derived, a small quantity of each of these compounds was heated at 135° with a drop of nitro-benzene and a drop of strong sulphuric acid, the melt then dissolved in water, and the solution made slightly alkaline,—whereupon resorcinol gave a bright red solution with yellow fluorescence, catechol a blue-violet, and quinol a yellow liquid. Now cœrulignol treated in like manner gave a reaction exactly like that of catechol, and may therefore perhaps be regarded as a homologue of guaiacol (methyl-catechol); but whether it contains a propyl-group or some other groups, must for the present remain undecided.

H. W.

Action of Sodium on Camphor. (Preliminary Notice.) By J. Kachler and F. V. Spitzer (*Monatsh. Chem.*, **4**, 494—496).—When sodium acts at ordinary temperatures on camphor dissolved in absolute ether or in partially purified petroleum of low boiling point, the products always consist of compounds containing large proportions of sodium and oxygen; and even when a solvent quite free from oxygen such as light petroleum previously distilled over sodium, is used for dissolving the camphor, the action being conducted in a stream of hydrogen, and completed by heating the product in a reflux apparatus, on the water-bath for several days, a sodium salt is obtained, still containing a considerable quantity of oxygen. This salt dissolves readily in water, with separation of a small quantity of camphor (or borneol?) and the alkaline liquid, when treated with an acid, yields a flocculent precipitate which ultimately collects into a yellow viscid mass yielding by dry distillation two substances, viz.: (1.) Shining laminæ melting at 141°, insoluble in water, soluble in alcohol and ether, and having the composition $C_{20}H_{30}O_2$. (2.) Camphoric anhydride, $C_{20}H_{14}O_3$. The investigation will be continued. H. W.

Mode of Formation of the Isomeric Dibromocamphors. By J. KACHLER and F. V. SPITZER (*Monatsh. Chem.*, **4**, 480—486).—The results obtained by Swarts (p. 214 of this volume) on the formation of the two dibromocamphors differ from those of the authors (1882, Abstr., 864), inasmuch as Swarts never obtained α-dibromocamphor melting at 61° by heating monobromocamphor at 100—150° with the requisite quantity of bromine, the product being always the β-modification, at whatever temperature the action took place. The α-modification was however produced when camphor or its monobromo-derivative was heated with bromine in open vessels, and Swarts supposes that its formation was facilitated by the elimination of the hydrogen bromide produced in the reaction. For the preparation of α-dibromocamphor Swarts recommends the process adopted in Schuchardt's factory, which consists in heating 1200 g. camphor in a reflux apparatus with 640 g. bromine and a little chloroform, adding another 640 g. bromine after the escape of the resulting hydrogen bromide, and recrystallising the product from absolute alcohol.

The authors, in following these directions, never obtained α-dibromocamphor, the product invariably consisting of monobromocamphor: in fact, the quantity of bromine employed is not more than sufficient to convert the whole of the camphor into the monobromo-derivative. This latter treated in like manner with the requisite quantity of bromine, yields a good product of α-dibromocamphor; but camphor itself similarly treated with the quantity of bromine required to form dibromocamphor, yields merely a dark-coloured product which crystallises with difficulty or not at all.

The authors now prepare β-dibromocamphor by heating monobromocamphor for 6—10 hours in sealed tubes with 1½ times the calculated quantity of bromine, mixing the liquid with alcohol, which throws down the dibromo-compound as a heavy powder, and purifying this product by recrystallisation from boiling alcohol. To obtain α-dibromocamphor by a similar process, it is necessary that the capacity of the sealed tubes should be sufficiently great in proportion to the volume of the hydrobromic acid formed, to keep the resulting pressure below that which is required for the formation of the β-modification. For preparing larger quantities of α-dibromocamphor, it is advisable to use the process already described, namely to heat monobromocamphor dissolved in chloroform in a reflux apparatus, with the theoretical quantity of bromine. H. W.

Reaction of the Two Isomeric Dibromocamphors with Nitric Acid. By J. Kachler and F. V. Spitzer (*Monatsh. Chem.*, **4**, 554—569).—α-Dibromocamphor heated with nitric acid yields the two non-brominated acids formed in like manner from camphor itself, viz., camphoronic acid, $C_9H_{12}O_5$, and hydroxycamphoronic acid, $C_9H_{12}O_6$, together with bromodinitromethane, $CHBr(NO_2)_2$, and products of more complete decomposition, viz., carbonic anhydride, hydrogen bromide, and nitrosyl bromide. H. W.

Hydroxycamphor from β-Dibromocamphor. By J. Kachler and F. V. Spitzer (*Monatsh. Chem.*, **4**, 643—651).—This compound is formed, as already described by the authors (Abstr., 1882, 865), by the action of sodium-amalgam on β-dibromocamphor dissolved in alcohol. It is a faintly yellowish oily liquid, having a turpentine-like odour and burning taste, easily soluble in alcohol and ether, insoluble in water. It has at 20° a density equal to that of water at the same temperature. Boiling point 265° (bar. 753·5 mm.). It dissolves in alkalis, yielding corresponding salts. $C_{10}H_{15}NaO_2$ is a white crystalline mass; $(C_{10}H_{15}O_2)_2Ba,4H_2O$ is a white hard crystalline salt. Hydroxycamphor heated in a reflux apparatus with excess of acetic chloride, yields colourless highly deliquescent crystals. Heated with hydrobromic acid in a sealed tube at 100°, it is converted into a brown viscid oil. Phosphorus pentachloride acts violently on it, yielding a liquid apparently consisting of monochlorocamphor, $C_{10}H_{15}ClO$; but mixed with condensation-products very difficult to separate. By the prolonged action of chromic acid mixture, hydroxycamphor is completely oxidised to carbonic and acetic acids. Fuming nitric acid acts violently on it, producing *nitro-hydroxycamphor*, $C_{10}H_{14}(OH)(NO_2)O$, together with oxalic acid; with less concentrated acid, the nitro-compound is also formed together with *hydroxycamphoronic acid*, $C_9H_{12}O_6$, and products of more complete oxidation.

Nitro-hydroxycamphor, $C_{10}H_4(OH)(NO_2)O$, crystallises from aqueous alcohol in white woolly needles, or by slow evaporation in monoclinic prisms, exhibiting the faces $\infty P\grave{2}$, $P\grave{\infty}$, $\infty P\bar{\infty}$, ∞P, $\infty P\grave{\infty}$, $2P\grave{\infty}$, $P\bar{\infty}$. Axial ratio $a : b : c = 0{\cdot}7617 : 1 : 0{\cdot}4310$. Angle $ac = 89^\circ\ 18{\cdot}5'$. It is insoluble in water, but dissolves readily in boiling alcohol and ether, also in alkalis, but with separation of nitrous acid. By boiling its solution in glacial acetic acid with tin, it is reduced to *Amidhydroxycamphor*, $C_{10}H_{14}(OH)(NH_2)O$, the hydrochloride of which,

$$C_{10}H_{15}(NH_2)O_2,HCl,$$

forms colourless laminæ, easily soluble in water and melting at 250°. The *platinochloride*, $2C_{10}H_{15}(NH_2)O_2,H_2PtCl_6$, forms yellow well-defined crystals or laminæ. H. W.

Addition-products of Quinoline. By A. Claus and F. Tosse (*Ber.*, **16**, 1277—1283).—*Quinoline Ethyl bromide*, $C_9H_7N,EtBr + H_2O$, formed by the direct union of its components in the cold, crystallises from water or alcohol in large rhombic tables, melts at 80°, and becomes anhydrous at 100°; it is then readily soluble in chloroform, but insoluble in ether. By the action of silver chloride it is converted into *quinoline ethyl chloride*, $C_9H_7N,EtCl + H_2O$. This also crystallises in large rhombic tables, and melts at 92·5°. The platinochloride, $(C_9H_7N,EtCl)_2,PtCl_4$, is obtained as a bright yellow precipitate, scarcely soluble in water, and melting at 226° to a dark yellow liquid. *Quinoline ethyl nitrate*, $C_9H_7N,EtNO_3$, prepared from the bromide by treatment with silver nitrate, forms large colourless rhombic crystals, melts at 89°, and deliquesces rapidly on exposure to air.

Quinoline amyl bromide, $C_9H_7N,C_5H_{11}Br$, is best prepared by heating a mixture of quinoline and amyl bromide with absolute alcohol in sealed vessels at a moderate temperature. It crystallises in yellowish needles, and melts at 87°, but does not resolidify above 67°. The melting point of the anhydrous compound is 140°. The platinochloride, $(C_9H_7N,C_5H_{11}Cl)_2,PtCl_4$, is obtained as a reddish-yellow crystalline precipitate, and melts at 220° to a dark yellow liquid.

Quinoline benzyl chloride is obtained, as already described, in large tabular crystals containing 3 mols. H_2O, and melting at 65°. On exposure to air these lose 1 mol. H_2O, and melt constantly at 129—130°. From an alcoholic solution thick rhombic crystals of the formula $C_9H_7N,C_7H_7Cl + 2H_2O$, are obtained, melting at 130°. The anhydrous salt melts at 170°.

By the action of moist silver oxide or of alkalis on these compounds, bases are obtained having at once the characters of quaternary ammonium oxides and of tertiary bases; they are very unstable, oxidising rapidly on exposure to air to red resins, but when freshly prepared yield the original salts on neutralisation with acids. Freshly prepared aqueous solutions have a strongly alkaline reaction, precipitate all metallic salts, with exception of the alkalis, and expel ammonia from its salts, even in the cold. Analyses of the amyl and benzyl compounds dried over potash gave in each case numbers intermediate between that required for the amine ($C_9H_6N.C_5H_{11}$ and $C_9H_6N.C_7H_7$), and the hydrate ($C_9H_7N,C_5H_{11}OH$ and C_9H_7N,C_7H_7OH). The carbonates appear to be only stable in presence of water, a solution of the base eagerly absorbing carbonic anhydride, but losing it again on expulsion of the water. A. J. G.

Oxidation of Quinoline Benzyl Chloride. By A. Claus and F. Glyckherr (*Ber.*, **16**, 1283—1286).—By oxidation of quinoline benzyl chloride in aqueous solution with potassium permanganate (best in such amounts as to give 5 at. oxygen per mol. chloride), benzoic acid is obtained in small quantity, together with formylbenzylamidobenzoic acid and some benzylamidobenzoic acid.

Formylbenzylamidobenzoic acid, $N(COH)(C_7H_7).C_6H_4.COOH$, crystallises in slender colourless needles or large tables, melts at 196° (uncorr.), is sparingly soluble in water, readily in hot alcohol, the solution showing a fine blue fluorescence. Treatment with alcoholic potash decomposes it into *benzylamidobenzoic acid*,

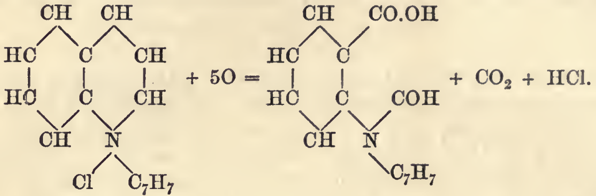
$$C_6H_4(NH.C_7H_7).COOH,$$

crystallising in groups of long thin needles or in thick prisms melting at 176° (uncorr.). The hydrochloride crystallises in large tables, and melts at 104—106° (uncorr.); the platinochloride,

$$[COOH.C_6H_4.NH(C_7H_7)]_2,H_2PtCl_6,$$

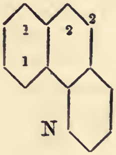
crystallises in orange-yellow tables, and melts at 158° (uncorr.).

From these results, it follows that the benzyl-group in benzylquinoline chloride must be in direct union with the nitrogen-atom, and the oxidation to formylbenzylamidobenzoic acid is represented by—

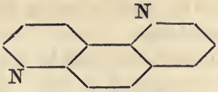


A. J. G.

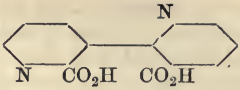
α- and β-Naphthaquinoline. By Z. A. SKRAUP and A. COBENZL (*Monatsh. Chem.*, **4**, 436—479).—Skraup has described, under the name α-naphthaquinoline, a base of the quinoline series, produced by heating a mixture of α-naphthylamine, α-nitronaphthalene, glycerol, and sulphuric acid (*Monatsh.*, **2**, 139; *C. J.*, **40**, 920). This base has the composition $C_{13}H_9N$, and may be derived from anthracene or phenanthrene in the same manner as quinoline from naphthalene or pyridine from benzene, *i.e.*, by the introduction of an atom of nitrogen in place of a CH-group. Its constitution is therefore analogous to that of phenanthrene, and may be represented by the formula—



As a derivative of naphthalene, it may be expected to yield by oxidation a quinoline-dicarboxylic acid, just as naphthalene yields phthalic acid, and, on the other hand, in accordance with its phenanthrenic structure, it should yield by direct oxidation a dicarboxylic acid analogous to diphenic acid. The first of these changes takes place when the C-atoms (1) are oxidised to COOH-groups, the second when the oxidation affects the C-atoms (2). The second of these transformations is perhaps that which may be expected to occur most frequently, inasmuch as Skraup has shown (*C. J.*, **42**, 1112) that the similarly constituted base *phenanthroline*, which may be regarded as phenanthrene having two CH-groups replaced by N, is transformed in a similar manner into an acid analogous to diphenic acid, viz., dipyridyl-dicarboxylic acid—



Phenanthroline.



Dipyridyl-dicarboxylic acid.

The first-mentioned transformation may, however, likewise occur, inasmuch as α-naphthaquinoline contains two benzene rings, and therefore also two groups of atoms susceptible of comparatively easy oxidation.

To give greater generality to their results, the authors have also prepared β-naphthaquinoline from β-naphthylamine, and examined the products of its oxidation.

β-Naphthaquinoline is best prepared by heating a mixture of 28 g. β-naphthylamine, 13 g. nitrobenzene, 50 g. glycerol, and 40 strong sulphuric acid in an oil-bath for about five hours, ultimately at 150—160°, then adding 3 vols. water and a strong solution of 20 g. potassium hydroxide; filtering; covering the light brown filtrate with a layer of ether; adding caustic potash to alkaline reaction, the liquid being at the same time agitated and kept cool; drying the ethereal solution with potassium carbonate; evaporating off the ether on the water-bath; and distilling the residue over an open flame. The β-naphthaquinoline then passes over, above the range of the thermometer, as a nearly colourless easily solidifying oil, which may be purified by a second distillation, or better by converting it into the sulphate, which is sparingly soluble in alcohol. As thus prepared, it is a nearly colourless radio-crystalline substance, very soluble in ether, alcohol, and benzene, slowly in dilute acids, very slightly in water. From a boiling aqueous solution, it crystallises on cooling in snow-white scales, which soon acquire a reddish or yellowish to light yellow-brown colour. It is nearly scentless when cold, but smells like α-naphthaquinoline when heated. It melts at 90°, and readily solidifies to a crystalline mass on cooling. When pure it distils almost without decomposition. The alcoholic solution is coloured brown by ferric chloride, and gives a gelatinous precipitate with silver nitrate. The *hydrochloride*, $(C_{13}H_9N)_2,2HCl + H_2O$, crystallises in long brittle needles; the *chromate*, $(C_{13}H_9N)_2Cr_2O_7$, is a yellow crystalline precipitate; the *picrate* is a light yellow crystalline precipitate, and crystallises from solution in alcohol or benzene in slender prisms melting at 251—252°. The *methiodide*, $C_{13}H_9N,MeI + 2H_2O$, crystallises in pale yellow needles, melting at 200—205°, and giving off their water at 100°. Its aqueous solution has a faint blue fluorescence.

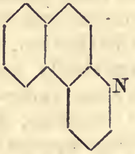
β-Naphthaquinoline is very slowly oxidised by chromic acid, but quickly by a cold dilute solution of potassium permanganate, being converted thereby into β-phenylpyridine-dicarboxylic acid, $C_{13}H_9NO_4$, which is sparingly soluble in cold water, but dissolves somewhat readily in hot water and in alcohol, and separates from the aqueous solution in colourless jagged irregular crystals, often white and opaque; from alcohol, in short limpid better-shaped prisms. It is but very slightly soluble in ether and in benzene. The aqueous solution is coloured orange-red by ferric chloride, and gives a yellowish-white flocculent precipitate with ferrous sulphate.

The following salts of this acid are described :—$C_{13}H_7K_2NO_4,3H_2O$; white crystalline powder, which gives off its water at 300°, and may be heated without decomposition to 360°.—$C_{13}H_8KNO_4,2H_2O$; microscopic laminæ, becoming anhydrous at 170°.—$C_{13}H_7CaNO_4,3H_2O$; shining prisms, very slightly soluble in water even at boiling heat.—$C_{13}H_7BaNO_4,4\frac{1}{2}H_2O$; elongated microscopic plates, moderately soluble in boiling water.—$C_{13}H_8AgNO_4,C_{13}H_9NO_4$; small thick laminæ, sparingly soluble in cold water.—$C_{13}H_7CuNO_4,4H_2O$; light green crystalline precipitate, insoluble in water, but dissolving readily with blue colour in aqueous cupric acetate.—$C_{13}H_7CuNO_4,(C_{13}H_9NO_4)_2Cu$; of a light violet colour.—$C_{13}H_9NO_4,HCl$; small crystalline grains, sparingly soluble in hydrochloric acid, easily in water, sparingly in alcohol.—$(C_{13}H_9NO_4)_2H_2PtCl_4 + 2\frac{1}{2}H_2O$; separates from hot aqueous solution in a yellow oil, which slowly crystallises.

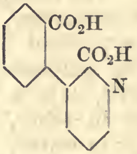
The easy conversion of β-naphthaquinoline into a dicarboxylic acid, $C_{13}H_9NO_4$, shows that the former is analogous in constitution to phenanthrene, and that the latter may be regarded as a diphenic acid of the pyridine series.

The connection between β-naphthylamine, β-naphthaquinoline, and β-phenylpyridine-dicarboxylic acid may be represented by the following formulæ :—

β-Naphthylamine.



β-Naphthaquinoline.



β-Phenylpyridine-dicarboxylic acid.

β-Phenylpyridine-monocarboxylic acid,

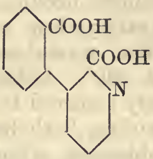
$$C_{12}H_9NO_2 = C_{11}H_8N.COOH,$$

is formed, with evolution of CO_2, when the dicarboxylic acid is heated at 180—185°, and remains as a fused mass which solidifies on cooling and crystallises from aqueous solution in long brittle prisms, which may be purified by recrystallisation from alcohol. It separates from alcohol in soft white crystalline threads, from water in brittle needles, or sometimes in large short prisms. It dissolves sparingly in cold, more freely in hot water, still more in alcohol. The aqueous solution is coloured brownish-yellow by ferric chloride, and gives a light blue precipitate with cupric acetate. The acid is anhydrous, distils without decomposition, and solidifies to a vitreous mass, but becomes crystalline on rubbing with a glass rod. The *calcium salt,*

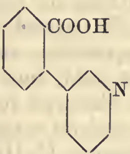
$$(C_{12}H_8NO_4)_2Ca,2H_2O,$$

separates from concentrated solutions in long slender needles, which give off their water at 130°, and begin to turn brown at 250°. The light blue *copper salt,* $(C_{12}H_8NO_4)_2Cu$, is insoluble in water, appears to contain water, but remains unaltered at 170°, even in colour.

By oxidation with a very strong solution of chromic acid, this acid is converted into nicotinic acid, $C_4H_4N.COOH$ [N : COOH = 1 : 3], a result which indicates that in the decomposition of the phenyldicarboxylic acid by heat, the carboxyl-group which escapes is separated from the pyridine residue, and that in the subsequent oxidation of the monocarboxylic acid, the phenyl residue undergoes complete decomposition, its carboxylic group remaining attached to the pyridine—



β-Phenylpyridine-dicarboxylic acid.



β-Phenylpyridine-monocarboxylic acid.

Nicotinic acid.

The arrangement [COOH : N = 1 : 3] in nicotinic acid thus deduced is in accordance with the conclusion previously drawn by Skraup from the behaviour of the pyridinecarboxylic acid on dry distillation, and from the behaviour of the three pyridine-monocarboxylic acids.

β-Phenylpyridine, $C_{11}H_9N = C_5H_4PhN$, is obtained by heating the calcium salt of β-phenylpyridine-dicarboxylic acid with quicklime in very refractory glass tubes, as an oil, which when purified by a method for which the original paper must be consulted, is nearly colourless when recently distilled, smells like diphenylamine, boils at 269—270° (uncorr.; bar. 748—9 mm.), is heavier than water and insoluble therein, but dissolves readily in alcohol, ether, and dilute mineral acids. Its alcoholic solution forms with picric acid a crystalline precipitate, which dissolves with moderate facility in hot alcohol, and crystallises therefrom on cooling in a pulpy mass of soft light yellow needles melting at 161—163·5°. The *platinochloride*,

$$(C_{11}H_9N_2)_2,H_2PtCl_6,$$

crystallises in orange-yellow needles, nearly insoluble in water and in dilute hydrochloric acid, and containing 3 mols. H_2O, which they give off at 100°.

The formation of the β-phenylpyridine is accompanied by that of another body which separates from the alcoholic solution in brownish crystals, apparently consisting of the diketone of β-phenylpyridine.

β-Phenylpyridine is converted by oxidation with permanganate into nicotinic acid, according to the equation $C_{11}H_9N + O_{12} = 2H_2O + 5CO_2 + C_6H_5NO_4$, the acid thus obtained being identical with that which is produced by the oxidation of β-phenylpyridine-monocarboxylic acid, and having the constitution [COOH : N = 1 : 3].

α-NAPHTHAQUINOLINE.—This base is best prepared by heating in an oil-bath a mixture of 28 g. α-naphthylamine, 13 g. nitrobenzene, 50 g. glycerol, and 40 g. sulphuric acid, the mixture, after the first reaction is over, being left to itself at 160° for five hours, the resinous portions of the product removed by partial precipitation with potash-lye, and unaltered naphthylamine by converting the bases into sulphates, treating the product with water, which leaves the greater part of the naphthylamine salt undissolved, and adding to the filtrate at boiling heat a solution of potassium dichromate, as long as the blue oxidation-product of α-naphthylamine continues to separate. The filtered liquid treated with ammonia yields an oil which solidifies on cooling, and after one distillation furnishes pure α-naphthaquinoline. The *chromate* of this base, $(C_{13}H_9N)_2H_2Cr_2O_7$, is moderately soluble in boiling water, and crystallises in long soft yellow needles. The *methiodide*, $C_{13}H_9N,MeI,2H_2O$, crystallises in faintly yellow needles, which suffer partial decomposition at 100°. The crystal-water is not given off over sulphuric acid, but readily at 100°. Other salts of this base are described in Skraup's paper, already referred to.

By the action of chromic acid on α-naphthaquinoline, both dissolved in glacial acetic acid, a quinone, $C_{13}H_7NO_2$, is obtained, which dissolves somewhat readily in alcohol, benzene, and ether, sparingly in dilute alcohol, not at all in water; it dissolves also in dilute mineral acids, sparingly in acetic acid, and is precipitated by water from its solution in glacial acetic acid. It may be distilled, with a certain amount of decomposition, and melts, also with decomposition, at 205—207°. Concentrated sulphurous acid converts it into a white substance, which is coloured deep yellow by ferric chloride, and probably consists of the quinol of naphthaquinoline. This body crystallises from alcohol in small indistinct prisms, from dilute alcohol in long needles, from benzene in thick prisms.

α-Phenylpyridine-dicarboxylic acid, $C_{13}H_9NO_4$, is prepared like the β-acid by the action of potassium permanganate on α-phenylpyridine. It is much less soluble in water and in alcohol than the β-acid, more soluble in alcohol than in water, and crystallises from both solvents in small chalk-white indistinct crystals. The aqueous solution is coloured faintly reddish by ferric chloride, deep blue by cupric acetate, and gives with bromine-water a precipitate of crystalline flocks. The acid when heated melts, with intumescence, to a yellowish liquid, quickly changing to dark indigo-blue, and giving off dark blue vapours which condense on the upper part of the tube; at a higher temperature it gives off dark violet vapours, and is in great part decomposed, with separation of charcoal. In consequence of this decomposition, the melting point is difficult to determine; it lies, however, between 230° and 235°, and brisk effervescence sets in at 236°.

The following salts have been prepared: The *normal* and *acid potassium salts* form transparent uncrystallisable varnishes. The *calcium salt*, $C_{13}H_7CaNO_4,2H_2O$, is obtained by neutralisation and evaporation, as a thick syrup which slowly deposits small crystals.—$C_{13}H_7CuNO_4,4H_2O$ forms violet crystals.—$C_{13}H_7Ag_2NO_4,1\frac{1}{2}H_2O$ is a crystalline precipitate, quickly turning violet-grey on exposure to light, and decomposing quietly when heated.—$(C_{13}H_9NO_4)_2,H_2PtCl_6 + 3H_2O$, forms orange-yellow shining laminæ, easily soluble in cold, still more in hot water, and giving off their crystal-water at 100°.

α-Dibromophenylpyridine-dicarboxylic acid, $C_{13}H_7Br_2N_2O_4$, obtained by direct combination, forms anhydrous crystalline grains, becomes light sulphur-yellow at 100°, dissolves very sparingly in water, more freely than the non-brominated acid in warm alcohol, from which it separates on spontaneous evaporation in transparent crystalline granules. Heated in a capillary tube, it melts at 204—205° to a brownish liquid; in a test-tube over an open flame, it froths up, becomes partly carbonised, and yields a yellow-brown oily distillate which readily solidifies to a radio-crystalline mass. The solution of its ammonium salt gives with *cupric salts* a light green, with *lead salts* a white pulverulent, with *silver salts*, a white gelatinous precipitate, becoming crystalline on boiling. The *nickel salt* is whitish-green; the *calcium salt* crystallises after long standing in small yellowish-white needles. Ferrous sulphate produces a faint transparent yellow coloration; ferric chloride throws down yellowish-red flocks.

α-Phenylpyridine-dicarboxylic acid when heated gives off water and carbonic anhydride, and leaves a blue-black substance from which chloroform extracts a dark-coloured compound, insoluble in water, very slightly soluble in alcohol, more freely in chloroform and glacial acetic acid, the solutions having a dark blue colour. Its composition has not been exactly determined.

The calcium salt of this acid distilled with five times its weight of quicklime yields a dark brown oil in which crystals soon begin to separate. The oil consists of α-phenylpyridine, $C_{11}H_9N$, and the crystals of the ketone of that compound, $C_{11}H_7NCO$, these bodies being formed according to the following equations:

$$C_{11}H_7N(COOH)_2 = 2CO_2 + C_{11}H_9N.$$
$$C_{11}H_7N(COOH)_2 = CO_2 + H_2O + C_{11}H_7NCO.$$

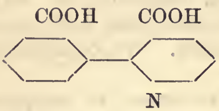
α-Phenylpyridine, separated from solution in hydrochloric acid by potash, and dried with potassium carbonate, distils almost completely between 270° and 275°, leaving a small quantity of the ketone, which separates out completely after standing for some days. The oily base thus freed from the ketone boils at 268·5—270·5° (bar. 749 mm.). It has a faint yellow colour when freshly distilled, but gradually becomes darker; it is heavier than water, and insoluble therein, but soluble in alcohol and ether. It has a pleasant odour, very much like that of diphenylamine, and volatilises slowly with steam, but more quickly than β-phenylpyridine. Its alcoholic solution gives with picric acid small yellowish needles, sparingly soluble in cold, easily in hot alcohol. Heated in a capillary tube, they cake together at 160° and melt at 169—172°. The solution of this base in hydrochloric acid crystallises after long standing in long soft threads which are extremely soluble in water, but not deliquescent. The *platinochloride*, $(C_{11}H_9N)_2,H_2PtCl_6$, crystallises in hydrated needles which give off their water at 100 .

α-Phenylpyridine ketone, $C_{12}H_7NO$, purified by distillation and repeated crystallisation from alcohol, forms large irregular soft laminæ, having a sulphur-yellow colour. Like α-phenylpyridine it emits, even at ordinary temperatures, and more strongly when heated, a fruity odour resembling that of diphenylamine. It is very slightly soluble in cold, rather more freely in hot water, somewhat abundantly in boiling alcohol. It boils without decomposition at 315°, and melts in a capillary tube at 140—142° to a yellow liquid which solidifies on cooling.

The *picrate*, when slowly formed in alcoholic solution, separates as a crystalline precipitate melting at 195—199°. The *chromate* forms red prisms. The *platinochloride*, $(C_{12}H_7NO)_2,H_2PtCl_6$, closely resembles that of α-phenylpyridine in colour and solubility. The ketone offers great resistance to the action of oxidising agents.

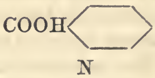
α-Phenylpyridine is very slowly oxidised by potassium permanganate, more readily by chromic acid in aqueous solution, yielding picolinic acid, $C_5H_4N.COOH$, identical with that which is prepared from picoline (m. p. 137·5 to 136°).

The constitution of α-phenylpyridine, of the dicarboxylic acid from which it is obtained, and of the monocarboxylic acid into which it is converted when its phenyl-residue is replaced by a carboxyl-group, may be represented by the following formulæ:—



α-Phenylpyridine-dicarboxylic acid.

α-Phenyl-pyridine.



α-Pyridinemonocarboxylic acid.

α-Pyridine-carboxylic acid, as just observed, is identical with picolinic acid [1 : 2], and β-pyridine-carboxylic acid [1 : 3] has been shown to be identical with nicotinic acid: hence the γ-acid [1 : 4] must be identical with cinchomeronic acid. H. W.

Caffeïne and Theobromine. By R. Maly and R. Andreasch (*Monatsh. Chem.*, **4**, 369—387). I. *Action of Dilute Alkalis on Caffeïne.*—The bodies hitherto obtained by the action of alkalis on caffeïne are products of decomposition due to secondary actions: thus Wurtz by distilling caffeïne with potash obtained methylamine, and Rochleder obtained the same base by treating caffeïne with chlorine. Strecker, by heating caffeïne with baryta-water, obtained a new base, caffeïdine, $C_7H_{12}N_4O$, formed according to the equation $C_8H_{10}N_4O_2 + H_2O = CO_2 + C_7H_{12}N_4O$. Secondary actions however take place at the same time, giving rise to methylamine, formic acid, and sarcosine, $C_3H_7NO_2$, the formation of these products being represented by the equation—

$$C_8H_{10}N_4O_2 + 6H_2O = C_3H_7NO_2 + 2CH_5N + CH_2O_2 + 2CO_2 + NH_3.$$

The process, as usually conducted, yields only a small quantity of caffeïdine; but the authors of the present paper find that by moderating the action of the alkali, and especially by keeping down the temperature, the formation of secondary products may to a great extent be avoided. Moreover, they find that caffeïdine itself is only a secondary product, and that caffeïne when subjected to the gentle action of alkalis, simply takes up 1 mol. water, and is converted into an acid, $C_8H_{12}N_4O_3$, which is resolved by boiling with water into carbonic anhydride and caffeïdine; ($C_8H_{12}N_4O_3 = CO_2 + C_7H_{12}N_4O$) and may therefore be called Caffeïdine-carboxylic acid.

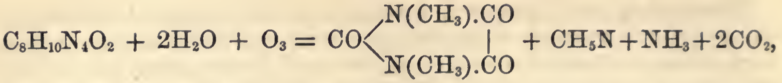
This acid is easily prepared by digesting finely divided caffeïne at 30° in a dilute solution of potash and soda, neutralising with acetic acid, adding a solution of cupric acetate, and decomposing the copper salt thereby precipitated with hydrogen sulphide; it may be purified by solution in chloroform and precipitation with benzene, and is thus obtained in the form of a thick oil, which on exposure to the air solidifies to a yellowish-white, slightly crystalline mass, very easily soluble in water. On boiling its aqueous solution, carbonic anhydride is evolved, and there remains a reddish oil, which when stirred up with a small quantity of sulphuric acid and treated with alcohol, solidifies to a white acicular mass of caffeïdine sulphate. This reaction forms an easy way of preparing caffeïdine: it is merely necessary to decompose the copper salt with hydrogen sulphide, evaporate the filtrate quickly, and treat it with strong sulphuric acid.

Cupric Caffeïdine-carboxylate, $(C_{10}H_{11}N_4O_3)_2Cu$, is a pale-blue rather heavy powder, appearing under the microscope as a mass of crystalline grains or nodules: it is nearly insoluble in water, quite insoluble in alcohol. The calcium, barium, zinc, cadmium and magnesium salts are similarly constituted, and nearly insoluble in water. The silver salt is very unstable. The lead salt is soluble in water.

A solution of mercuric chloride affords a delicate test for caffeïdine-carboxylic acid, forming with its soluble salts a copious white precipitate, which is not a simple mercuric salt, but also contains chlorine, and appears to have the composition $(C_8H_{11}N_4O_3)_2Hg,2HgCl_2$. When decomposed by hydrogen sulphide, it yields a filtrate which on evaporation leaves caffeïdine hydrochloride.

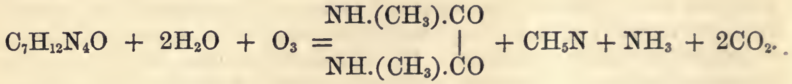
Action of Alkalis on Theobromine.—The behaviour of this compound to bases is totally unlike that of caffeïne; in fact it reacts with alkalis and alkaline earths like an acid, forming definite salts. The *sodium salt*, obtained by adding theobromine to soda-lye in such quantity that a portion remains undissolved after long standing, and evaporating the filtrate under the air-pump, forms milk-white crusts and rings destitute of crystalline structure. It is extremely soluble in water; has a strong alkaline reaction; absorbs carbonic anhydride from the air, and is decomposed thereby. Its aqueous solution forms precipitates with silver nitrate, lead acetate, and zinc chloride, and after a while with mercuric chloride. The *barium salt*, $(C_7H_7N_4O_2)_2Ba$, separates on adding theobromine to baryta-water, as a mass of microscopic needles, and on dissolving this in hot water, filtering, and leaving the filtrate to cool slowly, the compound is obtained in somewhat larger needles; forming a snow-white loosely coherent mass having a somewhat silky lustre. It is but sparingly soluble in cold water, has an alkaline reaction, and the solution when quickly cooled, solidifies to a stiff jelly like gelatinous silica. When heated it melts to a liquid which solidifies by slow cooling to the above-mentioned mass of needles, and by rapid cooling to the jelly, which latter however gradually passes into the former. On pouring a little of the hot solution upon a cold surface, it solidifies and may be pulled off like a membrane.

Oxidation of Caffeïdine with Chromic Acid.—The authors have previously shown that caffeïne is converted by oxidation with chromic acid mixture into cholestrophane, according to the equation—



$$C_8H_{10}N_4O_2 + 2H_2O + O_3 = CO\left\langle\begin{array}{l} N(CH_3).CO \\ \qquad\quad | \\ N(CH_3).CO \end{array}\right. + CH_5N + NH_3 + 2CO_2,$$

and they now find that caffeïdine is converted in like manner into dimethyloxamide:



$$C_7H_{12}N_4O + 2H_2O + O_3 = \begin{array}{l} NH.(CH_3).CO \\ \qquad\qquad | \\ NH.(CH_3).CO \end{array} + CH_5N + NH_3 + 2CO_2.$$

Behaviour of Caffeïne in the Animal Organism.—From experiments in which caffeïne was mixed with the food of a dog, the authors infer, in accordance with the results obtained by other experimenters, that the greater part, if not the whole, of the caffeïne passes unchanged through the organism, and may be recovered in the urine.

H. W.

Notes on Cinchona Alkaloïds. By C. H. Wood and E. L. Barret (*Chem. News*, **48**, 4; comp. Abstr., 1882, 404).—In the abstract referred to, the authors state that the crystals obtained from an ethereal extract of cuprea bark were composed of equal quantities of quinine and quinidine. They have since then investigated this subject more closely, and publish the results, &c., in the present paper. In the first case equal quantities of quinine and quinidine sulphates were dissolved separately in acidulated water, the solution shaken with ether, excess of soda added, and the whole agitated; as soon as the precipitates had dissolved in the ether, the ethereal solutions were decanted off and mixed. The crystals deposited from this mixed solution yielded on analysis numbers approximating to the composition 1 mol. quinine + 1 mol. quinidine + $2\frac{1}{2}H_2O$. In another experiment equal weights of the alkaloïds were dissolved together in 50 per cent. spirit. The crystals obtained from this solution, after 48 hours' exposure over sulphuric acid, were similar in constitution to those described above. Whilst in a third experiment equal weights of the two sulphates were dissolved, &c., as in the first experiment, but the alkaloïds were taken up with warm benzene. This time the crystals, even after three days' exposure, were found to contain 1 mol. quinine + 1 mol. quinidine + $2H_2O$ + C_6H_6. From these facts the authors infer that the crystals always contain water, and therefore this compound is a hydrate of the two alkaloïds.

When anhydrous, a mixture of quinine and quinidine has a lower melting point than either of the constituent alkaloïds. Some of the anhydrous double body dissolved in dry benzene had deposited only a very few crystals, after remaining corked up ten days, but on removing the cork and exposing the contents of the flask to the air plenty of crystals soon formed, and in two days the solution was half filled with them. Quinine, prepared from the sulphate, when dissolved in warm benzene, forms rhomboidal crystals of the composition 2 mols. quinine + $2OH_2$ + C_6H_6. They lose the benzene slowly; a sample after being kept for some time had lost all odour of benzene, but gave evidence of the presence of the hydrocarbon when treated with an acid. The authors remark on the analogy these crystals bear to those of the quinine and quinidine compound when crystallised from the same menstruum. When anhydrous quinine is dissolved in dry benzene, it crystallises out in needles containing a large quantity of benzene, which is gradually given off until only 1 mol. benzene is retained. Cinchonidine crystallises from benzene without water, but with 1 mol. benzene, with which it readily parts. The benzene employed in these experiments was carefully purified. The authors recommended the following test for the purity of quinine:—0·7 gram of the quinine sulphate to be tested is dissolved in 20 drops of hydrochloric acid and 7 c.c. of water; 7 c.c. of benzene are added, and the whole warmed, and then shaken up with 3½ c.c. of dilute ammonia. The benzene layer is separated, the quinine hydrate allowed to crystallise out and filtered off; the separation of feathery crystals then indicates the presence of cinchonidine. These crystals contain a large quantity of quinine. Less than 1 per cent. of cinchonidine can be recognised in this way. The crystals must be sought for within the liquid, not on the surface. The quantities and method of procedure given above must be strictly followed in order to ensure success. Absolutely pure benzene is not necessary for this test: the benzene should, however, crystallise when placed in a freezing mixture. D. A. L.

Alkophyr, and the True and so-called Biuret Reaction. By E. BRÜCKER (*Monatsh. Chem.*, 4, 203—222).—The author some years ago (this Journal, 1871, p. 410) described a substance (*alkophyr*) obtained from peptones, which gives conspicuously the biuret reaction of those bodies (purple coloration with cupric oxide and potash); and in the present paper he describes in considerable detail the methods of obtaining this substance in the pure state. H. W.

Physiological Chemistry.

Composition of the Ash of the Entire Animals, and of certain Separate Parts of some of the Animals used as Human Food. By J. B. LAWES and J. H. GILBERT (*Proc. Roy. Soc.*, 35, 342—344).—This is simply an abstract of a paper which itself is a supplement to a former communication (*Phil. Trans.* [ii], 1859). In the paper referred to, the authors have given the percentage of total ash of the internal organs and of some other separate parts. Ten animals were selected, out of 326, for chemical examination, viz., a fat calf; a half fat and a fat ox; a fat lamb; a store, a half fat, a fat, and a very fat sheep; a store and a fat pig. It was shown that as the animal matured, the percentage of ash, like the nitrogenous matter, decreased, both in the entire body and especially in the collective carcase; and it is now shown that the fatter the animal the less is the quantity of every one of the mineral constituents in greater or less degree in a given live weight. The present paper records the results of the complete analyses, 40 in number, of the collective carcass parts, of the collective offal parts, and of a mixture of all parts of each of the ten animals.

Phosphoric acid, lime, and magnesia comprise more than 80 per cent. of the ashes. They are present to the largest extent in ash of oxen, less in that of sheep, and still less in that of the pig. If the phosphoric acid be calculated as tribasic, ruminants have an excess of base, whilst pigs have not such excess. From separate analyses of the ash of the chiefly bony and of the chiefly soft offal parts of the pigs, it is shown that the ashes of the non-bony portions contain a considerable excess of acid, especially phosphoric, probably due to the oxidation of phosphorus during incineration. No such analyses were made with the other animals; it has, however, been shown that, although oxen and sheep have a higher percentage of nitrogenous substance than pigs, yet the amount of ash from the non-bony parts is less in proportion to that from the bones in the case of the ruminants than in that of the pigs, because the latter animals have only a relatively small proportion of bone. Comparing the percentage composition of the ashes of the entire bodies of the different animals, the chief points of distinction are—that the ash of the pig contains more sulphuric acid, chlorine, potash, and soda than the ash of the other animals; on the other hand, the ash from the ruminants contains more lime than pig ash, whilst in the ash of pigs and oxen there is a higher percentage of phosphoric acid than in that of sheep. It is shown that a given live weight of oxen contains more mineral matter than the same weight of sheep, but that a given weight of sheep has much more than the same weight of pigs. The loss of mineral constituents to a farm by the production and sale of mere fattening increase is estimated to be very small, greater of course in the case of growing than of only fattening animals. Approximately it may be stated that the loss of phosphoric acid per acre would be more in milk, and four or five times more in wheat or barley grain or in hay, than in the fattening increase of oxen or sheep. The land would lose about twice as much lime in the animal's increase as in milk or wheat or barley grain, but only about one-tenth as much as in hay. Of potash the land would lose only a fraction of a pound per acre in animal increase, 6 or 8 times as much in milk, 20 or 30 times as much in wheat or barley grain, and more than 100 times as much in hay. D. A. L.

Distribution of Poisons in the Human Organism in Cases of Poisoning. By C. Bischoff (*Ber.*, **16**, 1337—1356).—The subject of the distribution of poisons amongst the various organs of the body has hitherto received but little attention. The author in particular wishes to ascertain which organ or organs is of special importance in the search for any given poison. The exact estimation of the amount of poisons is of great importance, when it is remembered that such substances may occur in small quantity in food or medicine, or may occur normally or otherwise in the human body. Many of the methods recommended for the estimation of poisons have been tried; those found most satisfactory will alone be quoted. The present paper deals with cases of poisoning by phenol, potassium chlorate, oxalic acid, and potassium binoxalate, and by hydrocyanic acid, potassium cyanide, and essential oil of bitter almonds.

Acute Poisoning by Carbolic Acid.—For the determination of phenol from organs and their contents, the author recommends Landolt's method (*Ber.*, **4**, 770), but finds it necessary to continue the distillation until the distillate gives no further precipitate of tribromophenol on addition of bromine-water. (To isolate 0·5 gram phenol from 1 kilo. of substance about 2 litres of distillate is required.)

Of four cases of poisoning by phenol investigated, in one only were the organs examined separately. A man had died 15 minutes after taking 15 c.c. of officinal carbolic acid (100 parts phenol + 10 parts water). The organs were quite fresh.

242 grams contents of stomach and small intestine, gave 0·1711 gram phenol; 112 grams blood, 0·0259 gram phenol; 1480 grams liver, 0·637 gram phenol; 322 grams kidney, 0·201 gram phenol; 508 grams heart muscle (free from blood), 0·1866 gram phenol; 1445 grams brain, 0·314 gram phenol; 420 grams gluteal muscle, traces; 125 grams urine, 0·0014 gram phenol.

In cases of alleged poisoning by phenol it has to be remembered that it occurs normally in minute quantity in urine, and that along with its next homologues it is formed during putrefaction; 100 grams each of fresh pancreas and of fresh fibrin having yielded, after six days' putrefaction, 0·0208 and 0·022 gram of phenol respectively, and that a liver of 2000 grams in the same time yielded 0·72 gram phenol. In two cases where putrefaction had set in before the post-mortem, either traces only or no phenol could be found in the organs.

Poisoning with Potassium Chlorate.—Potassium chlorate is best estimated by dividing the dialysate from the organs into two parts, estimating the chlorine of the chlorides directly with silver solution in one, reducing the other with sulphurous acid, adding not too dilute nitric acid, and estimating the total silver as silver chloride. From the difference, the chlorate can be calculated. Direct experiments show that potassium chlorate is very soon reduced by moist organic substances, and especially by blood, so that chemical evidence may not be obtainable in undoubted cases of poisoning with potassium chlorate.

Four cases were investigated in which death had occurred in from twelve hours to six days after the use of considerable quantities of potassium chlorate for gargling, &c. In two cases not a trace could be detected; in one case traces were found; and in a fourth slight traces of chlorate could be isolated from the stomach and intestines, and their contents, but none from the liver, kidneys, or pancreas.

In cases of *poisoning with oxalic acid* or oxalates, quantitative estimation is essential on account of the wide diffusion of oxalic acid in the vegetable kingdom, and its consequent ingestion in food or medicine. Salt of sorrel consists more frequently of potassium tetroxalate than of dioxalate, and the tetroxalate on treatment with absolute alcohol is completely decomposed into free oxalic acid and insoluble dioxalate. On finding oxalic acid in an alcoholic extract, therefore, further experiments are needed to ascertain if the poison was oxalic acid or salt of sorrel. The organs are best extracted with alcohol (without addition of acid) to dissolve free oxalic acid and the "half bound" acid of tetroxalates, then digested with water to dissolve any alkaline oxalate, and finally with dilute hydrochloric acid to dissolve any calcium oxalate, the oxalic acid being estimated in each extract. The following cases are given:—I. Person 24 years of age, poisoned with oxalic acid. Death occurred in less than one hour. Analysis commenced two days after death. There was obtained from 358 grams stomach and contents, 0·75 gram oxalic acid, but little calcium oxalate; from 412 grams liver, pancreas, kidneys, and heart, 0·0135 gram calcium oxalate, 0·95 gram oxalic acid as alkaline salt; from 100 grams blood, 0·0467 oxalic acid as alkali salt, traces of calcium oxalate. II. Case of poisoning with phosphorus and oxalic acid. Analysis two days after death. From 215 grams stomach and contents 0·446 gram oxalic acid (total); 100 grams intestines and contents, 0·4 gram oxalic acid (total); 400 grams liver and blood, 0·012 gram oxalic acid as Ca salt. III. Poisoning by oxalic acid. From 2240 grams stomach, œsophagus, intestines, and contents, 2·28 grams oxalic acid (mainly free); from 770 grams liver, 0·285 gram combined oxalic acid; 180 grams blood from heart, 0·0435 gram combined oxalic acid; 350 grams heart, 0·0206 gram combined oxalic acid; 290 grams kidneys, 0·0145 gram combined oxalic acid; 40 grams urine, 0·0076 gram combined oxalic acid; and from 730 grams brain and 590 grams gluteal muscle no result. IV. Poisoning with salt of sorrel. Investigation 25 days after death. Numerous microscopic crystals of calcium oxalate on walls of stomach, duodenum, and kidneys. 142 grams of stomach and contents gave of oxalic acid 0·5555 gram free or from tetroxalate, 0·311 gram as alkaline oxalate, 0·3021 gram as calcium salt; 16 grams duodenum, traces of calcium oxalate; 52 grams mixture of liver and kidney, traces of combined oxalic acid. V. Attempted poisoning with potassium tetroxalate. 340 grams stomach and contents and intestines gave 0·0275 gram total oxalic acid; 40 grams urine, 0·0162 gram oxalic acid as Ca salt; 525 grams mixed blood, liver, kidney, pancreas, brain, and heart, 0·0595 total oxalic acid.

Poisoning with Hydrocyanic Acid, Cyanides, &c.—The best method for the quantitative estimation of hydrocyanic acid in these cases is to mix with excess of alcohol, acidulate with tartaric acid, and distil, a constant stream of air or carbonic anhydride being passed through the apparatus, and the distillate received into a concentrated solution of silver nitrate. The results obtained in five cases are tabulated below. I, II, and III were cases of poisoning with potassium cyanide, IV with hydrocyanic acid, V with essential oil of bitter almonds, the investigations being commenced in from 2—4 days after death.

	I.		II.		III.		IV.		V.	
	Weight of organ employed.	Hydrocyanic acid found.	Weight of organ employed.	Hydrocyanic acid found.	Weight of organ employed.	Hydrocyanic acid found.	Weight of organ employed.	Hydrocyanic acid found.	Weight of organ employed.	Hydrocyanic acid found.
	gram.	gram.	gram.	gram.	gram.	gram.	gram.	gram.	gram.	gram.
Stomach and contents, œsophagus, and duodenum	97	0·0044	223	0·0692	347	0·041	520	0·04	250	0·36*
Intestines and contents	257	0·0077	595	0·0186	249	traces			—	—
Blood	30	0·0028	—	—	85	0·0004	140	0·013	100	traces
Kidneys	43	0·002	122	0·0031	132	0·0024	390	0·0125	100	—
Liver	229	0·0078	505	0·017	445	0·0044			400	slight traces
Pancreas	23	0·0013	—	—	—	—				
Heart muscle	30	0·00088	138	0·0025	145	0·0016	190	0·0091	—	—
Crural muscle	—	none	—	none	207	traces	—	—	—	—
Brain	207	0·002	352	0·0144	220	traces	—	—	—	traces
Urine	—	none	—	none	—	none	—	—	—	none

* 0·13 gram of oil of bitter almonds was isolated containing about 3 per cent. of hydrocyanic acid.

A. J. G.

Chemistry of Vegetable Physiology and Agriculture.

Constituents of the Beans of the Soja hispida. By E. Meissl and F. Böcker (*Monatsh. Chem.*, 4, 349—368).—The Soja-bean, imported from Japan, is a very valuable fodder, inasmuch as, like all leguminous fruits, it contains a large amount of proteïds, and is moreover very rich in fatty constituents. The authors have made an elaborate investigation of these fruits, the results of which are summarised as follows:—

1. The Soja-bean contains no gluten proteïds, and only very small quantities of amido-compounds.

2. By exhaustion with dilute aqueous potash, or with pure water, or with a 10 per cent. solution of sodium chloride, it yields a caseïn nearly resembling the legumin of ordinary leguminous fruits, and containing, when freed from ash, 51·24 per cent. C, 6·99 H, 16·38 N, 0·47 S, and 24·92 O.

3. The solution filtered from the caseïn deposits, on being boiled, an albuminous substance differing essentially in composition and properties from ordinary albumin, but closely resembling the albumin of peas. This albumin is perhaps formed by transformation of the caseïn, and contains 52·58 per cent. C, 7·00 H, and 17·27 N.

4. The mother-liquors of the caseïn and albumin treated with copper salts yield nitrogenous precipitates, consisting for the most part of a cupric compound of caseïn which has escaped precipitation, contaminated with non-azotised substances.

5. The residue left after exhausting the beans with dilute potash contains nitrogen belonging to caseïn which has been rendered insoluble. By prolonged keeping, or by roasting of the beans, the quantity of this insoluble caseïn is increased, and finally the whole of the caseïn is converted into the insoluble modification.

6. Of the nitrogenous constituents of the Soja-beans which are soluble in dilute potash, more than 90 per cent. consists of caseïn, and 1·5 to 2 per cent. of albumin.

7. Combustion with soda-lime cannot be employed for estimating the nitrogen of the caseïn, but is well adapted for estimating the amount of nitrogen in the entire bean.

8. The portion of the Soja-bean soluble in ether consists of 90—95 per cent. neutral fat and 5—10 per cent. cholesterin, lecithin, wax, and resin.

9. The other non-azotised constituents of the bean are cellulose, a small quantity of sugar, about 10 per cent. dextrin, and less than 5 per cent. starch in very small rounded separate grains.

10. The composition of the Soja-bean is, in round numbers, as follows:—

Water	10·0 p. c.
Soluble caseïn	30·0 „
Albumin	0·5 „
Insoluble caseïn	7·0 „
Fat	18·0 „
Cholesterin, lecithin, resin, wax	2·0 „
Dextrin	10 p. c.
Starch (less than)	5 „
Cellulose	5 „
Ash	5 „
Sugar, amides, &c., small quantities.	

H. W.

Chemistry of Globularia. By HECKEL and SCHLAGDENHAUFFEN (*Ann. Chim. Phys.* [3], **28**, 67—81).—The paper describes the analyses of stalks and leaves of *Globularia alypum* and *G. vulgaris*, and the properties of certain of the constituents. In the former plant, Walz in 1857 found a new glucoside, *globularin*. The authors recognise the presence of some substances overlooked by Walz, and they find that the tannin of the plant is no special modification. The substances separated and estimated by them are globularin, cinnamic acid, potassium and sodium cinnamates, tannin, mannite, glucose, chlorophyll, resins, colouring matters, and fixed salts. The presence of the volatile compound detected by Walz was confirmed, but it exists in quantity too small for examination, at least with the amount of material at the authors' disposal; they think it may be cinnamic aldehyde, and that it may be the cause of the peculiar excitement produced by the administration of the extract. The *gobularetin* and *paraglobularetin* of Walz are merely products of decomposition. R. R.

Phoma Gentianæ: a newly observed Parasitic Fungus. By J. KÜHN (*Landw. Versuchs.-Stat.*, **28**, 455—456).—The writer describes a newly-discovered fungus, having its habitat on the stems, leaves, and buds of *Gentiana ciliata*, and takes the opportunity of denying that plants grown in mountainous districts are freer from such parasites than those of the lowlands. J. F.

Artificial Digestion of Meadow Hay. By KERN (*Landw. Versuchs.-Stat.*, **28**, 460—461).—At the experimental station of Gottingen, experiments were made with two sheep, fed for one period on meadow hay and another on lucerne hay; and the digestible and undigestible proteïn matter was estimated according to Stutzer's method, by treatment with acid pepsine. As the excrement contains nitrogenous matters not directly obtained from the food, it was digested for half an hour with 1 per cent. hydrochloric acid, extracted with alcohol and ether and then examined, the unextracted dung being also examined: it was found that the process of natural and artificial digestion yields very similar results. J. F.

Decomposition of the Diffusion Residues from Beetroot. By M. MÄRCKER (*Landw. Versuchs.-Stat.*, **28**, 465—467).—It is found that the residues from the making of beet-sugar by the diffusion process, lose considerable portions of their weight when stored in either pits or barns; as the substance is considered a valuable food for cattle, the author undertook the investigation of the cause, and believes it to be due to fermentation, which is greater in warehouses built of porous materials admitting air, and particularly in pits thatched with straw; he recommends that the residues be used for feeding purposes when fresh, and if that is not possible that they should be dried in a special apparatus before being stored. J. F.

Culture of Various Descriptions of Sugar-beet. By D. v. Koeth (*Landw. Versuchs.-Stat.*, **28**, 451—453).—In order to test the value of different kinds of beet, a large field of limey clay was manured with 200 kilos. of precipitated phosphate and 150 kilos. Chili saltpetre, equal to 64 kilos. of phosphoric acid and 23 kilos. of nitrogen, divided into five parcels, in each of which 77 plants were placed, a different sort in each plot. When ripe, they were weighed; the season being very wet, they showed it in their contents and quality of juice. The differences between the qualities are considerable. The sugar contents were estimated in the juice by a saccharometer, a polariscope not being available, as this instrument would have shown a sugar result of 20 per cent. too little.

The accompanying table gives the figures :—

Name.	Total weight.	Percentage juice.	Specific gravity.	Dry sub. in juice per cent.	Sugar by saccharometer.
	kilos.	kilos.	kilos.	kilos.	kilos.
Oberndorfer	199·5	96·1	1·044	9·8	10·8
Bes Barres	185	96·0	1·041	10·4	10·1
Cylindrical Beets.....	163·5	95·8	1·040	11·2	9·9
Giant Mangold	157	96·8	1·043	11·9	10·6
Giant Mammoth	142	96·0	1·036	7·4	8·9

J. F.

Hay and Ensilage from a Poor Quality of Grass. By F. Sutton (*Chem. News*, **47**, 287).—In the present paper, the author publishes the comparative composition, &c., of hay and ensilage made from the same inferior grasses. Grass 1, from which the corresponding hay and ensilage were made, grew in a wood from which the trees were partially removed, and was very coarse and rank. Grass 2 grew in a rough meadow, was poor and coarse, but somewhat better than 1.

The two samples of hay were coarse and poor in quality, and destitute of the sweet odour and taste usually found in well-made hay; the texture of No. 2 was preferable to No. 1. The hays contained a trace of ready formed sugar, which was considerably increased by digestion with acid: distilled with water they yielded no essential oils, nor any flavour except those of decaying grass.

Both specimens of ensilage were highly odorous from the essential oils, and had a vinous fragrance accompanied by a slight but pleasant acidity. When steam distilled, essential oils passed over, but although powerful in flavour they were too small in quantity to separate. No ready formed sugar could be detected, but after prolonged digestion with acid a substance was formed which reduced copper solution. The following are the analytical data (comp. Abstr., 1882, 330):—

	Hay 1.	Hay 2.	Ensilage 1.	Ensilage 2.
Water	22·20	24·90	74·30	65·95
Albumin and albuminoïds soluble in water	0·73	0·88	1·60	2·12
Insoluble albuminoïds	5·03	7·09	1·41	1·43
Sugar, gum, and extractive matter, soluble in water	7·48	8·87	4·64	7·05
Oil, wax, chlorophyll, &c.	1·29	1·34	0·72	0·89
Digestible fibre	20·80	19·80	8·28	10·62
Indigestible woody fibre	33·92	30·27	6·50	9·24
Alcohol	—	—	—	(0·06)
Acidity, taken as acetic acid	—	—	(0·34)	(0·36)
Soluble inorganic matter	4·05	3·15	1·78	1·88
Insoluble inorganic matter	4·50	3·70	0·77	0·82
	100·00	100·00	100·00	100·00

The author then points out the manifold benefits derived from the ensilage in the present case. Firstly, what would have been tasteless, dry forage is rendered a fragrant appetising and succulent food; then comparing the composition of the dry hay and dry ensilage, he draws attention to the much larger proportion of soluble albuminoïds, soluble extractive matter, and digestible fibre in the latter as compared with the former, and finally infers that what amounts to a partial digestion has been effected in the silo. The author, alluding to the composition of the dried materials, refers to two apparent anomalies; firstly, the increase in fatty matter in the ensilage (*ibid.*) as against the hay, which he thinks is probably due to some of those substances becoming insoluble during the drying of the hay; secondly, the high percentage of nitrogen in ensilage 1, as compared with the corresponding hay, which is probably due to the ensilage containing more seed-vessels or other richer nitrogenous portions of the plant, or perhaps is due to different periods of growth. D. A. L.

Effect of Water containing Zinc Sulphate and Common Salt on Soils and Plants. By C. KRAUCH (*Landw. Versuchs.-Stat.*, 28, 468—472).—The injurious effect of drainage water from mines and chemical works on vegetation is well known, and is believed to be in great measure due to the solvent power of such waters on the valuable constituents of the soil, as well as their directly poisonous properties. A series of experiments was undertaken with samples of earth containing different proportions of common salt and zinc sulphate. It was found that half a gram of salt added to a litre of water, and shaken up with a sample of soil, dissolved more potash, phosphoric acid, and lime, than pure water, and that in a similar experiment with zinc sulphate the zinc became chemically combined with the soil, setting free equivalent quantities of lime, magnesia, and potash.

The injurious effects of the common salt were not so evident in water culture, but when large quantities were used, the plants did not grow. The results with zinc sulphate were much the same, so that it would appear that comparatively large quantities are necessary to produce decidedly injurious effects. Instances of plants which bore treatment with zinc sulphate without injury were mentioned to the author, and suggestions that some plants are more sensitive to the poison than others. J. F.

Analytical Chemistry.

Nitrogen Estimation, a Method of General Application. By H. GROUVEN (*Landw. Versuchs.-Stat.*, **28**, 343—367).—This method is an adaptation to the purposes of analysis of an arrangement employed by the author on a commercial scale in a factory in Bürgerhof, for the purpose of obtaining sulphate of ammonia from peat, the results of which were so satisfactory as to induce him to try to bring it to a sufficient state of perfection that it might replace the so largely used soda-lime process, which he thinks yields rather low results and requires too much care in its execution. The author has employed his method for three years in more than 3000 estimations with very satisfactory results. It consists in burning the nitrogenous matters in contact with steam in a suitable apparatus. The theory is that superheated steam when forced over glowing carbon gives up its oxygen; the nascent hydrogen and nitrogen are brought into intimate molecular contact, and the hydrogen is in such excess that the whole of the ammonia is obtained. The apparatus cannot be very well understood without the accompanying illustrations, but may be described as consisting of two iron gas-pipes connected by a branch at one end. One tube acts as a steam generator and superheater; the water being fed into it gradually from a burette with which it is connected by an india-rubber tube. This generator is filled with broken pumice, which receives the drops of water and presents a very large surface to the heat. The superheated steam passes through the connecting branch into the analysing tube and over the substance, which is contained in a platinum boat: the fore part of this tube is filled with a substance which the author calls the "contact mass," a composition of certain earths with peat, highly burned, very light, and porous. The evolved gases are thoroughly mixed during their passage through this substance, and pass thence through an ordinary bulb arrangement; the pumice in the generator and the contact mass in the analyser are seldom changed. The substance to be examined is put in at the hinder end of the tube, pushed beyond the connecting branch so that the current of steam will play on it; the opening is then closed with an asbestos stopper. These stoppers are a great feature of the apparatus. They are made of the best American asbestos millboard, punched out similar to gun-wads, made as thick as necessary, and connected by screw-rivets, trimmed neatly with a file to closely fit the openings in the tubes. These stoppers last for hundreds of operations. Tubes of various materials have been tried, but ordinary gas-tubes protected by cast-iron cases of good quality are found to last better than any.

A few precautions are recommended. The bulb-tube should be cooled during the process by a stream of water; the "contact mass," although useful for 50 operations, should be cleansed at about every sixth operation by passing a stream of air through it for about 15 minutes while the tube is at a red heat. The hinder portion of the analyser tube is cooled before putting in the substance, by placing a cold iron rod in it and damping the fuel, whilst the portion which contains the "contact mass" is left glowing. This is to prevent the too sudden evolution of gas. The substance under examination should not be previously dried, as the author believes moisture in the sample to be favourable to the operation, and has employed with success samples containing as much as 80 per cent. of water. Fresh vegetable matter, flesh, blood, and all similar materials can be placed at once in the platinum boat without the tedious process of drying and powdering; grain, seeds, bread, and air-dried manures should be damped; fluids of the consistence of milk, such as beer, beet-juice, &c., are concentrated to one-third of their original bulk with addition of a couple of grams of the broken "contact mass." The use of gypsum, sulphate of magnesia, and other substances which yield oxygen to organic matter at a red heat should be avoided; the chlorides should not be employed. The sample should be about 3 grams. The duration of the process is from 20 to 30 minutes, according to the nature of the substance; in very few cases 40 minutes are required. The end is known by the slowness with which the gas bubbles pass. The oven employed is one heated by a fuel composed of 3 parts coke and 1 part wood charcoal; the author prefers it to a gas-oven on the score of cheapness and convenience. Directions are given as to firing and arrangement of the oven: the heat should be moderate, neither very high nor very low, but a low heat is less dangerous to the results than if too high; a coloured and tarry distillate shows the heat to be too low, and that some ammonia is being lost. The tube when all goes right appears of a clear red, and the author estimates the temperature then at about 700—800°; the gases leave the "contact mass" at about 300—350°. The ash of the substance is perfectly pure, and as well burned as in the best muffle, so that it can be weighed directly on cooling.

The author is very strongly convinced of the great accuracy of his process, which always yields a somewhat higher result in ammonia. Five samples exactly alike, examined one after the other, agreed within one-tenth c.c., whilst the soda-lime process carefully carried out with a similar series of five samples showed larger differences, and the author mentions that a difference in the latter process leads to errors fourfold as great as in his, as in his process four times the quantity of organic matter can be burned.

The author believes that the application of this process to the analysis of feeding-stuffs has certain advantages—the easy separation of the more valuable proteïn from the less useful amides, alkaloïds, ammonium salts, nitrates, &c. His method consists in cutting the sample very small, and dividing it into two parts; the one is introduced immediately into the apparatus for determination of total nitrogen; the other is boiled for 10 minutes in distilled water containing 1 c.c. of acetic acid, filtered on a paper filter, and washed with boiling water; the washed filter and substance is then placed wet in the tube, and the nitrogen determined; this represents the true proteïn matter, the difference between it and the total nitrogen, the amides, nitrates, &c.

The nitrogen in raw and dissolved guano, and in many kinds of ammonia superphosphate exists in the form of nitric acid to the amount of $\frac{1}{4}$ to $\frac{1}{2}$ per cent.; the author says that the soda-lime process is quite unsuitable for its determination, even with the precautions recommended by Ruffle—admixture with charcoal, sulphur, and sulphide of soda—yielding unsatisfactory results. Manure merchants and manufacturers complain of this, but hitherto no remedy has been found. The author takes 2 grams of the manure in the dry state, mixes it in the platinum boat by means of a glass rod with 0·5 gram of pure powdered sugar and 3 grams of acetate of soda, and introduces into the tube; the process is finished in about a quarter of an hour. Superphosphate manures of this class are poor in organic matter, but contain much acid gypsum, which has a reducing effect, counteracted by the addition of the sugar and the sodium acetate.

The analysis of sodium nitrate and saltpetre by this method requires a slow and regular evolution of gas, and a considerable excess of carbon gases in the steam while brought into the "contact mass," wherein the dissociation of the aqueous particles takes place. 500 milligrams of the sample are dissolved in 12 c.c. of water and 7 grams of pure sugar added, to this solution as much Dinas clay is added as will make it into a stiff paste. (Dinas clay is rich in magnesia and highly plastic.) This paste is rolled on a porcelain plate to a cylinder 20 mm. thick aud 150 mm. long, placed on a thin piece of sheet-iron and run into the tube previously well cooled. Experience shows that this produces a slow and regular decomposition. The process is completed in 30 minutes and the results are very satisfactory. J. F.

Comparative Estimations of Nitrogen in Guano. By J. Konig (*Landw. Versuchs.-Stat.*, **28**, 461—462).—Raw Peruvian guano contains a considerable proportion of its nitrogen in the form of nitric acid, difficult of estimation by common methods of analysis. Manufacturers of fertilisers have employed Ruffle's method for its estimation, but there are objections to it by reason of the numerous weighings and the retention of a not inconsiderable part of the nitrogen by the mixture of carbon and sulphur. The author recommends a method which yields accurate and higher results than the process referred to, and is preferable for use in commercial analyses. It consists in combustion of the sample with 100 grams finely powdered soda-lime, 12 grams potassium xanthate, and 5 grams tartaric acid; if saltpetre has been added to the guano, the results are too low. J. F.

Nitrogen Estimation in Saltpetre by Potassium Xanthate. By E. A. Grete (*Landw. Versuchs.-Sat.*, 28, 462—463).—The author recommends his process after further trials, as superior to Ruffle's, which he looks on as a modification of his own. He recommends the use of xanthate in quantity about half as much as the sample and soda-lime together, some xanthate behind the mixture in the tube, and ordinary soda-lime in the front of the sample. A. Mayer doubts the wisdom of adopting the process, thinking it would lead to the extensive mixture of Chili saltpetre with guano. M. Maercker advises its adoption on the ground that ammonium sulphate is already mixed with many guanos, and why not saltpetre. J. F.

Phosphoric Acid Determination. By E. A. Grete (*Landw. Versuchs.-Stat.*, 28, 467—469).—The author proposes a new method for the determination of phosphoric acid in presence of iron and alumina. The solution is made in the ordinary way, or should the destruction of organic matter be necessary, 20 grams of the substance is well moistened with a concentrated solution of soda and potassium nitrate, gently ignited in a platinum or silver capsule, and the residue dissolved in hydrochloric or nitric acid; after dilution to 500 c.c., it is filtered, 50 c.c. of the filtrate nearly neutralised is treated with 50 c.c. of ordinary sodium acetate solution, and the precipitate collected on a large filter (a slight washing with water is advantageous but not absolutely necessary), the acetic solution is put aside in a half-litre flask for later treatment; the precipitate is washed from the filter with hot hydrochloric acid by means of a wash-bottle, well washed, treated with ammonia, then with tartrate or citrate of ammonia until the iron or aluminium phosphate is dissolved, and the phosphoric acid in this solution is precipitated by magnesia mixture in presence of much ammonia; when freed by frequent washing (by decantation) the precipitate is dissolved in a small quantity of hydrochloric or acetic acid, and added to the reserved filtrate from the first part of the process, filled to the mark and determined by the uranium process. The rapidity of the process and its small liability to error from the large quantity of substance employed, recommend the process for use. J. F.

Specific Gravity of Minerals and their Mechanical Separation. By P. Gisevius (*Landw. Versuchs.-Stat.*, 28, 369—449).—This paper consists of two divisions, the first being a review of several previously known methods of ascertaining the sp. gr. of minerals by immersing them in certain solutions of known density so that they float midway in the fluid; the second is occupied with a description of various precautions taken by the author to avoid errors, and of an apparatus devised by him to effect the separation of particles of different sp. gr. contained in the sample under analysis. He commences by dwelling on the importance to the agriculturalist of knowing, not only the chemical substances present in his soil, but also their actual state of combination, and he asserts that the methods now in use do not afford the required information.

Amongst the methods reviewed are those of—Senft by washing;

Fleuriau de Bellevue and Cordier by differences in sp. gr.; Schaffgotsch by means of a solution of mercuric nitrate; Sonnstadt by a solution of iodide of potassium and mercury; Church with the same solution; Bréon with molten lead and zinc chloride; but the solution which of all others seemed most suitable was Klein's (Abstr., 1881, p. 1168), by which, with certain precautions, particles of densities between 2·2 and 3·3 sp. gr. can be separated, solutions of any desired density within these limits being easily made up by dilution or concentration of the original preparation. As a check upon his own determinations, he made repeated estimations of the sp. gr. of nine minerals which were given in Naumann's work edited by Zirkel, employing Joly's spring balance, the pyknometer, and the hydrostatic balance. In all of them he found considerable margins of error, and dismisses them as not being sufficiently accurate: this leads to a description of an instrument of his own invention, which he calls "*Volumeometer*." Without the illustration accompanying the paper it would be difficult to understand it; it may be described as a bent tube, one arm much wider and shorter than the other; the solution stands at a certain mark in the wider tube; the sample is placed in it with the usual precautions, and the fluid forced to the mark at which it first stood by means of a caoutchouc ball and a micrometer screw arranged over the aperture of the larger arm; this causes the solution to rise in the other arm, which being very narrow and marked in cubic millimeters, gives at once the volume of the sample, the reading of the scale being aided by a microscope provided with cross-wires; from the volume the sp. gr. is calculated: of the nine minerals examined the agreement with Zirkel's careful determinations was very close.

The second portion of the paper is occupied by a description of the mechanical separation of mineral particles by means of Klein's solution. He describes the preparation of the original solution, the manner of diluting it to the required density, and the various modes of separating the heavier and lighter particles; for this purpose he has devised another instrument, also worked by pressure of air on one arm of a **U**-shaped receptacle, the other arm of which forms the cylinder in which the sample is placed. By varying the pressure, the fluid is agitated, and when the lighter particles rise to the surface, is caused to overflow and carry them into a suitable basin; those particles which are of the same sp. gr. as the fluid can be removed in a similar manner, and the heavier remain at the bottom.

The remainder of the paper is occupied with instructions for the preparation of the sample, from which carbonates must be removed by treatment with dilute acetic acid, but which otherwise contains nothing novel, and with test analyses and estimations, all of which are intended to show the suitability for the estimation of sp. gr. in small samples, and the mechanical separation of their particles, but which scarcely admit of useful abstraction. J. F.

New Method for the Estimation of Minute Quantities of Carbon in Iron or Steel, and a New Form of Chromometer. By J. E. Stead (*Chem. News*, **47**, 285—286).—The ordinary colour method for the estimation of minute quantities of carbon in steel is not accurate, owing to the colour of the iron nitrate interfering with that due to the carbon. In the course of some investigations, the author found that this colouring matter is soluble in alkali, and therefore by treating the nitric acid solution of the steel with soda it can be separated from the iron. Moreover the colour is much deeper in the alkaline than in the acid solution. Upon this discovery the author has based the following method for the determination of carbon in iron or steel. The standard solutions required are—nitric acid, sp. gr. 1·20; and sodium hydroxide, sp. gr. 1·27. One gram of the metal to be tested is dissolved in 12 c.c. of the standard acid, with the aid of heat (90—100°). At the same time some standard iron containing a known quantity of carbon is treated in a similar manner, and when both are dissolved 30 c.c. of hot water and 13 c.c. of soda solution are added to each. They are well shaken, diluted to 60 c.c., well mixed, and after standing ten minutes in a warm place are filtered through dry filters.

The filtrates are compared by pouring them into two separate measuring tubes in such quantities that on looking down the tubes the colours appear equal, and from the difference in height of the columns the amount of carbon is calculated, the amount of carbon being inversely proportionate to the bulk of the steel solution under examination compared with that of the standard. Thus if the steel to be tested contains half as much carbon as the standard, and 50 mm. of the standard be used, then 100 mm. of the steel solution will be required to give the same tint, and then the amount of carbon in the standard multiplied by 50 and divided by 100, would give the amount in the steel. Several experiments were made to test the efficacy of the method. To test the effect of heating, five separate portions of steel were dissolved in 12 c.c. of the standard acid; solution was complete in five minutes: one solution was immediately treated as above described, the others were heated for different periods, and then treated in the same way, the results were as follows:—

	5 mins.	10 mins.	15 mins.	20 mins.	25 mins.
Carbon per cent...	0·098	0·110	0·110	0·110	0·108

In another series, the effect of excess of nitric acid was tested with the following results:—

C.c. of nitric acid used	12	15	18	21	25
Carbon per cent...........	0·41	0·41	0·41	0·402	0·380

whilst excess of soda had the following effect:—

C.c. of soda used	13	15	18	21
Carbon per cent.	0·110	0·110	0·110	0·115

Less than 13 c.c. of soda precipitate the colour along with the iron.

Hydrochloric acid affects the quantity but not the quality of the colour, showing that chlorides are harmless, but that nitrohydrochloric acid even in small quantity prevents the formation of the full amount of colour which would be produced by the nitric acid alone. Several samples of iron have been examined by this method, the results are very slightly lower than the figures obtained by the combustion process. The colours from low carbon irons are different in tint from those from higher carbon steels, and therefore a low carbon iron must be used as a standard for comparison in such cases. When steel is heated to redness and chilled, the colour from the chilled steel is less than that from the original steel, but this difference is not so marked in low carbon steels. The author has detected two distinct colouring matters in all nitric acid steel solutions, one yellow like potassium chromate, the other dark brown-red. In some solutions the yellow preponderates, in others the brown.

For these colorimetric carbon determinations, the author suggests a chromometer, in which a fixed length of liquid column of the carbon solution under examination is used, and a variable standard column of the suitable standard solution is employed; the amount of carbon is deduced from the length of the latter required to make a colour column equal in depth to the former, and the percentage is read off directly from a graduated scale. The apparatus consists of two parallel tubes of any convenient diameter, one of which is 9 inches long and is closed at the lower end; the other tube is contracted at a point 9 inches from the top and is open at both ends, the lower end passes through an india-rubber cork to the bottom of a bottle containing the standard solution; a second tube also passing through the cork into the bottle is connected with a syringe, used for adjusting the height of the standard column. Just above the contracted part of the open tube, and at the bottom of the closed one, a glazed porcelain cylinder is placed. When the tubes are placed in a parallel position the length from the flat surface of the clay to the upper ends is equal in each. A small looking-glass fixed at an angle of 45° over the open ends of the tubes facilitates the observations.

D. A. L.

Electrolysis of Bismuth Solutions. By N. W. THOMAS and E. F. SMITH (*Chem. News*, **48**, 10).—The authors employ solutions of the sulphate or citrate of bismuth, the latter either alkaline or acid. In some experiments, the solutions to be examined were put in a platinum crucible, which was surrounded by a coil of wire in connection with the negative pole of a battery, the positive electrode being suspended in the solution; on the passage of the current, metallic bismuth is deposited on the interior of the crucible, and can be washed, dried, and weighed. In other experiments, the platinum crucible is suspended, from a wire connected with the negative pole, in the solution in a beaker, the positive electrode being likewise in the solution; in this case, the bismuth is deposited on the outside of the crucible. The authors find that the method works well and accurately. The time required to deposit the bismuth varies according to the strength of the solution, and is not shortened by application of heat.

D. A. L.

New Volumetric Method for the Estimation of Arsenic. By L. W. McCAY (*Chem. News*, **48**, 7—9).—The author has success-the most important ingredients, beyond the silica, are calcium and magnesium carbonates, which, filling up the interstices between the particles of sand, form a firm mass; they amount to 0·52 to 12·58 per cent. of the whole. Alumina varies from 0·32 to 1·77 per cent., and is either a component of admixed minerals, or else of clay, which is injurious to the durability of the stone. Iron oxides are contained in all sandstones, in white stones apparently as silicates, and in red stones partially at least, as free ferric oxide or hydrate. The colour of the stone affords no indication of the amount of iron contained; thus a white stone from Kenmure contained 2·62 per cent. ferric oxide, another from Ravenscrag 0·14 per cent., and a red-brown stone from Bothwell Park only 0·98 per cent. Some stones become disfigured with patches of ferric oxide; this arises from the oxidation of pyrites and the action of calcium carbonate and the air on the sulphate produced. Calcium sulphate and phosphate exist in small quantities, viz., about 0·1 per cent. The sp. gr. of the air-dried stone varies from 2·048—2·318, and the amount of water capable of being absorbed varies from 3·4 to 7·2 per cent. It may fairly be taken that the durability of a stone depends on its impermeability to water, its density and the amount of binding material contained. It is noticeable that building stones begin first to decay immediately below any flat projecting surfaces, which allow the rain to collect and then percolate *through* them, and thus dissolve or alter the binding materials. All such horizontal ledges and protections should therefore not be made flat, but have a steep slope given to them. In order to render the stone impervious, it may be painted, or treated with silicate of soda or a preparation called "Alexinoton," but the stone must first be allowed to dry as completely as possible. H. B.

Utilisation of Butter-milk in Bread Making. By A. MÜLLER (*Landw. Versuchs.-Stat.*, **28**, 458—460).—An examination of an excellent specimen of milk-bread from an official farm near Berlin led to the present paper. Butter-milk from cows' milk contains 4 to 5 per cent. of milk-sugar and half per cent. of mineral salts, and after setting for cheese-making it also contains 1 per cent. of nitrogenous matter, and nearly as much butter-fat. The value of this article as food has not been fully investigated; a very small proportion of the quantity produced is drunk or used in bakeries, but the greater part is used for pig and calf feeding, and much of it is allowed to run off into the sewers. The difficulties in the way of its more extensive use are its large percentage of water and its rapid acidification when stored: both difficulties are removed by concentration; this is practised in the North, particularly in Norway, where the butter-milk is boiled over a naked fire in the same way as fruit juices. This process is troublesome and expensive, and would not find acceptance in Germany. The evaporation in a vacuum apparatus, similar to that employed in sugar-boiling, would be much more economical, and would yield a cleaner extract, easy of transport and storage, ready for preparation of milk-sugar, or as food in many forms. The daily evaporation of 40 hectolitres would reduce the cost of the operation to about 1 mark per hectolitre. The author induced a friend to try the new process as applied to bread making, and for several months bread made with it and wheat and rye was sold to the public of Berlin, of excellent quality and at moderate prices. The consumers were pleased with the results, and the bread was pronounced sweet and tasteful.

The daily process consists in evaporating 300 litres of butter-milk to one-seventh of its volume, and mixing to a stiff paste with double its weight of flour. Whole or skimmed milk can be added if butter fat or albuminous matter is desired in the bread. J. F.

Action of Certain Vegetable Acids on Lead and Tin. By F. P. HALL (*Chem. News*, **47**, 290—291; and 300—302).—Taking into consideration the large quantities of tinned food which are constantly being consumed, the author has thought it expedient to study the action of various organic acids on the materials which are exposed in the interior of the cans, viz., tin and lead. The present paper contains the results of experiments on this subject, and also investigations on the quality of tin-plate and tin-foil used as covers for food products.

The first series of experiments were conducted to determine quantitatively the action of the more common vegetable acids on the metals in question, all previous quantitative work in this direction having been made with acetic acid only. First of all, in order to test the effect of alloying on the corrosion of the metals, the amount of tin dissolved, when pure, was compared with the amount dissolved under the same conditions from an alloy exposing the same surface of the metals in question. This was effected by proportioning the size of the plates of pure metals according to the composition of the alloy. Three alloys were made, taking into consideration the specific gravities of the metals, one with equal parts of each metal, one with excess of tin, and one with excess of lead. The metals were fused, well mixed together, cast into thin sheets in iron moulds, rolled into thin strips, and cut into pieces 1·2 inch wide and 12 inches long, thus exposing one-fifth of a square foot surface. The tin and lead strips were of the same width, but varied in length for the reason stated above. The acetic acid solution employed contained 5·75 per cent. of acid, the solutions of tartaric and citric acids were made to an equal degree of acidity. After an exposure of two weeks to the action of the acids at 25—35°, all the metals were found to be tarnished more or less, the tin more so than the lead; two of the alloys were sprinkled with small black crystals of lead; the smallest pieces of lead in tartaric acid were covered with transparent crystals of lead tartrate. The solutions containing tin were yellowish, whilst those with lead were clear and colourless; the pieces of tin were covered with a dusty powder. The strips of metals were taken out, washed, dried, and weighed. The solutions were precipitated with hydrogen sulphide. The lead gave dense black precipitates, finer in the tartaric and citric acids than in the acetic. The tin came down brown in acetic, and yellow and flocculent in the tartaric and citric acids. With the alloys, the precipitates were dark brown in acetic and light-coloured and flocculent in the other acids. The results are given in the following table:—

Surface exposed in sq. inches.		Per cent. composition.		Acetic acid.				Tartaric acid.				Citric acid.			
				Percentage of dissolved metals.		Total amount dissolved (in grams) from		Percentage of dissolved metals.		Total amount dissolved (in grams) from		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
Lead.	Tin.	Lead.	Tin.	Lead.	Tin.	Alloys.	Pure metals.	Lead.	Tin.	Alloys.	Pure metals.	Lead.	Tin.	Alloys.	Pure metals.
7·2 7·2 —	— 21·6 21·6	100·0 34·1 —	— 65·9 100·0	11·54	88·46	0·3744	0·7122	9·73	90·27	0·0298	0·0664	10·15	89·85	0·1626	0·4785
14·4 14·4 —	— 14·4 14·4	100·0 60·8 —	— 39·2 100·0	13·57	86·42	0·4110	0·8242	11·23	88·77	0·0374	0·0750	13·42	86·58	0·1565	0·5439
21·6 21·6 —	— 7·2 7·2	100·0 80·84 —	— 19·16 100·0	75·46	24·54	0·6476	0·8073	22·92	77·08	0·0349	0·0787	44·58	55·42	0·2203	0·5946
7·2	21·6	34·1	65·9	15·25	84·74	0·0341	0·1332	17·65	82·35	0·0102	0·0400	6·74	93·25	0·0267	0·0644

Some similar experiments were now conducted in stoppered bottles. In order to exclude air as much as possible, the bottles were heated, filled with acid while hot; boiled; and at once tightly stoppered. The results are given in the last line of the above table. Another series of experiments proved conclusively that galvanic action did not influence the rapidity of the corrosion, the action generally being slight at first, and increasing as time went on. Dilute acids, if in sufficient quantities, cause more corrosion than stronger ones. Some experiments were next tried on the tins themselves. 200 c.c. of the acids were put into three empty tins, tied over with paper, and examined after two weeks. The citric and tartaric acids had removed the tinning. A white powder was deposited in the citric acid solution, soluble in hydrochloric acid. The quantities of lead and tin dissolved were as follows:—

	Grams dissolved by		
Metals.	Acetic acid.	Tartaric acid.	Citric acid.
Lead	0·0117	0·0873	0·1559
Tin	0·4178	1·0430	0·6828

In addition to these metals, there was a good deal of iron dissolved. The lead was derived from the solder.

The result of the analysis of various samples of tin-plate showed that the superior class or "Bright plate" was tinned with pure tin, and that this quality is the one almost universally used for tin-ware; the inferior class or "Terne plate," as is understood, contains lead to the extent of 70 per cent.; it is considerably duller than bright plate, and is used almost exclusively for roofing purposes. The analysis of commercial tin-foil proves it to be of a very mixed character, from pure tin to stuff containing 90 per cent. of lead; the latter would prove deleterious if used for cheese or like substances.

D. A. L.

General and Physical Chemistry.

Refractive Power of Organic Compounds in Solution. By J. Kanonnikoff (*J. pr. Chem.* [2], **27**, 362—364).—The author is re-investigating the refractive powers of organic substances in order to confirm the results already obtained, and to settle some questions still open. In the present communication, he confirms the rule that the specific refractive power of a substance can be calculated from that of its solution, provided that the solvent has no action on the dissolved substance. The specific rotary power of quinic acid shows the absence of double carbon union. A. J. G.

Cause of the Anomalous Double Refraction of Certain Salts Crystallising in the Regular System. By R. Brauns (*Jahrb. f. Min.*, 1883, **2**, Mem., 102—111).—F. Klocke, who described the double refraction occurring in alum, lead nitrate, and other salts of the regular system (*Jahrb. f. Min.*, 1880, **1**, 53), considered this phenomenon to be due to the state of tension of the crystals in question. The author, however, is of opinion that chemically pure crystals are optically isotropic, and that the anomalous double refraction occurs only in those crystals with which an isomorphic salt is mixed. This conclusion was based on the examination of more than a thousand crystals, including some of Klocke's original crystals. He found that none of them were chemically pure, but that an appreciable amount of isomorphic material was always present. The ammonia-alum was always mixed with potash-alum, and the lead nitrate with nitrate of barium. B. H. B.

Relation between the Composition of Organic Compounds and their Absorption Spectra. By G. Krüss and S. Oeconomides (*Ber.*, **16**, 2051—2056).—One of the authors has already shown that the absorption spectrum of a mixed solution of two coloured substances is not equal to the spectrum of each solution taken separately, but that displacements and concentrations of the bands frequently occur (Abstr., 1882, 1018). These changes are ascribed to chemical reactions within the solution, and it would thus be interesting to decide, if possible, by spectrum analysis the nature of these reactions. As a preliminary stage to this inquiry the authors have examined the changes experienced in an absorption spectrum by the alteration in the composition of a compound, viz., the replacement of a hydrogen-atom by the groupings Me, Et, NO_2, NH_2, &c. This subject has been partially investigated by Dunstan, Soret, and others. The authors have selected for their experiments indigo and its derivatives, which give an absorption-band between C and D, a slight absorption in the red, and a stronger absorption between F and G. The experiments were conducted with a Krüss' universal spectrum apparatus (the slit of which is placed symmetrically to the optical axis), fitted with a micrometer. Measurements were made of the positions of *minimum brightness*, which for dilute solutions lies between well defined and narrow limits. Thus, for example, a solution of indigo in chloroform gives an absorption band from $C_{65}D$—$C_{90}D$ or $\lambda_1 = 613·4$ and $\lambda_2 = 596·7$; and the position of minimum brightness can be taken approximately as the mean of these two numbers, $\lambda_3 = \frac{\lambda_1 + \lambda_2}{2} = 604·8$.

The following table contains the authors' results for λ_1, λ_2, and $\frac{\lambda_1 + \lambda_2}{2}$, for indigo and its various derivatives dissolved either in chloroform or in sulphuric acid:—

	Solution in chloroform.			Solution in sulphuric acid.		
	λ_1.	λ_2.	$\frac{\lambda_1 + \lambda_2}{2}$.	λ_1.	λ_2.	$\frac{\lambda_1 + \lambda_2}{2}$.
Indigo..............	606·9	602·8	604·8	613·4	596·7	605·1
m-Methyl-indigo	628·5	610·8	619·7	—	—	—
m-Oxymethyl-indigo..	658·1	643·4	656·8	—	—	—
Ethyl-indigo	660·9	644·2	652·6	—	—	—
Monobrom-indigo	614·9	597·7	606·3	—	—	—
Dibrom-indigo	628·5	617·5	623·0	—	—	—
Amido-indigo	—	—	—	595·4	582·3	588·9
Dibromoamido-indigo.	—	—	—	590·0	580·2	586·1

The above numbers show that the introduction of the methyl, oxymethyl, or ethyl groupings and of bromine displace the position of minimum brightness to the less refrangible end, while the nitro- and amido-groupings have a reverse action.

It is remarkable that the introduction of an ethyl in the methyl group produces the same effect as the replacement of a hydrogen-atom by oxymethyl: secondly, the introduction of one atom of bromine causes but little change, whilst the effect of the second atom is equal to that of a methyl-group. This difference is to be ascribed to the nearness of position of this latter bromine-atom to the imido-group. A similar phenomenon has been observed by Baeyer and Oeconomides in the case of mono- and di-bromisatin. V. H. V.

In the abstract referred to above, the word *colourless* (fourth line in abstract) is an obvious misprint for *coloured.*—V. H. V.

Electrolytic Researches. By HANS JAHN (*Monatsh. Chem.*, **4**, 679—694).—The starting point of all theories of electrolysis is the well-known law of Faraday, from which, when expressed according to existing conceptions, we learn that *equal quantities of electricity are capable of setting free equal numbers of combining units or quantivalencies;* whence also it follows directly that currents of equal intensity must separate at the electrodes equivalent quantities of the two ions composing an electrolyte,—and, consequently, that the work done by the current in decomposing chemically equivalent quantities of the electrolytes is the same for all electrolytes, and quite independent of the chemical nature of the ions contained therein.

If, however, we admit, according to the ordinary assumption, that the atoms or radicles of an electrolyte are held together by a peculiar force (affinity) depending only on the chemical nature of those atoms, the explanation of electrolytic phenomena in the sense of Faraday's law is attended with considerable difficulty.

Solutions of copper sulphate and zinc sulphate subjected to the action of currents of equal strength yield equal quantities of oxygen and sulphuric acid at the anode, and chemically equivalent quantities of zinc and copper at the cathode. But the quantities of work which must be expended by the current in order to resolve these two salts into their constituents, viz., metal, oxygen, and sulphuric acid, are very different, the zinc salt requiring the expenditure of nearly twice the amount of work that suffices for the decomposition of the copper salt; and in accordance with this fact, it has been shown by Thomsen that the formation of zinc sulphate from zinc, oxygen, and sulphuric acid, is attended with the evolution of nearly twice the amount of heat that is evolved in the formation of the copper salt, viz.:—

$$(Zn, O, SO_3, Aq) = 106{\cdot}01 \text{ heat-units.}$$
$$(Cu, O, SO_3, Aq) = 55{\cdot}96 \quad ,,$$

Granting, however, the existence of different *forces of affinity*, it follows that, in the electrolytic decomposition of a salt, the current must loosen these forces of affinity by restoring the component atoms and molecules to their original conditions of movement. But since the decomposition of zinc sulphate requires the expenditure of an amount of working force nearly double of that required to decompose the copper salt, it seems to follow that equal quantities of electricity will decompose twice as much of the latter salt as of the former, a result which appears at first sight to be in direct contradiction to Faraday's law of electrolysis. The author, however, suggests that in the decomposition of equivalent quantities of the salts under consideration, part of the electric force is expended in the purely chemical work of neutralising the forces of affinity, and another part in overcoming the resistance to conduction and other antagonistic forces,—a view which indeed was suggested by Faraday himself in his classic researches on electrolysis; and as the first of those amounts is directly, and the second inversely proportional to the affinity of the ions, the sum of the two components must remain constant for all electrolytes, and consequently the quantities of electricity required for the decomposition of equivalent quantities of different electrolytes must be the same in all cases,—which is Faraday's law.

With the view of throwing further light on this matter, the author has made a series of experiments on the quantities of heat evolved in the electrolysis of the sulphates of zinc and copper, using a calorimeter of peculiar construction, for the description of which we must refer to the original paper.

The main result of his experiments is that the quantities of electricity used up, or rather converted into heat, in overcoming the resistance to conduction and other secondary influences, are inversely proportional to the forces of affinity of the ions of the electrolyte. Hence it appears that in spite of the different amounts of chemical work which must be supplied by the current for the decomposition of the two salts above mentioned, the entire loss of energy in the circuit is the same in both cases, and therefore that Faraday's law holds good, even if we admit the existence of a determinate affinity between the ions to be overcome by the electric current.

The author has also subjected this inference to a further test. If the quantity of electricity converted into heat by the resistance to conduction, the secondary actions, &c., in the circuit, is less as the affinity between the ions concerned is greater, the amount of heat evolved in the electrolysis of copper sulphate and zinc sulphate with copper and zinc electrodes respectively, must be the same for both salts. For it is clear that if the development or abstraction of heat due to the solution of the anode, with reproduction of the original salt, increases in the same ratio as the quantity of heat due to the resistance to conduction diminishes, the total amount of heat evolved must be the same in both cases.

This conclusion is fully borne out by the author's experiments. In solutions containing respectively $CuSO_4 + 200H_2O$ and $ZnSO_4 + 200H_2O$, the quantities of heat evolved in the deposition of equivalent weights of copper and zinc were found to be: for copper, 39·497; and for zinc, 39·958 heat-units; and solutions containing $CuSO_4 + 100H_2O$ and $ZnSO_4 + 100H_2O$ gave for copper, 37·95 and for zinc 39·39 heat-units. A solution of silver nitrate containing $Ag_2N_2O_6 + 200H_2O$, gave for the deposition of an equivalent weight of silver, 34·03 heat-units. This somewhat smaller result is regarded by the author as probably due to the fact observed by Hittorff, that in the electrolysis of copper and zinc solutions equal proportions of the working force are converted into kinetic energy of the ions, whereas in silver solutions a larger proportion of the working force is thus converted, and consequently only a smaller proportion is converted into heat.

In the electrolysis of mixed solutions of zinc and copper sulphates, the deposit on the cathode consists wholly of copper. H. W.

Relation of the Heat of Combustion of Isomeric Organic Compounds to their Densities. By MÜLLER-ERZBACH (*Ber.*, **16**, 758—761).—From a careful comparison of all the available determinations of heat of combustion of various compounds, the author draws the conclusion that "of isomeric bodies, that one which has the lowest density will show the greatest heat of combustion and the least heat of formation." He also considers this to be another proof of the correctness of his law that "the changes brought about by chemical affinity, acting in accordance with the law of 'smallest space,' force together the active masses, causing continued increase in the mean density." L. T. T.

Molecular Volume of Liquid Substances. By R. SCHIFF (*Annalen*, **220**, 71—112).—After some remarks on the advance made within the last few years in tracing the interdependence of physical constants and the arrangement of the atoms within the molecule, the author proceeds to sum up the various results as follows :—

1. In isomeric substances, the boiling point and index of refraction have a lower value the less continuous the arrangement of the carbon-atoms within the molecule, and a maximum value when these atoms are perfectly continuous or normally disposed.

2. The optic constants (atom refraction and molecular polarisation) and the thermic constants (heat of combustion) are increased by every so-called double affinity (or bond) between two carbon-atoms.

The author has carried on a series of investigations chiefly with a view of ascertaining how far this latter generalisation holds good in the case of molecular volume, as suggested originally by Buff, and further investigated by Thorpe (this Journal, Trans., 1880), and Schröder.

As the dilatometer method requires costly apparatus, a number of observations and measurements at various temperatures, and a series of calculations, the author has devised another method of measuring the volume occupied by a known weight of a liquid at its boiling point. The method is, however, merely a more accurate modification of that proposed by Ramsay (Trans., 1879, 463). With this apparatus the author has made more than 200 observations, and the results obtained agree with those of Kopp, Pierre, and Thorpe.

Great care was used to obtain perfectly pure samples of the liquids investigated; fractional distillation was avoided whenever any substance could be obtained directly by synthesis; and the degree of purity was controlled by vapour-density determinations. The results of the investigation are given in the table below.

Hydrocarbons.

Name.	Molecular volume $\frac{M}{D}$.	Name.	$\frac{M}{D}$
Secondary pentane, C_5H_{12}	117·17	Xylene, C_8H_{20}	139·74
Normal hexane, C_6H_{14}	139·71	Ethylbenzene, C_8H_{10}	138·93
Di-isobutyl, C_8H_{18}	184·47	Styrene, $CHPh.CH_2$	130·91
Di-isoamyl, $C_{10}H_{22}$	231·31	Normal propylbenzene, C_6H_5Pr	161·82
Amylene, C_5H_{10}	110·01		
Caprylene, C_8H_{16}	117·22	Paraethyl-toluene, C_6H_4MeEt	161·94
Diamylene, $C_{10}H_{20}$	211·18	Mesitylene, $C_6H_3Me_3$	162·41
Diallyl, C_6H_{10}	125·82	Cymene, $C_6H_4Me\ Pr^{\alpha}$	184·46
Benzene, C_6H_6	95·94	Terpene, $C_{10}H_{16}$	182·83
Toluene, C_7H_8	117·97	Carvene, $C_{10}H_{16}$	190·32

Chloro-derivatives of Hydrocarbons.

Name.	Molecular volume $\frac{M}{D}$.	Name.	$\frac{M}{D}$.
Chloroform, $CHCl_3$	84·56	Propyl chloride, C_3H_7Cl	91·43
Tetrachloromethane, CCl_4	103·66	Allyl chloride, C_3H_5Cl	84·22
Ethylene chloride, $CH_2Cl.CH_2Cl$	85·24	Chlorobenzene, C_6H_5Cl	114·27
		Parachlortoluene, C_6H_4ClMe.	134·91
Ethylidene chloride, $CHCl_3Me$	88·50	Benzylic chloride	133·47
Trichlorethane, $CH_2ClCHCl_2$	102·77	Epichlorhydrin, C_3H_5CCl	87·67
Tetrachlorethylene, CCl_2CCl_2	114·18		

Alcohols.

Methyl alcohol, MeOH	42·71	Allyl alcohol, C_3H_5OH	74·10
Ethyl alcohol, EtOH	62·00	Amyl alcohol, $C_5H_{20}OH$	122·74
Normal propyl alcohol, $Pr^{\alpha}OH$	81·28	Dimethyl ethyl carbinol, CMe_2EtOH	121·26
Isopropyl alcohol, $Pr^{\beta}OH$	80·75		
Normal butyl alcohol, C_4H_9OH	101·57	Methyl hexyl carbinol, $CMeC_6H_{16}H.OH$	191·28
Isobutyl alcohol, CMe_2CH_2OH	101·63		

Ketones, Aldehydes, and their Derivatives.

Acetone, Me_2CO	77·08	Paraldehyde $(C_2H_4O)_3$	150·72
Methyl hexyl ketone, $MeCOC_6H_{13}$	186·61	Dimethyl acetal, $MeCH(OMe)_2$	110·81
Furfuraldehyde, $C_5H_4O_2$	95·52	Diethyl acetal, $MeCH(OEt)_2$	159·88

Acids.

Normal butyric acid, $C_4H_8O_2$	107·85	Isobutyric acid, $C_4H_8O_2$	108·57

Ethers.

Anisoïl, PhOMe	125·18	Phenetoïl, PhOEt	148·47

Ethereal Salts.

Methyl formate, HCOOMe	62·57	Propyl acetate, MeCOOPr	128·55
Ethyl formate, HCOOEt	84·57	Allyl acetate, $MeCOOC_3H_5$	121·37
Butyl formate, $HCOOC_4H_9$	130·74	Butyl acetate, $MeCOOC_4H_9$	152·51
Amyl formate, $HCOOC_5H_{11}$	153·21	Amyl acetate, $MeCOOC_5H_{11}$	174·57
Methyl acetate, $MeCOOCH_3$	83·65	Methyl propionate, EtCOOMe	104·23
Ethyl acetate, MeCOOEt	105·70	Ethyl propionate, EtCOOEt	127·82
Ethyl chloracetate, CH_2ClCO_2	123·09	Propyl propionate, EtCOOPr	150·69
Ethyl dichloracetate, $CHCl_2.COOEt$	143·42	Amyl propionate, $EtCOOC_5H_{11}$	196·95
		Ethyl butyrate, $EtCOOC_4H_9$.	150·23
Ethyl trichloracetate, $CCl_3.COOEt$	163·86	Ethyl isobutyrate, C_4H_9COOEt	150·68

In conclusion the author discusses the magnitude of the errors in the determination of the boiling point, measurement of the volume of the liquid, and its weight. If each of the several possible errors were in the same direction, the total would reach a maximum value of 0·16 unit, a difference which was never observed in two separate determinations of the molecular volume of the same liquid. V. H. V.

Variation of the Constant of Capillarity of the Surfaces, Water-Ether, and Water-Carbonbisulphide under the Action of Electromotive Force. By KROUCHKOLL (*Compt. rend.*, **96**, 1725—1728).—The author finds that insulating liquids, such as carbon bisulphide, ether, and turpentine, which are not miscible with water, acquire a distinct conductivity when placed in contact with it. He finds that the capillarity constants of the surfaces, water-ether, and water-carbonbisulphide vary under the action of electromotive force in the same way as the capillarity constant of the surface, water-mercury. Lippmann's well-known experiments with mercury can indeed be repeated with ether or carbon bisulphide. The enormous resistance of the ether or carbon bisulphide, even when saturated with metallic salts as in these experiments, exercises considerable effect on the rapidity of the movements of the meniscus. C. H. B.

Experiments on the Diffusion of some Organic and Inorganic Compounds. By J. D. R. SCHEFFER (*Ber.*, **16**, 1903—1917). —A continuation of the author's investigations (comp. Abstr., 1882, 1159). The mean results of the author's determinations are collected in the following table:—

Substance employed.	Grams of substance in 100 c.c. solution.	Temperature.	Diffusion constant, *k*.
Hydrochloric acid	4·55	3·5°	1·622
,, ,,	22·7	,,	2·008
Sodium chloride	5·45	5·5	0·756
,, ,,	6·1	,,	0·756
,, ,,	12·53	,,	0·727
,, ,,	26·3	,,	0·732
,, nitrate	10·35	2·5	0·622
,, ,,	49·09	,,	0·565
Silver nitrate	4·96	7·5	0·899
,, ,,	35·95	,,	0·774
,, ,,	68·58	,,	0·649
Sodium thiosulphate	5·6	10·5	0·630
,, ,,	38·97	,,	0·543
Urea	3·3	7·5	0·810
Tartaric acid	(5 per cent. solution)	5·0	0·374
Racemic acid	,,	,,	0·388
Sodium sulphobenzoate	5·16	14·5	0·674
Sodium formate	2·47	8·0	0·691

The author in conclusion compares his results for hydrochloric acid, sodium chloride, nitrate, and thiosulphate, and silver nitrate with those of Graham and Schulmeister. For sodium chloride, both Graham's and the author's results point to a very slight influence of concentration on the velocity of diffusion; Schulmeister, however, concludes that with increase of concentration the value for k increases. In the case of sodium nitrate, and more so for sodium bisulphate and silver nitrate, the effect of concentration is greater. The author considers that the variation in the values of k for the same substance in solutions of various degrees of concentration are probably due to a separation caused by dilution of larger with smaller molecular aggregates. V. H. V.

Affinity, and its Relation to Atomic Volume, Atomic Weight, and Specific Gravity. By E. DONATH and J. MAYRHOFER (*Ber.*, **16**, 1588—1596).—After mentioning the views held by Mohr, Kopp, Gmelin, Wächter, and others, the authors compare the elements with reference to their specific volumes, *i.e.*, the quotient of the atomic volume divided by the atomic weight, or in other words the reciprocal of the specific gravity. The order in which the elements are arranged is such that those in which $\frac{1}{D}$ has the highest values, and the properties of which are more opposed, are placed at the two ends of the list, whilst the elements with lowest specific volumes are placed in the centre, forming a series which in many respects resembles the electro-chemical series of elements. A. K. M.

Inorganic Chemistry.

Activity of Oxygen. By F. HOPPE-SEYLER (*Ber.*, **16**, 1917—1924).—This paper is an answer to Traube's criticisms on the author's results (this vol., p. 900). The author has repeated his experiments (this vol., p. 848), and is satisfied as to their accuracy and the deductions drawn therefrom. V. H. V.

Lecture Experiments. By A. LADENBURG (*Ber.*, **16**, 1478—1483).—I. A description of a mercurial trough and apparatus for gas analysis, which could not be described without the aid of the accompanying cuts.

II. *Synthesis of Water by Weight.*—A modification of the ordinary apparatus for illustrating the synthesis of water, in which the weight of hydrogen required to form water by uniting with the oxygen of the copper oxide is directly determined. Two glass gasholders are used, one filled with hydrogen the other with water. Each is weighed before the experiment begins. The hydrogen is driven out of one gasholder in the usual way by means of water; this passes through the apparatus, and the unused hydrogen displaces the water in the second gasholder. When the experiment is complete, the gasholders are again weighed. From the increase in weight, the volume and weight of hydrogen employed can be calculated. The upper part of the gasholders must be empty when the weighings are made.

W. C. W.

Unobserved Resemblance between Carbonic Anhydride and Carbon Bisulphide. By J. TYNDALL (*Proc. Roy. Soc.*, **35**, 129—130).—The author has examined the question whether compounds of like chemical constitution possess like vibrating periods of their constituent molecules. Carbonic anhydride, although the most transparent of gases, is the most opaque to the radiation from hot carbonic anhydride produced by the burning of carbonic oxide; carbon bisulphide, whether as liquid or gas, is the most diathermous. But the author has proved by experiment that carbon bisulphide absorbs 75 per cent. of the heat radiated from a carbonic oxide flame, but only 10 per cent. of the heat from a hydrogen flame. Thus carbon bisulphide transcends as an absorbent of heat from carbonic anhydride many substances which for all other sources of radiation far transcend it.

V. H. V.

Phosphorus Sulphides. By ISAMBERT (*Compt. rend.*, **96**, 1771—1772).—The author admits Lemoine's claim for priority. He points out, however, that there is a considerable difference between the liquid sub-sulphide formed by mixing phosphorus and sulphur at 100°, and that formed by heating the mixture to a temperature higher than 130°, or by mixing phosphorus and phosphorus trisulphide: the latter is much more stable than the former, a difference due to the fact that in the first case there is no real chemical combination. When a mixture of phosphorus with even a large excess of sulphur is distilled at 100° in a vacuum, all the phosphorus distils over, and a residue of sulphur is left; but on distilling a mixture of phosphorus and phosphorus trisulphide in the same way, phosphorus distils over and carries with it some of the trisulphide and a residue of the trisulphide is left. The heat developed by the union of P_2 with S_3, 18·4 cals., is sufficient to account for the explosion which accompanies combination, for since the specific heat of the mixture is only about 0·2 and the combination takes place at about 130°, the temperature of the mass is suddenly raised to 965°. Solution of iodine in carbon bisulphide rapidly attacks phosphorus trisulphide, yielding phosphorus tri-iodide, but has no action on compact red phosphorus, a difference due to the fact that the formation of phosphorus tri-iodide develops less heat than the conversion of ordinary phosphorus into red phosphorus. The phosphorus does not exist in the trisulphide as red phosphorus, all the latter having been converted into the ordinary variety at the moment of combination.

C. H. B.

Phosphorus Subsulphide. By H. SCHULZE (*Ber.*, **16**, 2066—2068).—This communication is for the most part a polemic directed against Lemoine, who has recently maintained the existence of phosphorus subsulphide as a chemical entity. Isambert and the author have, however, shown that the formation of the subsulphide is not accompanied with evolution of heat and by distillation at 100° in a vacuum all the phosphorus may be separated from the sulphur. The author has further shown that the liquid sulphides prepared in accordance with the assigned formula P_4S and P_2S do not solidify as a homogeneous mass; from the former, phosphorus, and from the latter, sulphur separate out. Also the liquids obtained from phosphorus with excess of sulphur deposit phosphorus on cooling; and by treatment with carbon bisulphide and chloroform can be separated into their two components. Hence these liquids are solutions of the one element in the other, and not chemical compounds.

V. H. V.

Preparation of Phosphoric Acid by the Oxidation of Phosphorus with Air in Presence of Moisture. By W. T. WENZELL (*Pharm. J. Trans.* [3], **14**, 24—26).—Some years back Moir suggested that phosphoric acid could be prepared by the oxidation of phosphorus with moist air; and effected it by placing sticks of phosphorus in glass tubes contracted at one end, and several of these tubes were placed in a funnel, the end of which dipped into a flask of water. Doebereiner, with the same object in view, filled a flat porcelain dish to the depth of an inch with powdered glass, which was nearly covered with water, sticks of phosphorus being laid on the wet glass, so as not to touch one another, and the whole covered with a bell-jar. These processes are not only impracticable but dangerous, on account of there being no arrangement for regulating the air supply. The author now suggests the use of infusion jars for this purpose; the sticks of phosphorus are laid on the diaphragm, and sufficient water is poured on to leave half the diameter of the sticks exposed. The lip of the jar is closed with an india-rubber stopper, whilst the top of the jar, which is ground even and smooth, is covered with a porous disc of plaster of Paris, which regulates the air supply. The phosphorus soon begins to oxidise, and after a week disappears to the surface of the water; the acid liquid is poured off so as to expose more phosphorus, and the operation is continued until all the phosphorus is oxidised. For large quantities, the author proposes the use of shallow glazed pottery trays which can be covered with a plaster of Paris tile, the phosphorus being arranged on cross bars and the liquid run out by means of a tube let in the side. Lead does not answer, on account of lead phosphate being formed.

The products of the oxidation are *phosphoric acid* in largest proportion, next *phosphorous acid*, *ozone*, and *hydrogen peroxide* in molecular proportions, and besides these, *ammonium nitrate* and *arsenic acid* are present in the final product. The ozone, hydrogen peroxide, and ammonium nitrate are the products of the oxidation due, as the author suggests, to atomic oxygen, which is set free by the breaking up of the ordinary oxygen molecule to supply the phosphorus atoms with the uneven number of oxygen-atoms required to form phosphoic and phosphorus anhydrides. The porous cover to the apparatus not only permits the gradual admission of air, but also dialyses the ozone from the hydrogen peroxide; the former diffuses through and can be recognised by the odour and by test-paper, whilst the latter remains within the apparatus, forming the white vapour which is present during the oxidation. It runs into the liquid and of course takes part in the oxidation; its presence is rendered evident by agitating some of the liquid with chromic acid and ether, &c.

The arsenic acid is got rid of by heating for a short time at 160°, when the arsenic is completely precipitated as metal; at 170° and above, the phosphorous acid is decomposed into phosphoric acid and spontaneously inflammable hydrogen phosphide. The next operation is the conversion of the phosphorous acid into phosphoric; the acid solution is heated to about 130°, a small quantity is reserved, the remainder is treated with nitric acid until no more nitrous fumes are formed, and the excess of nitric acid is got rid of by adding the reserved portion of the acid solution. During this operation, nitric oxide is produced and acts as a carrier of oxygen as it does in the sulphuric acid chambers, and thus economises the nitric acid; it is therefore advisable to add the nitric acid gradually so as to avoid the escape of the nitrous fumes. The process is tedious. D. A. L.

Thionyl Chloride and Pyrosulphuryl Chloride. By K. Heumann and P. Koechlin (*Ber.*, **16**, 1625—1631).—Thionyl chloride acts readily on powdered antimony, with formation of antimony trichloride: $3Sb_2 + 6SOCl_2 = 4SbCl_3 + Sb_2S_3 + 3SO_2$. On warming mercury-diphenyl with an excess of thionyl chloride, an energetic reaction sets in and a yellowish mass is obtained from which, after the addition of water, crystals of mercury-phenyl chloride, HgPhCl, can be isolated, melting at 245°. A small quantity of an oily substance containing sulphur is also formed, giving a splendid blue coloration with concentrated sulphuric acid. A different reaction takes place with mercury-dinaphthyl, with formation of β-chloronaphthalene. By the action of thionyl chloride on butyric, benzoic, and cinnamic acids, the corresponding chlorides are produced, and from sodium paratoluene-sulphonate paratoluene-sulphonic chloride can be obtained. On passing the vapour of thionyl chloride through a red-hot tube, it is decomposed according to the equation: $4SOCl_2 = S_2Cl_2 + 2SO_2 + 6Cl$. Its vapour-density at 99° (steam), 154° (bromobenzene vapour) and at 442° (sulphur vapour), is respectively 3·95, 3·81, and 2·65, theory requiring 4·11 for $SOCl_2$ and 2·74 for $\frac{2}{3}SOCl_2$, showing that the vapour-density is normal up to 154°, whilst at 442° dissociation takes place according to the above equation.

In reply to Konowalow (*Ber.*, **16**, 1127), the authors state that they have distilled pyrosulphuryl chloride four times over phosphoric anhydride, and that the boiling point remains constant at 147°, whilst sulphuric anhydride at once raises the boiling point. This is explained by the presence of sulphuric acid in the anhydride. The authors are of opinion that from the mode of preparation adopted by Konowalow, the differences between his boiling point and vapour-density determinations and their own are due to the presence of sulphuric acid.

A. K. M.

Blue Rock Salt. By B. Wittjen and H. Precht (*Ber.*, **16**, 1454—1457).—The blue colour of certain pieces of Stassfurt rock salt has been ascribed to the presence of a sulphur compound by Ochsenius, to sodium subchloride by Johnson (*Gmelin Kraut*, **2**, 204), and to the presence of gases by Bischof (*Steinsalzwerke bei Stassfurt*, F. Bischof).

The authors prove that the salt contains very minute quantities of hydrogen and marsh-gas. It does not contain sulphur, neither does it contain any colouring matter soluble in ether or in carbon bisulphide. The authors conclude that the colour is not due to the presence of any blue colouring matter, but is a purely optical phenomenon.
W. C. W.

Silver Hypophosphate. By J. Philip (*Ber.*, **16**, 749—752).—Six grams of silver nitrate are dissolved in 100 c.c. of nitric acid (sp. gr. 1·2) diluted with 100 c.c. water, and heated on the water-bath. 8—9 grams of phosphorus are introduced, when at a little below 100° a violent reaction takes place, the phosphorus being oxidised to phosphorous, phosphoric, and hypophosphoric acids, of which—if the phosphorus be maintained in excess, and the reaction stopped as soon as the violent evolution of gas ceases—the hypophosphoric acid forms the greater part. As the liquid cools, silver hypophosphate crystallises out, the phosphorous and phosphoric acid remaining in solution. When silver hypophosphate is heated, it decomposes into metallic silver and silver metaphosphate. L. T. T.

Iodide of Argentammonium. By A. Longi (*Gazzetta*, **13**, 86).—Rammelsberg (*Pogg. Ann.*, **48**, 151) found that dry silver iodide absorbed gaseous ammonia, with formation of a white easily decomposible substance of the formula $2AgI,NH_3$. The author, by digesting silver iodide with ammonia solution (sp. gr. 0·960), obtained another white compound of the formula NH_3AgI. It is easily decomposed when exposed to the air, or when left in contact with water.
C. E. G.

Hydrates of Baryta. By H. Lescœur (*Compt. rend.*, **96**, 1578—1581).—The author has measured the tension of dissociation of barium oxide in various states of hydration, with a view to determine how many definite hydrates of baryta actually exist: At 100° two definite hydrates exist: the hydroxide BaH_2O_2 with practically no tension of dissociation, and the hydrate BaH_2O_2,H_2O with a tension of dissociation of about 45 mm.: this hydrate is completely converted into the hydroxide when heated at 100° in a vacuum. At 75°, the hydroxide, BaH_2O_2, has practically no tension of dissociation, and that of the hydrate, BaH_2O_2,H_2O, is less than 1 mm. A third hydrate, $BaH_2O_2,8H_2O$, however, exists at this temperature, and has a tension of dissociation of 213 mm. Barium oxide therefore forms three definite compounds: BaO,H_2O; $BaO,2H_2O$, and $BaO,9H_2O$, and these are the only definite hydrates which can exist at 75°. C. H. B.

Hydrates of Baryta. By E. J. Maumené (*Compt. rend.*, **96**, 1730—1732).—Barium hydroxide fused at a dull red heat has the percentage composition BaO 87 49, H_2O 12·51, corresponding with the formula $BaO(H_2O)_{1\cdot214}$. If the hydrate crystallised from water is placed under a small bell-jar over some of the fused hydroxide until it ceases to lose weight, it yields the hydrate $BaO(H_2O)_{2\cdot83}$. The crystallised hydrate, dried in a similar manner over this second hydrate, has the composition $BaO,(H_2O)_{8\cdot5}$. The behaviour of baryta is not exceptional: the crystallised hydrate of sodium oxide obtained by Terreil has the composition $Na_2O,(H_2O)_{3\cdot44}$, and by fusion in a platinum crucible it yields the hydrate $Na_2O,(H_2O)_{1\cdot14}$. According to the author, hydrates containing 1 H_2O are very rarely formed. C. H. B.

Platinised Magnesium as a Reducing Agent. By M. BALLO (*Ber.*, **16**, 694).—Pure water is not decomposed by magnesium, but if a trace of platinum chloride be added, decomposition takes place freely. The author recommends this as a very useful reducing agent for organic substances. L. T. T.

Dried Alum. By E. BAILEY (*Pharm. J. Trans.* [3], **13**, 838—839).—There has been some contention with regard to the dried alum of the B.P.; some say that it is almost insoluble in water, but recovers its solubility on boiling, others contend that it is slowly but completely soluble in water. From several experiments, the author comes to the following conclusions:—1. That commercial dried alum almost always leaves some insoluble residue varying from 6·5 to 0·5 per cent. 2. That boiling increases the quantity of insoluble matter. 3. That when alum is dried carefully, not exceeding the limit allowed by the Pharmacopœia (400° F.), a freely but slowly soluble product is obtained; and he therefore asserts that dried alum ought to be soluble, the insolubility being solely due to carelessness in preparation.

Judging from his samples, he remarks that it is apparent that potassium alum has replaced ammonium alum in the preparation in commerce. D. A. L.

Thorium Sulphate. By E. DEMARÇAY (*Compt. rend.*, **96**, 1859—1862).—A dilute neutral solution (0·5 per cent.) of thorium sulphate becomes turbid when heated, and at 100° deposits a flocculent basic salt, the formation of which is prevented by the presence of a very small quantity of free acid. The composition of this salt has not yet been determined. A solution of the crystallised sulphate, $Th(SO_4)_2,9H_2O$, in 10 or 15 times its weight of water, is converted at 60° into a spongy mass which if heated at 100° for 24—48 hours, changes to a pulverulent precipitate, which no longer dissolves on cooling. This precipitate has the composition $3Th(SO_4)_22H_2O + Th(SO_4)O,2H_2O$. The quantity of thorium remaining in solution is very small, and varies with the proportion of water present, and with other conditions. The formation of the basic salt is prevented to some extent by the presence of 3—4 per cent. of free acid. The basic salt when once formed is almost unaltered by cold water, and is only slowly attacked by acids.

The solubility in water of the hydrate, $Th(SO_4)_2,9H_2O$, increases with the temperature up to 55°, at which point the solution becomes turbid. The hydrate, $Th(SO_4)_2,4H_2O$, described by Chydenius, and probably identical with the hydrate, $2Th(SO_4)_2,9H_2O$, of Delafontaine, is readily obtained by heating the preceding hydrate for some time at 100° in presence of dilute sulphuric acid (5 per cent.). The solubility of this hydrate diminishes as the temperature increases from 17° to

100°, but above 60° the results are affected by the decomposition of the salt. It would appear that a solution of the hydrates of thorium sulphate contains, at a given temperature, a definite quantity of each hydrate, the relative proportions of the different hydrates depending on the temperature. C. H. B.

Solubility of Cupric Sulphide in Alkaline Thiomolybdates. By DEBRAY (*Compt. rend.*, **96**, 1616—1617).—Cupric sulphide dissolves somewhat easily in solutions of alkaline thiomolybdates, the maximum solubility corresponding with the formation of a definite cupric thiomolybdate. On adding hydrochloric acid to the solution, copper thiomolybdate is precipitated. Prolonged boiling of a solution of cupric sulphide in ammonium thiomolybdate causes the precipitation of a crystalline double copper ammonium thiomolybdate, slightly soluble in water. This double thiomolybdate is green by reflected, red by transmitted, light. C. H. B.

Colloidal Copper Sulphide. By L. T. WRIGHT (*Ber.*, **16**, 1448). —A question of priority.

Hydrogen Gold Chloride. By J. THOMSEN (*Ber.*, **16**, 1585—1587).—According to previous researches of the author, this compound crystallises with 4 mols. H_2O (*Ber.*, **10**, 1633); whereas, according to Schottländer (this vol., p. 853), it contains only $3H_2O$. The author has repeated his experiments, and finds that hydrogen gold chloride does crystallise with $4H_2O$, but that it gradually loses 1 mol. on exposure to dry air. A. K. M.

Separation of Gallium. By L. DE BOISBAUDRAN (*Compt. rend.*, **96**, 1696—1698, 1838—1840).—*From Iridium.*—(1.) The gallium is precipitated by potassium ferrocyanide in presence of a large excess of hydrochloric acid, the precipitate decomposed by potash, dissolved in hydrochloric acid, and the precipitation repeated two or three times. (2.) The gallium is precipitated from a hot solution by cupric hydroxide, the traces of iridium in the precipitate being removed by repeated precipitation. (3.) Metallic copper and cuprous oxide may be used instead of cupric hydroxide. (4.) The chlorides or sulphates of gallium and iridium are carefully heated to dull redness with a considerable excess of potassium hydrogen sulphate, and the mass dissolved in boiling water. The cold solution is then nearly neutralised with potash and allowed to stand, when the greater part of the iridium is precipitated as iridium potassium sulphate (this vol., p. 905). The precipitate is washed with a slightly acid solution of potassium sulphate, and the filtrate and washings are mixed, almost neutralised with potash, and boiled for 15 to 30 minutes in contact with the air. The liquid is then rendered alkaline and the boiling continued for some time, when iridium oxide is precipitated and gallium remains in solution. Traces of gallium in the precipitate are removed by repetition of the process.

From Ruthenium.—(1.) The ruthenium is precipitated as sulphide by passing hydrogen sulphide for some time into the boiling solution strongly acidified with hydrochloric acid. The precipitate is washed with a solution of hydrogen sulphide acidified with hydrochloric acid. (2.) The solution is mixed with a slight excess of potassium hydroxide and boiled for some time. The precipitate is dissolved in hydrochloric acid, and the precipitation repeated two or three times in order to remove traces of gallium. The gallium is precipitated from the filtrate by cupric hydroxide. (3.) The gallium is precipitated as ferrocyanide in presence of a large excess of hydrochloric acid. If the ruthenium and gallium exist in an insoluble substance, the latter is fused at a dull red heat in a gold crucible with a mixture of potassium nitrate and hydroxide, the fused mass treated with water, the solution acidified with hydrochloric acid and boiled, and the ruthenium and gallium separated by one of the three methods.

From Osmium.—The osmium is precipitated as sulphide by passing hydrogen sulphide for some time into the strongly acid solution, which is gradually heated to boiling. The filtrate, even if colourless, may retain traces of osmium, which are removed by evaporating the liquid to a small bulk (a slow current of hydrogen sulphide being passed through), then adding a small quantity of solution of hydrogen sulphide, and filtering off the precipitate. This method is applicable to both osmic acid and osmic chloride.

From Arsenic.—The arsenic is precipitated as sulphide from the strongly acid solution, and the precipitate is washed with dilute hydrochloric acid.

From Selenium.—The selenium, which should be in the state of selenious acid, is either precipitated as sulphide from a hot strongly acid solution, or is reduced by passing sulphurous anhydride into the hot solution acidified with hydrochloric acid. C. H. B.

Oxidation of Titanic Acid. By A. PICCINI (*Gazzetta*, **13**, 57—65).—Pure titanic acid prepared from rutile, or from the tetrachloride by precipitation with ammonia, is dissolved in sulphuric acid, and digested in the cold with pure crystallised barium peroxide in excess, which may be recognised by the solution containing hydrogen peroxide. The deep-red solution thus obtained is filtered to remove barium sulphate, and partially precipitated with an alcoholic potash solution (1 : 10); this precipitate, when washed and dried, is of a deep yellow colour. On adding more potash solution to the filtrate, a precipitate is thrown down which is more flocculent than the first, and when dried forms a bright yellow powder, with a slightly greenish tinge. These both contain water and titanic acid, with excess of oxygen, which they lose when strongly heated, leaving titanic acid behind. On boiling them with water, oxygen is evolved, and a white powder is left. They dissolve in sulphuric acid, yielding solutions of the colour of potassium dichromate, and with hydrochloric acid they evolve chlorine. The sulphuric acid solution may be concentrated by slow evaporation, but at a certain stage oxygen begins to be evolved and the solution is gradually decolorised, and a white gelatinous mass is left. With hydrofluoric acid the precipitates give colourless solutions containing hydrogen peroxide. The sulphuric acid solution gives a white precipitate of normal potassium fluotitanate with potassium fluoride; a yellowish precipitate with disodium phosphate, provided the solution be not too acid; liberates iodine from alkaline iodides; and decolorises potassium permanganate with liberation of oxygen.

The proportion of oxygen to titanic acid was determined either by the amount of permanganate required to decolorise the solution, or by means of ammonioferrous sulphate, the titanic acid being subsequently precipitated by boiling the dilute solution; or the estimations were made directly by heating the substance in a vacuum, measuring the amount of oxygen evolved, and weighing the residue of titanic acid. In this way it was found that the first precipitate of a deep yellow colour contained about 5·0 per cent. oxygen, corresponding with the ratio $4TiO_2 : O$, whilst the second pale yellow precipitate contained 10 per cent., corresponding with $2TiO_2 : O$. This applies only to the freshly-prepared precipitates: if they are dried they lose oxygen, the deep yellow precipitate ultimately approximating to the ratio $5TiO_2 : O$. The author also obtained another compound, in which the ratio was $3TiO : O$.

When pure hydrogen peroxide solution is added to a solution of titanic acid, or of either of the two yellow precipitates in sulphuric acid, until it is in very slight excess (as may be seen by the fugitive bluish cloud produced on testing it with a drop of potassium dichromate solution), a red liquid is obtained, in which the proportions of titanic acid and oxygen are represented by $TiO_2 : O$.

If we leave out of consideration the water present in these various compounds, we have the following series of acids:—

$$4TiO_2,TiO_2 = Ti_5O_{11}.$$
$$3TiO_2,TiO_3 = Ti_4O_9.$$
$$2TiO_2,TiO_3 = Ti_3O_7.$$
$$TiO_2,TiO_3 = Ti_2O_5.$$
$$TiO_3.$$

These results establish the existence of coloured unstable compounds in which titanic acid is combined with more or less oxygen, and the author is inclined to place titanium in the periodic system, thus:

Ti. V. Cr.

It is known that the vanadates are coloured red by hydrogen peroxide, and the study of this reaction may possibly reveal the existence of a peroxide more stable than that of titanium. C. E. G.

Atomic Weight of Antimony. By J. Bongaril (*Ber.*, **16**, 1942—1945).—The author at the commencement of his paper reviews the various methods proposed for the determination of the atomic weight of antimony, their incidental errors, and their results. The process adopted by him consists in the oxidation of the sulphide by ammoniacal hydrogen peroxide as suggested by Classen (this vol., p. 934), and precipitation in the form of barium sulphate. Metallic antimony was first prepared by the electrolysis of a solution of the sulphide in excess of ammonium sulphide, and purified by fusion with sodium carbonate. The regulus was washed with dilute hydrochloric acid, cleansed with sand, and dried. The metal was dissolved in potassium sulphide, and the solution precipitated with sulphuric acid. The precipitated sulphide was then oxidised by hydrogen peroxide, in an apparatus of the form proposed by Classen, and the solution precipitated by barium chloride. The results of twelve determinations (Ba = 136·8, S = 31·98, O = 15·96) gave a mean of 120·193, the number varying from a minimum 120·09 to a maximum 120·39.

V. H. V.

Chemistry of the Platinum Metals. By T. Wilm (*Ber.*, **16**, 1524—1531).—This is a continuation of work previously published by the author (Abstr., 1880, 854, and 1881, 514). On treating precipitated platinum residues with chlorine and sodium chloride according to Wöhler's method, a black powder is obtained which resists further action of these reagents. It is readily acted on by fused sodium carbonate, and on exhausting the melt with water, filtering, and evaporating, a grey powder is obtained soluble in hydrochloric acid. After oxidising the solution with nitric acid and adding ammonium chloride, a crystalline precipitate can be obtained on evaporation, which is probably a mixture of ruthenium ammonium chloride and iridium ammonium chloride. On treating the insoluble residue from the melt with hydrochloric acid, a portion is dissolved, yielding a solution from which a double salt of ammonium chloride can be obtained forming blackish-violet crystals closely resembling those of iridium ammonium chloride. The mother-liquor yields, on evaporation in a desiccator, brownish-yellow crystals, consisting of a double salt of iron with a platinum-metal (ruthenium ?). The blackish-violet crystals abovementioned are, however, distinguished from the iridium salt by their greater transparency, by their more ready solubility in water, and by certain reactions, such as that with ammonia. Its properties also do not agree with those of ruthenium ammonium chloride. The abnormal reactions are probably due to the presence of a peculiar compound of rhodium and iron, and perhaps of an unknown metal.

A. K. M.

Violet Iridium Sulphate. By L. de Boisbaudran (*Compt. rend.*, **96**, 1551—1552).—The pale blue colour produced by adding potassium hydroxide to a cold solution of green iridium sulphate (this vol., p. 905) is due to the formation of a bulky pale blue precipitate which contracts to a greenish powder, and gradually becomes blue-violet in colour. This change of colour is due to oxidation. When a boiling solution of potassium hydroxide is added to a boiling solution of the green iridium sulphate, only a very faint violet tint is at first produced, but if the liquid is agitated in contact with air, the blue-violet colour is gradually developed. The change of colour does not take place in an atmosphere of hydrogen, and if a current of hydrogen is passed through the liquid containing the blue-violet oxide, the latter is decolorised. Sulphurous acid changes the colour of the blue-violet sulphate to blue, and finally decolorises it. An aqueous solution of the deep violet sulphate becomes almost colourless on prolonged boiling, but on adding potassium hydroxide the colour reappears and an abundant blue-violet precipitate is formed, soluble in dilute sulphuric acid. The same changes take place in the cold, although more slowly.

Hydrochloric acid dissolves the blue-violet oxide, forming a deep violet liquid, which gradually becomes blue, then green, and finally orange-yellow, the change being accelerated by heat. If the blue-violet oxide is dried, or is subjected to prolonged ebullition, it becomes partly insoluble in dilute sulphuric acid. C. H. B.

Contributions to the Chemistry of the Rhodammonium Compounds. By S. M. Jörgensen (*J. pr. Chem.* [2], **27**, 433—489).—I. *Chloropurpureorhodium Salts.* — *Chloropurpureorhodium chloride*, $Cl_2(Rh_2,10NH_3)Cl_4$, is prepared by evaporating a solution of rhodium chloride and ammonium. It crystallises best from a solution containing a trace of free hydrochloric acid, when it forms small yellow rhombic crystals isomorphous with the corresponding cobalt salt (sp. gr. at 18·4, 2·075). They can be heated for a day at 100° without losing weight. When heated in dry chlorine, they yield rhodium chloride; in dry hydrochloric acid gas metallic rhodium is produced. Chloropurpureorhodium chloride does not part with all its chlorine when treated with silver nitrate. When ground with an excess of freshly precipitated silver oxide, it yields a strongly alkaline yellow solution, containing chloropurpureorhodium hydroxide and traces of roseorhodium hydroxide; the former is a base resembling potassium hydroxide, and when heated yields a mixture of roseorhodium chloride and roseorhodium hydroxide. Roseorhodium salts are very readily detected by means of potassium ferrocyanide. *Chloropurpureorhodium nitrate*, $Cl_2(Rh_2,10NH_3)4NO_3$, is prepared by pouring a hot solution of the chloropurpureo-chloride into well-cooled concentrated nitric acid. The precipitate so obtained consists of small octohedral crystals. They are only sparingly soluble in water. When boiled with soda solution they form the roseo-salt. *Chloropurpureorhodium silicofluoride*, $Cl_2(Rh_2,10NH_3)2SiF_6$, is obtained when a hot solution of the chloride (60°) is filtered into an excess of strong hydrofluosilicic acid. It forms glittering rhomboïdal plates of a straw-yellow colour. It is isomorphous with the corresponding cobalt and chromium salts. The salt remains unaltered at 100°; and when heated to redness it leaves rhodium oxide. *Chloropurpureorhodium platinochloride*, $Cl_2(Rh_210NH_3),2PtCl_6$, is a buff-coloured precipitate insoluble in cold water. It is isomorphous with the corresponding cobalt and chromium salts. *Chloropurpureorhodium sulphate*, the acid salt, $2Cl_2(Rh_2,10NH_3)2SO_4,3H_2SO_4$, is prepared by grinding the chlorochloride with concentrated sulphuric acid. On diluting the mixture and allowing it to cool, glittering yellow prismatic crystals separate out. They are slightly soluble in cold water. *The normal salt*, $Cl_2(Rh_2,10NH_3)2SO_4,4H_2O$, is obtained by neutralising the chloropurpureo-hydroxide with dilute sulphuric acid. It crystallises in sulphur-coloured prisms. *Chloropurpureorhodium carbonate*,

$$Cl_2(Rh_2,10NH_3)2CO_3,2H_2O,$$

is prepared by grinding the chlorochloride with silver carbonate freshly precipitated from an acid solution. It forms a bright yellow crystalline powder.

II. *Bromopurpureorhodium Salts.—Bromopurpureorhodium bromide*, $Br_2(Rh_2,10NH_3)Br_4$, can be prepared by heating rhodium zinc with a solution of bromine in hydrobromic acid, and subsequently proceeding as in the preparation of the chloro-compound. It is more conveniently obtained by treating the basic roseorhodium salt, formed by heating the chloropurpureo-chloride with soda solution, with hydrobromic acid, and then heating the roseorhodium bromide so formed at 100°, or boiling the aqueous solution. The bromo-bromide forms yellow rhombic crystals. It is more sparingly soluble in water than the chloropurpureo-chloride. It only loses traces of hygroscopic moisture when heated at 100°. It closely resembles the chloropurpureo-chloride in all its reactions. *Bromopurpureorhodium nitrate*, $Br_2(Rh_2,10NH_3)4NO_3$, is prepared in a similar manner to the chloropurpureo-salt. It crystallises from water in large octohedra. *Bromopurpureorhodium silicofluoride*, $Br_2(Rh_2,10NH_3)2SiF_6$, is prepared in a similar manner to the chloro-compound. The *platino-bromide* is obtained by filtering a solution of the bromo-bromide into sodium platino-bromide.

III. *Iodopurpureorhodium Salts.—Iodopurpureorhodium iodide*,

$$I_2(Rh_2,10NH_3)I_4,$$

is prepared by treating a solution of roseorhodium hydroxide with hydriodic acid, and heating the mixture for about two hours on a water-bath. When pure, it forms small rhombic crystals with a colour resembling that of potassium dichromate. They are more soluble in hot water than in cold. When boiled with soda, it is converted into the roseo-salt. On triturating it with moist silver oxide, a strongly alkaline yellow solution is obtained, which doubtless contains iodopurpureo-hydroxide.

Iodopurpureorhodium chloride, $I_2(Rh_2,10NH_3)Cl_4$, is, when dry, a dark yellow crystalline powder. It is freely soluble in hot water, but insoluble in hydrochloric acid and in alcohol. *Iodopurpureorhodium nitrate*, $I_2(Rh_2,10NH_3)4NO_3$, is prepared by filtering a solution of the iodochloride into dilute nitric acid. It crystallises from hot water in small octohedra. *Iodopurpureorhodium silicofluoride*, $I_2(Rh_2,10NH_3)2SiF_6$, is formed when a warm solution of the iodochloride is filtered into strong cold hydrofluosilicic acid. It forms bright glittering yellow plates, which are almost insoluble in cold water. *Iodopurpureorhodium platino-iodide*, $I_2(Rh_2,10NH_3)2PtI_6$, is prepared by treating the iodochloride with calcium platino-iodide. It forms a black precipitate consisting of masses of small crystals. It is quite insoluble in water and in alcohol. *Iodopurpureorhodium sulphate.*—The hydrated normal salt, $I_2(Rh_2,10NH_3)2SO_4 + 6H_2O$, is obtained by grinding together 3·6 grams of precipitated iodochloride and 10 grams of concentrated sulphuric acid; the product is then dissolved in 40 c.c. of water, and 1 c.c. of alcohol added to the solution. After 24 hours large orange-yellow crystals separate out. The anhydrous salt is formed when a larger quantity of alcohol is present. It forms orange-yellow quadratic plates.

IV. *Dichloropyridine Rhodium Salts.—Dichlorotetrapyridine-rhodium chloride*, $Cl_4(Rh_2,8C_5H_5N)Cl_2$, is prepared by dissolving rhodium-zinc in aqua regia, and, after removing the nitric acid, heating the aqueous solution with pyridine; on cooling, the solution deposits the pyridine salt in yellow prisms. The salt melts when heated and forms a black oil, which leaves metallic rhodium on being heated to redness. When the salt is ground with freshly precipitated moist silver oxide, it yields a yellow strongly alkaline solution containing dichlorotetrapyridine-rhodium hydroxide; this absorbs carbonic anhydride from the air, and evolves ammonia from solutions of its salts. *The dichloronitrate*, $Cl_4(Rh_2,8C_5H_5N)2NO_3$, is obtained by filtering a solution of the chloride into dilute nitric acid. *The dichloro-bromide*,

$$Cl_4(Rh_2,8C_5H_5N)Br_2,$$

is prepared in a manner similar to the nitrate. *The dichloro-sulphate*, $Cl_4(Rh_2,8C_5H_5N)SO_4$, is precipitated from a saturated aqueous solution of the chloride on adding dilute sulphuric acid. It can also be prepared in a manner similar to iodopurpureorhodium sulphate. *The platinochloride*, $Cl_4(Rh_2,8C_5H_5N)PtCl_6$, forms a buff-coloured crystalline powder.

V. *The Atomic Weight of Rhodium.*—Chloropurpureorhodium chloride and the corresponding bromine compound can be readily prepared in a state of great purity; and as the other elements which they contain, in addition to rhodium, are such as have had their atomic weights accurately ascertained, the author considered that they offered an excellent opportunity to determine the atomic weight of rhodium. The amount of rhodium contained is readily determined by simply heating in the air, and afterwards in hydrogen and carbonic anhydride. The mean result of five determinations made by the author gives 103·04 as the atomic weight of rhodium. J. I. W.

Mineralogical Chemistry.

Application of a Solution of Barium and Mercury Iodide to Petrographical Purposes. By C. Rohrbach (*Jahrb. f. Min.*, 1883, **2**, Mem., 186—188).—Instead of a solution of mercury iodide with the alkali iodides, the author employed a solution of barium-mercury iodide for the preparation of heavy solutions, for which a still higher sp. gr. than that of Thoulet's solution was to be expected, seeing that the atomic weight of barium is so much greater than that of potassium. In practice he found that the new solution gave a maximum sp. gr. of 3·588. B. H. B.

Optical Properties of Nocerine. By E. Bertrand (*Jahrb. f. Min.*, 1883, **2**, Ref., 160).—Nocerine is the name given by Scacchi to the double fluoride of calcium and magnesium. It occurs in extremely small hexagonal crystals, which the author observed to be optically uniaxial and negatively double refracting. B. H. B.

Analyses of Magnetic Pyrites. By C. BODEWIG (*Jahrb. f. Min.*, 1883, **2**, Ref., 161).—The author found that freshly distilled carbon bisulphide dissolved 0·01 to 0·021 gram of sulphur from 10 grams of the magnetic pyrites from Bodenmais, while the magnetic pyrites from Schreibershau and crystallised magnetic pyrites from Pallanza gave up no sulphur. The magnetic pyrites from the three localities were treated with carbon bisulphide, dried, and very carefully analysed. The results were as follows:—

1. Magnetic pyrites from Bodenmais contained 38·45 per cent. of sulphur and 61·53 per cent. of Fe, corresponding to the formula $Fe_{11}S_{12}$.

2. Magnetic pyrites from Schreibershau, in Silesia, gave 38·560 per cent. sulphur, 61·325 Fe, and 0·290 Co. Then Fe + Co : S = 1·1019 : 1·2057 = $Fe_{11}S_{12}$.

3. Magnetic pyrites from Pallanza gave 38·75 per cent. S, 60·59 Fe, 0·63 Co. Then Fe + Co : S = 1·0964 : 1·2117 = $Fe_{11}S_{12}$.

B. H. B.

Tinder Ore from the Harz. By O. LUEDECKE (*Jahrb. f. Min.*, 1883, **2**, Mem., 116—118).—Tinder ore is found at Clausthal and St. Andreasberg in the Upper Harz, and at Wolfsberg in the Lower Harz. Hausmann regarded it as a mixture of 82·04 plumosite, 13·46 mispickel, and 4·3 red silver ore. Roesing (Abstr., 1881, p. 24) regarded it as a lead antimony sulphide, and showed that the analysis agreed with the formula $Pb_4Sb_6S_{17}$, the lead being partially replaced by Cu, Fe, Ag, and Zn. He inferred that it was the final product of the decomposition of an antimonial galena. The author, after a microscopic examination of the tinder ore from Clausthal, comes to the conclusion that it is not a mixture, but a distinct mineral, the composition of which is expressed by the formula $(PbAgFeZnCu)_4Sb_6S_{17}$.

B. H. B.

Brucite from Cogne. By C. FRIEDEL (*Jahrb. f. Min.*, 1883, **2**, Ref., 161).—The analysis of the brucite from Cogne, in the Aosta Valley, after the removal of a small amount of silica, gave the following results:—

MgO.	FeO.	H_2O.	Total.
68·53	1·15	30·18	99·81

B. H. B.

Brucite. By A. WEISBACH (*Jahrb. f. Min.*, 1883, **2**, Mem., 119—120).—A boiler incrustation from Zwickau gave on analysis the following results:—

MgO.	Fe_2O_3.	SO_3.	SiO_2.	H_2O.	Total.
66·09	0·31	3·49	1·31	28·80	100·00

This represents 93·15 per cent. of magnesium hydroxide, so that brucite is the main constituent.

The feed-water of the boiler contained 0·5306 per cent. of fixed constituents, the greater portion of which was magnesium chloride.

B. H. B.

The Inclusions in Sapphire, Ruby, and Spinel. By W. PRINZ (*Jahrb. f. Min.*, 1883, **2**, Ref., 156—157).—The sapphire contains numerous inclusions of liquid carbonic anhydride in large cylindrical cavities, the longitudinal axis of which is perpendicular to the main axis of the crystal or in the form of the crystal itself. In the ruby these large fluid inclusions are almost entirely wanting. Small ones occur only to a slight extent; they also contain liquid carbonic anhydride. In the inclosed fluids crystal needles, small opaque hexagonal tablets, and more rarely tetrahedrons are met with. On the other hand, as Sorby showed, the ruby is very rich in solid enclosures. Sorby distinguished four varieties, which may, according to the author, be referred to two kinds: (1) rutile, and (2) doubly refracting round grains, rhombohedral and columnar crystals, which are regarded as microscopic rubies and sapphires according to their colour. The spinel is characterised by frequently enclosing two fluids which do not mix, a colourless one and a dark orange one. These fluids frequently contain small cubes, doubly refracting prismatic crystals, and an opaque black substance. The yellow fluid appears to be viscous, and is regarded as a very concentrated salt solution. The colourless fluid does not expand like liquid carbonic anhydride. When heated strongly, the yellow fluid becomes converted into an aggregate of doubly refracting crystals, while the colourless fluid is enclosed in drops in the yellow material. When heated more slowly, the crystals thus separated out dissolve, and the isolated drops of the colourless fluid combine again. At a lower temperature, the yellow fluid again crystallises.

B. H. B.

Artificial Production of Barytes, Celestine, and Anhydrite. By A. GORGEU (*Compt. rend.*, **96**, 1734—1737).—The artificial production of hausmannite (this vol., p. 859) is not impeded by the presence of iodine or bromine, or of the chlorides of the alkalis or alkaline earths, and the product retains only very small quantities of these foreign substances. The sulphates of barium, strontium, and calcium dissolve quickly in many fused metallic chlorides, and by gradually cooling the fused mass and extracting the residue with water, barytes, celestine, and anhydrite are obtained in crystals identical in form and properties with those of the natural minerals. The crystals contain no chlorine, and the aqueous solution of the fused mass is free from more than traces of the alkaline earth.

C. H. B.

Optical Properties of Cobalt Carbonate. By E. BERTRAND (*Jahrb. f. Min.*, 1883, **2**, Ref., 161).—The small rhombohedrons of this mineral are optically uniaxial with negative double refraction. A section parallel to *c* showed distinct pleöchroism.

B. H. B.

New Locality for Hayesine, and its Novel Occurrence. By N. H. HARTON (*Amer. J. Sci.*, 1882, **23**, 458—459; *Jahrb. f. Min.*, 1883, **2**, Ref., 161—162).—Hayesine occurs at Bergen Hill, New

Jersey, with datholite and calcite in cavities in the trap rock. The analysis gave the following results:—

CaO.	B_2O_3.	H_2O.	SiO_2. Na_2O. MgO.	Total.
18·39	46·10	35·46	trace	99·95

The sp. gr. was between 1·5 and 1·7. The analysis corresponds to the formula: $CaB_2O_7 + 3H_2O$. B. H. B.

Two New Minerals, Monetite and Monite, with a Notice of Pyroclasite. By C. U. Shepard (*Amer. J. Sci.*, 1882, **23**, 400—405).—The prevailing rock of the islands of Moneta and Mona, in the West Indies, is a tertiary limestone covered with guano, and the two minerals were formed by infiltration. The monetite crystallises in the triclinic system. The general form is that of a thin rhomboid. The fracture is uneven. The mineral is semitransparent, has a vitreous lustre, and a pale yellowish-white colour; H. = 3·5; sp. gr. = 2·75. The chemical analysis corresponds to the formula:

$$2CaO,H_2O,P_2O_5.$$

The analysis of *monite* corresponded to the formula $Ca_3P_2O_8 + H_2O$. This mineral resembles kaolin in colour and density. Its fracture is earthy; hardness below 2, and sp. gr. 2·1. Before the blowpipe it melts with difficulty to an opaque white enamel.

Two stalactites of *pyroclasite* were found in the same caves as monite and monetite. They strongly resemble the impure stalactites of our limestone caves. The sp. gr. is 2·62, H. 3·5—4. Before the blowpipe it decrepitates, emits a decidedly organic odour, and fuses to a white enamel. The chemical analysis corresponds with the formula:

$$3(Ca_2H_2P_2O_8) + Ca_3P_2O_8 + H_2O.$$

Whether this forms a true mineral species, or is only a mechanical mixture of monetite and monite, must be determined by more extended examination. B. H. B.

Analysis of a Pyromorphite from Zähringen in Baden. By C. Baerwald (*Jahrb. f. Min.*, 1883, **2**, Ref., 152).—This mineral occurs in a concentric aggregate covered by a brown layer. It has been called *eusynchite*. The analysis gave:—

SiO_2.	PbO.	ZnO.	V_2O_3.	P_2O_5.	Al_2O_3.	CaO.	Cl.	Total.
3·70	76·39	1·39	3·05	11·24	1·93	0·21	1·40	99·31

B. H. B.

Analysis of Crocoisite. By C. Baerwald (*Jahrb. f. Min.*, 1883, **2**, Ref., 152).—The analysis of crocoisite from Berjósowsk gave the following results:—

PbO.	Cr_2O_3.	Total.
68·82	31·16	99·98

B. H. B.

Notes on some North Carolina Minerals. By W. E. Hidden (*Jahrb. f. Min.*, 1883, **2**, Ref., 148—149; *Amer. J. Sci.*, 1882, **24**, 372—374).—A remarkable crystal of *beryl* was found lying loose in the surface-soil on the land known as Pendergrass land. The large development of the planes, $3P\frac{3}{2}$ and $4P\frac{4}{3}$ is unprecedented. Other planes observed were:—P, 2P, 2P2, 0P, ∞P and ∞P2.

The mineral thought to be *aeschynite*, from Ray's mica mine, Yansey Co., proves, on analysis, to be columbite.

The sp. gr. of three different specimens of *uranite* from Mitchell Co. was found to be 8·968, 9·05, and 9·218.

An analysis was made of the so-called *euxenite* from Wiseman's mica mine, with results differing widely from those obtained by J. L. Smith:—

Nb_2O_5.	$SnO_2 + WO_3$.	Y_2O_3.	Ce_2O_3.	$Di_2O_3 + La_2O_3$.
47·09	0·40	13·46	1·40	4·00

U_2O_3.	FeO.	CaO.	H_2O.	Total.
15·15	7·09	1·53	9·55	99·67

The so-called euxenite is probably only altered samarskite.

An analysis of the fergusonite from the Brindletown gold placer gave the following results:—

Nb_2O_5.	Ta_2O_5.	$SnO_2 + WO_3$.	Y_2O_3, &c.	Ce_2O_3.
43·78	4·08	0·76	37·21	0·66

$Di_2O_3 + La_2O_3$.	U_2O_3.	FeO.	H_2O.	Total.
3·49	5·81	0·65	1·62	99·87

The form occurring is a very acute octohedron. The colour is brown-black, and sp. gr. 5·87.

The author has lately found *allanite* at two new localities, at the beryl locality and at Wiseman's mica mine. The mineral occurs in small well-polished prisms of a light brown colour in the felspar of the gneiss, and contains 14 per cent. La_2O_3. B. H. B.

New Sublimates from the Crater of Vesuvius. By A. Scacchi (*Jahrb. f. Min.*, 1883, **2**, Ref., 157—160).—Among the sublimates from Vesuvius in October, 1880, the author found four new ones on the same slag. The most important is of a bright blue colour, and mixed with this is always a white substance of granular structure, the former often covering the latter. A third species spreads over the slag in the form of a layer 2 to 4 mm. thick, formed of a white crystalline mass resembling cork. It appears to be a variety of hornblende. The fourth species consists of very thin yellowish-brown crystals firmly fixed to the slag or mixed with the other minerals. The white granular substance consists of amorphous, transparent, infusible and hard grains. At a red heat it loses 0·51 to 0·72 per cent. H_2O; sp. gr. = 2·287. All the reactions in the dry way indicate SiO_2. The author does not regard this mineral as opal, but as a special kind of amorphous silica. Silica has, up to the present time, rarely been observed at Vesuvius. It was found only in 1767, 1794, and 1860.

From the examination of another specimen formed in April, 1882, the author comes to the conclusion that the mineral is identical with the variety of silica which is obtained on decomposing silicates with acids, and for which he suggests the names of *granuline*.

B. H. B.

Calculation of Analyses of Augites and Amphiboles from Finland. By A. KENNGOTT (*Jahrb. f. Min.*, 1883, **2**, Mem., 171—172).—From the analyses given by Wiik (Abstr., 1883, 560) of augites and amphiboles from Finland, the author calculates that they correspond with the generally accepted formula RO,SiO_2. B. H. B.

Formation of Bauxite and of Pisolitic Iron Ore. By S. MEUNIER (*Compt. rend.*, **96**, 1737—1740).—Bauxite and pisolitic iron ore have probably been formed by the action of marble or limestone on water holding aluminium and ferric chlorides in solution. This reaction can readily be produced on a small scale. The aluminic and ferric chlorides are probably formed by the action of superheated water charged with chlorides on the rocks in the interior of the earth; this water would also dissolve from the older rocks the small quantities of titanium and vanadium usually found in bauxite, and might carry up with it the granitic sand with which bauxite is frequently associated. The clay mixed with the bauxite or limonite may have been formed by the alteration of limestone or by the partial decomposition of felspathic rocks. C. H. B.

Notes on some Interesting Minerals Occurring near Pike's Peak, Colorado. By W. CROSS and W. F. HILLEBRAND (*Amer. J. Sci.*, 1882, **24**, 281—286).—The following minerals have been found in this region:—Microcline, albite, biotite, quartz, fluorspar, columbite, göthite, hæmatite, limonite, arfvedsonite, astrophyllite, and zircon. The authors can now add to this list topaz, phenacite, cryolite, thomsenolite, and others not yet fully determined.

Three crystals of topaz have been examined, all of them remarkable for size and clearness. In the most perfect one the prisms ∞P and $\infty P\breve{2}$ are not developed. The terminations are drusy; the pyramid 2P has been recognised with certainty, while $\frac{4}{5}P$ and 2P4 are probably also present. The sp. gr. is 3·578, and the chemical composition normal.

The two crystals of phenacite examined were found together. The forms appearing have been identified as R, $-\frac{1}{2}R$, $-R$, and $\frac{2}{3}P2$. The crystallographic determination of these crystals as phenacite is confirmed by the chemical analysis and physical characteristics. There is an imperfect cleavage parallel to $\infty P2$. The crystals are clear and colourless; H. = 8; sp. gr. = 2·967.

Zircon was found in a vein of white quartz in granite. The crystals are of a deep reddish-brown colour, occasionally deep emerald-green. The crystals are perfectly developed and wonderfully transparent. The observed forms are P, 3P, 3P3, ∞P, and $\infty P\infty$. The rare face 0P is less frequently developed, and is constantly accompanied by a pyramid $\frac{14}{25}P$. The chemical analysis of the zircon shows it to be very pure, and the sp. gr. is 4·709. B. H. B.

Mineralogical Notes. By E. Claassen (*Amer. J. Sci.*, 1882, **23**, 67; *Jahrb. f. Min.*, 1883, **2**, Ref., 151).—1. *Analysis of Orthoclase.* —The orthoclase occurs in crystals on hæmatite at Isapemeng, Marquette County, Michigan. The forms observed were ∞P and 2P∞. The colour is white, reddish, and red. The reddish and red crystals contain:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.
63·712	17·546	1·644	0·714	0·172

K_2O.	Na_2O.	P_2O_5.	H_2O.	Total.
13·807	0·233	0·612	0·606	99·046

2. *Regular Polyhedral Cavities in Hæmatite.*—The author proves by measurement of the angles that the cavities observed in the micaceous hæmatite of Lake Superior once contained crystals of pyrites. Access of air and water effected their disappearance, and not the smallest particle of pyrites can now be met with. B. H. B.

Chemical Composition of a Green Mica from Syssert in the Ural Mountains. By A. Damour (*Jahrb. f. Min.*, 1883, **2**, Ref., 180—181).—The mineral is of an emerald-green colour, and has a sp. gr. of 2·88. The analysis gave:—

SiO_2.	Al_2O_3.	CrO_3.	Fe_2O_3.	MgO.	K_2O.	Volatile constituents.	Total.
46·17	29·71	3·51	2·03	2·28	10·40	5·42	99·52

B. H. B.

Saussurite. By A. Cathrein (*Jahrb. f. Min.*, 1883, **2**, Ref., 177—179).—The author examined microscopically and chemically a number of specimens of saussurite from Tyrol. The study of thin sections showed that numerous crystals of zoisite or, in some cases, epidote, occur in a colourless ground-mass. In several specimens, a gradual transition from zoisite to epidote could be observed. At Wildschönau, the author observed a gradual transition from saussurite to albite. The result of his researches is that the so-called saussurite is not a mineral species, but a mixture of plagioclase, more rarely of orthoclase, with zoisite, chlorite and other minerals occurring as accessory constituents. The chemical composition of the saussurite resembles mostly that of the lime-soda felspar, but is poorer in silica and richer in lime; saussurite also is distinguished from the members of the albite-anorthite series corresponding to it in chemical composition by a much higher sp. gr. The saussurite is a product of the alteration of the felspars by an interchange of silica and alkalis for lime, iron, and water. The conversion of the felspars into epidote is also a process of alteration which is intimately connected with the genesis of the saussurite, and which is only distinguished by taking up more iron. B. H. B.

Jadeite. By Krenner (*Jahrb. f. Min.*, 1883, **2**, Mem., 173—174). —From the examination of a nephrite-like mineral from Upper Burmah, the author came to the conclusion that it consisted of nephrite. This conclusion, however, does not agree with Damour's analyses

(*Ann. Chim. Phys.*, 1881), which give a percentage of 21 to 24 of alumina and 9 to 14 of soda, thus indicating that the mineral is jadeite. On comparing Damour's analyses with the author's examination, he concludes that the so-called jadeite is an entirely new mineral, a soda alumina augite, having the formula $Na_2Al_2Si_4O_{12}$.

B. H. B.

Nepheline in the Oligoclase of Dénise. By DES CLOIZEAUX and JANNETTAZ (*Jahrb. f. Min.*, 1883, **2**, 172—173).—In the basalt of Dénise in Haute-Loire enclosures of decomposed granite occur, containing cordierite and also glassy masses containing nepheline in large grains. Analyses of the nepheline (i) and of the accompanying oligoclase (ii) are given :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.
I.	43·18	33·50	—	1·50	—	0·90	18·61	0·80	98·49
II.	62·1	20·2	0·5	0·8	0·4	1·0	12·7	1·4	99·1

B. H. B.

Idocrase from Kedabék in the Caucasus. By O. KORN (*Jahrb. f. Min.*, 1883, **2**, Ref., 170—171).—This mineral occurs in greenish-yellow crystals, and in compact masses in limestone. The following forms were observed :—

$$P,\ 2P,\ 3P,\ P\infty,\ 2P2,\ 3P3,\ \infty P,\ \infty P\infty,\ \tfrac{9}{5}P,\ 4P,\ \tfrac{5}{4}P\tfrac{5}{4},\ \tfrac{17}{4}P\tfrac{17}{4}.$$

The last four are now observed in idocrase crystals for the first time. 3P3 often predominates. The chemical analysis gave the following results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	FeO.	MnO. K_2O.	H_2O.	Total.
36 81	15·46	5·42	35·57	3·66	0·69	traces	2·06	99·67

Sp. gr. = 3·25. From this analysis is calculated the formula—

$$8RO,2R_2O_3,7SiO_2 + 1\tfrac{1}{4}H_2O.$$

B. H. B.

Discovery of Fluorine in the Idocrase from Vesuvius. By P. JANNASCH (*Jahrb. f. Min.*, 1883, **2**, Mem., 123—135).—The analysis of idocrase from Vesuvius gave the following results :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
36·81	16·42	3·00	2·07	0·66	36·22	2·17

H_2O.	F.	Li_2O.	K_2O.	Na_2O.	Total.
1·57	1·06	0·08	trace	0·42	100·48

The presence of fluorine is not confined to the Vesuvian idocrase, for the author found 1·23 per cent. in the idocrase from Christiansand in Norway, and 0·23 per cent. in the variety from the River Wilui in Siberia. He was, however, unable to find any in the idocrase from the Ala valley, recently investigated by Ludwig and Renard.

B. H. B.

Analysis of a Green Pyroxene from the Diamond Mines of the Cape. By JANNETTAZ (*Jahrb. f. Min.*, 1883, **2**, Ref., 170).—This mineral resembles diopside in its optical properties. It has a distinct basal cleavage. H. = 5·5, and sp. gr. = 3·26. It gave on analysis:—

SiO_2.	Cr_2O_3.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
52·4	2·8	0·6	6·5	20·5	15·5	1·5	99·8

The mineral is, therefore, a chromium-diopside. B. H. B.

Chemical Composition of Walujewite. By D. P. Nicolajew (*Jahrb. f. Min.*, 1883, **2**, Ref., 181—182).—The analysis of this mineral gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.	Total.
16·39	43·40	1·57	0·60	20·38	13·04	4·39	99·77

Sp. gr. = 3·075. B. H. B.

Nephrite. By W. v. Beck and J. W. v. Muschketow (*Jahrb. f. Min.*, 1883, **2**, Ref., 171—172).—The authors give microscopic descriptions and analyses of a large number of nephrites from various localities, and come to the conclusion that all the nephrites from the province of Irkutsk and from Turkestan must, from their chemical composition and sp. gr., be regarded as actinolites and not as diopsides. The nephrites from the Jarkand valley may be distinguished from the Siberian varieties by greater homogeneity in the structure, by a smaller percentage of FeO and absence of chromite, by enclosures of diopside, and by a cloudy milky appearance. The Siberian nephrites, on the other hand, are characterised by the presence of chromate and limonite and enclosures of asbestos. B. H. B.

Chemical Composition of Diallage. By A. Cathrein (*Jahrb. f. Min.*, 1883, **2**, Ref., 180).—The results obtained from the analysis of three specimens of diallage were as follows:—I and II are from Wildschönau in Tyrol, III from Ehrsberg in Baden.

	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.	Sp. gr.
I.	49·25	0·70	5·60	0·20	0·45	7·15	21·31	14·41	0·82	1·86	0·30	102·05	3·343
II.	50·41	0·88	4·05	0·60	0·11	6·57	21·34	15·33	0·42	1·55	0·37	101·63	3·337
III.	51·34	0·58	5·35	0·43	0·48	4·42	21·12	14·08	0·15	0·84	0·70	99·49	3·178

B. H. B.

Analyses of Humite. By A. Kenngott (*Jahrb. f. Min.*, 1883, **2**, Mem., 174—176).—In Sjögren's analyses of minerals of the chrondrodite groups (Abstr., 1883, 436), the loss is so great as to render the analyses unsuitable for the calculation of formulæ. They are, however, valuable in confirming the view that all these minerals contain more than 2R to 1Si, if they are compared with olivine, and that the percentage of fluorine is variable and is not, as Rammelsberg states, essential to the group. B. H. B.

Pseudomorph of Nacrite after Fluorspar. By F. E. GEINITZ (*Jahrb. f. Min.*, 1883, **2**, Ref., 160—161).—In his memoir on mineral pseudomorphs (Abstr., 1877, **1**, 691), the author described a crystal of fluorspar partially filled with nacrite. At that time he regarded the nacrite as originally deposited there. Further studies have now led him to believe that it is an alteration-product of the fluorspar.

B. H. B.

Analysis of the Mansfeld Copper Slate. By SCHEERER (*Jahrb. f. Min.*, 1883, **2**, Ref., 197—198).—The analysis of a sample of unburnt copper slate from the Ernst mine gave—

SiO_2.	Al_2O_3.	CaO.	MgO.	CO_2.	Fe.	Cu.	Ag.	S.	Bitumen.
33·15	12·90	14·39	2·32	10·47	3·31	2·90	0·016	2·15	9·89

B. H. B.

Dioritic Rocks of Klausen in South Tyrol. By F. TELLER and C. v. JOHN (*Jahrb. f. Mim.*, 1883, **2**, Ref., 200—205).—The eruptive masses in the neighbourhood of Klausen are composed of triclinic felspar, enstatite, hypersthene, diallage, augite, biotite, magnetite, apatite, and generally free quartz. The plagioclase from a granular norite rock proved on analysis to be intermediate between labradorite and andesine. The rocks are partly quartz-mica-diorites, partly norites and partly norite-porphyrites; these types being connected by various intermediate members. An analysis is given of a granular norite from Oberhofer (I). This rock is composed of diallage, augite, biotite, hypersthene and a little quartz, passing over into the norite porphyrite. (Analysis II.) A quartz norite from the Vildarthal was also analysed (III.): from this rock, the quartz-mica-diorites are developed by the retirement of the pyroxenes. An analysis of a quartz-mica-diorite, also from the Vildarthal, is given (IV). The difference in the eruptive magma is very great, it has an acid dioritic character in the larger masses and in the central portions, while in the narrower veins and on the periphery of the principal mass it has a basic noritic character.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.
I.	56·72	16·90	4·14	6·28	7·25
II.	56·85	16·70	5·92	7·13	5·97
III.	59·97	16·93	2·41	4·83	5·10
IV.	70·17	11·10	1·92	2·86	3·34

	MgO.	Na_2O.	K_2O.	Loss on ignition.	Total.
I.	4·62	4·65	0·63	0·75	101·94
II.	3·25	2·78	1·91	0·54	101·05
III.	3·61	3·87	1·32	1·60	99·64
IV.	1·23	3·77	3·23	1·87	99·49

B. H. B.

Metalliferous Vein Formation at Sulphur Bank. By J. Le Conte and W. B. Rising (*Jahrb. f. Min.*, 1883, **2**, Ref., 195—197).—The attention of geologists has been called by J. A. Phillips to the fact, that metalliferous veins are even now forming at Steamboat Springs in Nevada, and at Sulphur Bank in California. The mines at Sulphur Bank, formerly mere open surface excavations, have been recently developed in a systematic way, thus affording the authors opportunities of study which were not enjoyed by any previous observers. The lava stream of Sulphur Bank is 300 yards wide, 600 yards long, and 100 feet thick. The surface consists of pure silica, the residue from the complete decomposition of the volcanic rock. Deeper down, the rock consists of decomposed blocks of andesite, in every crevice of which sulphur is found in abundance. Still deeper, the rock assumes its natural square-jointed structure. Cinnabar now appears mixed with the sulphur. At a greater depth cinnabar is found without sulphur; together with this, impregnations of iron pyrites and bitumen occur. Still deeper, beyond the influence of atmospheric agencies, although still within the lava stream, the decomposition is no longer universal, but only in streaks along the waterways; the result of decomposition is now tough unctuous blue clay, and finally the earthy residuum is no longer acid from down-going waters, but alkaline from up-coming solfataric waters. In this region, irregular fissures running in all directions are filled with opal, nearly always clouded with cinnabar. Here, then, mineral veins are undoubtedly being formed with quartz vein-stuff and ore. B. H. B.

The Klausenburg Meteorite. By F. v. Hauer, A. Brezina, A. Koch, G. Tschermak, and E. Döll (*Jahrb. f. Min.*, 1883, **2**, Ref., 184—188).—At 3.45 P.M. on the 3rd of February, 1882, a meteorite fell between Gyulatelka and Mócs, 38 km. east of Klausenburg in Transylvania. The sky was perfectly cloudless at the time. The stones spread over an area 20 km. long and 4 km. broad, and the lustre of the ball of fire was visible throughout Western Transylvania. When the fiery phenomenon disappeared, the path (N.W.—S.E.) was for a long time marked by a greyish-white cloud. Three minutes after the appearance of the intense light, a series of detonations followed. The heaviest stone fell two miles south of Mócs; it weighed 38·534 kg. The smallest stone found weighed only 0·95 grm. Koch estimates the number of stones fallen at 3,000, and their weight at 300 kg. The larger ones are described at length.

In order to obtain the average composition, the material for analysis was taken from six of the larger stones. The results obtained were as follows:—

Fe.	Mn.	Ni.	Co.	SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.
7·93	0·57	1·38	trace	42·74	trace	20·86	1·12	15·95

CaO.	Na_2O.	K_2O.	Li_2O.	S.	P.	C.	Chromite.	Total.
2·78	1·20	0·21	trace	2·61	0·41	0·19	1·56	99·51

52·3 per cent. was soluble in acid. This analysis corresponds with a percentage of 9·88 nickel-iron, 6·63 magnetic pyrites (Fe_7S_8), and 83·49 silicates. B. H. B.

The Meteorites of Alfianello. By J. GALLIA and A. BREZINA (*Jahrb. f. Min.*, 1883, **2**, Ref., 188).—A fall of meteoric stones took place on the 16th of February, 1883, at 2.55 P.M. at Alfianello, near Brescia, with the usual appearances, but without any visible fiery phenomenon. The stone was 260 kg. in weight and of a conical shape, ½ m. high, and 75 cm. in basal diameter. It buried itself 1 m. deep in the earth, singeing the grass in its neighbourhood. Although the meteorite passed through the air in a S.S.E. direction, it forced its way into the earth obliquely in the opposite direction. When dug out, the stone was still warm; it was covered with a smooth black crust, and the smell of sulphur was distinctly noticeable.

B. H. B.

Mineral Water at Montrond (Loire). By A. TERREIL (*Compt. rend.*, **96**, 1581—1582).—The mineral water at Montrond rises from a depth of 502 m., and issues from the bore-hole in the form of a jet, which rises several meters above the surface of the soil, the water being driven to this height by the pressure of the carbonic anhydride with which it is charged. The water has the following composition :—

CO_2 (free).	CO_2 (combined).	Na_2O.	K_2O.	Li_2O.	CaO.
0·9356	2·1994	1·5408	traces	traces	0·0336

MgO.	Al_2O_3.	FeO.	Cl.	I.	SO_3.
0·0224	traces	0·0118	0·0390	traces	traces

P_2O_5.	As_2O_5.	SiO_2.	Non-nitrogenous organic matter.
0·0005	0·0003	0·0386	0·0090 = 4·8310.

Arranging the constituents in the usual way, the composition of the water is—

Free carbonic anhydride	0·9356 gr. = 473 c.c.
Sodium bicarbonate	3·5502
Potassium ,,	traces
Lithium ,,	traces
Calcium ,,	0·0864
Magnesium ,,	0·0716
Ferrous ,,	0·0262
Alumina	traces
Sodium chloride	0·0640
Sodium iodide	traces
Sodium sulphate	traces
Sodium phosphate	0·0010
Sodium arsenate	0·0004
Sodium silicate	0·0787
Non-nitrogenous organic matter	0·0090
	4·8231

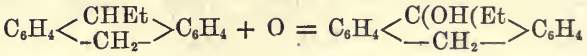
The water is an alkaline carbonated water of unusual purity. It differs, however, from other waters of the same class by its strongly chalybeate taste, due to the presence of ferrous carbonate.

C. H. B.

Organic Chemistry.

Hydroxylation by Direct Oxidation. By R. MEYER (*Annalen*, **220**, 1—71).—The main portion of this paper has already been abstracted from the *Berichte* (comp. Abstr., 1881, 45 and 818; 1882, 195; this vol., p. 983). At its conclusion, the author offers some general remarks of interest.

Besides those cases examined or mentioned by the author in his former memoir, analogous examples have been investigated by other chemists. For example, the conversion of ethyl-methacetic and isobutylformic acids into their corresponding hydroxy-acids, thus: $CHMeEt.COOH + O = CMeEt(OH).COOH$ and $CHMe_2.CH_2.COOH + O = CMe_2(OH).CH_2.COOH$ (Miller), of ethylanthracene dihydride into ethylhydroxanthranile—



$$C_6H_4<\genfrac{}{}{0pt}{}{CHEt}{-CH_2-}>C_6H_4 + O = C_6H_4<\genfrac{}{}{0pt}{}{C(OH(Et}{-CH_2-}>C_6H_4$$

(Liebermann), of hydratropic into atrolactic acid, $CHMePh.COOH + O = CMePh(OH).COOH$ (Ladenburg and Kügheimer).

The peculiarity of the hydrogen-atom in a CH-group in yielding generally a hydroxyl-compound can be traced to its isolated position and to the well-known instability of compounds containing more than one hydroxyl-group associated with one carbon-atom: for the groups $CH(OH)_2$ or $C(OH)_2$, which might be formed during oxidation are immediately converted into the aldehydic CHO or ketonic CO group, with elimination of a molecule of water.

It might, however, be objected that the transformation of the primary alcoholic into the aldehydic group, or the formation of glycollic acid from ethyl alcohol, are examples of hydroxylation by direct oxidation in substances not containing the so-called tertiary hydrogen-atom. But the author suggests in answer that both aldehyde and glycollic acid are prone to oxidation, and thus can be considered only as intermediary products.

This hydroxylation by direct oxidation cannot, however, be used as a final means for determining the existence of a CH-group in the molecule: for in one case, in ordinary cymene, the normal propyl was converted into the isopropyl-group, a change analogous to the formation of isopropyl bromide by the action of bromine and aluminium bromide on cymene.

The author remarks that although the basicity of the acid formed by the oxidation of aromatic compounds determines the number of so-called side chains, yet in few cases is any light thrown on the intimate constitution of these groupings. This arises from the restricted use of partial oxidation, for generally the substances to be oxidised are only moderately soluble in the reagent used, nitric or chromic acid. The reaction thus proceeds slowly, and an intermediate product is therefore more readily oxidised completely into the COOH-group.

Hydroxylation by direct oxidation is the first step of a series, and the substance formed can be converted stage by stage into the final product of oxidation. As an example, the author adduces the conversion of cumic acid into hydroxypropylbenzoic acid, which further yields acetylbenzoic and finally terephthalic acid.

This transformation of the CH- into the C(OH)-group is characteristic not only of the side chains of the aromatic derivatives, but also of the paraffin compounds. V. H. V.

Caucasian Ozokerite. By F. Beilstein and E. Wiegand (*Ber.*, **16**, 1547—1551).—The raw ozokerite occurring on the island Tscheleken, in the Caspian Sea, is a brownish-black sticky mass, almost entirely soluble in boiling benzene. On extracting it with ether, the oily portion and the colouring matter are dissolved, leaving a hard residue. The paraffin, named by the authors *leken*, is obtained from the latter by boiling with ethyl acetate, and can be obtained pure and of constant melting point by repeated treatment with animal charcoal and precipitation from benzene; it forms lustrous crystals, melting at 79°, sp. gr. 0·93917. It is very readily soluble in benzene, carbon bisulphide, and chloroform, also in alcohol, ethyl acetate, light petroleum, aniline, and nitrobenzene. It can be distilled in a vacuum, but is partially decomposed at the ordinary pressure. Leken is very stable, dilute nitric acid having very little action on it after a week's heating on a water-bath. Chromic mixture and 4 per cent. permanganate solution scarcely act on it at 100°, whilst if sulphuric acid is added, the manganate oxidises the leken to carbonic anhydride and water; fuming sulphuric acid decomposes it, with formation of a black carbonaceous mass. On heating a mixture of leken (6 grams), bromine (3 grams), and water (2 c.c.) at 100°, a crystalline product is obtained melting at 74·5°, and containing 5·7—6·2 per cent. bromine. A second experiment with double the amount of bromine and water yielded a compound containing 12·6 per cent. bromine, half the bromine being evolved as hydrobromic acid.

The oil obtained on extracting ozokerite with ether contained after distillation in a vacuum 86·13 per cent. carbon and 13·70 per cent. hydrogen, leken containing 85·1 per cent. carbon and 14·57 per cent. hydrogen. A. K. M.

Hydrocarbon, $C_{10}H_{18}$, prepared from Allyl Dipropyl Carbinol. By S. Reformatsky (*J. pr. Chem.* [2], **27**, 389—407).—This hydrocarbon has already been obtained by Saytzeff and Nikolsky (Abstr., 1879, 214), by the action of sulphuric acid on allyl dipropyl carbinol. The author has now investigated it further. Its purification presented great difficulty, as it readily absorbs oxygen, but was at last effected by digesting the fraction distilling between 160—170° with sodium in sealed tubes at 175° for two days, and subsequently distilling it in an atmosphere of carbonic anhydride. The pure hydrocarbon, $C_{10}H_{18}$, is a colourless liquid of sp. gr. 0·7870 at 0°, 0·7740 at 16°, and 0·7705 at 21° (water at 0° = 1), boils at about 158°, is insoluble in water, readily soluble in alcohol, ether, and benzene. Its vapour-density is 4·83, and it oxidises rapidly on exposure to air. When treated with bromine in ethereal solution, it yields a tetrabromide, $C_{10}H_{18}Br_4$, as a thick heavy liquid. On oxidation with chromic mixture, the hydrocarbon yields butyric and propionic acids, together with a small quantity of acetic acid. A. J. G.

Hydrocarbon, $C_{12}H_{20}$, prepared from Allyl Dimethyl Carbinol. By W. NIKOLSKY and A. SAYTZEFF (*J. pr. Chem.* [2], **27**, 380—389).—A preliminary communication has already appeared (Abstr., 1879, 214) on the hydrocarbons C_6H_{10} and $C_{12}H_{20}$, obtained by the action of sulphuric acid on allyl dimethyl carbinol. The compound $C_{12}H_{20}$ is best obtained by heating a mixture of 1 vol. allyl dimethyl carbinol and 2 vols. sulphuric acid (1 part H_2SO_4 + 1 part water) in sealed tubes for about three days at 100°. By fractionation, an oil boiling at 194—199° is obtained, still mixed with an oxygen compound; by treatment with phosphoric anhydride and subsequent fractionation, the pure hydrocarbon, $C_{12}H_{20}$, is obtained as a colourless mobile liquid, not solidifying in a freezing mixture; its odour somewhat resembles that of turpentine. It boils at 196—198°, has a sp. gr. 0·8530 at 0°, and 0·8385 at 21° (water at 0° = 1), vapour-density, found 5·55, calculated 5·67. It is insoluble in water, readily soluble in alcohol and ether. An ethereal solution absorbs bromine readily, but decomposition ensues on attempting to remove the ether from the liquid. By heating the hydrocarbon with concentrated hydrochloric acid at 100° for two days, a substance was obtained whose analysis gave numbers not agreeing very well with the formula $C_{12}H_{21}Cl$. By oxidation with chromic acid it yields a small quantity of acetone, acetic and propionic acids, and mainly a non-volatile acid of the formula $C_{10}H_{16}O_6$ or $C_{10}H_{14}O_6$. This forms a colourless syrupy liquid, readily soluble in water, alcohol, and ether. All the salts yet prepared crystallised badly, and so could not be purified.
A. J. G.

Conversion of Fulminates into Hydroxylamine. By A. STEINER (*Ber.*, **16**, 1484—1486).—When fulminating mercury is dissolved in cold strong hydrochloric acid, a mixture of hydroxylamine hydrochloride and a double chloride of mercury and hydroxylamine is formed. Pure hydroxylamine hydrochloride may easily be obtained by expelling the excess of acid from this solution, and removing the mercury by means of sulphuretted hydrogen.

This reaction indicates that fulminic acid is an isonitroso-compound, $HON\colon C\colon C\colon NOH$. W. C. W.

Preparation of Ammonium Thiocyanate. By J. SCHULZE (*J. pr. Chem.* [2], **27**, 518).—In preparing ammonium thiocyanate by the action of ammonia on carbon bisulphide in alcoholic solution, the author finds that it is not necessary to use such large quantities of alcohol and ammonia as Claus recommends. He finds that the best yield is obtained by employing 600 grams of 95 per cent. alcohol, 800 grams of ammonia (sp. gr. 0·912), and 350—400 grams of carbon bisulphide. J. I. W.

Normal Primary Hexyl Alcohol. By J. FRENTZEL (*Ber.*, **16**, 743—746).—The author obtained the alcohol as follows: Ricinoleïc acid, obtained from castor oil, was dry-distilled; the œnanthaldehyde thus obtained oxidised to œnanthic acid, which was then converted into hexylamine by Hofmann's method (Abstr., 1882, pp. 822, 950, and 1052). Hexylammonium chloride was converted into the nitrite by double decomposition with silver nitrite in aqueous solution, and the solution thus obtained was subjected to distillation when it yielded hexyl alcohol as soon as it became concentrated. *Hexyl alcohol* boils at 157·3° (corr.), and solidifies at − 30°. Its sp. gr. is 0·813 at 17°. The yield was 40—50 per cent. of theory.

Hexyl formate boils at 146°, has a sp. gr. of 0·8495 at 17°, and an odour of apples. *Sodium hexylate* is produced by the action of sodium on the alcohol, and with benzoic chloride yields *hexyl benzoate.* The latter boils at 272° (bar. 770 mm.), has a sp. gr. of 0·99846 at 17°, and a smell of apples. *Hexyl chloride* boils at about 130°, but was not obtained in a pure state.

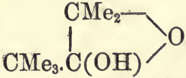
Hexylammonium hexylthiocarbamate, $C_6H_{13}.NH.CS.SH.C_6H_{13}.NH_2$, was prepared by the action of carbon bisulphide on hexylamine. It is a white crystalline body, which on being heated yields *dihexylthiocarbamide*, $CS(NH.C_6H_{13})_2$; this crystallises in glistening white plates melting at 40°. *Hexylthiocarbimide*, $CS\!:\!N.C_6H_{13}$, prepared by decomposing copper hexylthiocarbamate with steam, boils at 212° (bar. 578 mm.). Alcoholic ammonia converts the carbimide into *monhexylthiocarbamide*, $NH_2.CS.NH.C_6H_5$, which crystallises in white plates melting at 83°. L. T. T.

Preparation of Normal Primary Decyl, Dodecyl, Tetradecyl, Hexdecyl, and Octodecyl Alcohols. By F. KRAFFT (*Ber.*, **16**, 1714—1726).—To prepare normal *decyl alcohol*, $C_{10}H_{22}O$, the aldehyde is first obtained by the dry distillation of a mixture of barium caprate and formate under reduced pressure (8—15 mm.). The crude aldehyde (b. p. 106° under a pressure of 15 mm.) is dissolved in 10 times its weight of glacial acetic acid, and 3 to 4 parts of zinc-dust are gradually added. To complete the reduction, it is necessary to boil the mixture gently for about a week. The cold acid solution is separated from the solid zinc salt, and poured into water; the oily liquid is washed with water, dried, and distilled under reduced pressure. *Decyl acetate* is a colourless, strongly refractive, mobile liquid, which boils at 125° under a pressure of 15 mm. The alcohol obtained by saponifying the acetate with alcoholic potash is a viscous liquid (b. p. 119° under 15 mm. pressure). It has a sweet smell, and is powerfully refractive. It crystallises in transparent rectangular plates which melt at 7°. *Decyl chloride* formed by the action of phosphorus pentachloride on the alcohol is converted into the olefine, $C_{10}H_{20}$, which yields normal decane, $C_{10}H_{22}$, on treatment with hydriodic acid and phosphorus.

By a series of reactions analogous to the preceding, the following compounds were prepared. (The boiling points are determined under a pressure of 15 mm. unless otherwise stated.) *Dodecyl alcohol* melts at 24° and boils at 143·5°. The sp. gr. of the alcohol in the liquid state is 0·8309 at 24° and 0·8201 at 40°. The *acetate* boils at 151°. Normal *dodecane* melts at − 12° and boils at 98°. *Tetradecyl acetate* melts at 13° and boils at 176°. The *alcohol*, $C_{14}H_{30}O$, melts at 38°, and boils at 167°. The sp. gr. of the alcohol is 0·8236 at 35° and 0·8153 at 50°. *Hexdecyl acetate* is sparingly soluble in cold alcohol. It melts at 22—23° and boils at 200°. The alcohol has been previously described. *Octodecyl alcohol* forms silvery plates, sparingly soluble in alcohol. It melts at 59° and boils at 210·5°. Its sp. gr. is 0·8124 at 59° and 0·7849 at 99·1. The acetate melts at 31° and boils at 222°.

In conclusion, the author points out that the influence of diminished pressure on the boiling points of the alcohols increases with the molecular weight. W. C. W.

Bye-product of the Preparation of Allyl Dimethyl Carbinol. By W. DIEFF (*J. pr. Chem.* [2], **27**, 364—380).—This substance, which appears to be *isopropyl allyl dimethyl carbinol*, $C_4H_4Me_2Pr^{\beta}.OH$, and is formed by the action of zinc and isopropyl iodide on allyl dimethyl carbinol, was observed several times when impure allyl iodide containing isopropyl iodide had been employed in the manufacture of allyl dimethyl carbinol. The complete purification of the substance could not be effected; it boils about 76°; combines with 2 atoms bromine; is converted into the chloride, $C_9H_{17}Cl$ (?), by the action of phosphoric chloride; and on oxidation gives butyric acid and other acids not identified. A. J. G.

Oxoctenol. By V. MEYER and E. NÄGELI (*Ber.*, **16**, 1622—1624).—According to Butlerow (Abstr., 1882, 937) the constitution of oxoctenol is either  $\begin{array}{l} CMe_2\text{—} \\ \quad | \qquad\qquad \rangle O \\ CMe_3.C(OH) \end{array}$, or $CMe_3.CO.CMe_2(OH)$. If the second formula is correct, this substance should yield an isonitroso-derivative with hydroxylamine, whilst a compound having the first formula would not be acted on by this reagent. The authors have experimented under various conditions, but the oxoctenol remained unattacked, showing that no CO-group is present, and that the first formula is the correct one. In order, however, to ascertain whether the presence of hydroxyl in a ketone interferes with the hydroxylamine reaction, the authors have examined the action of the latter on benzoyl carbinol, and have obtained *isonitrosophenylethyl alcohol*,

$$PhC(NOH).CH_2.OH.$$

It is insoluble in light petroleum, readily soluble in ether, alcohol, water, and hot benzene, crystallising from the latter in lustrous scales melting at 70°. Acids dissolve it on warming, with liberation of hydroxylamine. A. K. M.

Preparation of Chlorhydrins. By A. LADENBURG (*Ber.*, **16**, 1407—1408).—Ethylene chlorhydrin is best prepared by passing a slow current of dry hydrochloric acid gas through glycol heated at 148° in a retort, when water and ethylene chlorhydrin distil over. The temperature of the glycol is slowly raised to 160°. About 16 hours are required to convert 100 grams of glycol into the chlorhydrin. The distillate is mixed with 2 or 3 times its volume of ether, allowed to stand over potassium carbonate to remove free hydrochloric acid, dried over fused potassium carbonate, and then distilled. The yield is 60 per cent. of the theoretical. W. C. W.

Effect of Temperature and Concentration of Acid on the Rate of Inversion of Saccharose. By F. URECH (*Ber.*, **16**, 762—766).—The author gives a number of equations to obtain the different coefficients under varying conditions. Of these, the following are the principal: If u_0 = the original quantity of saccharose, u that remaining after an interval of time t expressed in minutes, and a the coefficient of rate of inversion:

$$a = \frac{\log \dfrac{u_0}{u}}{(\log 2{\cdot}7182)\,.\,t},$$

or if u_0 be taken as 100—

$$\log a = \log(2 - \log u) - (\bar{1}{\cdot}63774 + \log t).$$

L. T. T.

Fermentation of Cellulose. By H. TAPPEINER (*Ber.*, **16**, 1734—1740).—Finely divided cotton-wool or paper is introduced into a flask containing a neutral one per cent. solution of extract of meat. The vessel is heated at 110°, and when cold a small quantity of the contents of the pancreas is added. Fermentation begins in a few days: the gases evolved consist chiefly of marsh-gas and carbonic anhydride. These two gases are in the ratio of 1 to 7·2 at the beginning of the process, but the carbonic acid afterwards diminishes to the ratio of 1 : 3·4.

The actual figures are—

	Commencement.	End.
CO_2	85·48	76·98
SH_2		
H	0·03	—
CH_4	11·86	23·01
N	2·73	—

Acetic and isobutyric acids are the chief products of the fermentation, 5·5 grams of cotton-wool yielding 5·8 grams of volatile acids. Acetaldehyde is also formed. Cellulose undergoes similar fermentation in the first stomach of ruminants and in the alimentary canal of herbivora. When the preceding experiments are varied by rendering the meat-extract feebly alkaline, by adding Nägeli's solution (potassium phosphate 0·2 gram, magnesium sulphate 0·04 gram, and calcium chloride 0·02 gram), or a solution containing in addition to the above salts, 0·35 per cent. of ammonium acetate, 0·3 acetamide, or 0·6 asparagine, the following results were obtained:—

	0·5 per cent. solution of meat extract.	Asparagine.	Acetamide.
CO_2 .... SH_2	55·39	86·47	78·14
H	42·71	5·73	13·68
N	1·90	7·80	8·18

No difference could be detected in the bacteria in the two kinds of fermentation. In addition to aldehyde, isobutyric and acetic acids, a small quantity of ethyl alcohol appears to be formed by the "hydrogen" fermentation of cellulose.

Alcohol, aldehyde and acetic acid are produced during the fermentation of hay. The gases evolved contain CO_2 51·15, H 44·58, CH_4 0·9, N 4·18 per cent. W. C. W.

Reduction of Saccharin. By C. LIEBERMANN and C. SCHEIBLER (*Ber.*, **16**, 1821—1825).—The authors confirm the accuracy of Kiliani's statement (*Annalen*, **218**, part 3) that the lactone obtained by the action of hydriodic acid on saccharin is α-methylvalerolactone. Methylpropylacetic acid (b. p. 190°) is also produced. W. C. W.

Some Anomalous Reactions. By G. MEYER (*Ber.*, **16**, 1439—1443).—*Methyl iodide and Sodium arsenite.*—If an alcoholic solution of methyl iodide is heated in sealed tubes at 75° with an aqueous solution of sodium arsenite containing a small quantity of free soda, and the crystalline contents of the tubes are dissolved in warm water and boiled with calcium chloride, *calcium methylarsenite*, $CaCH_3AsO_3 + H_2O$, is thrown down as a white crystalline precipitate. On treating another portion of the aqueous solution with sulphuretted hydrogen, a mixture of sulphur, methylarsine sulphide and the bisulphide, CH_3AsS_2, is precipitated. The precipitate is treated with carbon bisulphide, and the residue of methylarsine bisulphide is dissolved in ammonia and reprecipitated by the addition of hydrochloric acid. The bisulphide is decomposed by heat, yielding methyl sulphide and arsenious sulphide.

An alcoholic solution of methyl iodide acts at the ordinary temperature on stannous chloride dissolved in excess of sodium hydroxide. After the excess of alcohol and methyl iodide have been removed by boiling, carbonic acid precipitates methylstannic acid, $MeSnO_2H$, from the alkaline solution in the form of a crystalline powder. On passing sulphuretted hydrogen into the filtrate, a white sulphide is precipitated. On evaporating the hydrochloric acid solution of methyl stannic acid or the sulphide, a fuming crystalline mass is produced which probably consists of $MeSnCl_3$. W. C. W.

Base derived from Crotonaldehyde. By A. COMBES (*Compt. rend.*, **96**, 1862—1863).—A solution of crotonaldehyde in anhydrous ether is cooled to $-20°$, saturated with dry ammonia gas, and exposed to light in well-closed flasks for two or three days, when the liquid separates into two layers. When distilled, the lower layer yields water and an oily liquid which distils with difficulty at 200° in a vacuum. The same substance is obtained by evaporating the upper ethereal layer. This oily liquid has the composition $C_8H_{16}N_2O$, and is formed in accordance with the equation, $2C_4H_6O + 2NH_3 = C_8H_{16}N_2O + H_2O$. It has a distinctly alkaline reaction, and combines with water with development of heat, forming a white crystalline substance which can also be obtained by adding water to the ethereal solution. This hydrate is very soluble in water and combines readily with hydrochloric acid, forming a hydrochloride which crystallises easily; the yellow somewhat soluble platinochloride also crystallises readily. C. H. B.

Acetone-chloroform. By C. WILLGERODT (*Ber.*, **16**, 1585).—This compound previously described by the author (*Abstr.*, 1882, 492) contains half a molecule of water of crystallisation,

$$COMe_2,CHCl_3 + \tfrac{1}{2}H_2O,$$

and melts at 80—81°. On treating it with anhydrous solvents, such as chloroform, light petroleum, benzene and carbon bisulphide, it loses its water of crystallisation, and then melts at 96°.

A. K. M.

Condensation of Acetone. By A. PINNER (*Ber.*, **16**, 1727—1734).—Mesityl oxide obtained by the action of hydrochloric acid on acetone is identical with the mesityl oxide obtained by heating acetone with lime. The author finds that the reaction which takes place when cane-sugar is heated with lime is by no means so simple as Benedikt (*Annalen*, **162**, 303) represents, viz., $C_6H_{12}O_6 = C_3H_6O + 2CO_2 + CH_4 + H_2O$. Metacetone and phorone are, according to Benedikt, condensation-products of acetone. The residue in the retort contains, in addition to calcium carbonate and a small quantity of caproic acid, an acid of the composition $C_6H_{10}O_5$, which forms a crystalline hygroscopic potassium salt. The calcium salt is precipitated from an aqueous solution by the addition of alcohol. The white amorphous silver salt is somewhat soluble in water. It decomposes even in the dark, and turns brown. The volatile portion of the products of the dry distillation of sugar and lime contains, in addition to the compounds isolated by previous observers, acetaldehyde, metacetone, and several other bodies. W. C. W.

Action of Sodium on Methyl Ethyl Ketone. By J. SCHRAMM (*Ber.*, **16**, 1581—1582).—The methyl ethyl ketone was dissolved in benzene, and after the action of the sodium, the latter separated by distillation and the product fractioned, when the following compounds were obtained. The fraction 163—165° is a liquid of camphoraceous odour, insoluble in water, readily soluble in alcohol and in ether, and combines directly with bromine, forming a heavy dark coloured oil.

In its composition, $C_8H_{14}O$, and properties, it agrees with the homologue of mesityl oxide obtained by Pawlow (*Annalen*, **188**, 138). By the action of a freezing mixture on the fraction boiling at 200—205°, a white crystalline body is obtained, apparently identical with Lawrinowicz's methyl ethyl pinacone, $C_8H_{18}O_2$. It melts at 28—29°, boils at 201—203° (bar. 745 mm.), and does not again solidify at the ordinary temperature. It has an odour like that of camphor, is moderately soluble in water, readily in alcohol and in ether. The product boiling at 248—253° is an oily liquid which could not be solidified, and evidently contains a substance of the formula $C_{12}H_{20}O$ analogous to phorone. It is thus shown that the above reaction is at least for the most part analogous to the action of sodium on acetone, the chief products of which are mesityl oxide, pinacone, and phorone.

A. K. M.

Diethyl Ketone. By J. SCHRAMM (*Ber.*, **16**, 1583—1584).—Very different statements occur with regard to the combination of diethyl ketone with hydrogen sodium sulphite (*Annalen*, **161**, 286; **179**, 322; and **157**, 251; *Ber.*, **5**, 459). The author finds that the combination does not take place very readily, but that the temperature rises after continued shaking, and on cooling a mass of needles is obtained. The compound $C_5H_{10}O + NaHSO_3$ is very readily soluble in water, alcohol, and ether, and decomposes gradually on exposure to the air. In order to prove that the ketone experimented with was really diethyl ketone and not methyl propyl ketone, the author converted it into the corresponding pinacone and obtained a crystalline substance, $C_{10}H_{22}O_2$, melting at 27—28°, almost insoluble in water, readily soluble in alcohol and in ether. Methyl propyl ketone yields a liquid pinacone (*Jahresbericht*, 1869, 513). A. K. M.

Ethyl Acetate. By W. I. CLARK (*Pharm. J. Trans.* [3], **13**, 777—783).—The acetic ether of commerce is often impure, and in this paper the author describes various tests for the impurities, comments on the present modes of preparation and purification, and on some of the properties of ethyl acetate; he finally proposes a new process for its preparation.

The amount of ethyl acetate present is determined by saponifying a definite quantity of the ether with a measured volume of a solution of potassium hydroxide in pure alcohol, of known alkalinity; the loss of alkalinity represents the total acetic acid combined and free, the amount of the latter being ascertained by titrating the ethyl acetate dissolved in spirit with standard alkali, and is deducted from the total. The alcohol is determined by collecting the distillate from the saponification, the quantity of ethyl acetate having been determined, the total alcohol, less the alcohol used and the alcohol produced in the reaction, gives the quantity of free alcohol present. Most commercial samples contain large proportions of water, alcohol, and acetic acid; for this reason the author has investigated the methods of preparation. Methods which depend on the production of ethyl acetate direct from free acetic acid, alcohol, and sulphuric acid, are quite useless owing to the great quantity of ether, alcohol, and acetic acid inevitably present in the product. The action of carbonic anhydride on a solution of potassium acetate in absolute alcohol yields no ethyl acetate after 24 hours, but on adding water a trace of it is produced.

The British Pharmacopœia method of distilling a mixture of 8 parts of dry sodium acetate, 5 parts rectified spirit, and 10 parts of sulphuric acid, adding the distillate to half its weight of calcium chloride, and after 24 hours decanting and rectifying, is unsatisfactory; firstly, it is not economical, for the B.P. formula requires a considerable excess both of sulphuric acid and sodium acetate; secondly, this great excess of sulphuric acid is deleterious, the ethyl acetate being decomposed by it into ether, acetic acid, and numerous other products. The author therefore undertook a series of experiments with crystalline and dry sodium acetate, with rectified spirits of wine and absolute alcohol, and with various quantities of sulphuric acid under various conditions. From these he draws the following conclusions:—1. Dry sodium acetate should be used. 2. Great excess or deficiency of sulphuric acid are equally to be avoided; a slight excess being advantageous. 3. The advantage gained by the use of absolute alcohol in place of rectified spirits of wine is not worth the extra expense. 4. The yield is never more than 91·2 per cent. of the theoretical. 5. Delay (for example, the previous mixing of the alcohol with the sulphuric acid and allowing it to stand some time, as recommended by Frankland and Duppa, so as to favour the formation of ethyl hydrogen sulphate) lowers the yield. The product obtained by the authors, whether by the B.P. method or any other, was always far superior, even before purification, to that occurring in commerce; the plea that acetic ether decomposes when moist is inadmissible, for experiment proves that this decomposition is far too slow to account for the impurities.

The next point attacked is the removal of impurities; ether and secondary products of the action of the sulphuric acid are best removed by distillation, and acetic acid by agitation with potassium carbonate, the ether being slightly moist; standing over fused calcium chloride and subsequent distillation from it, as a means of removing the alcohol, cannot be recommended, as there is always a loss, also decomposition, which the author points out is due to the alkalinity of the calcium chloride; moreover, the distillation is always accompanied by bumping owing to the deposition of calcium chloride, although the ethyl acetate dissolves only 0·15 gram per 100 c.c. at 15°. The alcohol is best removed by a saturated solution of calcium chloride which also removes some of the water: the author finds that 47 c.c. of calcium chloride solution (saturated) only dissolve 1 c.c. of ethyl acetate at 15°, and very slightly more at 0°, but this increases directly with the dilution of the calcium chloride solution, that is, the more alcohol or alcohol and water present, the greater will be the quantity of acetate dissolved. Upon this fact he has constructed tables in which are given the quantities of ethyl acetate remaining undissolved when stated mixtures of the acetate with alcohol, or with alcohol and water are agitated with the calcium chloride solution. These tables can be used in a manner described in the paper to determine approximately the quantity of ethyl acetate present in such a mixture.

Removal of water: 1 c.c. of ethyl acetate dissolves in 8 c.c. of water at 0°, and in 9 c.c. at 15°; it is hence more soluble at 0° than at 15°. Water dissolves in ethyl acetate in proportions of 1 c.c. : 26 c.c. at 0°, and 1 c.c. : 24 c.c. at 15°; it is hence more soluble at 15° than at 0°. Digestion with potassium carbonate is recommended for the removal of the water, but distillation from it causes decomposition and loss. Sodium acetate is also an excellent dehydrant, and the ethyl acetate may be distilled from it; the sodium acetate being subsequently used for a fresh preparation of the ether.

The following is the process recommended by the author for the preparation of ethyl acetate:—283 c.c. of sulphuric acid are poured into 283 c.c. of rectified spirit contained in a flask, keeping it cool; as soon as the temperature has fallen to about 15° the sodium acetate is gradually added, agitating constantly, keeping the flask cool, and connecting it with a reflux condenser. The contents are then distilled, digested for three days with 2 oz. of freshly dried potassium carbonate, filtered, and distilled, stopping the distillation at the last ounce. The excess of sulphuric acid ensures the absence of alcohol in the distillate, whilst the action of this excess on the acetate itself is minimised by the above precautions. It is therefore only necessary to neutralise and free the ether from water as described. From several observations made on ethyl acetate, as pure as can be procured, purified both after admixture with alcohol, which would lower the sp. gr., and with water, which would raise the sp. gr., the author concludes that the sp. gr. of ethyl acetate is higher than 0·9004 and lower than 0·9012. It is exceedingly difficult to remove the last traces of water from the acetate. D. A. L.

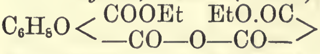
Action of Aldehyde-ammonia on Methyl Acetoacetate. By A. HANTZSCH (*Ber.*, **16**, 1946—1948).—By the action of 2 mols. of methyl acetoacetate on 1 mol. aldehyde-ammonia, *methyl dihydrocollidinedicarboxylate* is formed, thus: $CH_3.CO.CH_2.COOMe + CHMe(OH).NH_2 = C_5N.H_2Me_3(COOMe)_2$. This substance resembles the corresponding ethyl compound as regards its solubility, colour, and fluorescence, but differs in its melting point, 156°. By boiling with hydrochloric or nitrous acid, *methyl collidinedicarboxylate*,

$$C_5NMe_3(COOMe)_2$$

is obtained, which crystallises in white needles (m. p. 82°, b. p. 286°). This substance, although it has a neutral reaction, combines with acids to form well-defined salts. The *hydrochloride* crystallises in glistening prisms; the *platinochloride* in reddish-golden spangles, which melt at 200° with decomposition: the aurochloride in slender golden needles, which readily melt into an oil. V. H. V.

Halogen-substituted Ethyl Acetoacetates. By M. CONRAD and M. GUTHZEIT (*Ber.*, **16**, 1551—1555).—Duisberg showed that bromine is capable of displacing 5 atoms of hydrogen in ethyl acetoacetate (Abstr., 1882, 1192). In order to ascertain whether ethyl dichloracetoacetate, which at the ordinary temperature can take up no more chlorine, undergoes further substitution by bromine, the authors exposed a mixture of the former (20 grams) with bromine (50 grams) for some days to direct sunlight. Hydrobromic acid is evolved, and *ethyl dichlorodibromacetoacetate*, $C_6H_6Cl_2Br_2O_3$, is formed as a slightly yellowish liquid insoluble in water, and decomposed on boiling. With ammonia, it forms a white crystalline compound, soluble in ether. On heating ethyl dichlorodibromacetoacetate with hydrochloric acid, carbonic anhydride is given off with formation of the compound $C_3H_2Cl_2Br_2O,4H_2O$, which crystallises in six-sided plates of a vitreous lustre melting at 56°; it loses its water over sulphuric acid, and then forms a colourless liquid (*dichlorodibromacetone*), the vapour of which violently attacks the eyes. In its properties it agrees with the dichlorodibromacetone obtained by Claus and Lindhorst (Abstr., 1880, 862) by the action of bromine on dichlorhydrin, the constitution of which is $CH_2Cl.CO.CClBr_2$. This constitution is, however, not in accordance with what one would expect, since both chlorine-atoms in ethyl dichloracetoacetate are united to the same carbon-atom (*Annalen*, **186**, 232).

By the action of sodium on ethyl chloracetoacetate, the sodium compound is obtained, forming a white crystalline hygroscopic powder. An attempt to displace the bromine in ethyl bromacetoacetate by acetyl by boiling it with an alcoholic potassium acetate solution yielded ethyl succinylsuccinate. Chlorine acts on ethyl diethylacetoacetate with evolution of hydrochloric acid. The product distils for the most part between 245° and 255°, and apparently contains both mono- and di-chloro-substitution derivatives. A. K. M.

Condensation-products of Ethyl Acetoacetate. By A. HANTZSCH (*Ber.*, **16**, 740—742).—By the action of strong sulphuric acid on ethyl acetoacetate, the author has obtained *ethyl mesityloxidedicarboxylate*, $C_6H_8O(COEt)_2$, *ethyl mesityloxideanhydrodicarboxylate*,  $C_6H_8O<\genfrac{}{}{0pt}{}{COOEt\quad EtO.OC}{—CO—O—CO—}>C_6H_8O$, and a crystalline body of the empirical formula C_2H_2O, *i.e.*, isomeric with dehydracetic acid. This acid is dibasic, and appears to have the molecular formula $C_{14}H_{14}O_7$: the author proposes for it the preliminary name of *metadehydracetic acid*. Ammonia forms a peculiar compound with ethyl mesityloxidedicarboxylate, having the formula $COOEt.C_6H_8O.COO.NH_4,NH_3$, and giving with mineral acids the acid $COOH.C_6H_8O.COOEt$. The three mesityl-acids give *mesityloxide-dicarboxylic acid*, $C_6H_8O(COOH)_2$, when saponified with excess of potash. L. T. T.

Action of Trimethylene Bromide on Ethyl Acetoacetate, Ethyl Benzoylacetate, and Ethyl Malonate. By W. H. PERKIN (Jun.), *Ber.*, **16**, 1787—1797).—*Acetotetramethylenecarboxylic acid*, obtained by the action of trimethylene bromide on ethyl sodacetoacetate (*Ber.*, **16**, 208) is decomposed by distillation, yielding acetotetramethylene, $CH_3.COC_4H_8$, and carbonic anhydride.

The ethylic salt of benzoyltetramethylenecarboxylic acid is prepared by the action of trimethylene bromide (21) on a mixture of ethyl benzoylacetate (20), and a solution of sodium (2·5) in absolute alcohol. The sodium bromide which is deposited is removed by filtration and the alcohol distilled off: 2·5 grams of sodium, dissolved in alcohol, are added to the residue, and the mixture is heated at 100° until it ceases to exhibit an alkaline reaction. After removing sodium bromide and alcohol, the mixture is diluted with water and extracted with ether. From the ethereal solution, the ethyl salt, $PhCO.C(COOEt)<{}^{CH_2}_{CH_2}>CH_2$, is obtained in colourless prisms (m. p. 60°), which dissolve freely in the usual solvents. On saponification with alcoholic potash, *benzoyltetramethylenecarboxylic acid*,

$$\overline{Bz}C(C_3H_6).COOH,$$

is obtained as a crystalline mass, which melts at 143°, decomposing into carbonic anhydride and benzoyltetramethylene. The acid is soluble in alcohol, chloroform, benzene, carbon bisulphide, and ether. *Benzoic tetramethylene*, $C_6H_5COCH<{}^{CH_2}_{CH_2}>CH_2$, is a colourless oil boiling at 259°.

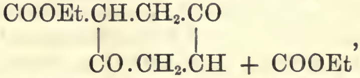
By the action of trimethylene bromide on the disodic derivative of ethyl malonate, ethyl tetramethylenedicarboxylate,

$$CH_2\colon(CH_2)_2\colon C(COOEt)_2,$$

is obtained as a colourless oil (b. p. 224°). On saponification, it yields *tetramethylenedicarboxylic acid*, $CH_2\colon(CH_2)_2\colon C(COOH)_2$, which melts at 155° with decomposition, and is converted into *tetramethylenemonocarboxylic acid* at a temperature of 210°. The acid dissolves freely in ether and benzene, but is precipitated from its solution on the addition of light petroleum. It is also readily soluble in water. The ammonium salt forms needle-shaped crystals. The silver salt is sparingly soluble in water.

Tetramethylenemonocarboxylic acid, $CH_2<{}^{CH_2}_{CH_2}>CH.COOH$, is a colourless oil boiling at 194°. It is sparingly soluble in water, but dissolves freely in alcohol and ether. The silver salt is sparingly soluble in water. The calcium salt forms crystalline needles, which are very soluble in water.

A comparison of the melting points and boiling points of these compounds with the corresponding allyl derivatives shows that these bodies contain tetramethylene, and are not allyl derivatives. Their behaviour with bromine indicates that they differ in constitution from allyl compounds. W. C. W.

Constitution of Ethyl Succinosuccinate. By F. HERRMANN (*Ber.*, **16**, 1411—1415).—The substance previously described by the author as *diethyl succinosuccinate* (*Annalen*, **211**, 308) has been proved to be identical with ethyl oxytetrolate obtained by Duisberg (*Ber.*, **16**, 133) from ethyl monobromacetate. As the constitution of the body is represented by Duisberg as  $\begin{array}{l}COOEt.CH.CH_2.CO\\ \qquad\quad\ \ | \qquad\quad\ \ |\\ \qquad\quad CO.CH_2.CH + COOEt\end{array}$, the author suggests that the compound should be called *diethylquinone tetrahydridedicarboxylate*. The monethyl salt can be split up into carbonic anhydride and *ethyl quinonetetrahydridemonocarboxylate*, formerly called ethyl succinopropionate. The author also proposes to substitute the name of *diethyl quinonedihydridedicarboxylate* for that of diethylquinonehydrodicarboxylate for the compound derived from diethylquinonetetrahydridedicarboxylate by the loss of two atoms of hydrogen. W. C. W.

So-called Tetric, Pentic, and Hexic Acids. By R. FITTIG (*Ber.*, **16**, 1939—1941).—Demarçay has recently described (*Ann. Chem. Phys.* [5], **20**, 433) a series of new acids obtained by the action of bromine and alcoholic potash on the alcoholic derivatives of ethyl acetoacetate, to which he assigns the composition $3C_4H_6O_2,H_2O$, tetric acid; $3C_5H_6O_2,H_2O$, pentic acid; $4C_6H_8O_2,H_2O$, hexic acid. The author, with the assistance of Schultz, has repeated Demarçay's work as regards tetric acid, and arrives at the same results as regards the melting point and other physical properties, but finds that the acid contains no water, and five not four carbon-atoms, viz., a composition $C_5H_6O_3$. It is monobasic, its salts having the formula $C_5H_5O_3M$. Its formation from ethylbromomethacetoacetate can be represented by the equation $C_4H_6BrO.COOEt + H_2O = C_4H_5O.COOH + HBr + EtOH$. In a postscript the author notices that his results agree with those of Pawlow, which were published recently and independently.

V. H. V.

Formation of Disodium Glycollate. By DE FORCRAND (*Compt. rend.*, **96**, 1728—1730).—Disodium glycollate, $C_2H(NaHO)NaO_2 + 2H_2O$, obtained by adding sodium hydroxide to neutral sodium glycollate in the required proportion, forms small deliquescent needles which lose their water at 180°. Its heat of solution is — 0·36 cal. at 20°. The heat developed on adding a quantity of sulphuric acid sufficient to combine with half the sodium is + 15·17 cal. The subsequent addition of an equal quantity of sulphuric acid causes a further development of + 2·19 cal. These results prove that the compound is really a bibasic glycollate. From these data, it also follows that $2NaHO$ solid + $C_2H_4O_3$ solid = $C_2H(NaHO)NaO_2.2H_2O$ solid, developes + 31·42 cal. The heat of solution of the anhydrous salt is + 9·18 cal., from which it follows that the formation of the solid anhydrous salt develops + 24·76 cal. This value is practically the same as the heat of formation of the normal salt, and consequently the conversion of the latter into the anhydrous bibasic salt is accompanied by practically no thermal disturbance. The heat developed by the hydration of the bibasic salt (+ 6·62 cal.) is, however, sufficient to explain its formation. The heat of formation of the anhydrous bibasic salt from the normal salt and anhydrous sodium oxide, is precisely the same as the heat of hydration of the sodium oxide (+ 17·27 cal.). It follows that $C_2H_4O_3 + Na_2O = C_2H_2Na_2O_3 + H_2O$ solid, develops + 58·92 cal. C. H. B.

Basic Potassium Beryllium Oxalate. By J. PHILIPP (*Ber.*, **16**, 752—753).—A solution of hydrogen potassium oxalate dissolves beryllium oxide easily, and from the solution a basic salt,

$$Be_4K_6C_{12}O_{27} + 8H_2O,$$

is obtained, forming large glass-like crystals, which have a high refractive power. The author considers the constitution of this body to be $Be_2(C_2O_4)_3 + 3K_2C_2O_4 + Be_2(HO)_6 + 5H_2O$. L. T. T.

Lithium Citrate. By C. THOMPSON (*Pharm. J. Trans.* [3], **13**, 783—786).—In this paper, the author reviews the various modes of preparing this salt, and describes the processes for making lithium carbonate from lepidolite. When pure, lithium citrate crystallises well, and is not deliquescent; the ordinary salt, however, is generally impure, containing lithium carbonate (or citric acid), along with salts of potassium, sodium, and calcium; the methods for detecting and estimating those impurities are fully described in the paper.

D. A. L.

Melanuric Acid. By E. BAMBERGER (*Ber.*, **16**, 1703—1704).—Melanuric acid is sparingly soluble in hot water, not insoluble as stated by Wöhler and Liebig. It is deposited from boiling water in white microscopic crystals. Dicyanodiamidocarboxylic acid from dicyanodiamide is identical with melanuric acid. W. C. W.

Action of Sulphuric Acid on Di- and Tri-allylamine. By C. LIEBERMANN and A. HAGEN (*Ber.*, **16**, 1641—1642).—This is a continuation of Liebermann and Paal's experiments (this vol., p. 908). Di- and tri-allylamine were prepared by the action of allyl chloride on allylamine. The separation of lustrous plates during the fractioning was again observed (*loc. cit.*), and found to be due to hydrochlorides of the above bases. Concentrated sulphuric acid reacts in the same way as in the case of the alkylallylamines; hydroxypropylallylamine and hydroxypropyldiallylamine being formed in the first phase of the reaction, but decompose with separation of the elements of water. A complicated series of bases is produced, the chief fraction of the product from diallylamine boiling at 130—170°, that from triallylamine at 170—200°. They are not hydroxy bases, and they have a penetrating odour resembling that of conine, so that it is probable they may be derivatives of pyridine and piperidine; no pure products have as yet been obtained. The authors prove the presence of pyrroline-like substances soluble in dilute sulphuric acid to a red solution.

A. K. M.

New Glyoxalines. By B. RADZISZEWSKI (*Ber.*, **16**, 747—749).—In a former paper (this vol., 308), the author showed that gloxaline was the first member of a homologous series of compounds obtainable by the action of ammonia on a mixture of glyoxal and an aldehyde. He now describes three new members of the series.

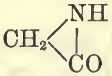
Glyoxalisobutyline, $C_6H_{10}N_2$, boils between 240—265°, and by further purification is obtained as a crystalline body melting at 129°, easily soluble in alcohol, ether, and boiling water. The platinochloride is crystalline, and easily soluble in water.

Glyoxalisoamyline, $C_7H_{12}N_2$, boiled between 250—270°. Further purified it forms long, slightly bent needles melting at 120—121°. It is sparingly soluble in boiling water. The platinochloride is less soluble than that of the previous base, and crystallises in needles.

Glyoxaliso-œnanthyline, $C_9H_{16}N_2$, is easily soluble in alcohol, sparingly in ether, and insoluble in water. It crystallises in needles and melts at 84°.

The author is now studying the action of bromine on these bodies in the hope of throwing new light on their constitution, and so deciding between the formulæ proposed respectively by Wallack, Japp, and himself. L. T. T.

Glycocine. By T. Curtius (*Ber.*, **16**, 753—757).—If ethyl acetylamidacetate (m. p. 48°; b. p. 260°), in hot alcoholic solution, is treated with hydrochloric acid gas, it splits up into ethyl acetate, and the *hydrochloride of ethyl amidacetate*, $CH_2(NH_3Cl).COOEt$. This body is also produced quantitatively by acting on a solution of glycocine in absolute alcohol with hydrochloric acid. It is very soluble in water and alcohol; crystallises well, sublimes undecomposed, and melts at 144°. It forms an easily soluble platinochloride; and is decomposed into glycocine and alcohol when boiled with aqueous alkali. If an aqueous solution of this substance be shaken with exactly the calculated quantity of silver oxide, the solution extracted with ether or chloroform, and this extract, after drying, evaporated in a current of cold dry air, *ethyl amidacetate*, $CH_2(NH_2).COOEt$, is obtained as a colourless oil. This oil is strongly basic and volatile, and forms dense fumes with hydrochloric acid. With dilute hydrochloric acid, the original hydrochloride is reproduced, concentrated mineral acids split off carbonic anhydride, and silver nitrate produces a precipitate of silver carbonate. It is very unstable, and can only be preserved in *dry* etheric solution. If any moisture is present, *glycocinimide-anhydride*,



$CH_2\left<\begin{matrix}NH\\ |\\ CO\end{matrix}\right.$

, is produced, and with acids it yields a base melting at a high temperature, and showing the biuret reaction. In aqueous solutions, this base is gradually converted into the imide. *Glycocinimide-anhydride* has a neutral reaction, but appears to possess feebly basic properties, and forms a platinochloride. It is easily soluble in boiling water and alcohol. When heated quickly it melts, and sublimes at about 280° to white needles; if slowly heated, partial decomposition sets in. It crystallises from its aqueous solution unchanged, only a small quantity of glycocine being obtained from the last mother-liquors on continued evaporation.

By the action of acetic chloride on silver amidacetate, the author obtained an acid analogous to the acid $C_{10}H_{12}N_3O_4$, which he formerly (this vol., p. 337) obtained with benzoic chloride. These acids are, however, obtained more easily and in a purer state by heating free glycocine with the ether of acetyl- or benzoyl-glycocine. When using benzoyl-glycocine, small quantities of another acid are obtained, having physically similar properties and the same melting point (172°) as hippurylamidacetic acid, but having the formula $C_{13}H_{15}N_3O_5,H_2O$. This acid loses its water of crystallisation at 110°, and forms a silver salt, $C_{13}H_{14}N_3O_5Ag$. The author believes it to be *benzoyldiamidoacetyl-*

amidacetic acid, $NH\overline{Bz}.CH_2.CO.NH.CH_2.CO.NH.CH_2.COOH$, standing in the same relation to hippuramidacetic acid,

$$NH\overline{Bz}.CH_2.CO.NH.CH_2.COOH,$$

as the latter does to hippuric acid, $NH\overline{Bz}.CH_2.COOH$.

Urea and ethyl benzoylamidacetate when heated together at 140—150°, yield *hippuryl carbamide*, $NH\overline{Bz}.CH_2.CO.NH.CONH_2$, which crystallises in silvery scales melting at 216°, and decomposing at the same time. Boiling with dilute acids splits it up into urea and hippuric acid.

The best method to prepare acetylglycocine is to boil a mixture of acetic chloride, glycocine, and benzene (the latter to prevent the temperature rising too high): the acid is thus obtained much freer from secondary products than when the silver salt of glycocine is employed. All the compounds of this acid are very soluble, and its ether distils without decomposition. L. T. T.

Preparation of Acetamide and other Amides of the Acetic Series. By SCHULZE (*J. pr. Chem.* [2], **27**, 512—517).—By heating 20 grams of ammonium acetate with 26 grams of acetic anhydride, 96 per cent. of the theoretical quantity of acetamide can be obtained. This mode of preparation, however, is costly, owing to the high price of acetic anhydride. It can be more cheaply prepared by heating 1 molecule of ammonium thiocyanate with $2\frac{1}{2}$ mols. of glacial acetic acid for three or four days at about the boiling point. The decomposition which takes place is shown by the equation $CNS.NH_4 + 2\overline{Ac}HO = 2\overline{Ac}NH_2 + COS + H_2O$. When ammonium thiocyanate is heated with formic acid, it readily yields formamide. If propionic acid be employed, propionamide is formed. J. I. W.

Derivatives of Ethyloximide and Ethylsuccinimide. By A. PINNER (*Ber.*, **16**, 1655—1659).—The formation of ethylsuccinimide hydrochloride, $NH:C(OEt).CH_2.CH_2.C(OEt):NH,2HCl$, and of succinamidine hydrochloride, $NH:C(NH_2).CH_2.CH_2.C(NH_2):NH,2HCl$, has been described by the author (this vol., p. 731), and also the conversion of the latter compound by water into succinimidine hydrochloride,  $\left.\begin{array}{l}CH_2.C:NH\\ |\\ CH_2.C:NH\end{array}\right>NH,HCl$.* An attempt to obtain *oximidine* by the method yielded negative results.

Oxamidine hydrochloride, $NH:C(NH_2).C(NH_2):NH,HCl + H_2O$, can be obtained by the action of alcoholic ammonia on ethyl oximide hydrochloride. It forms large plates, readily soluble in water, sparingly in alcohol. It easily decomposes, especially in solution, but can be recrystallised from water without being converted into oximidine.

On adding an ammoniacal solution of silver nitrate to an aqueous solution of succinimidine hydrochloride, a white precipitate of *silver*

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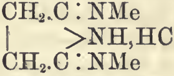
* The errors in the formulæ previously given are due to misprints in the original paper.

succinimidine, $C_4H_6N_3Ag$, is obtained, sparingly soluble in ammonia, more readily in water, and very readily in nitric acid. Succinimidine hydrochloride is decomposed by platinic chloride with formation of succinic acid and precipitation of ammonium platinochloride. By the action of methylamine on ethyl succinimide hydrochloride, *dimethylsuccinimidine hydrochloride*,  $\begin{array}{l}CH_2.C:NMe\\ | \qquad\quad >NH,HCl\\ CH_2.C:NMe\end{array}$, is obtained, and not the expected tetramethylsuccinamidine. It gives no precipitate with ammoniacal solution of silver nitrate, but is decomposed by platinic chloride in the same way as succinimidine. A. K. M.

Conversion of Nitrils into Imides. By A. PINNER (*Ber.*, **16**, 1643—1655).—The preparation of ethylformimide hydrochloride has been previously described by the author (this vol., p. 731); also its reactions with alcohols, with ammonia, and with amines. By means of the same reaction he has prepared the following compounds:—*Methylformimide hydrochloride*, $NH:CH.OMe,HCl$, forming short thick lustrous prisms; *propylformimide hydrochloride*, an oil crystallising at low temperatures, moderately soluble in ether; *isobutylformimide hydrochloride*, also moderately soluble in ether, and crystallising on cooling to lustrous scales; *amylformimide hydrochloride*, crystallising in scales, sparingly soluble in ether; and *benzylformimide hydrochloride*, forming scales almost insoluble in ether. By the action of alcohols on these, orthoformates are obtained. In the preparation of *mixed* orthoformates by the action, *e.g.*, of methyl alcohol on ethylformamide, a number of products are formed (*i.e.*, dimethyl ethyl orthoformate and also the trimethyl and triethyl derivatives), so that the author has not succeeded in obtaining them all in a state of purity. The following list contains the formulæ and boiling points of the orthoformates obtained:—

$CH(OMe)_3$	102°	$(PrO)_2CH.OEt$	185—187°
$(MeO)_2CH.OEt$	116—120	$(PrO)_2CH.OC_5H_{11}$	222—230
$(MeO)_2CH.OPr$	150—155	$(C_4H_9O)_2CH.OPr$	207—208
$(MeO)_2CH.OC_5H_{11}$	234—240	$(C_4H_9O)_2CH.OPr$	212—214
$CH(OEt)_3$	145	$(C_4H_9O)_2CH.OC_5H_{11}$	230—235
$(EtO)_2CH.OPr$	165—170	$(C_5H_{11}O)_2CH.OEt$	253—255
$CH(OPr)_3$	192—196	$(C_5H_{11}O)_2CH.OPr$	254—255
$(PrO)_2CH.OMe$	180—182	$CH(OC_5H_{11})_3$	260—265

Dimethylformamide obtained by the action of an alcoholic solution of methylamine on ethylformimide yields a *platinochloride*,

$$(NMe:CH.NHMe)_2,H_2PtCl_6,$$

crystallising in short prisms, readily soluble in water. The *platinochloride* of the corresponding ethyl derivative,

$$(NEt:CH.NHEt)_2,H_2PtCl_6,$$

is only sparingly soluble in cold, but readily in hot water, from which it crystallises in thick red prisms. By the action of dimethylamine on ethylformimide hydrochloride, *isodimethylformamidine hydrochloride*, $NH\colon CH.NMe_2,HCl$, is produced, melting at 168—169°. It is deliquescent, readily soluble in water and in alcohol, and crystallises in prisms of a vitreous lustre. Different results are obtained by the action of diethylamine and of methylaniline; the former yielding a compound of the formula $C_{10}H_{21}N_3,HCl$, and the latter *methylformanilide*, CHO.NMePh, boiling at 243—244°. By the action of tertiary amines, ethylformimide is liberated, and salts of the amines produced. *Acetylformimide*, $NH\colon CH.O\overline{Ac}$, is obtained by the action of acetic anhydride on ethylformimide acetate, and forms short thick white prisms melting at 70°, and readily soluble in the ordinary solvents.

The author has also prepared the ethyl derivatives of acetimide, propionimide, capronimide, and benzimide, and from hydrocyanic acid and glycol he has obtained ethyleneformimide hydrochloride,

$$(NH\colon CH.O)_2C_2H_4,2HCl.$$

Ethylacetimide hydrochloride, $NH\colon CMe.OEt,HCl$, forms fern-like groups of lustrous rhombic plates; *ethylacetimide*, $NH\colon CMe.OEt$, is a liquid of peculiar odour boiling at 97°. *Ethylpropionimide hydrochloride*, $NH\colon CEt.OEt.HCl$, crystallises in prisms. It is decomposed by alcoholic ammonia with formation of *propionamidine hydrochloride*, $NH\colon CEt.NH_2,HCl$, a crystalline deliquescent compound. *Ethylcapronimide hydrochloride* is an oil. *Ethylbenzimide hydrochloride*,

$$NH\colon CPh.OEt,HCl,$$

forms large transparent prisms decomposing at 118—120° before melting. A. K. M.

Aldehyde-ammonium Bases. By G. MEYER (*Ber.*, **16**, 1444).—The author has not succeeded in again obtaining a good yield of trimethylaldehydeammonium iodide by the method he previously described (this vol., 568). W. C. W.

Dicyanodiamide. By E. BAMBERGER (*Ber.*, **16**, 1459—1464).—*Guanylthiocarbamide* (thiodicyanodiamidine) is best prepared by digesting dicyanodiamide with sulphuretted hydrogen water at 60—70°. The base is precipitated from the solution by the addition of ammonium oxalate and oxalic acid. The precipitate is decomposed by baryta-water, in order to obtain the free base. If ammonium sulphide is substituted for sulphuretted hydrogen, ammonium thiocyanate and thiocarbamide are also formed. Guanylthiocarbamide can also be prepared by heating a salt of guanylcarbamide (dicyandiamidine) with sulphuretted hydrogen water.

Ammonia and methylamine are formed when dicyanodiamide is reduced by zinc and hydrochloric acid, but the presence of guanidine could not be detected. A sodium salt, $C_2H_3N_4Na$, is precipitated when alcoholic solutions of sodium ethylate and dicyanodiamide are mixed; it is soluble in water and in dilute alcohol. It is decomposed by carbonic acid. With hydrochloric acid it yields guanylcarbamide.

The author considers that the constitution of dicyanodiamide is best represented by the formula $NH\colon C(NH_2).NH.CN$.

W. C. W.

Thiophene, a Substance contained in Coal-tar Benzene. By V. MEYER (*Ber.*, **16**, 1465—1478).—The fact that benzene from coal-tar has the power of yielding a deep blue coloration, due to the formation of indophenine, when shaken with isatin and strong sulphuric acid (this vol., 315), is owing to the presence of about 0·5 per cent. of a sulphur compound, C_4H_4S, to which the author has given the name *thiophene.* Benzene from benzoic acid does not contain this impurity, and consequently does not yield the indophenine reactions with sulphuric acid and isatin.

In order to obtain thiophene in sufficient quantity for investigation, 250 litres of the purest commercial benzene were shaken with 25 litres of strong sulphuric acid for four hours. The layer of acid was separated from the benzene, diluted with water, and a lead salt of thiophenesulphonic acid precipitated. The oily liquid obtained by distilling the lead salt with ammonium chloride is washed with water and with potash, to remove mercaptan. It is then dried over calcium chloride and distilled. The distillate (b. p. 84°) consists of a mixture of thiophene (70 per cent.) and benzene (30 per cent.). It does not solidify when surrounded by a freezing mixture of ice and salt. It dissolves in strong sulphuric acid at the ordinary temperature, but the solution soon decomposes, evolving sulphuretted hydrogen and sulphurous anhydride. Decomposition does not, however, ensue if the liquid is diluted with 100 times its volume of light petroleum. Pure thiophene is obtained by converting this sulphuric acid solution into lead thiophenesulphonate, and distilling the lead salt with ammonium chloride. Thiophene is a colourless mobile oil boiling at 84°, immiscible with water. Its sp. gr. at 23° is 1·062 compared with water at the same temperature. Thiophene is not attacked by sodium, but is readily oxidised by nitric acid, and yields two substitution-products when acted on by bromine. *Monobromothiophene* (b. p. 150°) is produced in small quantities in the preparation of the dibromo-compound. It bears a close resemblance to monobrombenzene. The sp. gr. of the compound is 1·652 at 23°. *Dibromothiophene* (b. p. 211°) closely resembles dibromobenzene in its chemical and physical properties. Like this substance, it does not readily wet glass. The sp. gr. of dibromothiophene is 2·147 at 23°.

In consequence of the author's discovery that the formation of indophenine is entirely due to the presence of thiophene in the benzene used, Baeyer has examined his specimen of indophenine, and found that it contains sulphur. W. C. W.

Tetrethylbenzene and Hexethylbenzene. By K. GALLE (*Ber.*, **16**, 1744—1748).—To prepare tetrethylbenzene, a mixture of aluminium chloride, benzene, and ethyl bromide is heated at 100° in sealed tubes for nine hours. The tubes are opened three or four times, and fresh ethyl bromide introduced. The crude product is purified by treatment with strong sulphuric acid and fractional distillation. The portion boiling above 255° is again heated for six hours to convert it into hexethylbenzene. The portion boiling between 250° and 255° is dissolved in double the volume of fuming sulphuric acid at 60°. By carefully adding one-fourth of the volume of water to the solution *tetrethylbenzenesulphonic acid* is obtained as a silky crystalline mass.

The *barium salt*, $(C_{14}H_{21}SO_3)_2Ba,6H_2O$, crystallises in flat prisms, which are sparingly soluble. The *sodium salt*, $C_{14}H_{21}SO_3Na,5H_2O$, forms microscopic quadratic plates, which effloresce on exposure to the air. The *copper salt*, crystallising in lustrous plates containing 8 mols. H_2O, and the *cadmium salt* in prisms containing 7 mols. H_2O, are less soluble than the barium sulphonate. The *sulphamide*,

$$C_{14}H_{21}.SO_2NH_2,$$

melting at 104—105°, crystallises in glistening scales which melt at 104°, and dissolve freely in alcohol and in glacial acetic acid.

Tetrethylbenzene, prepared from the sodium sulphonate, is a colourless oil, lighter than water, b. p. 251°. *Monobromotetrethylbenzene*, $C_{14}H_{21}Br$ (b. p. 284°), is a heavy liquid. The *dibromo*-derivative, $C_{14}H_{20}Br_2$, forms colourless prisms, soluble in alcohol. It melts at 74·5°, and boils at 330°. *Dinitrotetrethylbenzene* is deposited from an alcoholic solution in pale lemon-coloured rhombic prisms melting at 115°.

Prolonged boiling with a solution of potassium permanganate converts tetrethylbenzene into prehnitic acid.

In the preparation of tetrethylbenzene, an isomeride appears to be formed, which yields a dibromo-derivative crystallising in flat prisms melting at 110°.

Hexethylbenzene, $C_{18}H_{30}$, is deposited from alcohol in long monoclinic prisms, soluble in ether and in hot alcohol. It melts at 126°, and boils at 305° (corr.). It is identical with the hydrocarbon described by Allright, Margan, and Woolworth (*Compt. rend.*, **86**, 887). Hexethylbenzene dissolves in warm fuming sulphuric acid, and is deposited unaltered on cooling. Treatment with a mixture of strong nitric and sulphuric acids converts the hydrocarbon into dinitrotetrethylbenzene. Similarly dibromotetrethylbenzene is produced by the action of bromine on a dry mixture of iodine and hexethylbenzene. W. C. W.

Coal-tar Toluene. By V. MEYER (*Ber.*, **16**, 1624—1625).—The author finds that pure toluene does not give Laubenheimer's colour-reaction with phenanthraquinone (*Ber.*, **8**, 224), this property being destroyed by agitating toluene with concentrated sulphuric acid. It appears that coal-tar toluene contains a substance analogous to thiophene (this vol., p. 1091), which, like the latter, can be removed by sulphuric acid. A. K. M.

Chlorides of Ortho- and Meta-nitrobenzyl. By M. ABELLI (*Gazzetta*, **13**, 97—99).—Chloride of benzyl is allowed to drop slowly into five times its weight of nitric acid (sp. gr. 1·5), kept cool by immersion in water; the product is then precipitated by water, the solid paranitrobenzyl compound separated by a vacuum filter, and the oil, cooled by a frigorific mixture, is again filtered in the same manner to remove the portion of the para-compound which crystallises out. The oil could not be distilled *per se*, even under reduced pressure, but it passed over in a current of steam as a yellowish oil. On analysis it gave numbers corresponding with the formula $C_6H_4(NO_2).CH_2Cl$. When oxidised by potassium permanganate, it yielded a mixture of para-ortho- and meta-nitrobenzoic acids, showing that the oil is a mixture of ortho- and meta-nitrobenzyl chlorides holding some of the para-compound in solution. C. E. G.

Trinitrotoluene and Liquid Dinitrotoluene. By A. CLAUS and H. BECKER (*Ber.*, **16**, 1596—1598).—From a comparison of the crystalline form of trinitrotoluene with that of symmetrical trinitrobenzene, Friedländer concluded that the former must also have a symmetrical constitution, $C_6H_2Me(NO_2)_3$ [$Me : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6$]. With a view to establish this constitution, the authors heated trinitrotoluene with concentrated nitric acid in sealed tubes at 180°, and obtained symmetrical trinitrobenzene melting at 121—122°. It is evident from this constitution that the dinitrotoluene obtained by Staedel and Becker from the trinitro-compound must have the formula $C_6H_3Me(NO_2)_2$ [$Me : NO_2 : NO_2 = 1 : 2 : 6$], the only other possible one being the known [1 : 2 : 4] dinitrotoluene. From this *solid* dinitrotoluene, Staedel and Becker obtained, however, the same nitrotoluidine which Cunerth (*Annalen*, **217**, 205) and Bernthsen (*Annalen*, **172**, 223) prepared from *liquid dinitrotoluene*. From an examination of the latter, the authors find it to consist of a mixture of two solid dinitrotoluenes, trinitrotoluene, and orthonitrotoluene, its liquid condition being due to the presence of the mononitro-derivative. A. K. M.

Derivatives of Diethyl-toluene.* By W. DAFERT (*Monatsh. Chem.*, **4**, 616—629).—Diethyl-toluene, $C_{11}H_{16} = C_6H_5.CH(Et_2)$, discovered in 1867 by Lippmann and Louguinine (*Annalen*, **145**, 106), is prepared by the action of zinc-ethyl mixed with an equal volume of benzene on benzylidene chloride: $C_6H_5.CHCl_2 + ZnEt_2 = ZnCl_2 + C_6H_5.CHEt_2$. The process may be conducted either at ordinary temperatures, or at 40° in a flask filled with carbonic anhydride, the benzylidene chloride being added by drops, and the mixture cooled if the escape of vapour becomes violent. The pasty product is added to water acidulated with hydrochloric acid, and the pale yellow oil which rises to the surface is washed with aqueous sodium carbonate and with water, then filtered, dried, and fractionated, the fractions 170—190°, 190—210°, and 210° to beyond the ordinary thermometric range, being collected separately.

Fraction I (170—190°) is a turbid mobile yellow liquid, which may be freed from chlorinated products by heating it in a sealed tube at 100° with lead nitrate, and from benzaldehyde, formed in the treat-

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* Called by the author *Amyl-benzene;* but this name (or *Isopentyl-benzene*) belongs properly to the isomeric hydrocarbon, $C_6H_5.C_2H_4.CHMe_2$, obtained by the action of sodium on a mixture of monobromobenzene and isopentyl or amyl bromide, $C_2H_4.CHMe_2Br$.—H. W.

ment, by agitation with acid sodium sulphite. It is then several times fractionated, the greater part distilling at 178—180°. This portion is diethyl-toluene. It is a strongly refractive, colourless, aromatic liquid, having a density of 0·8731 at 21°, very slightly attacked by reagents, slightly soluble in sulphuric and nitric acids. It is not attacked by ordinary chromic acid mixture, but is slowly oxidised by chromic trioxide dissolved in glacial acetic acid, yielding the monosulphonic acid $C_{11}H_{15}.SO_3H$, the barium salt of which crystallises in large nacreous laminæ, having the composition

$$(C_{11}H_{15}.SO_3)_2Ba + \tfrac{3}{2}H_2O.$$

By the action of nitric acid on diethyl-toluene, soluble nitro-products are obtained, partly oily, partly solid, having a persistent odour, and reducible by zinc in acetic acid solution, yielding a base whose hydrochloride forms white needles, together with a deep purple dye-stuff.

Fraction II (b. p. 190—210°) consists chiefly of benzylidene chloride, showing that the action of the zinc-ethyl on that compound is by no means complete.

Fraction III (b. p. 210°) is a thick red oil, which has the odour of the paraffins, and when gently heated with fuming sulphuric acid yields a yellow oil, which, after solution in alcohol, precipitation with water, drying, and distillation, has the composition of bidiethyl-tolyl,* $C_{22}H_{30} = CHEt_2.C_6H_4—C_6H_4.CHEt_2$. This compound is a pale yellow oil, having a peculiar odour, miscible with alcohol and ether in all proportions, but not with water, boiling above 360°, and not solidifying at 0°. It dissolves, with aid of heat, in sulphuric and nitric acids, and yields substitution-products with bromine and iodine, in the latter case only when heated.

On adding bromine (1 mol.) to boiling diethyl-toluene, the latter is converted, with copious evolution of HBr, but without carbonisation, into a heavy dark-brown transparent oil; and on washing this with aqueous sodium carbonate and with water, then filtering, drying, and distilling in a vacuum, an oil is obtained, clear and colourless at first, but turning brown and opaque and decomposing towards the end. The colourless portion, when distilled, washed, and dried, gave by analysis numbers agreeing with the formula of *bromodiethyl-toluene* or *diethyl-tolyl bromide*, $C_{11}H_{15}Br = CH_2Me.CHPh.CHBrMe$.

When this last compound is added by degrees to boiling water, a fragrant oil is obtained, which floats on the water, and after washing, drying, and heating with sodium at 170—180° for a day or two, is free from bromine, and distils almost completely at 170—180°. The liquid thus obtained has the composition of a *pentenyl-benzene*, $C_{11}H_{14} = C_6H_5(C_5H_9)$, or a polymeride thereof, and is formed from the bromodiethyl-toluene by simple abstraction of HBr.

The same compound is formed, together with *di-pentenyl-benzene*, $C_{22}H_{28}$, by the action of alcoholic potash on bromodiethyl-toluene. The two compounds are separated by fractional distillation, the first, which has not been obtained quite pure, distilling at 173—177°, the second at 208—212°. The former has a density of 0·8458 at 23°, the

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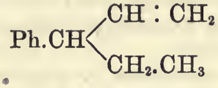
* Called in the original paper, *Diamylphenyl.*

latter 0·9601 at the same temperature. Pentenyl-benzene absorbs bromine, yielding the compound $C_{11}H_{14}Br_2$, in the form of an oil, which attacks the eyes strongly, and gives up its bromine to caustic potash. Dipentenyl-benzene is not acted on by bromine at ordinary temperatures, but yields substitution-products when heated therewith.

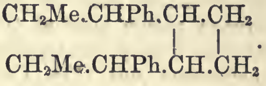
According to its synthesis from the bromide

$$CHPh.(CHBrMe).CH_2Me,$$

pentenyl-benzene and dipentenyl-benzene may be represented by the following formulæ:—



$$Ph.CH\begin{cases} CH:CH_2 \\ CH_2.CH_3 \end{cases}$$



$$\begin{array}{l} CH_2Me.CHPh.CH.CH_2 \\ \qquad\qquad\qquad\;\; | \quad\; | \\ CH_2Me.CHPh.CH.CH_2 \end{array}.$$

The polymerisation of pentenyl-benzene is in accordance with Perkin's view (*Chem. News*, 1877, 271), that polymerisation takes place with especial facility in those hydrocarbons which contain the group $—CH:CH_2$.

Pentenyl- and dipentenyl-benzene are but slowly oxidised by ordinary chromic acid mixture or by aqueous chromic acid; but chromic anhydride dissolved in glacial acetic acid acts violently on pentenylbenzene, yielding benzoic and acetic acids. Dipentenylbenzene similarly treated yields products the nature of which has not yet been determined. H. W.

Mesitylene. By ROBINET and COLSON (*Compt. rend.*, **96**, 1863—1864).—*Mesitylenic glycol*, $C_6H_3Me(CH_2.OH)_2$, is obtained by the prolonged ebullition of mesitylene dichloride (m. p. 41·5°) with an excess of lead carbonate suspended in water. It is a colourless viscous liquid, which boils at 190° under a pressure of 20 mm. and at 280° with partial decomposition under a pressure of 750 mm.; sp. gr. 1·23 at 25°. It has a bitter taste, is very soluble in alcohol, dissolves in twice its weight of anhydrous ether, and in about twenty times its weight of water. When treated with fuming hydrobromic acid, it yields mesitylene dibromide melting at 66·4°.

Mesitylene diacetate, $C_6H_3Me(CH_2.\overline{Ac}O)_2$, is obtained by prolonged ebullition of a mixture of mesitylene dichloride, acetic acid, and silver acetate. It is a colourless oily liquid, which boils at 244° under a pressure of 120 mm.; sp. gr. at 20° = 1·12. It is almost inodorous, but has a disagreeable burning taste. When saponified with potassium carbonate it yields the glycol previously described.

C. H. B.

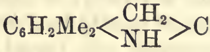
Derivatives of Mesitylene. By P. WISPEK (*Ber.*, **16**, 1577—1580).—*Mesityl bromide*, $C_6H_3Me_2.CH_2Br$, forms long white prisms melting at 37·5—38°, and boiling (with slight decomposition) at 229—231° under a pressure of 740 mm. It dissolves readily in alcohol, ether, and chloroform, and crystallises from hot ether in clusters of long needles. Its vapour is very irritating to the eyes. *Mesityl acetate*, $C_9H_{11}.O.\overline{Ac}$, is a colourless liquid of agreeable ethereal odour boiling at 228—231° (745 mm.); its sp. gr. is 1·0903 at 16·5°.

On saponification with alcoholic potash, a colourless liquid is obtained boiling at 218—221°. It is heavier than water, resembles benzyl alcohol in odour, and is doubtless mesityl alcohol, $C_9H_{11}.OH$. *Symmetrical dimethylphenylacetic acid*, $C_6H_3Me_2.CH_2.COOH$, dissolves readily in alcohol and in ether, very sparingly in cold water, moderately in boiling water; under hot water, it melts before dissolving, and crystallises in long prisms resembling phthalic anhydride. It melts at 100°, boils at 273° (735 mm.), and volatilises very slowly in a current of steam. When warmed with alkaline permanganate solution, it is readily oxidised, with formation of uvitic acid, whilst with dilute nitric acid it yields α-nitro-dimethylphenylacetic acid. Concentrated nitric acid at 0° dissolves it unchanged; at ordinary temperatures, with formation of two nitro-acids.

The *potassium salt*, $C_9H_{11}.COOK,H_2O$, crystallises in slender silky needles; the *calcium salt*, $(C_9H_{11}.COO)_2Ca,3H_2O$, in hard thick transparent well-formed needles, which are readily soluble in water, and lose half their water of crystallisation over sulphuric acid; the *barium salt*, $(C_9H_{11}.COO)_2Ba,4H_2O$, in well-formed characteristic transparent prisms, which lose their water of crystallisation over sulphuric acid; the *magnesium salt*, $(C_9H_{11}.COO)_2Mg,5H_2O$, in stellate groups of long slender silky needles, and the *silver salt*, $C_9H_{11}.COOAg$, in long thin needles soluble in boiling water.

α-Nitrodimethylphenylacetic acid,

$$C_6H_2Me_2(NO_2).CH_2.COOH\ [CH_2.COOH : NO_2 : Me : Me = 1 : 2 : 3 : 5],$$

obtained by warming dimethylphenylacetic acid with dilute nitric acid for 6—8 hours, crystallises from hot water in long slender yellowish-coloured needles melting at 139°, and readily soluble in alcohol and in ether, sparingly in boiling water, and insoluble in cold water. The *calcium salt*, $(C_9H_{10}NO_2.COO)_2Ca,4H_2O$, forms large thick transparent needles, which lose their water at 100°, and detonate when strongly heated; the *barium salt*, $(C_9H_{10}NO_2.COO)_2Ba,4\frac{1}{2}H_2O$, behaves in the same way, and crystallises in slender needles; the *silver salt*, $C_9H_{10}NO_2.COOAg$, melts on heating and burns, leaving a residue of spongy silver. On reducing α-nitrodimethylphenylacetic acid by means of tin and hydrochloric acid, and pouring the product into cold water, *carbomesyl*,  $C_6H_2Me_2<\genfrac{}{}{0pt}{}{CH_2}{NH}>CO$, is obtained as a voluminous white precipitate. It is very stable, crystallises from hot dilute alcohol in white needles, which become brown at about 215° and sublime; it melts at 231—232°. It is insoluble in cold water, very sparingly soluble in hot water, readily in hot alcohol or benzene, insoluble in ammonia, soluble in warm potash, in hot concentrated hydrochloric acid, and in cold concentrated sulphuric acid; water precipitates it unchanged from the two latter solutions.

A. K. M.

Reaction of Aromatic Amines with Lactic Acid. By O. WALLACH and M. WÜSTEN (*Ber.*, **16**, 2007—2010).—The authors have examined the reaction between hydroxyl-acids and aromatic amines with a view of preparing substances allied to oxindole or quinoline.

On heating a mixture of aniline, nitrobenzene, and lactic acid with concentrated sulphuric acid, a basic substance boiling at 246° was obtained, of the composition $C_{10}H_9N$, or a methylquinoline, which is probably identical with Döbner's quinaldine. On heating this base and benzaldehyde in molecular proportions with zinc chloride, a crystalline basic substance (m. p. 100°) of formula $C_{17}H_{13}N$ was obtained. This base combines directly with bromine to form an addition-product. $C_{17}H_3NBr_2$, crystallising in white iridescent leaflets melting at 173°. This shows that the base $C_{17}H_{13}N$ is an unsaturated compound, and if the original base be a methyl quinoline, its composition must be expressed by the formula $(C_9H_6N)CH \colon CHPh$, or a representative of a new series of compounds. The authors also briefly examined analogous substances obtained from metanitrobenzaldehyde and ortho- and para-hydroxybenzaldehyde. V. H. V.

Decomposition of Rosaniline by Water. By C. LIEBERMANN (*Ber.*, **16**, 1927—1931). In former experiments, on the decomposition of rosaniline by water, the author obtained, besides dihydroxybenzophenone, two nitrogenous substances whose separation not only from hydrobenzophenone, but also from one another, presented several difficulties. The author, working on a larger scale, has succeeded in separating them by processes described in full in the communication, and has isolated *diamido-* and *hydroxyamido-methylbenzophenone*. The former, $C_6H_4(NH_2).CO.C_6H_3Me.NH_2$, crystallises in needles of a pale red colour, which melt above 220° and are soluble in hydrochloric acid, insoluble in alkalis. With benzoic chloride, it gives a dibenzyl-derivative, $C_6H_4(NH\overline{Bz}).CO.C_6H_3Me.NH\overline{Bz}$, crystallising in needles melting at 226°. Hydroxyamidomethylbenzophenone,

$$C_6H_4(OH).CO.C_6H_3Me.NH_2,$$

forms colourless needles, soluble in soda, insoluble in acids and ammonia; it gives a dibenzyl-derivative,

$$C_6H_4(O\overline{Bz}).CO.C_6H_3Me.NH\overline{Bz},$$

which crystallises in needles melting at 192°.

Judging from the results obtained on the decomposition of rosolic acid by water, it would appear that in the corresponding decompositions of rosaniline, besides the three substances, dehydroxydiamidomethyl- and hydroxyamidomethyl-benzophenone, homologues of them are also formed. V. H. V.

The Violet Derivatives of Triphenylmethane. By O. FISCHER and L. GERMAN (*Ber.*, **16**, 706—710).—In a paper on methyl-violet derived from triphenylmethane (Abstr., 1879, 787), E. and O. Fischer came to the conclusion that this body was *pentamethylpararosaniline.* Several reasons, however, and especially the fact that the sixth amido-hydrogen-atom could not be replaced by methyl, led the authors of the present paper to doubt the correctness of that conclusion. They have therefore subjected methyl-violet to further investigation. It was prepared as before described; the melting point is 173°, not 163°, as erroneously given in the former paper. If this substance contained only five methyl-groups, the sixth hydrogen-atom should be replaceable. All the authors' endeavours to replace it by continued treatment, at all temperatures below that at which decomposition sets in, with acetic anhydride, acetic and benzoic chlorides, proved fruitless. Neither could the so-called hexmethylparaleucaniline be obtained by the action of metallic sodium and methyl iodide.

To show that the complexity of the molecule is not the cause of this difficulty of replacement, the authors have made the acetyl-compound of tetramethylparaleucaniline; this substance by exhaustive methylation yields the same end-product as methyl-violet, so that the two compounds must stand in close relationship.

Acetyltetramethylparaleucaniline, $C_{25}H_{29}N_3O$, is easily produced by boiling the base with excess of acetic anhydride. It crystallises in needles melting at 108°. It is still a strong base, and its dilute sulphuric acid solution, when treated with manganese dioxide, gives *acetyltetramethylpararosaniline*, a fine green colouring-matter. If this is boiled with concentrated hydrochloric acid, the acetyl-group is split off, and the same violet is obtained as by the direct oxidation of tetramethylparaleucaniline by chloranil. This is in agreement with the fact pointed out by E. and O. Fischer that it is the *free* amido-groups in the triphenylmethane-derivatives which are the colour-determining elements. The green colour to which methyl-violet turns on addition of hydrochloric acid is without doubt due to the acid becoming added to one of the amido-groups, and thus neutralising it.

From all these facts, the authors believe that methyl-violet is not a penta-methyl-compound, but is *hexmethylpararosaniline*, and that the above-mentioned hexmethylparaleucaniline is really an *ethane* derivative, and is converted into a *methane* derivative only during the oxidation. Finally the authors believe that the colouring-matter Wichelhaus obtained (Abstr., 1882, 58) by acting on dimethylaniline with chloranil is really the leuco-base of methyl-violet, and has not the formula $C_{16}H_{20}N_2$, which Wichelhaus adopted. His analyses agree just as well with the formula $C_{25}H_{31}N_3$ as with $C_{16}H_{20}N_2$.

L. T. T.

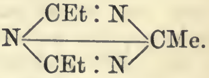
Dye-stuff from Dimethylaniline and Chloranil. By H. WICHELHAUS (*Ber.*, **16**, 2005—2007).—In some former experiments, the author was unable to prepare in a sufficiently pure state a crystalline substance formed by the action of dimethylaniline on chloranil. By an improvement in the method, this base was successfully purified, and obtained in the form of small colourless prisms melting at 190°, having the composition $C_{21}H_{29}N_3O$, insoluble in water and sparingly soluble in alcohol. As this base and rosaniline have the same composition, the author has re-examined the latter, and proved that it is a mixture of two isomeric substances, one of which is identical with the product from dimethylaniline and chloranil, whilst the other is a red-brown powder melting at 130°. These two substances can be separated by frequent solution in sulphuric acid and reprecipitation by alcohol, and then boiling the precipitate frequently with petroleum, which leaves the red-brown powder undissolved. When reduced with tin and hydrochloric acid, the dye-stuffs give isomeric substances, the one forming glistening leaflets melting at 173°, which readily assume a violet colour, the other, steel-grey prismatic crystals melting at 155°. V. H. V.

Formation of Nitrile Bases from Organic Acids and Amines. By A. Bernthsen (*Ber.*, **16**, 767—769).—In a former paper (this vol., p. 580) the author described the formation of a base $C_{19}H_{13}N$, by the abstraction of water by means of zinc chloride from benzoyldiphenylamine, $N\overline{Bz}Ph_2$. The author, in conjunction with F. Bender, has now prepared the same substance directly from benzoic acid and diphenylamine by heating them with zinc chloride. This reaction appears to be a general one. Formic acid and diphenylamine (and also ready-formed formyl diphenylamine) yield a base with an exceedingly burning taste, and having the formula $C_{13}H_9N$. It forms an easily soluble hydrochloride and a yellowish-green platinochloride. Ammonia precipitates the base from a solution of its hydrochloride in the form of a white crystalline powder. O. Fischer has recently (*Ber.*, **16**, 74) obtained the analogous base, $C_{14}H_{11}N$, from diphenylamine and glacial acetic acid. L. T. T.

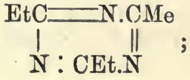
Action of Acetic Anhydride on the Amidines. By A. Pinner (*Ber.*, **16**, 1659—1663).—Pinner and Klein showed that dibenzimidine, NH : CPh.NH.CPh : NH, is produced by the action of acetic anhydride on benzamidine (*Ber.*, **11**, 8). With a view to examine other amidines in the same direction, the author heated a mixture of acetic anhydride, formamidine hydrochloride, and sodium acetate, but, instead of the desired product, he obtained *diacetylformamidine*, $N\overline{Ac} : CH.NH\overline{Ac}$, crystallising in short thick lustrous prisms sparingly soluble in cold water, moderately in hot water, and very sparingly in alcohol. It sublimes at a high temperature without melting. From propionamidine hydrochloride, sodium acetate, and acetic anhydride, a compound is obtained of the formula $C_8H_{13}N_3$. It is very sparingly soluble in cold water, more readily in hot water, and readily in alcohol and in acids; it melts at 204° and sublimes in the form of long white prisms. The *platinochloride*, $C_8H_{13}N_3,H_2PtCl_6 + 3H_2O$, crystallises in large red rhombic plates. The formation and constitution of this substance may probably be explained by the following equations:—

$$2NH : CEt.NH_2 + \overline{Ac}_2O = NH : CEt.NH.CEt : NH + \overline{Ac}NH_2 + \overline{Ac}OH$$

and $NH : CEt.NH.CEt : NH + \overline{Ac}OH = 2H_2O +$



in which case it must be regarded as *ethenyldipropionimidine*, or it may be assumed to be a homologue of cyanethine, thus



but its high melting point and the composition of its platinochloride are opposed to the latter formula. A. K. M.

Azylines. By E. Lippmann and F. Fleissner (*Ber.*, **16**, 1421—1434). —By the cautious addition of potassium nitrite to a solution of dimethylanilineazyline in glacial acetic acid, *paranitrodimethylaniline* is produced. By a similar reaction, diethylanilineazyline is converted into *paranitrodiethylaniline*, identical with the nitrodiethylaniline obtained by the oxidation of nitrosodiethylaniline. This substance (m. p. 76°) crystallises in monoclinic needles [$a : b : c = 1·0342 : 1 : 0·8245$, $\gamma = 99° 27'$]. The crystals are yellow in colour and dissolve freely in warm alcohol. The nitro-products form platinochlorides crystallising in triclinic prisms.

Nitrous acid acts on azylines as an oxidising agent; the acid being reduced to nitric oxide; but as no nitrogen is liberated during the reaction, the nitro-product must be produced by the direct union of oxygen with the nitrogen-atoms occupying the para-position.

Diethylanilineazyline is converted into *diethylparaphenylenediamine* by treatment with stannous chloride. This base, which can also be prepared by the reduction of nitrosodiethylaniline, boils at 260—262°. It exhibits the following reactions:—With sodium hypochlorite a brown coloration, with potassium chromate a violet coloration, with iodine and copper sulphate a red coloration. Ferric chloride first produces a red coloration, which is followed by a precipitate. The platinochloride forms red or yellow triclinic plates. When a mixture of diethylanilineazyline (1 mol.), ethyl iodide (4 mols.), and a small quantity of alcohol is heated at 100° in sealed tubes, free iodine, resinous bye-products, and tetrethylphenylenediamine hydriodide, $C_6H_4(NEt_2)_2,2HI$, are formed.

Tetrethylphenylenediamine prepared by the addition of potash to this iodide, or from diethylphenylenediamine, melts at 52° and boils at 280°. It forms monoclinic plates which sometimes resemble cubes in appearance [$a : b : c = 0·99 : 1 : 1·833$, $\gamma = 90° 30'$]. The base is very soluble in ether, chloroform, benzene, and light petroleum. It is best purified by recrystallisation from a mixture of alcohol and water. The *platinochloride*, $C_6H_4(NEt_2)_2,H_2PtCl_6$, forms pale yellow cubical crystals. The double mercuric chloride, $C_6H_4(NEt_2)_2,2HCl,2HgCl_2$, crystallises in the monoclinic system. The periodide, $C_6H_4(NEt_2)_2,I_6$, forms black prisms sparingly soluble in alcohol. The iodide produced by the action of methyl iodide on diethylanilineazyline does not yield a base on the addition of potash, but bases were obtained in this way from the iodides prepared by the action of ethyl iodide on dimethylanilineazyline and on dipropylanilineazyline, which boil at 275° and at 295—300° respectively. Azylines do not alter on exposure to the air. When azyline is oxidised by potassium permanganate, ammonia, and acetic, carbonic, and oxalic acids are formed. The constitution of these azylines may be represented by the type

$$\overset{4}{N}Et_2.C_6H_4.\overset{1}{N} : \overset{1}{N}.C_6H_4.\overset{4}{N}Et_2$$

W. C. W.

Substitution-products of Azobenzeneparasulphonic Acid. By J. V. JANOVSKY (*Ber.*, **16**, 1486—1490).—The author has previously pointed out (*Ber.*, **15**, 2575) that in the nitration of azobenzeneparasulphonic acid, two nitro-derivatives are formed, viz., a meta-compound, $C_6H_4(NO_2)N \colon NC_6H_4.SO_3H$ [$NO_2 : N . N : SO_3H = 3 : 1 : 1 : 4$], and the isomeric α-acid [$NO_2 : N : N : SO_3H = 4 : 1 : 1 : 4$]. The best conditions for obtaining the α-acid are to keep the temperature of the mixture below 100°, and not to use a large excess of nitric acid (1 of azobenzenesulphonic acid to 5—6 parts of nitric acid, sp. gr. 1·4). The α-acid crystallises in beautiful needles of a fiery hue. It is deposited from dilute nitric acid in rhombic plates. A warm concentrated aqueous solution gelatinises on cooling. The salts of this acid crystallise readily; $NO_2.C_{12}H_8N_2.SO_3K$ forms orange-coloured rhombic plates, sparingly soluble in water. 100 c.c. of water at 17° dissolve 0·161 gram of the salt. $NO_2.C_{12}H_8N_2.SO_3Na + 2H_2O$ crystallises in monoclinic plates or needles, which are sparingly soluble in water. The addition of potash or soda to a moderately-concentrated aqueous solution of the acid produces a crystalline precipitate of the potassium or sodium salt respectively. The barium salt, $(NO_2.C_{12}H_8N_2.SO_3)_2Ba$, forms crystalline scales, sparingly soluble in water. On reduction with tin and hydrochloric acid, the α-nitro-acid is converted into paraphenylenediamine and sulphanilic acid; but on cautious treatment with stannous chloride, it yields the hydrazamido-acid, $NH_2.C_{12}H_8N_2H_2.SO_3H$. This substance forms microscopic rhombic crystals, which are very sparingly soluble in water; 100 parts of water at 97° dissolve 0·39 gram of the acid. The potassium salt forms golden crystals, sparingly soluble in cold water. The sodium salt is freely soluble. The barium salt forms flat rhombic prisms, containing 4 mols. H_2O.

If, however, an alcoholic solution of the nitro-acid is reduced by ammonium sulphide, *amidazobenzeneparasulphonic* acid is produced: 100 c.c. of water at 22° dissolve 0·0168 gram of the acid. From hot water, it is deposited in salmon-coloured plates. The potassium salt, $NH_2.C_{12}H_8N_2.SO_3K + H_2O$, forms golden rhombic plates. The sodium salt crystallises in needles; both salts dissolve freely in water. The barium salt, $(NH_2.C_{12}H_8N_2.SO_3)_2Ba + 6H_2O$, forms brilliant needles, resembling potassium chlorobromate; 100 c.c. water at 24° dissolve 0·064 gram of the salt. The calcium salt crystallises in beautiful efflorescent yellow plates, containing 4 mols. H_2O; 100 c.c. water at 18·5° dissolve 0·2589 gram. The lead salt forms monoclinic plates of an orange colour; its solubility is 0·0642 gram per 100 c.c. water at 18·5°. Since this acid yields sulphanilic acid and paraphenylenediamine on reduction, its constitution may be represented by the formula $C_6H_4(NH_2).N_2.C_6H_4.SO_3H$ [$NH_2 : N : N : SO_3H = 4 : 1 : 1 : 4$]; but this is identical with the formula for the sulphonic acid obtained by the action of aniline on the compound obtained from sulphanilic acid by means of the diazo-reaction. A comparison of their salts shows, however, that the two acids are not identical. W. C. W.

Amidazobenzeneparasulphonic Acid. By J. V. JANOVSKY (*Monatsh. Chem.*, **4**, 652—659).—The author has already obtained (p. 324 of this volume) by reduction of paranitrazobenzeneparasulphonic acid, a product agreeing nearly in composition, either with amidazobenzenesulphonic acid, $C_{12}H_8N_2(NH)_2.SO_3H$, or with amidhydrazobenzenesulphonic acid $C_{12}H_8N_2H_2(NH_2).SO_3H$. This acid may be prepared either with stannous chloride or with ammonium hydrosulphide, and its chemical relations show that it is really a hydrazo-compound, inasmuch as, when treated with potassium nitrite, it oxidises in the first instance to an amido-acid, which may then be converted into a diazo-compound. Whether the action of stannous chloride gives rise to an azo- or a hydrazo-compound depends on the duration of the process, but on the whole the hydrazo-acids appeared to be formed most readily by the action of stannous chloride in acid solutions.

Amidazobenzene-p-*sulphonic acid*, $C_6H_4(NH_2).N : N.C_6H_4.SO_3H$ [4 : 1 : 1 : 4′], is most readily obtained in the pure state by the action of ammonium hydrosulphide on the corresponding nitro-acid, the product obtained with stannous chloride consisting almost wholly of the hydrazo-acid. The resulting dark brown-red solution boiled with hydrochloric acid deposits nearly all the amido-acid, together with sulphur, and the acid may be purified by boiling the filtered solution with barium carbonate, and decomposing the resulting barium salt, after crystallisation, with hydrochloric acid. It then separates as a salmon-coloured precipitate, made up of microscopic crystalline scales, containing 1 mol. H_2O. Its solutions are faintly yellow; those of its salts have a deep yellow colour, and crystallise well. The *potassium salt*, $C_{12}H_8(NH_2)N_2.SO_3K + H_2O$, crystallises in gold-coloured plates belonging to the orthorhombic system, and exhibiting the faces $P\breve{\infty}$, $\infty P\breve{\infty}$, $\infty\bar{P}\infty$. It dissolves very readily in water and is very hygroscopic. The *barium salt*, $(NH_2.C_{12}H_8N_2.SO_3)_2Ba + 6H_2O$, crystallises in fiery-coloured needles, exhibiting very fine colours in polarised light. The *calcium salt*, $(NH_2.C_{12}H_8N_2.SO_3)_2Ca + 4H_2O$, crystallises in nacreous yellow laminæ, or from dilute solution in large rhombic plates, P, $\infty P\breve{\infty}$, or in very flat pyramids. The *strontium salt* forms very long flexible needles, containing 2 mols. water. The *lead salt* crystallises in small laminæ, exhibiting in the polarising microscope a remarkable striation, appearing half light and half dark. H. W.

Diazo-derivatives. By P. Griess (*Ber.*, **16**, 2028—2036).—*Azobenzenephenylenediaminebenzene*, $PhN : N.C_6H_2(NH_2)_2.N : NPh$, formed by the action of diazobenzene nitrate on azobenzene-metaphenylenediamine (the so-called chrysoïdine), crystallises in dull-red glistening needles melting at 250°, sparingly soluble in most solvents. Its hydrochloride forms a violet amorphous mass; the platinochloride a violet-brown amorphous precipitate.

By the action of diazobenzene nitrate on azoparatoluene-phenylenediamine on the one hand, and of diazotoluene nitrate on azobenzene-phenylenediamine on the other, two identical substances are formed as subsidiary products, but the chief products are isomeric.

From the former reaction, α-azobenzenephenylenediamineparatoluene, $PhN : N.C_6H_2(NH_2)_2.N : NC_7H_7$ is obtained in the form of dark-red glistening needles melting at 192°, insoluble in alcohol, soluble in ether; from the latter, azoparatoluenephenylenediaminebenzene, $C_7H_7N : N.C_6H_2(NH_2)_2.N : NPh$, which crystallises also in red needles (m. p. 214°). From both the above reactions is obtained β-azobenzenephenylenediamineparatoluene, which forms delicate hairy needles, melting at 225°.

Azoparatoluenephenylenediamine β-naphthalene,

$$C_7H_7N : N.C_6H_2(NH_2)_2.N : NC_{10}H_7,$$

obtained by the action of paradiazotoluene nitrate on β-azonaphthalenephenylenediamine, forms copper-red glistening leaflets, soluble in chloroform, insoluble in alcohol. A solution of this substance, although of a deep colour, possesses no tinctorial properties, but must be converted into the sulphonic acid, the salts of which may be used as dyes.

Azo-parasulphobenzenephenylenediaminebenzene, prepared by the action of paradiazobenzenesulphonic acid on chryosïdine hydrochloride, forms small microscopic grains; its potassium salt crystallises in red-brown leaflets.

Azophenylenediaminebenzenemetabenzoic acid, prepared by the action of metadiazobenzoic acid on chrysoïdine, forms a brown-red crystalline precipitate.

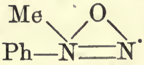
Azodibenzenephenylenediamine, $PhN : N.C_6H_4.N : N.C_6H_3(NH_2)_2$, obtained by the action of diazoazobenzene on phenylenediamine, crystallises in brown-red needles melting at 105°, easily soluble in ether and alcohol; it dyes silks and wools of a brown-red colour. Its *dihydrochloride* forms a black-brown amorphous mass; its *monohydrochloride*, steel-grey glistening needles; its *platinochloride*, brown leaflets.

Azoparasulphobenzenephenylenediamine,

$$C_6H_4(SO_3H).N : N.C_6H_4.N : N.C_6H_2(NH_2)_2,$$

formed by the action of *m*-diamidobenzene on paradiazoazobenzenesulphonic acid, is a dark red amorphous mass; its potassium salt crystallises in copper-red needles, characterised by their remarkable solubility in water; the solution of this substance dyes wools a brown-red colour.

Azosulphobenzenetoluenediamine, prepared by the action of paradiazoazobenzenesulphonic acid on metadiamidotoluene, forms reddish-brown needles. V. H. V.

Constitution of the Nitrosamines. By E. ERLENMEYER (*Ber.*, **16**, 1457—1459).—The author is of opinion that nitrosamines contain the group , methylphenylnitrosamine would be represented by the formula . Methylphenylhydrazine would consequently be $NHMePh : NH$, instead of $NMePh.NH_2$. The primary hydrazine would have the constitution $NH_2Ph : NH$, and the salts of the hydrazine $NH_2R : NH_2R'$. W. C. W.

Aldoximes. By B. LACH (*Ber.*, **16**, 1780—1787).—Phthalylhydroxamic acid is produced by the action of hydroxylamine on a warm concentrated alcoholic solution of phthalic anhydride. Camphoric anhydride yields a resinous substance which slowly crystallises when similarly treated. Lactones are not converted into aldoximes by the action of hydroxylamine. Unsaturated acids, *e.g.*, oleic and stearolic, do not combine with hydroxylamine.

Salicylaldoxime, $OH.C_6H_4.CH \vdots NOH$ [$OH : NOH = 1 : 2$], is prepared by adding sodium carbonate to a concentrated alcoholic solution of salicylaldehyde and hydroxylamine hydrochloride. As the reaction is very energetic, it is best to cool the vessel containing the mixture. After 24 hours, the solution is rendered feebly acid by hydrochloric acid; a portion of the alcohol is removed by evaporation, and the residue is extracted with ether. From the ethereal solution, the salicylaldoxime is obtained in white crystals melting at 57°, soluble in alcohol, ether, and benzene. The base also dissolves easily in hydrochloric acid, but decomposition takes place on warming the solution. The hydrochloride is prepared by passing dry hydrochloric acid gas into an ethereal solution of the base: it is a hygroscopic body, and is decomposed by water. The sodium salt, $ONa.C_6H_4.CHNONa + 3H_2O$, is obtained in yellow crystalline scales when salicylaldoxime is boiled with sodium and absolute alcohol. It decomposes on exposure to the air. The aqueous solution gives a white precipitate with lead acetate; with cobalt and ferric salts brown precipitates; and with silver nitrate a white precipitate which changes to black when heated. The methyl and ethyl salts are aromatic oils. Salicylaldoxime appears to form an acetic derivative. *Paroxybenzaldoxime* forms white needles which melt at 65°. The sodium salt is more stable than that of the ortho-compound. *Vanillinaldoxime*, $OH.C_6H_3(OMe).CH \vdots NOH$, melts at 117°. Resorcylaldehyde and resorcyldialdehyde yield nitrogenous compounds when they are acted on by hydroxylamine. Thiobenzaldehyde resembles benzaldehyde in its behaviour with hydroxylamine, yielding benzaldoxime, but thioacetones are not acted on.

W. C. W.

Paranitrobenzaldoxime and Amidobenzaldehyde. By S. GABRIEL and M. HERZBERG (*Ber.*, **16**, 2000—2004).—The authors have shown that paranitrobenzaldehyde in an alkaline solution reacts with hydroxylamine hydrochloride to form paranitrobenzaldoxime. This latter substance when reduced with ammonium sulphide yields *paramidobenzaldoxime*, $C_7H_8ON_2$, which forms golden crystals melting at 124°, and soluble in alcohol and ether; when these are dissolved in acids, the originally clear liquid is converted into a blood-red jelly in which crystalline needles appear. These crystals, however, could not be obtained in a state of perfect purity, but they appear to have the composition of *paramidobenzaldehyde*, C_7H_7NO. This compound dissolves in acetic anhydride to form paracetamidobenzaldehyde,

$$NH.\overline{Ac}C_6H_4 : CHO = [4 : 1],$$

which crystallises in long glistening needles; these melt at 154°, and form *paracetamidobenzaldoxime* with hydroxylamine. V. H. V.

Metamidobenzaldoxime. By S. Gabriel (*Ber.*, **16**, 1997—2000).—The author in a previous research has shown that orthamidobenzaldehyde may be obtained by the oxidation of orthamidobenzaldoxime, the nature of the reaction being—

$$C_6H_4(NH_2).CH : NOH + H_2O = C_6H_4(NH_2).CHO + NH_3O$$

and $2NH_3O + O_2 = N_2O + 3H_2O$. In the present paper, he examines the corresponding meta-derivatives; he was, however, unable to obtain the metamidoaldehyde. *Metamidobenzaldoxime*,

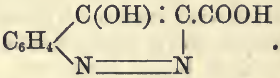
$$(1)NH_2.C_6H_4.CH : NOH(3),$$

obtained by the reduction of nitrobenzaldoxime, crystallises in snow-white needles (m. p. 88°), soluble in alcohol and ether; its platinochloride crystallises in orange-golden needles. V. H. V.

Cinnoline-derivatives. By V. v. Richter (*Ber.*, **16**, 677—683).—The author describes a number of derivatives (obtained from orthamidophenylpropiolic acid) of a new base having the formula

$$C_6H_4<\begin{matrix}CH : CH\\ N{=\!=}N\end{matrix}>.$$

This base may be looked upon as quinoline in which one CH-group has been replaced by N, and the author therefore proposes the name cinnoline for it.

Hydroxycinnoline-carboxylic acid,  $C_6H_4<\begin{matrix}C(OH) : C.COOH\\ |\\ N{=\!=}N\end{matrix}$. Orthamidophenylpropiolic acid (2 grams) is dissolved in hot hydrochloric acid (5—6 parts acid to 15—20 of water), and to the crystalline mass obtained on cooling, a concentrated solution of sodium nitrite (1 gram) is added. The resulting diazo-chloride is diluted and heated to about 70°, when hydroxycinnoline-carboxylic acid is gradually deposited in slightly coloured needles. The yield is from 80 to 85 per cent. of theory. Purified by crystallisation from 50 per cent. acetic acid, it forms colourless prisms or slender needles almost insoluble in water, and but slightly soluble in boiling alcohol and ether. It melts with evolution of carbonic anhydride at 260—265°, being converted into *hydroxycinnoline*.

Hydroxycinnoline,  $C_6H_4<\begin{matrix}C(OH) : CH\\ N{=\!=}N\end{matrix}>$, is easily soluble in alcohol and ether, from which solvents it crystallises with difficulty. It crystallises from water in small scales or prisms, melting at 225° and subliming to white crystalline flocks. Hydroxycinnoline resembles α-hydroxyquinoline (carbostyril) in possessing both basic and acid properties, both in a more marked degree. It dissolves in caustic alkalis and also in solutions of the carbonates. Warm dilute hydrochloric acid dissolves it easily, *hydroxycinnoline chloride* crystallising out in colourless needles which effloresce in the air. *Hydroxycinnoline platinochloride* crystallises in groups of small prisms.

On reducing hydroxycinnoline by distillation with zinc-dust, an oil containing small quantities of oxindole is obtained. Dissolved in dilute hydrochloric acid, and freed from the last traces of oxindole by washing with ether, it colours pine-shavings an intense orange. From the hydrochloric solution sodium hydroxide throws down a white flocculent precipitate having a peculiar smell reminding one at once of nicotine and quinoline. The author is not at present able to say whether this is actually the base $C_8H_6N_2$ sought for.

The formation of these compounds from orthamidophenylpropiolic acid is somewhat similar to that of carbostyril discovered by Baeyer and Bloem (this vol., p. 196).

In the preparation of orthamidophenylpropiolic acid by the reduction of the nitro-compound with ammonaical ferrous sulphate solution, the author advises the gradual introduction of the nitro-acid into the reducing solution as giving a much better yield of the amido-acid than the reverse operation. L. T. T.

Orthotolylhydantoïn. By A. EHRLICH (*Ber.*, **16**, 742—743).—The author has prepared the above body by Swebel's reaction, by heating together equal weights of orthotolylglycocine and carbamide. The ingredients were well mixed in a mortar, and then heated at 180°; at 170° frothing commenced and continued for about two hours when the reaction was completed.

Orthotolylhydantoïn, $C_{10}H_{10}N_2O_2$, crystallises in pale-yellow plates melting at 176°. It is soluble in alkalis, ammonia, alcohol, boiling water, and hot hydrochloric acid; sparingly so in ether and acetic acid. Boiled with barium hydroxide, it forms a barium compound, but is thrown down again unchanged on adding a mineral acid; no hydantoic acid being produced. Neither could the author obtain glycollic acid by treatment with alcoholic potash, or monotolylcarbamide by boiling with concentrated hydrochloric acid. In both cases the hydantoïn remained unchanged. L. T. T.

Products of the Decomposition of Mixed Aromatic Thiocarbamides by Acids. By K. MAINZER (*Ber.*, **16**, 2016—2028).—In a former research, the author has shown that when mixed aromatic thiocarbamides are heated with hydrochloric acid, they are decomposed into two thiocarbamides and two amines (Abstr., 1882, 1212—1213). In the present communication, it is shown that phosphoric acid effects the same change very completely, the yield of the product of the decomposition varying from 70—100 per cent. of that required by theory.

Diparaphenylethylthiocarbamide, $C_6H_4Et.NH.CS.NH.C_6H_4Et$, from phenylethylamine and carbon bisulphide crystallises in long needles melting at 144°: it is decomposed by phosphoric acid into phenylethylthiocarbimide and phenylethylamine.

Phenylethylphenylthiocarbamide, $NHPh.CS.NH.C_6H_4Et$, from phenylthiocarbimide and aniline, crystallises in leaflets (m. p. 103°) soluble in alcohol and ether; it is decomposed into phenyl- and phenyl-ethylthiocarbamides with aniline and phenylethylamine.

Phenylethyl-α-naphthylthiocarbamide, $C_6H_4Et.NH.CS.NH.C_{10}H_7$, from phenylethylamine and α-naphthylthiocarbimides crystallises in needles, decomposed by phosphoric acid into phenylethyl- and α-naphthyl-thiocarbimides with phenylethylamine and α-naphthylamine.

Phenyl-β-naphthylthiocarbamide, from phenylethylamine and α-naphthylthiocarbamide, crystallises in leaflets melting at 158°, decomposed by phosphoric acid into phenyl-β-naphthyl and β-naphthylthiocarbamides with phenylethylamine and β-naphthylamine.

Phenisobutylphenylthiocarbamide, $C_6H_4(C_4H_9).NH.CS.NHPh$, from phenylisobutylamine and phenylthiocarbamide, crystallises in leaflets (m. p. 152), decomposed by phosphoric acid into phenyl- and phenylisobutyl-thiocarbamide with aniline and phenylisobutylamine. Phenylisobutylthiocarbimide crystallises in large white needles melting at 266°.

Phenisobutylparatolylthiocarbamide, $C_6H_4(C_4H_9).NH.CS.NH.C_7H_7$, from phenylisobutylamine and paratolylthiocarbimide, crystallises in glistening leaflets melting at 137°, decomposed by phosphoric acid into paratolyl- and phenylisobutyl-thiocarbimides with paratoluidine and phenylisobutylamine.

Phenisobutylphenethylthiocarbamide, $C_6H_4(C_4H_9).NH.CS.NH.C_6H_4Et$, from phenylisobutylamine and phenylethylthiocarbimide, crystallises in white glistening prisms melting at 140°, decomposed by phosphoric acid into phenylisobutyl- and phenylethyl-thiocarbimides with phenylethyl- and phenyliso-butylamine.

Phenisobutyl-β-naphthylthiocarbamide,

$$C_6H_4(C_4H_9).NH.CS.NH.C_{10}H_7,$$

from β-naphthylthiocarbamide and phenylisobutylamine, forms small white leaflets melting at 153°, decomposed by phosphoric acid into phenyl-isobutyl- and β-naphthyl-thiocarbamide with isobutylamine and β-naphthylamine. V. H. V.

Action of Phenylthiocarbimide on Amido-acids. By O. Aschan (*Ber.*, **16**, 1544—1545).—When alanine (4 grams) is heated with phenylthiocarbimide (6·2 grams) until no more water is given off (the temperature being kept below 140°), the following reaction takes place:—

$$CH_3.CH(NH_2).COOH + CS\colon NPh = H_2O + C_{10}H_{10}N_2OS.$$

The product melts at 184°, dissolves in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, also in the fixed alkalis, and more sparingly in ammonia.

Corresponding compounds, $C_9H_8N_2OS$ and $C_{13}H_{16}N_2OS$, have likewise been obtained from glycocine and leucine, the former of which is yellow, dissolves in alkalis to a pink solution, and decomposes without melting when heated above 200°. The body obtained from leucine melts at 179°. A. K. M.

Diphenylcarbamide and Triphenylguanidine. By W. Hentschel (*J. pr. Chem.* [2], **27**, 498—503).—When ethyl carbanilate is heated with sodium phenate it yields symmetric diphenylcarbamide, and the latter, when heated with sodium ethylate, forms triphenylguanidine.

If a mixture of sodium phenate and ethyl carbanilate in equivalent proportions is distilled, pure phenetol passes over at 220°. When the distillation is complete, the residue in the retort is boiled several times with water, whereby sodium carbonate is dissolved and prismatic crystals of diphenylcarbamide are left. The reactions are expressed by the following equations:—

(1.) $NHPh.COOEt + PhONa = PhOEt + NHPh.COONa.$
(2.) $2(NHPh.COONa) = CO(NHPh)_2 + Na_2CO_3.$

The author has prepared large quantities of diphenylcarbamide according to Hofmann's method, and finds that it is advisable to act with phosgene gas on aniline suspended in water, instead of in the dry state. Although Merz and Weith state that diphenylcarbamide is decomposed by heat into carbonic anhydride, aniline and triphenylguanidine, the author was able to distil it without decomposition at 260°, or even maintain it at 220° for several hours. When it is heated with sodium ethylate at 220° in a current of hydrogen, a clear oily distillate passes over boiling at 180°, and having all the properties of aniline. The residue in the retort dissolves in hot dilute hydrochloric acid, and on adding concentrated hydrochloric acid the hydrochloride of triphenylguanidine crystallises out. The action of sodium ethylate is shown by the equation $2CO(NHPh)_2 + EtONa = CNPh(NHPh)_2 + ONa.COOEt.$* In addition to triphenylguanidine, sodium ethyl carbonate is formed. If sodium phenate be present, sodium salicylate will be produced.

(1.) $CO(NHPh)_2 + EtONa = CNPh(NHPh)_2 + NH_2Ph + COONa.OEt.$

(2.) $COONa.OEt + C_6H_5.ONa = ONa.C_6H_4.COONa + EtOH.$

J. I. W.

Phenolic Phosphates. By R. Heim (*Ber.*, **16**, 1763—1770).—The neutral phosphates of phenyl, cresyl, and naphthyl are best prepared by the action of phosphorus oxychloride on the phenols in slight excess, 90 per cent. of the theoretical yield of triphenyl phosphate, and of triortho- and tripara-cresyl phosphates can be obtained. *Triorthocresyl phosphate* is a brown oil which is partially decomposed by distillation. In preparing α- and β-*trinaphthyl phosphates* $(C_{10}H_7)_3PO_4$, the retort containing the mixture of naphthol and phosphorus oxychloride, must be heated on a sand-bath or layer of asbestos, so as to cause the liquid to boil very gently. If the retort is heated too strongly, a slight explosion may occur. The yield is 60—65 per cent. of the theoretical.

W. C. W.

Chlorophenols obtained by the Action of Alkaline Hypochlorites on Phenol. By T. Chandelon (*Ber.*, **16**, 1749—1753).—If a 3 per cent. solution of phenol in an alkali is mixed with sodium hypochlorite in molecular proportions, orthomonochlorophenol is produced. By increasing the quantity of hypochlorite a mixture of orthoparadichlorophenol, $C_6H_3Cl_2.OH$ [OH : Cl : Cl = 1 : 2 : 4], b. p.

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* The numbers of C, H, and N-atoms on the two sides of this equation do not agree. The error is in the original paper.—[Ed.]

210°, and orthodichlorophenol [1 : 2 : 6], boiling at 218°, is obtained. A still larger proportion of hypochlorite yields trichlorophenol,

$$C_6H_2Cl_3.OH.$$

W. C. W.

Action of Iodine on Sodium Phenate. By C. SCHALL (*Ber.*, **16**, 1897—1902).—On adding iodine to sodium phenate suspended in carbon bisulphide, a mixture of mono-, di-, and tri-iodophenols is formed. In order to separate these constituents, the oil obtained after filtration of the sodium iodide and evaporation of the carbon bisulphide, is shaken up with potash and ether, which separates the moniodophenol. The fraction taken up by potash is acidified and then distilled in a current of steam; the distillate separates into a liquid orthiodophenol, and a solid orthodiiodophenol. The residue left in the distillation flask consists of triiodophenol.

Action of Chlorine on β-Sodium Naphthol.—If chlorine gas is passed into β-sodium naphthol suspended in carbon bisulphide, and the crude product after evaporation of the latter is steam-distilled, the distillate consists of a monochloronaphthol crystallising in needles, which melt at 68°.

Action of Nitric Peroxide on Sodium Phenate.—If nitric peroxide be brought into sodium phenate in carbon bisulphide kept cool, there is formed orthonitro- and paranitro-phenol, which may be separated by the usual method of steam distillation. The reaction is as follows:—$2NO_2 + C_6H_5.ONa = NaNO_2 + C_6H_4(NO_2).OH$; the presence of sodium nitrite was recognised by Liebermann's reaction.

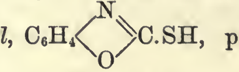
V. H. V.

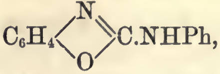
Diiodophenol. By C. SCHALL (*Ber.*, **16**, 1902—1903).—Diiodophenol can be conveniently prepared from iodine and sodium phenate, the sodium iodide being separated by carbon bisulphide. On heating diiodophenol with acetic chloride, *acetyldiiodophenol*, $C_6H_3I_2.O\overline{Ac}$, is formed; it crystallises in small prisms (m. p. 107°). The benzoyldiiodophenol, $C_6H_3I_2.O\overline{Bz}$, prepared by a similar process melts at 95·96°. The potassium diiodophenate crystallises in needles.

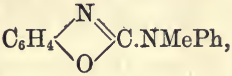
V. H. V.

Reduction of Monobromorthonitrophenol. By F. SCHOFF (*Ber.*, **16**, 2069—2070).—Pfaff has established that monobromometanitrophenol yields metamidophenol when reduced, and states that the relative position of the substituting groups can have no effect on the reaction. On the other hand, the researches of Staedel prove that in the reduction of bromamido-anisoïl and phenetoïl the bromine-atom is not replaced by hydrogen. On account of this discrepancy, the author has examined the action of tin and hydrochloric acid on parabromorthophenol; the resultant substance was proved by various characteristic tests to be parabromorthamidophenol. V. H. V.

Amidophenols. By F. A. KALCKHOFF (*Ber.*, **16**, 1825—1833).—

Thiocarbamidophenol,  $C_6H_4{<}\overset{N}{\underset{O}{\diamond}}{>}C.SH$, prepared by moistening a mixture of amidophenol hydrochloride and potassium xanthate, is identical with the "oxyphenylthiocarbimide" which Bendix (Abstr., 1879, 314) obtained by heating orthoxythiocarbamide above its melting point, and also with the compound which Dünner (*Ber.*, 9, 465) obtained by the action of carbon bisulphide on orthamidophenol.

Analidocarbamidophenol,  $C_6H_4\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle C.NHPh$, formed by boiling a mixture of aniline and thiocarbamidophenol, crystallises in long needles melting at 173°, soluble in alcohol, ether, and glacial acetic acid. Although it dissolves in acids and yields a platinochloride, it can be extracted from acid solutions by ether. By substituting methyl aniline in the preceding experiment, *methylanilidocarbamidophenol*,



$$C_6H_4\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle C.NMePh,$$

is obtained in the form of a blue fluorescent liquid, which boils above 360°. The platinochloride is crystalline. *Amidocarbamidophenol* has been described by Bendix under the name of phenylene carbamide. *Acetothiocarbamidophenol*, $C_6H_4(NO)CS\overline{Ac}$, crystallises in transparent plates melting at 120°, soluble in alcohol and acetic acid. Benzoic chloride acts on thiocarbamidophenol, yielding the benzoic-derivative of orthamidophenol, $\overline{Bz}O.C_6H_4.NH.COPh$ (m. p. 182°) the "orthobenzamidobenzoic phenol" of Morse and Güssefeld (*Ber.*, **15**, 370), and also phenylcarbamidophenol (m. p. 105°). *Oxycarbamidophenol*, described by Groenvik (*Bull. Soc. Chim.*, **25**, 178), is formed when oxyphenylcarbamide is heated.

In the preparation of orthhydroxythiocarbanilide, less than the theoretical quantity of phenylthiocarbimide must be taken, in order to prevent the formation of thiocarbamidophenol and thiocarbanilide by a secondary reaction. Hydroxythiocarbanilide, $C_{13}H_{12}N_2OS$, crystallises in white pearly plates melting at 146°, soluble in alcohol. It is decomposed by heat or by the action of mercuric oxide into anilidocarbamidophenol and sulphuretted hydrogen.

Derivatives of Paramidophenol. — Diparahydroxyphenylthiocarbamide, $CS(NH.C_6H_4.OH)_2$, prepared by digesting paramidophenol with carbon bisulphide, crystallises in plates which melt at 222° with decomposition. The compound is soluble in alkalis and in alcohol. It is desulphurised by mercuric oxide, and is apparently converted into dihydroxyphenylcarbamide.

Acethydroxythiophenylcarbimide forms white glistening plates melting at 36°, soluble in alcohol, ether, and glacial acetic acid. It unites with aniline, yielding *paracethydroxythiocarbanilide*,

$$NHPh.CS.NH.C_6H_4.O\overline{Ac},$$

(m. p. 137°). This substance dissolves in alcohol, ether, and glacial acetic acid. By the action of alcoholic ammonia on acethydroxyphenylthiocarbimide, parahydroxyphenylthiocarbamide is produced.

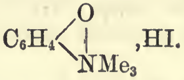
Free metamidophenol has not yet been obtained pure.

Reactions of the Amidophenol Hydrochlorides.

	Ortho.	Para.	Meta.
Ferric chloride....	Violet, changing to brown	Violet	Brownish-yellow solution.
Potassium dichromate	Brown solution....	Dark precipitate, brownish-violet solution	Dark brown solution.
Bleaching powder .	Violet-red-brown solution, dark precipitate	Violet-green-yellow solution	Red-brown solution.
Ammonia and silver nitrate	Dark brown precipitate	Grey precipitate, violet solution	Grey precipitate, green solution.

W. C. W.

Reaction of Ethyl Acetoacetate with Orthamidophenol. By A. Hantzsch (*Ber.*, **16**, 1946—1952).—The formation of pyridine-derivatives from ethyl acetoacetate and orthamidophenol led the author to examine a similar reaction in the case of an amidophenol, in order to form an ethereal salt of a carboxyl-derivative of skatole. The substance formed by heating orthamidophenol with ethyl aceto-acetate, has the composition $C_{12}H_{15}O_3N$, and for want of a better name may be called *anhydro-orthamidophenol ethyl aceto-acetate.* It crystallises in flat prisms (m. p. 107°), and is readily decomposed into orthamidophenol and ethyl acetoacetate. It forms a potassium compound of the composition $C_{24}H_{29}KO_6N_2$, derived from the original substance by the replacement of one hydrogen-atom of an amido-group in 2 mols. by one potassium-atom. This latter reacts with methyl iodide to form ortho-bromethylphenol ammonium iodide,



$$C_6H_4<\begin{matrix}O\\ |\\ NMe_3\end{matrix},HI.$$

V. H. V.

Conversion of Phenols into Nitrils and Acids. By R. Heim (*Ber.*, **16**, 1777—1780).—Benzonitril may be prepared by heating triphenyl phosphate with dried potassium cyanide or ferrocyanide in a current of hydrogen or carbonic anhydride. The yield is about 25 per cent. of the theoretical. Tolunitril and α- and β-naphthonitrils may be obtained by a similar process from tricresyl and trinaphthyl phosphates. A small quantity of phenol, cresol, &c., is always obtained as a bye-product. W. C. W.

Dichloroparacresol and Dichlororthocresol. By A. Claus and P. Riemann (*Ber.*, **16**, 1598—1603).—These compounds are obtained by the action of chlorine on para- and ortho-cresol heated to boiling in a large flask provided with an inverted condenser; an abundant evolution of hydrochloric acid takes place, whilst the liquid assumes a red colour, changing to dark brown, and finally becoming nearly black. When the liquid becomes thick, the reaction is stopped, and the product steam-distilled. Under these conditions the substitution takes place in the benzene ring and not in the side chain. *Dichloroparacresol*, $C_7H_6Cl_2O$, is readily soluble in alcohol, ether, and glacial acetic acid, sparingly in hot water, and crystallises in large prismatic needles. From a hot concentrated solution in light petroleum, it crystallises in long transparent needles, melting at 39°, whilst by the slow evaporation of a dilute solution, large transparent prisms are formed melting at 42°; the latter, however, soon become opaque, fall to pieces, and then melt at 39°. It forms a characteristic compound with ammonia, $C_7H_5Cl_2.ONH_4$, crystallising in long colourless needles, melting at 125° and subliming unchanged. It dissolves very readily in water. Dichloroparacresol is oxidised by nitric acid, with formation of oxalic acid, whilst a solution of chromic acid in glacial acetic acid oxidises it to *dichloroparahydroxybenzoic acid*, crystallising in long white needles melting at 156°. The *sodium salt* forms small lustrous needles readily soluble in water and in alcohol; the *silver salt*, obtained by precipitation from the latter, has the formula $C_7H_3Cl_2O_3Ag$. *Dichlororthocresol*, $C_7H_6Cl_2O$ (m. p. 55°) forms silky needles, readily soluble in alcohol, ether, benzene, chloroform, and light petroleum, sparingly in hot water. It is distinguished from the para-compound by forming no compound with ammonia. Nitric acid oxidises it to oxalic acid, whilst with chromic acid it yields *trichlorotoluquinone*, $C_7H_3O_2Cl_3$, crystallising in gold-coloured scales, readily soluble in ether and in hot alcohol. *Trichlorotoluhydroquinone*, obtained on heating the latter compound with sulphurous acid, forms white feathery crystals melting at 211—212°. A. K. M.

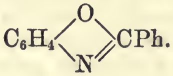
Thymol-derivatives. By A. K. Richter (*J. pr. Chem.* [2], **27**, 503—511).—Hentschel (*J. pr. Chem.* [2], **27**, 42) has found that ethyl phenyl carbonate and diphenyl carbonate, when treated with alkaline oxides of alcohol radicals are readily converted into salicylic acid. The author finds that ethyl thymyl carbonate and dithymyl carbonate when treated in a similar manner do not yield thymolic acid, but salicylic acid.

Ethyl thymyl carbonate is prepared by gradually adding an excess of ethyl chlorocarbonate to sodium thymol, the oil which separates being fractionally distilled. The carbonate boils at 259—262°.

Dithymyl carbonate is prepared by passing carbonyl chloride into an aqueous solution of sodium thymol, washing the oil which is formed with dilute soda solution, and finally distilling it; a clear liquid passes over above 270°, and solidifies on cooling to a striated crystalline mass. It has a faint odour, and melts at 48°. It dissolves in hot alcohol, ether, and chloroform, and crystallises from all of them in long needles or prisms. The author finds that if the liquid boiling above 270° be allowed to solidify slowly, a certain quantity of liquid of an unpleasant odour can be abstracted from the crystalline mass; it consists of ethyl thymyl carbonyl chloride. The same body has been previously observed by Kemp, but he was unable to obtain it sufficiently pure for analysis. He did not convert it into the amido-derivative, as he did the corresponding phenol and cresol bodies. The author has done so by passing dry ammonia gas into an ethereal solution of the substance. After filtering off the ammonium chloride and evaporating, the filtrate deposits slender needles of ethyl thymyl carbamic acid, $C_{11}H_{13}O_2Cl$. J. I. W.

Preparation of Phenetoïl. By H. KOLBE (*J. pr. Chem.* [2], **27**, 424—425).—Crude sodium ethyl sulphate is mixed with a thick solution of sodium phenol and heated in an autoclave under seven atmospheres' pressure for some hours at 150°. On opening the vessel, the phenetol is found floating on the semi-solid saline mass, and can be purified by washing with water and rectifying. A. J. G.

Molecular Transformations. By W. BÖTTCHER (*Ber.*, **16**, 1933—1939).—The author has previously observed that orthonitrobenzophenol, $C_6H_4(NO_2).O\overline{Bz}$, undergoes a molecular transformation when reduced, yielding orthobenzamidophenol, $C_6H_4(OH).NH\overline{Bz}$, a change which is attributed to the intermediate formation of benzamidophenol,



$$C_6H_4\Big\langle{}^{O}_{N}\Big\rangle CPh.$$

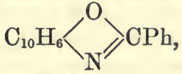
In order to see whether the reaction is general and the interpretation is correct, the behaviour of analogous substances under similar conditions is examined.

Orthonitroacetophenol, $C_6H_4(NO_2).O\overline{Ac}$, formed by the action of acetic chloride on sodium orthonitrophenate, forms asymmetrical crystals which melt at 40°, and boil at 255° with partial decomposition. It was not found possible to effect a molecular transformation with this substance.

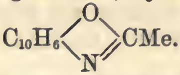
α-Nitro-β-benzonaphthol, $C_{10}H_6(NO_2).O\overline{Bz}$, prepared from the sodium salt of α-nitro-β-naphthol and benzoic chloride, crystallises in colourless needles melting at 142°, sparingly soluble in ether, easily soluble in boiling alcohol. When reduced with zinc-dust and acetic acid, it yields by molecular transformation *benzoyl-α-amido-β-naphthol*,

$$C_{10}H_6(NH\overline{Bz}).OH,$$

which crystallises in colourless leaflets (m. p. 245°).

Besides the latter substance, the intermediate compound, *benzenylamidonaphthol*,  $C_{10}H_6\Big\langle{}^{O}_{N}\Big\rangle CPh$, was formed, which confirms the author's interpretation of his results. A better yield of material is obtained by the sublimation of benzoylamidonaphthol; it crystallises in long colourless needles (m. p. 136°), soluble in ether and benzene, insoluble in water. The platinochloride forms golden needles.

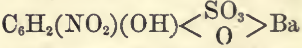
α-Nitro-β-acetonaphthol, $C_{10}H_6(NO_2).O\overline{Ac}$, from acetic chloride and the sodium salt of nitronaphthol, crystallises in long colourless needles, melting at 61°, soluble in alcohol and ether, insoluble in water. On reduction with zinc-dust and acetic acid, it is converted by a transformation analogous to that of the benzoyl-compound into acetyl-α-amido-β-naphthol, $C_{10}H_6(NH\overline{Ac}).OH$ [$NH\overline{Ac} = \alpha$, $OH = (5)$].

This latter substance crystallises in leaflets melting at 225°; by sublimation, it is converted into *ethenylamidonaphthol*,  $C_{10}H_6<\overset{O}{\underset{N}{}}>CMe$.

V. H. V.

Nitroresorcinolsulphonic Acid. By K. HAZURA (*Monatsh. Chem.*, **4**, 610—615).—Mononitroresorcinol heated at 80—90° with strong sulphuric acid, dissolves, with red-brown colour, and, on pouring the product into water, a small quantity of crystalline dinitroresorcinol separates out, while mononitroresorcinolsulphonic acid remains in solution.

Dinitrodiresorcinol, $C_{12}H_4(NO_2)_2(OH)_4$, is slightly soluble in water and in alcohol, easily soluble in ammonia, and is precipitated from the ammoniacal solution by acetic acid. It turns brown at 170°, and carbonises, without melting, at a higher temperature. It is formed by oxidation of the mononitroresorcinol, according to the equation $2C_6H_3(NO_2)(OH)_2 + O = H_2O + C_{12}H_4(NO_2)_2(OH)_4$.

Nitroresorcinolsulphonic acid, $C_6H_2(NO_2)(OH)_2.SO_3H$, is obtained by evaporating the filtrate to a syrup, and leaving it to cool, whereupon the whole solidifies to a thickish pulp, which may be freed from excess of sulphuric acid by draining on earthenware plates, then dissolved in the smallest possible quantity of water, and crystallised under the air-pump. As thus obtained, it contains $1\frac{1}{2}$ mol. H_2O; crystallises in white scales unctuous to the touch, dissolves very readily in water and in alcohol, but is insoluble in benzene and in chloroform. It melts at 124—125°. It forms three barium salts, viz.: α. $[C_6H_2(NO_2)(OH)_2.SO_3]_2Ba + 4H_2O$, obtained by adding caustic baryta to a strong solution of the acid as long as the crystalline precipitate exhibits a sulphur-yellow, and not a lemon-yellow colour. It dissolves readily in water, and crystallises from boiling water in large sulphur-yellow needles.—β.  $C_6H_2(NO_2)(OH)<\overset{SO_3}{\underset{O}{}}>Ba$ $+ 2H_2O$, obtained by adding a large quantity of baryta to the sulphur-yellow solution, is slightly soluble in cold, easily in hot water, and crystallises in lemon-yellow scales.—γ. $(C_6H_2NO_2)_2(SO_3)_2Ba.(O_2Ba)_2 + 10H_2O$, is obtained by adding an excess of baryta-water to a hot solution of the lemon-yellow salt in boiling water, and crystallises in blood-red needles.—These three salts differ remarkably in their behaviour when heated, the first carbonising at 125°, the second sustaining a temperature of 145°, while the third may be heated without decomposition to 180°. The potassium, copper, cobalt, and nickel salts are soluble in water, and may be obtained by decomposing the first barium salt with the corresponding soluble sulphates. The copper, cobalt, and nickel salts crystallise in long needles. By decomposing the potassium salt thus formed with potassium hydroxide, two potassium salts may be obtained analogous to the β and γ barium salts.

When nitroresorcinolsulphonic acid is treated with *bromine* it is converted, not into a brominated sulphonic acid, but into dibromonitroresorcinol, melting at 147°.

Amidoresorcinolsulphonic acid, $C_6H_2(NH_2)(OH)_2.SO_3H$, is obtained by heating the nitro-acid with tin and hydrochloric acid, the greater part separating from the liquid while still hot, the remainder on cooling. It crystallises in reddish-white, anhydrous, dimetric prisms, exhibiting the faces 0P, ∞P∞, ∞P. It is nearly insoluble in cold, and but slightly soluble in hot water, but dissolves readily in aqueous potash, forming a solution colourless at first, but quickly turning blue, green, and finally black. With ferric chloride, it gives a brown precipitate, which acquires a violet tinge on addition of sodium carbonate; with basic lead acetate a white precipitate becoming violet-blue on exposure to the air.

On passing hydrogen sulphide into the mother-liquor of amidoresorcinolsulphonic acid, filtering from tin sulphide, and concentrating the filtrate in a stream of carbonic anhydride, needle-shaped crystals were obtained, soluble in water, exhibiting with potash the same colour-reactions as amidoresorcinolsulphonic acid, and giving with basic lead acetate a violet-blue solution, which after some time deposited a blue precipitate, gradually turning black. These crystals gave by analysis numbers agreeing approximately with the formula of *diamidoresorcinol hydrochloride*, $C_{12}H_4(NH_2)_2(OH)_4$. By prolonged treatment with tin and hydrochloric acid, amidoresorcinolsulphonic acid is converted into a non-sulphuretted body, which however differs in its reactions with potash, from the last-mentioned compound. Further experiments on these two bodies are promised. H. W.

Sulphonic Acids of Quinol. By A. Seyda (*Ber.*, **16**, 687—694). —For the preparation of quinol, the following modification of Nietzki's process was found to give the best results. 1 part of aniline is dissolved in 8 parts sulphuric acid previously diluted with 10 parts water, and when the mixture is cold, 3½ parts of potassium dichromate dissolved in 20 of water is gradually added, the whole being left at rest for 12 hours, and the quinone extracted with ether. After distilling off the ether, 2 parts of boiling water are added, and sulphurous anhydride passed into the mixture until all the quinone is dissolved. After decoloration with animal charcoal the quinol is extracted with ether. The yield is about 60 per cent.

Quinol dissolves in mixed sulphuric acid very slowly in the cold, easily on heating, easily and with evolution of heat in fuming sulphuric acid; in both cases, however, mixtures of the mono- and di-sulphonic acids are produced, the complete separation of which is almost impossible. The author has therefore sought to find conditions more favourable for obtaining each acid alone.

Quinol-monosulphonic Acid.—1 part of quinol is heated with 8 parts mixed sulphuric acid at 50° for three hours with constant stirring, allowed to stand for 24 hours, and diluted. The liquid is then heated to boiling, and barium carbonate added to saturation; the filtered solution on being concentrated out of contact with the air, and allowed to cool, yields the barium salt in a crystalline state. *Barium quinolsulphonate*, $[C_6H_3(OH)_2.SO_3]_2Ba$, is easily soluble in hot water and dilute alcohol. In the cold ferric chloride produces a deep blue coloration, which gradually disappears on standing. It reduces mercury and silver salts. Its reaction is neutral, and it is decomposed at 110°. The *zinc salt*, $[C_6H_3(OH)_2,SO_3]_2Zn + 4H_2O$, is obtained from the barium salt by double decomposition with zinc sulphate, and is easily soluble in water and alcohol. It gives the same reactions as the barium salt. It effloresces over sulphuric acid, but does not lose all its water of crystallisation below 135°: it decomposes at 140°. The *potassium salt*, $C_6H_3(OH)_2.SO_3K$, crystallises well, and is the best means of purifying the acid; the barium salt is decomposed with potassium carbonate, and the concentrated filtrate is mixed with double its volume of alcohol, whereby a brown flocculent precipitate is produced, which is filtered off, and the alcohol removed by distillation out of contact with the air, when the concentrated aqueous solution deposits large, anhydrous, monoclinic crystals on cooling. the axis-ratios of these crystals are $a : b : c = 0·960028 : 1 : 2·225665$ and $\angle \beta = 107° 23' 9·1''$. This salt has a bitter taste, and is easily soluble in cold water. It is not decomposed at 170°. The *sodium salt* crystallises in minute octohedra; the *lead salt* is amorphous. *Quinolsulphonic acid*, obtained from the lead salt, solidifies over sulphuric acid to a crystalline mass, which deliquesces in the air, and gives an evanescent blue coloration with ferric chloride.

Quinoldisulphonic acid is best obtained by heating 1 part quinol with 5 parts fuming sulphuric acid for an hour at 100—110°. Water is added to the cold crystalline magma, the whole saturated with barium carbonate, the filtrate concentrated on the water-bath, and allowed to cool, when the barium salt of the disulphonic acid crystallises out.

Barium quinoldisulphonate, $C_6H_2(OH)_2(SO_3)_2Ba + 3\frac{1}{2}H_2O$, is sparingly soluble in cold water, easily in hot, and is precipitated even from dilute aqueous solutions by alcohol (difference from the monosulphate). It crystallises in long needles or prisms belonging to the monoclinic system. Ferric chloride gives a deep blue colour, which is permanent in the cold. Silver and mercury salts are reduced by it on boiling. It effloresces slowly over sulphuric acid, but only becomes anhydrous at 160°. The *zinc salt* crystallises with $6H_2O$ in white concentrically grouped needles. It is soluble in hot water, insoluble in alcohol. The *potassium salt* crystallises in prisms containing $4H_2O$, which they lose over sulphuric acid, or at 130°. It is not decomposed at 165°. The *sodium salt* is amorphous, soluble in water, insoluble in alcohol. The *lead salt* appears to have the formula

$$C_6H_2(OH)_2(SO_3)_2Pb + 3Pb(OH)_2.$$

Quinoldisulphonic acid prepared from the barium salt crystallises over sulphuric acid in long needles, of astringent taste, which deliquesce in the air.

From a comparison of his results with those already obtained, the author concludes that his (β) disulphonic acid is identical with that obtained by Graebe from potassium thiocronate; isomeric with the (α) acid obtained by Hesse from quinic acid; and that the third (γ) acid is at present unknown.

The author also endeavoured to replace the sulphonic groups by hydroxyl or the amido-group, but without success. Aqueous potash has no action, fusing potash re-forms quinol from both acids. Heating in closed tubes at 180° with aqueous or alcoholic ammonia also reproduces quinol. The potassium monosulphonate when heated with alcoholic potassium cyanide at 160° gives small quantities of a crystalline acid, soluble in alkalis, with a dark blue colour. L. T. T.

Chlorine and Bromine-derivatives of Quinone. By S. LEVY (*Ber.*, **16**, 1444—1448).—*Metadichloroquinone* prepared by Weselsky's method (*Ber.*, **3**, 646) may be best purified by recrystallisation from benzene or light petroleum. It is deposited from these solvents in yellow rhombic crystals. Dichlorquinol yields a diacetic derivative, $C_6H_2Cl_2(O\overline{Ac})_2$, crystallising in slender needles melting at 66·5°, and a dibenzoic-derivative, which crystallises in colourless opaque needles melting at 105°. Metadichloroquinone is formed by the oxidation of metadichloroparaphenylenediamine with sulphuric acid and potassium chromate.

Metadichlorometadibromoquinone, $C_6O_2Cl_2Br_2$, is easily prepared by boiling metadichloroquinone dissolved in acetic acid with bromine; when the liquid cools, the dichlorodibromoquinone is deposited, and by recrystallisation from benzene is obtained in reddish-yellow monoclinic plates isomorphous with tetrachloroquinone,

$$a : b : c = 1·1445 : 1 : 3·0286. \quad \beta = 74° \ 31'.$$

On reduction with stannous chloride solution, the metadichlorometadibromoquinol described by Krause (*Ber.*, **12**, 56) is formed. This substance is deposited from alcoholic chloroform in transparent monoclinic crystals isomorphous with tetrachlorhydroquinone,

$$a : b : c = 2·976 : 1 : 2·7813. \quad \beta = 77° \ 22'.$$

Chlorobromanilic acid from metadichlorometabromoquinone is identical with that obtained by Krause. W. C. W.

Action of Amines on Quinones. By T. ZINCKE (*Ber.*, **16**, 1555—1562).—By the action of dry ammonia on dry quinone, a black apparently crystalline substance is formed, together with quinhydrone and hydroquinone; its composition agrees with the formula $C_{12}H_9NO_4$. If the action takes place in anhydrous ether or in chloroform, a brown amorphous substance is obtained resembling the above in its properties, but of different composition, $C_6H_3(NH_2)O_2$. The nature of these compounds is not understood. *Dianilidoquinone*, $C_6H_2O_2(NHPh)_2$, obtained by the action of aniline on quinone, is nearly insoluble in hot alcohol, but can be crystallised from hot glacial acetic acid or from aniline, forming small bluish-violet scales. Nitrous acid does not act on it in suspension in alcohol except in the presence of acetic acid, when a reddish-yellow substance is formed almost insoluble in the ordinary solvents; it melts at about 245°. The numbers obtained on analysis indicate the formula $C_6HO_2(NO)(NH.C_6H_4.NO_2)_2$. It dissolves in ammonia, sodium carbonate, and sodium hydroxide solutions with decomposition and formation of ortho- and para-nitraniline. *Dinitranilides* are readily obtained by the action of nitraniline on quinone, and from the orthonitraniline compound a *dinitranilidodinitroquinone* can be formed by means of nitric acid. It resembles the above-mentioned compound obtained from dianilidoquinone. From ortho- and para-toluidine, compounds of the formula

$$C_6H_2O_2(NH.C_7H_7)_2$$

are obtained analogous to the aniline-derivative. From toluquinone and aniline in alcoholic solution, *dianilidotoluquinone*, $C_6HMeO_2(NHPh)_2$, is obtained melting at 232—233°, and crystallising from hot alcohol in brownish-yellow needles. A small quantity of the *monoanilide* is simultaneously formed. *Anilidohydroxytoluquinone*,

$$C_6HMeO_2(OH)(NHPh),$$

obtained by boiling dianilidotoluquinone with alcoholic sulphuric acid (20 per cent.), crystallises in deep blue lustrous needles decomposing at 250°; it forms soluble potassium and sodium derivatives and insoluble barium, copper, and silver compounds. *Dianilidotoluquinone-anilide*, $C_6HMeO(NPh)(NHPh)_2$, is formed by the action of aniline on toluquinone in alcoholic acetic acid solution. It crystallises in dark-brown broad leaflets melting at 167°, and forms well characterised salts. The *hydriodide* forms hard, brown lustrous crystals, the *hydrobromide* dark-green needles of metallic lustre, the *platinochloride*, $(C_{25}H_{21}N_3O)_2,H_2PtCl_6$, small dark prisms of metallic lustre. *Anilidoethoxytoluquinoneanilide*, $C_6HMeO(NPh)(NHPh).OEt$, is obtained by the action of alcoholic sulphuric acid on the trianilide, forming red silky needles readily soluble in alcohol, and melting at 115—116°. The *hydriodide* crystallises from alcohol in dark-blue coloured leaflets, sparingly soluble in water; the *nitrate* forms similar crystals also sparingly soluble; the *hydrochloride* and *sulphate* are readily soluble; the *picrate* forms blue-coloured needles; the *platinochloride*,

$$(C_{21}H_{20}N_2O_2)_2,H_2PtCl_6,$$

separates from alcohol in blue granular crystals. The *methoxy-derivative*, $C_6HMeO(NPh)(NHPh).OMe$, and the *isobutoxy-derivative*, $C_6HMeO(NPh)(NHPh).OBu$, have also been prepared, the former crystallising in long delicate brownish-red needles melting at 131°, and the latter in small red needles melting at 117°. Anilidohydroxytoluquinoneanilide, $C_6HMeO(NPh)(NHPh).OH$, crystallises from hot dilute acetic acid in brownish needles, which decompose without melting when heated. It forms metallic derivatives, which are mostly insoluble or sparingly soluble. When it is treated with dilute potash solution *dihydroxytoluquinone*, $C_6HMeO_2(OH)_2$, is formed, crystallising in broad brownish-yellow lustrous leaflets melting at 177°. It yields easily soluble salts with the alkalis; the *calcium salt* forms small dark-coloured crystals. A. K. M.

Halogen Derivatives. By R. Benedikt and M. v. Schmidt (*Monatsh. Chem.*, **4**, 604—615).—1. *Displacement of Bromine by Chlorine.*—It is known that when tribromoresorcinol or tribromophenol suspended in water is treated with chlorine gas, part of the bromine is replaced by chlorine; and the authors find that when chlorine is passed into a solution of tribromophenol in glacial acetic acid at the boiling heat, the whole of the bromine is expelled, the liquid on cooling depositing a small quantity of chloranil, and the mother-liquor as it cools, yielding crystals of trichlorophenol.

2. *Action of Potassium Iodide on Tribromophloroglucol.*—Iodine-derivatives of the fatty series have repeatedly been obtained by heating the corresponding chlorine- or bromine-derivatives with potassium iodide; and the same reaction takes place with aromatic compounds, like benzyl chloride, in which the substituting element is situated in a side-chain. The following experiments were made with the view of ascertaining whether a similar result can be obtained with aromatic derivatives having the substituting element in the nucleus:—

Tribromophenol undergoes no alteration, and tribromoresorcinol very little, when boiled with aqueous potassium iodide. Tribromophloroglucol, on the contrary, is somewhat strongly attacked by potassium iodide, the course of the reaction depending on the proportions used. When 1 part of tribromophloroglucol (1 mol.) is boiled with 15 parts water and 0·8—1 part KI (2—2½ mols.), considerable quantities of iodine are evolved, and a heavy precipitate is formed, consisting of *bromodiiodophloroglucol*, $C_6BrI_2(OH)_3$, which crystallises in brown needles and decomposes, when heated, with evolution of iodine. The same body, and not tri-iodophloroglucol, is formed, in smaller quantity, when tribromophloroglucol is boiled with 3 or 4 mols. potassium iodide; indeed, as the proportion of potassium iodide is increased, larger quantities of a soluble body are formed; and finally with 7 mols. KI this latter body is the sole product of the reaction, the whole remaining dissolved on cooling. By acidulating with sulphuric acid, agitating with ether, and leaving the ether to evaporate, a residue is obtained which, when washed with carbon bisulphide to remove adhering iodine, and then recrystallised from water, yields crystals of pure phloroglucol, probably formed according to the equation:—$2C_6Br_3H_3O_3 + 7KI + 6H_2O = 2C_6H_6O_3 + 6KBr + KIO_3 + 3I_2 + 3H_2O$.

3. *Action of Chlorine on Pentachlorophenol.*—When chlorine is passed for several days into pentachlorophenol suspended in hydrochloric acid, the pentachlorophenol is mostly converted into a tear-exciting oil, which does not solidify. In one experiment, however, a solid body was obtained, which, when crystallised from boiling benzene, was found to consist of pentachlorophenol, while the mother-liquor yielded large yellow crystals having the composition C_6Cl_6O, and melting at 46°. This substance, heated with tin and hydrochloric acid, is converted into pentachlorophenol, and may therefore be regarded as *chloroxy-pentachloro-benzene*, $C_6Cl_5O.OCl$, but its melting point is considerably below those of the corresponding compounds, $C_6H_2Br_3.OBr$, $C_6HBr_4.OBr$, $C_6Br_5.OBr$, and $C_6H_9Cl_3.OCl$, which range from 118° to 128°. Langer, by passing chlorine into a solution of aniline in glacial acetic acid, obtained a body C_6Cl_6O, melting at 106°, approaching, therefore, more nearly in this respect to the compounds just mentioned. The author, however, in repeating Langer's experiment, obtained, not C_6Cl_6O, but C_6Cl_8O, probably *hexchlorophenol chloride*, C_6Cl_6O,Cl_2. This compound forms large well-defined shining colourless to wine-yellow prisms, melting at 102°,

distilling undecomposed when slowly heated, and reduced by tin and hydrochloric acid to pentachlorophenol. On agitating the mother-liquors of this body with water and light petroleum and distilling off the latter, there remained a small residue, which, when recrystallised, yielded a body containing 70·03 per cent. chlorine, and, melting at about 100°, probably therefore identical with Langer's hexchlorophenol. H. W.

Paranitrobenzaldehyde and Acetone. By A. BAEYER and P. BECKER (*Ber.*, **16**, 1968—1971).—Claisen has observed that benzaldehyde reacts with acetone to form methyl cinnamyl ketone with elimination of a molecule of water; whereas under similar conditions Baeyer and Drewsen obtained from orthonitrobenzaldehyde an aldol; or the methyl ketone of orthonitro-β-phenyl lactic acid, without elimination of water. Baeyer and Drewsen consider that in both these changes an aldol is formed, but that in the latter case the presence of the nitro-group adds to its stability. The author has investigated a similar change in the para-derivatives, in order to examine the correctness of the above hypothesis. By the action of nitrobenzaldehyde on acetone, paranitro-β-phenyllactyl-methyl ketone is formed thus: $C_6H_4(NO_2).CHO + CH_3.COMe = C_6H_4(NO_2).CH(OH).CH_2.COMe$; this substance forms colourless crystals melting at 58°, soluble in ether and alcohol, insoluble in petroleum. When boiled with acids or water, it gives off a molecule of water, and yields *paranitro-cinnamyl methyl ketone*, thus:

$$C_6H_4(NO_2).CH(OH).CH_2.COMe - OH_2 = C_6H_4(NO_2).CH\colon CH.COMe,$$

which melts at 110°. If the aqueous solution of the lactyl ketone be mixed directly with potash or soda, *paranitrodicinnamylketone* is formed, which crystallises in golden glistening needles melting at 254°), sparingly soluble in alcohol, soluble in acetic acid. As this substance yields paranitrobenzoic acid on oxidation, it follows that the nitro-group remains intact; in this respect, the para- differs most markedly from the corresponding ortho-derivative, which under similar conditions yields the characteristic indigo-grouping. V. H. V.

Benzil. By H. GOLDSCHMIDT and V. MEYER (*Ber.*, **16**, 1616—1617).—Wittenberg and Meyer (this vol., p. 804) showed that benzil differs from glyoxal in its reaction with hydroxylamine, only one oxygen-atom of the former becoming replaced by the group NOH, whilst in the case of glyoxal both oxygen-atoms become substituted with formation of glyoxime. This led them to doubt the correctness of the formula PhCO.COPh. The authors find, however, that when powdered hydroxylamine hydrochloride and a drop of hydrochloric acid are added to a solution of Wittenberg and Meyer's compound, PhC(NOH).COPh, in wood spirit and the mixture heated to boiling, it yields *diphenylglyoxime*, $C_{14}H_{12}N_2O_2$. This forms white lustrous scales melting at 237°, sparingly soluble in cold wood-spirit, alcohol, and ether. It dissolves in strong soda solution, and is precipitated by the addition of an acid. Ammonia dissolves it sparingly, the solution giving a yellowish precipitate with silver nitrate. A. K. M.

Derivatives of Orthotoluic Acid. By O. JACOBSEN and F. WIERSS (*Ber.*, **16**, 1956—1962).—*Bromorthotoluic acid*,

$$C_6H_3BrMe,COOH\ [Me : COOH : Br = 1 : 2 : 3],$$

prepared by the direct action of bromine on orthotoluic acid, crystallises in long needles melting at 167°, soluble in alcohol and ether, sparingly soluble in water; its salts do not crystallise readily. *Nitro-orthotoluic acid*, formed by nitrating toluic acid, although it has a well-defined melting point, 146°, is a mixture of two isomerides, which can be separated only by frequent fractional crystallisation from alcohol. *α-Nitro-orthotoluic acid*, $C_6H_3(NO_2)Me.COOH$ [NO_2 : Me : COOH = 1 : 2 : 3], forms small needles melting at 179°, soluble in hot water and alcohol; its barium, calcium, and potassium salts crystallise in needles. *β-Nitro-orthotoluic acid*, [NO_2 : Me : COOH = 1 : 4 : 5], also forms needles melting at 145°, more soluble in dilute alcohol than its isomeride. *α-Amidorthotoluic acid* crystallises in flat prisms, melting at 196°; the β-acid in glistening needles. Both α- and β-nitro-orthotoluic acid give the same dinitro-acid,

$$C_6H_3Me(NO_2)_2.COOH\ [NO_2 : NO_2 : Me : COOH = 1 : 3 : 4 : 5],$$

which forms long needles, melting at 206°.

Sulpho-orthotoluic acid, $C_6H_3Me(HSO_3).COOH$, prepared by the action of ordinary sulphuric acid on orthotoluic acid, forms a crystalline mass; the disulphonic acid fine microscopic needles. On melting the latter substance with potash, a dihydroxyorthotoluic or *cresorsellinic acid*, $C_6H_2Me(OH)_2.COOH$, is obtained, which crystallises in hard glistening needles melting at 245°. A solution of the acid, heated with concentrated sulphuric acid, forms a beautiful magenta-red colour; on dilution with a further quantity of acid, the red solution gives two strong absorption-bands in the green part of the spectrum. This reaction with sulphuric acid resembles that of its homologue dihydroxybenzoic acid. The *ammonium* salt of cresorsellinic acid crystallises in thick transparent prisms, which at 155° are dissociated completely into ammonia and the free acid; the *barium* salt forms microscopic needles. Cresorsellinic acid is not identical with any of the known bromodihydroxybenzoic acids. Experiments made with a view of determining its constitution were unsuccessful.

V. H. V.

Benzyl Derivatives. By S. GABRIEL and O. BORGMANN (*Ber.*, **16**, 2064—2066).—The authors have prepared the third or metanitrophenylacetic acid, taking as their starting point the metanitrobenzyl alcohol, prepared by the action of sodium hydroxide on metanitrobenzaldehyde. The crude alcohol was converted into the *chloride*, $C_6H_4(NO_2).CH_2Cl$ [NO_2 : CH_2Cl = 1 : 3], which crystallises in long golden needles melting at 45—47°, soluble in alcohol and ether. The *nitrophenylacetic acid*, $C_6H_4(NO_2).CH_2.COOH$, prepared from the chloride through the medium of the cyanide, forms colourless needles melting at 117°; its silver salt forms colourless silky crystals. *Metamidophenylacetic acid*, $C_6H_4(NH_2).CH_2.COOH$, obtained by the reduction of the nitro-derivative, forms pale golden tabular crystals melting at 148°.

The authors suggest, as a convenient material for the preparation of the corresponding ortho-compounds, the oil obtained from the crude metanitrobenzaldehyde by pressure. V. H. V.

Formation of Phenylamidopropionic Acid by the Action of Stannous Chloride on Albuminoïds. By E. Schulze and J. Barbieri (*Ber.*, **16**, 1711—1714).—By boiling 2 kilos. of the albuminous matter contained in beans with stannous chloride and hydrochloric acid, the authors have obtained an acid which is identical with the phenylamidopropionic acid they have previously extracted from germinating lupins. W. C. W.

Phenylamidopropionic Acid, Phenylamidovaleric Acid, and other Nitrogenous Constituents of Lupine Shoots. By E. Schulze and J. Barbieri (*J. pr. Chem.* [2], **27**, 337—362).—The authors have already described the phenylamidopropionic acid from this source (Abstr., 1882, 189), they regard it as identical with phenylalanine. The yellow residue left on melting the acid consists of *phenyllactimide* (?), C_9H_9NO; it is soluble in boiling alcohol, and crystallises in thin needles, melts at 280°, and sublimes if strongly heated. The mother-liquor from the copper salt of phenylamidopropionic acid contains an amidovaleric acid, $C_5H_{11}NO_2$. This crystallises in transparent brilliant plates, resembling leucine in appearance, moderately soluble in water, sparingly in strong alcohol, readily in hot dilute alcohol; when heated, it volatilises completely, yielding a white woolly sublimate. It is readily distinguished from leucine by its yielding a soluble copper salt. The *hydrochloride*, $C_5H_{11}NO_2,HCl$, crystallises in small prisms, and is readily soluble in alcohol and water. The authors have also found lecithine and peptones in the shoots, and have confirmed the presence of xanthine, hypoxanthine, leucine, tyrosine, and asparagine. A. J. G.

Perkin's Reaction. By R. Fittig (*Ber.*, **16**, 1436—1438).—A reaction takes place at the ordinary temperature, when benzaldehyde, sodium malonate, and acetic anhydride are mixed together, giving rise to the formation of cinnamic and carbonic acids. If sodium isosuccinate is substituted for malonate, phenylcrotonic acid is produced. If glacial acetic acid is substituted for acetic anhydride in the preceding reactions, the acid, $CHPh \vdots C(COOH)_2$, described by Claisen and Crismer (*Annalen*, **218**, 129), is obtained in the former case, and phenylcrotonic acid, as well as a small quantity of cinnamic acid in the latter case, if the reaction takes place at about 180°.

When a mixture of benzaldehyde, acetic anhydride, and sodium butyrate is heated at 100° for 60 hours, phenylangelic acid is produced, but no cinnamic acid could be detected. Another acid is also formed, probably an acetic derivative of phenyloxyvaleric acid, which is much more soluble than phenylangelic acid. The formation of cinnamic acid observed by Perkin, is due to a secondary reaction. At 150° a mixture of cinnamic and phenylangelic acids is obtained.

Valeraldehyde and œnanthal also have the power of acting on the sodium salts of the acetic series, but as the action does not take place below 180°, a large portion of aldehyde polymerises, and consequently a poor yield is obtained. By the action of acetic acid and sodium acetate on valeraldehyde, the acid,

$$CHMe_2.CH_2.CH : CH.COOH,$$

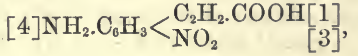
is formed, and in the same way the acid, $C_7H_{14} : CH.COOH$, is obtained from œnanthol. Both acids are colourless liquids, sparingly soluble in water, and volatile in a current of steam. W. C. W.

Derivatives of Cinnamic and Hydrocinnamic Acids. By S. Gabriel and M. Herzberg (*Ber.*, **16**, 2036—2043).—*Orthochlorocinnamic acid*, $C_6H_4Cl.C_2H_2.COOH$, prepared by the action of hydrochloric acid on orthodiazocinnamic acid, forms golden crystals, melting at 200°, soluble in alcohol and ether, insoluble in water; *orthochlorhydrocinnamic acid*, $C_6H_4Cl.C_2H_4.COOH$, crystallises in needles melting at 96·5°. The corresponding *iodocinnamic acid* is a crystalline solid melting at 212—214°, the *iodohydrocinnamic acid* forms leaflets melting at 102°; it is slowly converted into hydrocinnamic acid by nascent hydrogen.

Metachlorocinnamic acid forms golden needles melting at 167°, soluble in hot alcohol and ether; *metachlorhydrocinnamic acid* crystallises in leaflets. The corresponding *iodocinnamic* and *iodohydrocinnamic acids* melt at 181° and 65° respectively.

Parachlorocinnamic acid does not crystallise in a well-defined form; it melts at 241°, is sparingly soluble in cold water, readily in alcohol; parachlorhydrocinnamic acid melts at 124°; and the corresponding iodocinnamic and iodohydrocinnamic acids at 255° and 140° respectively.

Paracetamidocinnamic acid, $NH\overline{Ac}.C_6H_4.C_2H_2.COOH$, crystallises in long colourless needles melting at 259°, soluble in hot alcohol, insoluble in ether. Dinitroacetamidostyrole, $NH\overline{Ac}.C_6H_2(NO_2)_2.C_2H_3$, obtained by the action of nitric acid on the above compound, crystallises in needles melting at 211°. If the nitration be effected in the cold, an impure nitroparamidocinnamic acid is formed, which on boiling with sodium hydroxide yields sodium mononitroparamidocinnamate. By the action of hydrochloric acid, the corresponding acid,



$$[4]NH_2.C_6H_3<\begin{matrix}C_2H_2.COOH[1]\\ NO_2\qquad\quad[3]\end{matrix},$$

is obtained in red needles melting at 224—5°, and soluble in hot alcohol, less soluble in water; as this substance yields metanitrocinnamic acid when boiled with ethyl nitrate, the nitro-group is in the meta-position to the $C_2H_2.COOH$-group. *Metaparadiamidocinnamic acid*, obtained by the reduction of the above nitro-acid, crystallises in golden needles melting at 167°, soluble in water and alcohol, insoluble in ether and benzene.

Bromacetamidostyrole, $[4]NH\overline{Ac}.C_6H_3Br.C_2H_3[1]$, formed by the action of bromine on paramidocinnamic acid, crystallises in needles melting at 182·5°, insoluble in ammonia, soluble in alcohol and ether.

V. H. V.

Hydroxytoluic and Hydroxyphthalic Acid. By O. JACOBSEN (*Ber.*, **16**, 1962—1968).—*β-metahydroxytoluic acid*,

$$C_6H_3Me(OH).COOH\ [Me : COOH : OH = 1 : 2 : 5],$$

obtained from the corresponding bromo-, nitro-, or sulpho-toluic acids, crystallises in long glistening prisms melting at 168°; its solution gives a blue-violet colour with ferric chloride.

β-Orthohydroxytoluic acid, $C_6H_3Me(OH).COOH\ [OH : Me : COOH = 1 : 2 : 3]$, crystallises in long glistening needles melting at 183°; its aqueous solution gives a bright brown precipitate with ferric chloride. This acid, when heated with lime, yields a cresol convertible into salicylic acid. Its methyl-derivative, $C_2H_3Me(OMe)_3.COOH$, crystallises in small needles. On oxidation with potassium permanganate, this acid is converted into β-methoxyphthalic acid,

$$C_6H_3(OMe)(COOH)_2\ [OMe : COOH : COOH = 1 : 2 : 3],$$

which forms small prisms melting at 160° with partial decomposition into the anhydride and water. The former sublimes in needles melting at 87°. This methoxyphthalic acid gives precipitates with solutions of silver, lead, and barium salts.

β-Hydroxyorthophthalic acid,

$$C_6H_3(OH)(COOH)_2\ [OH : COOH : COOH = 1 : 2 : 3],$$

obtained from the methoxy-derivative by fusion with potash, crystallises in hard compact prisms, which melt at 200° when heated up quickly, but decompose at 150° into water and the anhydride when heated slowly. The anhydride melts at 145°. This hydroxyphthalic acid gives a cherry-red coloration with ferric chloride, thus differing from the α-acid. The salts of this acid are not readily obtained in a crystalline state; their solutions give precipitates with salts of lead and silver.
V. H. V.

Lævorotatory Mandelic Acid. By J. LEWKOWITSCH (*Ber.*, **16**, 1565—1568).—The mandelic acid was prepared from amygdalin by Wöhler's method (*Annalen*, **66**, 238), and melted at 132·8°, the melting point of the acid prepared from benzaldehyde being 118°. The acid obtained from amygdalin is lævorotatory, the specific rotatory power of an aqueous solution at 20° being $-[\alpha]_D = 212{\cdot}52 - 0{\cdot}57779$, and of a solution in glacial acetic acid $-[\alpha]_D = 209{\cdot}95 - 0{\cdot}27139$.
A. K. M.

Separation of Inactive Mandelic Acid into Two Optically Active Isomerides. By J. LEWKOWITSCH (*Ber.*, **16**, 1568—1577).—The author previously showed that dextrorotatory mandelic acid could be obtained from the inactive acid by the action of certain organisms (Abstr., 1882, 1076). He has now succeeded in separating both dextro- and lævo-rotatory acids from the inactive substance, and in reproducing the latter from equal parts of the two active isomerides. The dextrorotatory acid obtained by the action of *Penicillium glaucum* on inactive mandelic acid has the same specific rotatory power as the lævorotatory acid (see last Abstr.); both melt at 132·8°, show the same degree of solubility, and in fact agree in all their properties except in the direction in which they polarise a ray of light. The lævorotatory acid is obtained from the inactive mandelic acid by means of *Saccharomyces ellipsoïdeus* and of a *schizomycetes* (?) *vibrio*. When equal molecular weights of inactive mandelic acid and pure crystallised cinchonine are dissolved in boiling water, and a crystal of the cinchonine salt of the dextrorotatory acid added, an abundant separation of the latter salt takes place, forming rosette-like groups of anhydrous needles, from which the pure dextrorotatory acid can be obtained, melting at 133°. When the mother-liquor is concentrated, a deep yellow solution is obtained, which, after being exposed for some weeks in a vacuum, deposits crystals of the cinchonine salt of lævorotatory mandelic acid. It is much more readily soluble than the dextrorotatory salt; both are anhydrous and crystallise alike. The inactive mandelic acid obtained by the union of the two active varieties agrees in melting point (118°) and in its other properties with the inactive acid (*paramandelic acid*) prepared from oil of bitter almonds. From the close analogy thus exhiblited between mandelic and tartaric acids, the author assumes the possibility of converting lævomandelic acid into paramandelic and dextromandelic acids, and he has already succeeded in obtaining a partial conversion into an inactive variety.

A. K. M.

Dry Distillation of Sodium Dibromanisate. By L. Balbiano (*Gazzetta*, **13**, 65—72).—When a mixture of sodium dibromanisate with an equal weight of lime is cautiously heated in a retort, a violent reaction takes place, the mass becomes incandescent, and a small quantity of a yellowish liquid distils over, which on cooling becomes crystalline in great part. The yield is about 10 to 12 per cent. of the dibromanisate employed. The product dissolved in ether is washed by agitation with dilute soda solution, the ether distilled off, and the residue crystallised two or three times from alcohol. It forms small white lustrous needles melting at 91·5—92°, and insoluble in water. When saponified with alcoholic potash, it yields dibromanisic acid; this fact and the results of the analyses prove the substance to be *methyl dibromanisate*, $C_6H_2Br_2(OMe).COOMe$.

The carbonaceous residue in the retort is exhausted with boiling water, the solution concentrated, acidified with hydrochloric acid, and agitated with ether. On evaporating the ethereal solution and crystallising the residue from alcohol, a dibromhydroxybenzoic acid is obtained in colourless needles, melting at 266—268° with decomposition, but subliming at a lower temperature. It is almost insoluble in water. When this acid is carefully treated with sodium amalgam so as to replace the bromine by hydrogen, it yields parahydroxybenzoic acid melting at 211°, and having all the properties ascribed to it by Hlasiwetz and Barth. The calcium salt of dibromoparahydroxybenzoic acid is very soluble in water, and crystallises in small tables with 3 mols. H_2O.

In the mother-liquors from the crystallisation of the crude dibromoparahydroxybenzoic acid, there is a very small quantity of another acid which crystallises from ether in small needles melting with decomposition at 259°. Its alcoholic solution gives no coloration with ferric chloride.

From these results, it will be seen that the reaction by which the methyl dibromanisate and dibromoparahydroxybenzoic acid are produced is—

$$2[C_6H_2Br_2(OMe).COONa] = C_6H_2Br_2(OMe).COOMe + C_6H_2Br_2(ONa).COONa;$$

moreover, there is no intramolecular change, the dibromanisic acid obtained by the saponification of the methyl salt being identical with that originally employed. C. E. G.

Derivatives of Paracresolglycollic Acid. By M. NAPOLITANO (*Gazzetta*, **13**, 73—77).—The cresolglycolic acid is prepared by adding sodium hydroxide solution, sp. gr. 1·3 (400), to a mixture of paracresol (98) with monochloracetic acid (84); when cold, the sodium salt of the new acid is crystallised from water and decomposed by hydrochloric acid. *Sodium paracresolglycollate*, $C_9H_9O_3Na$, obtained as above, is sparingly soluble in cold, moderately in hot water, and forms thin plates or long slender prisms, the former containing one, the latter 0·5 mol. of water of crystallisation. The *barium salt*, prepared by neutralising the pure acid with barium hydroxide solution, crystallises in plates or prisms containing 2 mols. H_2O. The *lead salt* was prepared by decomposing the barium salt with sulphuric acid, and then neutralising with pure lead carbonate. It forms plates containing 1 mol. H_2O; it is moderately soluble in water, but does not crystallise readily. C. E. G.

Action of Phthalic Anhydride on Amido-acids. By E. DRECHSEL (*J. pr. Chem.* [2], **27**, 418—422).—By fusing phthalic anhydride with glycocine, *phthaluric acid* (phthalylglycocine),

$$C_6H_4 \vdots (CO)_2 \vdots N.CH_2.COOH,$$

is obtained. It crystallises in very long thin needles, is sparingly soluble in cold water and ether, readily in hot water, soluble in alcohol; it melts at 191—192°, and on further heating yields an oily sublimate crystallising on cooling. It is resolved into phthalic acid and glycocine when boiled with hydrochloric acid. The sodium salt crystallises in large flat prisms; the calcium salt, $(C_{10}H_6NO_4)_2Ca + 2H_2O$, forms very thin flat prisms; the platodiammonium salt,

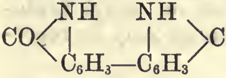
$$Pt[N_2H_6(C_{10}H_6NO_4)]_2$$

crystallises in large prisms or small needles, the copper salt,

$$(C_{10}H_6NO_4)_2Cu + 3H_2O,$$

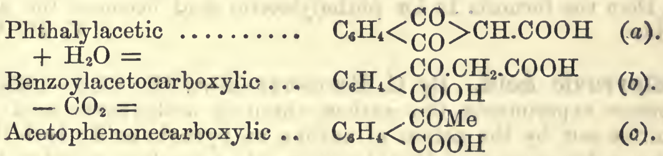
forms light blue rhombic tables. A. J. G.

Azophthalic Acid. By A. CLAUS and G. HEMMANN (*Ber.*, **16**, 1759—1762).—*Benzidinetetracarboxylic anhydride* is formed by the action of a concentrated solution of stannous chloride on azophthalic acid. It is a pale yellow powder insoluble in water, alcohol, ether, and in dilute acids. It dissolves in hot solutions of alkaline carbonates, yielding the acid potassium or sodium salt of benzidinetetracarboxylic acid. The *potassium salt*, containing 5 mols. H_2O, crystallises in prisms which effloresce at the ordinary temperature. The anhydrous salt is hygroscopic. The *sodium salt*, $Na_2C_{16}H_8N_2O_7$, forms microscopic needles which dissolve in water yielding a brown solution. The *silver salts*, $Ag_2C_{16}H_8N_2O_7$, and $Ag_4C_{16}H_6N_2O_8$, are easily decomposed by light. They are pale yellow powders insoluble in water. An ammonium salt of the composition $C_{16}H_6N_2O_6,NH_4.OH$, crystallises in yellow prisms.

When the anhydride is heated at 360°, water and carbonic anhydride are evolved, and a pale yellow sublimate of the anhydrimide,  is deposited in needle-shaped crystals. The anhydrimide (m. p. 283°) is soluble in alcohol and ether. It also dissolves in alkalis, forming a dark yellow liquid which grows darker on exposure to the air. On the addition of an acid a brown powder is obtained soluble in water and alcohol, and sparingly soluble in ether. It melts with decomposition at 235°. W. C. W.

Constitution of Phthalylacetic Acid. By S. GABRIEL (*Ber.*, 16, 1992—1997).—According as the complex grouping ⁚CH.COOH in phthalylacetic acid is associated with one or two carbon-atoms, so the acids benzoylacetocarboxylic and acetylphenonecarboxylic acid can be expressed by either of the formulæ written below :—

I.



$$\text{Phthalylacetic} \ldots\ldots\ldots\quad \mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}CH.COOH} \quad (a).$$

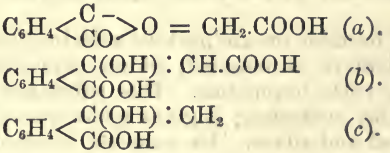
$$+ \mathrm{H_2O} =$$

$$\text{Benzoylacetocarboxylic} \ldots\quad \mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{CO.CH_2.COOH}{COOH}} \quad (b).$$

$$- \mathrm{CO_2} =$$

$$\text{Acetophenonecarboxylic} \ldots\quad \mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{COMe}{COOH}} \quad (c).$$

II.



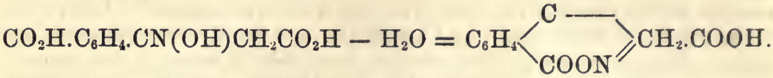
$$\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{C\,-}{CO}{>}O = CH_2.COOH} \quad (a).$$

$$\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)\,\vdots\,CH.COOH}{COOH}} \quad (b).$$

$$\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)\,\vdots\,CH_2}{COOH}} \quad (c).$$

Former researches of the author have established for acetophenonecarboxylic acid the formula I(*c*); the present paper not only confirms this view, but the formula I(*b*) for benzoylacetocarboxylic acid. V. Meyer's hydroxylamine reaction was used to recognise the presence of a CO grouping associated directly with the carbon atoms.

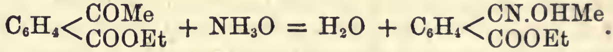
From the crude product of the action of hydroxylamine hydrochloride on benzoylacetocarboxylic acid in presence of soda, hydrochloric acid precipitates a crystalline substance of composition $C_{10}H_7O_4N$, whose formation can be expressed by the equation $C_{10}H_8O_5 + NH_{36} - 2H_2O = C_{10}H_7O_4N$. This compound is probably an anhydride of β-isonitrosopropiono-*o*-benzoic acid derived from an oximide compound $COOH.C_6H_4.C(N.OH).CH_2.COOH$, by the abstraction of 1 mol. of water thus:



$$CO_2H.C_6H_4.CN(OH)CH_2CO_2H - H_2O = C_6H_4\left\langle\begin{matrix}C\text{——}\\COON\end{matrix}\right\rangle CH_2.COOH.$$

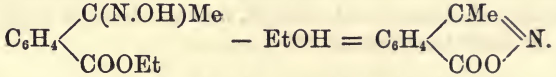
This substance is a monobasic acid forming salts of the composition, $C_{10}H_6NO_4N$. On melting, it is converted into an *anhydride of phenyl methyl acetoxime-orthocarboxylic acid*, a compound best obtained by the direct action of hydroxylamine hydrochloride on ethyl acetophenone carboxylate in presence of soda. This change may be represented thus:—

(I.)



$$C_6H_4<\begin{matrix}COMe\\COOEt\end{matrix} + NH_3O = H_2O + C_6H_4<\begin{matrix}CN.OHMe\\COOEt\end{matrix}.$$

(II.)



$$C_6H_4\left\langle\begin{matrix}C(N.OH)Me\\COOEt\end{matrix}\right. - EtOH = C_6H_4\left\langle\begin{matrix}CMe\\COO\end{matrix}\right\rangle N.$$

This substance crystallises in colourless needles melting at 157°, sparingly soluble in water; by the action of bromine it is converted into a dibromo-derivative, $C_9H_5Br_2NO_2$, which crystallises in needles melting at 223°.

As the above reactions are best explained on assuming the formulæ I(*b*) and I (*c*) for benzoylacetocarboxylic and acetophenonecarboxylic acids, then the formula I*a* for phthalylacetic acid becomes the more probable. V. H. V.

Anilpyruvic Acid. By C. Bottinger (*Ber.*, **16**, 1926—1927).—In former experiments the author obtained anilpyruvic acid and its aniline salt by the action of aniline on pyruvic acid; both these substances decompose on long keeping into a blackish powder, from which hydrochloric acid extracts the hydrochloride of aniluvitonic acid.

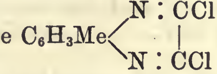
By the action of bromine on anilpyruvic acid in chloroform solution, a pentabromo-derivative is obtained, which crystallises in needles, always associated with impurities. This substance is insoluble in water, readily soluble in alcohol; it gives white precipitates with solutions of salts of lead and silver. Its solution in alcohol decomposes, with evolution of heat, into tribromaniline, dibromaldehyde, and carbonic anhydride. This decomposition points to the formula,

$$COOH.(CHBr)C : N.C_5H_3Br_3,$$

for the bromoanilpyruvic acid.

It is, however, noticeable that whereas tribromaniline is neutral, the above mentioned acid combines with hydrobromic acid to form a true salt. V. H. V.

Derivatives of Anhydro-amidotolyloxamic Acid. By O. HINSBERG (*Ber.*, **16**, 1531—1534).—This acid was obtained by the author on reducing nitrotolyloxamic acid (this vol., p. 323), and can also be prepared by heating the oxalic acid derivative of diamidotoluene, $C_6H_3Me(NH_3O.CO.COOH)_2 + H_2O$, to 160°, or by boiling it with glacial acetic acid. The *silver salt* is rather unstable; its formula is $C_6H_3MeN_2C_2O_2Ag_2$.

By the action of phosphorus pentachloride on the dry acid, the chloride  $C_6H_3Me\left\langle\begin{array}{l}N:CCl\\ \quad\;\;|\\ N:CCl\end{array}\right.$ is formed, melting at 114—115°. It crystallises in white needles insoluble in water, soluble in alcohol, ether, and chloroform; it can be boiled with water, dilute soda solution, or with ammonia without decomposition; silver nitrate and oxide are also without action on its boiling alcoholic solution. By the action of alcoholic potash, a substance still containing chlorine is obtained melting at 40°, long continued boiling with concentrated alkali being required for the displacement of the whole of the chlorine and reproduction of the original acid. By the reduction of the chloride by means of zinc and glacial acetic or hydrochloric acid, or of hydriodic acid and glacial acetic acid, dark blue solutions are obtained, whilst a part of the product is precipitated in black flocks dissolving in acetone to a blue solution. The colouring matter is unstable, and instantly decomposed by water. Sodium acts on the alcoholic solution of the chloride with formation of a solid neutral compound.

A. K. M.

Cymenesulphonic Acids. By A. CLAUS (*Ber.*, **16**, 1603).—A reply to Paternò (*Ber.*, **16**, 1297).

Isonitroso-acids. By A. MÜLLER (*Ber.*, **16**, 1617—1622).—In continuation of Meyer and Müller's experiments with nitrosomalonic acid (this vol., p. 790), the author has examined the action of hydroxylamine on two other ketonic acids. From levulic acid,

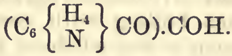
$$CH_3.CO.CH_2.CH_2.COOH,$$

he obtains *γ-isonitrosovaleric acid*, $CH_3.C(NOH).CH_2.CH_2.COOH$, melting at 95—96°. It is very readily soluble in water, less so in ether and in alcohol. The *barium salt*, $(C_5H_8O_3N)_2Ba,2H_2O$, decomposes when gently heated; the *silver salt*, $C_5H_8O_3NAg$, is obtained as a white precipitate, which blackens on exposure to light; the *ethyl derivative*, $C_5H_8O_3NEt$, is a liquid of an agreeable odour, which is decomposed by distillation. By the action of tin and hydrochloric acid on γ-isonitrosovalerianic acid, levulic acid is formed; sodium amalgam has no action; on boiling it with hydrochloric acid, it is converted into levulic acid and hydroxylamine. By the action of hydroxylamine on phenylglyoxylic acid, *isonitrosophenylacetic acid*,

$$PhC(NOH).COOH,$$

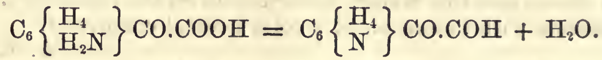
is obtained, melting at 127—128°. It is moderately soluble in ether, alcohol, and water, and has a slight, aromatic odour. It is decomposed when heated with hydrochloric acid, hydroxylamine being liberated. The *barium salt*, $[PhC(NOH).COO]_2Ba,1\frac{1}{2}H_2O$, crystallises in needles of silky lustre, and decomposes when gently heated; the *potassium salt*, $PhC(NOH).COOK,H_2O$, is crystalline, and very readily soluble in water; the *silver salt* obtained by precipitation has the formula $PhC(NOH).COOAg$. By the action of tin and hydrochloric acid on isonitrosophenylacetic acid, *phenylamidoacetic acid*, $CHPh(NH_2).COOH$ (m. p. 255—256°), is produced, together with ammonia and benzoic acid. Benzoic cyanide and hydroxylamine yield pure *dibenzhydroxamic acid* melting at 153°. A. K. M.

Isatin. By H. Kolbe (*J. pr. Chem.* [2], **27**, 490—497).—The author considers isatin to be a compound of formyl with benzoyl, the latter having one of its hydrogen-atoms replaced by an atom of monovalent nitrogen. It is therefore nitrogenbenzoyl-formyl,



$$(C_6\left\{\begin{matrix}H_4\\N\end{matrix}\right\}CO).COH.$$

He considers that when isatic acid loses water and forms isatin, the two hydrogen-atoms of the amido-group combine with the oxygen-atom of the hydroxyl-group, and that the carboxyl is converted into formyl according to the equation:—



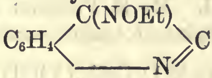
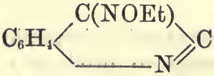
$$C_6\left\{\begin{matrix}H_4\\H_2N\end{matrix}\right\}CO.COOH = C_6\left\{\begin{matrix}H_4\\N\end{matrix}\right\}CO.COH + H_2O.$$

Amidobenzoylcarboxylic acid (Isatic acid). Nitrogenbenzoyl-formyl (Isatin).

When isatin is treated with phosphorus pentachloride, he considers that the trivalent-group CCl is formed, the formula of the chloride being $(C_6\left\{\begin{matrix}H_4\\N\end{matrix}\right\}CO.CCl)''.(C_6\left\{\begin{matrix}N\\H_4\end{matrix}\right\}CO.CCl)''$. On replacing the chlorine with hydrogen, the compound nitrogen-benzoyl-methine or indigo-blue is formed.

The author considers isatin, dioxindole, and indole to be analogously constituted formyl compounds, and represents their composition by corresponding formulæ. He considers indole to be a compound of nitrogen-benzoyl with the univalent radical $(CH)'$, its formula being $(C_6\left\{\begin{matrix}H_4\\N\end{matrix}\right\}CH_2)'.(CH)'$. J. I. W.

Oxindole and Isatoxime. By A. Baeyer and W. Comstock (*Ber.*, **16**, 1704—1711).—Oxindole is more soluble in alkalis than in water, but it can be extracted from the alkaline solutions by ether. It is converted into barium orthamidophenylacetate by the action of baryta-water at 150°. The ethyl derivative of oxindole, C_8H_6EtNO, prepared by heating alcoholic solutions of oxindole and sodium with ethyl iodide, is a colourless oil at the ordinary temperature, sparingly soluble in water. It is not decomposed by baryta at 200°, and it is only slowly attacked by strong hydrochloric acid at 150°, but oxindole is not found amongst the products of decomposition. As isonitrosoindole and isaxotime have been shown to be identical, and as the ethyl derivatives are easily converted into isatine, this compound must be regarded as a derivative of isatine. The name "*isaxotime*" will therefore be retained, and "*isonitrosoindole*" discarded. *Silver isatoxime* is thrown down when dilute ammonia is added to an alcoholic solution of silver nitrate and isatoxime. By the action of ethyl iodide on this salt, *monethylisatoxime*, $C_8H_5EtN_2O_2$, is produced. It is deposited from an alcoholic solution in yellow needles (m. p. 138°). Ethylisatoxime is soluble in alkalis, but is reprecipitated from the solution by carbonic acid. It dissolves in hot solutions of alkaline carbonates, but is deposited on cooling. It is easily converted into isatine by reducing it with zinc-dust and acetic acid, and oxidising the product with ferric chloride.

By a similar process, ethylisatoethyloxime can be prepared from the silver salt of isatoethyloxime. It is an unstable compound, and has not been obtained in a state of purity. It is converted into isatoethyloxime by boiling sodium hydroxide. The unstability of this compound, and the stability of the monethyl-derivative testify in favour of the formula  $C_6H_4\left\langle\begin{matrix}C(NOEt)\\ \text{———}N\end{matrix}\right\rangle C.OH$ for isatoethyloxime, and  $C_6H_4\left\langle\begin{matrix}C(NOEt)\\ \text{———}N\end{matrix}\right\rangle C.OEt$ for ethylisatoethyloxime.

Dibromisatoxime, $C_8H_4Br_2N_2O_2$, prepared by the action of sodium carbonate on an alcoholic solution of dibromisatine and hydroxylamine hydrochloride, forms pale yellow needle-shaped crystals, sparingly soluble in alcohol. It chars at 255° without melting. Dibromisatoxime is reprecipitated from its solution in an alkali by carbonic acid. *Dibromisatoethyloxime*, $C_{10}H_8Br_2N_2O_2$, forms yellow needles which melt at 252°. *Dibromethylisatoethyloxime* is deposited from acetone in long silky needles (m. p. 115°). It is a stable compound, and is converted into dibromisatine by reduction and oxidation. The presence of the oxime-group appears to increase the resistance which the isatine nucleus offers to the action of alkalis.

W. C. W.

Nitrosoxindole and Nitrosindoxyl. By A. BAEYER (*Ber.*, **16**, 769—770).—In reference to Gabriel's synthesis of nitrosoxindole from isatin and hydroxylamine, the author points out that he made that synthesis some time ago, and is now (in conjunction with Comstock and Sapper and with Victor Meyer's permission) investigating the constitution of nitrosoxindole and nitrosindoxyl with the help of that reaction. He finds that on the reduction and subsequent oxidation of the ether of nitrosoxindole isatin is obtained, whereas with diethylated nitrosindoxyl a new body, isomeric with isatin, is produced, the formula of which is probably  $C_6H_4<\begin{matrix}CO\\NEt\end{matrix}>CO$.

L. T. T.

New Synthesis of Skatole. By O. FISCHER and L. GERMAN (*Ber.*, **16**, 710—712).—100 grams of aniline were carefully mixed with 70—80° grams of zinc chloride to form the double salt: 100 grams of glycerol were then added and heated for some time at 160—170°, finally for two hours at 240°; the product was then acidified with very dilute sulphuric acid and steam-distilled. The distillate contained a mixture of various substances of which only *skatole* has yet been isolated. It fused at 93°, and showed all the reactions of skatole, but could not be obtained free from smell. The authors believe they have also identified methylketole in the mixture, and ascribe the odour of the skatole to traces of adhering methylketole. L. T. T.

Synthesis of Unsymmetrical Tetraphenylethane. By R. ANSCHÜTZ and F. ELTZBACHER (*Ber.*, **16**, 1435—1436).—Anthracene is produced by the action of aluminium chloride and benzene on symmetrical tetrabromethane. By a similar reaction tetraphenylethane can be obtained from unsymmetrical tetrabromethane.

W. C. W.

Ethylhydrocarbazostyril. By E. FISCHER and H. KUZEL (*Ber.*, **16**, 1449—1454).—*Nitrosoethylamidohydrocinnamic acid*,

$$C_6H_4(NEtNO).C_2H_4.COOH,$$

is prepared by treating an alkaline solution of ethylamidocinnamic acid with sodium-amalgam. When acetic acid ceases to produce a yellow coloration with a few drops of the mixture, the solution is acidified with dilute sulphuric acid and treated with sodium nitrite. By recrystallisation from benzene and from dilute sulphuric acid, nitrosoethylamidohydrocinnamic acid is obtained in colourless oblong plates which are freely soluble in alcohol, ether, benzene, and alkalis, but are less soluble in hot water.

The crystals melt at 78° and decompose at 150°. An alcoholic solution of this substance is converted into *ethylhydrazinhydrocinnamic acid* by reduction with zinc-dust and acetic acid. The operation is complete when a drop of the solution no longer exhibits Liebermann's reaction with phenol and sulphuric acid. The solution decomposes on evaporation; the crystalline residue consists of a mixture of *ethylhydrocarbazostyril* and zinc acetate. The zinc salt is dissolved out by water; the residue is treated with ether to remove small quantities of ethylhydrocarbostyril, and the crude product on recrystallisation from hot water yields the pure substance in white needles (m. p. 165·5°) freely soluble in alcohol. This compound closely resembles hydrocarbostyril, but is distinguished from it by its behaviour with hot hydrochloric acid. Hydrocarbostyril remains unchanged, and ethylhydrocarbazostyril unites with water, forming ethylhydrazinhydrocinnamic acid. A solution of ethylhydrocarbazostyril in strong cold hydrochloric acid is precipitated unaltered if water is at once added, but if the solution is left at rest for some hours a soluble crystalline hydrochloride is formed which melts at 146° and decomposes at 150° into water, hydrochloric acid, and hydrocarbazostyril.

Hydrocarbostyril yields a sulphonic acid, $C_{18}N_2H_{16}O_2S_2O_6H_2$, when it is treated with strong sulphuric acid at 100°. The barium salt of this acid is soluble in water and almost insoluble in alcohol and ether.

W. C. W.

Formation of Nitril Bases from Organic Acids and Amines. Synthesis of Acridines. By A. BERNTHSEN and F. BENDER (*Ber.*, **16**, 1802—1819).—The authors find that the base they obtained by the action of zinc chloride on a mixture of formic acid and diphenylamine (p. 1099) is identical with the *acridine* which Graebe and Caro (*Annalen*, **158**, 265; *Ber.*, **13**, 99) extracted from the high-boiling portion of coal-tar. The authors are of opinion that the composition of acridine should be expressed by the formula $C_{13}H_9N$, instead of $C_{12}H_9N$. The base, $C_{14}H_{11}N$, which Bernthsen and Fischer prepared from diphenylamine and glacial acetic acid (*Ber.*, **16**, 68), is *methylacridine*, and the base $C_{19}H_{13}N$, obtained from diphenylamine and benzoic acid (*Ber.*, **15**, 3011), is phenylacridine.

The close resemblance in the properties of these three compounds is shown by the following table:—

	Acridine.	Methylacridine.	Phenylacridine.
Pure base	Colourless	Colourless	Colourless.
Solubility in water	Slight	Very slight	0.
Salts	Yellow	Yellow	Yellow.
Fluorescence of salts	Blue-green	Blue-green	Green.
Dissociation	0	0	Partial.
Nitrate	Long needles, sparingly soluble	—	Long needles, sparingly soluble.
Precipitates with $K_2Cr_2O_7$,KI, or $HgCl_2$	Yellow	Yellow	Yellow.
Distilled with sodium hydroxide	Undecomposed	—	Undecomposed.
Strong HNO_3	0	0	0.

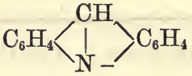
Phenylacridine melts at 181° and boils above 360° without decomposition. It is not attacked by acetic anhydride or by benzoic chloride, but it unites with methyl iodide, forming brilliant dark crystals of the ammonium iodide, $C_{19}H_{13}N,MeI$. The crystals are soluble in alcohol and in hot water. The addition of silver oxide or of caustic soda to the aqueous solution precipitates *methylphenylacridium hydroxide*, $C_{19}H_{13}NMe,OH$. This substance is deposited from its alcoholic solution in prisms melting at 108°, soluble in ether. The chloride crystallises in needles which dissolve freely in water, and the nitrate forms sparingly soluble needles of a yellow colour. Dilute solutions of the salts, with the exception of the iodide, exhibit a dark-green fluorescence. The reactions with potassium chromate, mercuric chloride, potassium chloride, and potassium iodoiodide, are similar to those exhibited by phenylacridine. The platinochloride is converted at 60° into phenylacridine platinochloride.

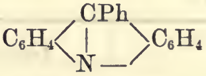
The yellow solution of phenylacridine hydrochloride is decolorised by zinc-dust, and all organic matter is removed from the solution.

By extracting the zinc-dust with boiling alcohol, *hydrophenylacridine*, $C_{19}H_{15}N$, is obtained in colourless needles. This substance has no basic properties. When boiled, it readily loses hydrogen, forming phenylacridine. *Hydromethylacridine*, $C_{14}H_{11}N$, resembles the preceding compound.

When hydrophenylacridine is heated at 130° with methyl iodide, it yields methylhydrophenylacridine, $C_{19}H_{14}MeN$. This substance is deposited from an alcoholic solution in needles or prisms (m. p. 104°). *Acetylhydrophenylacridine*, $C_{19}H_{14}\overline{Ac}N$ (m. p. 128°), dissolves freely in alcohol, ether, benzene, chloroform, and acetone. Methylhydrophenylacridine is converted into methylphenylacridinium hydroxide by oxidation with hydrochloric acid and sodium nitrite. Conversely the hydrochloride of methylphenylacridinium hydroxide is converted into methylhydrophenylacridine by reduction with zinc and hydrochloric acid.

Acridine resembles anthracene in constitution. It may be regarded as anthracene in which nitrogen replaces a CH-group.


Acridine.


Phenylacridine.


$C_6H_4<\begin{matrix}CHPh\\NH-\end{matrix}>C_6H_4$

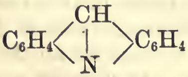
Hydrophenylacridine.


$C_6H_4<\begin{matrix}CHPh\\NMe-\end{matrix}>C_6H_4$

Methylphenylacridine.

Bases were also obtained by the action of diphenylamine on phthalic acid, ethylaniline on benzoic acid, and by methylaniline on acetic acid. W. C. W.

Acridine. By O. Fischer (*Ber.*, **16**, 1820—1821).—The base, $C_{14}H_{11}N$, obtained by the action of glacial acetic acid and zinc chloride on diphenylamine (*Ber.*, **16**, 68) bears such a close resemblance in its properties to acridine, recently described by Riedel (*ibid.*, **16**, 1612), that the author considers it may be regarded as *methylacridine*. The formation of methylacridine from acetyldiphenylamine is easily explained by means of Riedel's formula for acridine.

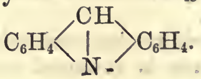

Acridine.

$C_6H_5N\overline{Ac}C_6H_5$

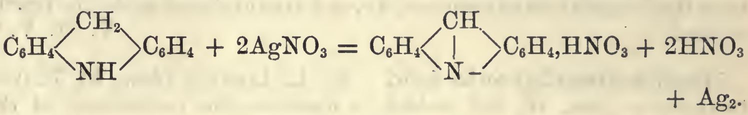
Acetyldiphenylamine.


Methylacridine.

W. C. W.

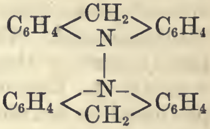
Acridine. By A. Bernthsen and F. Bender (*Ber.*, **16**, 1971—1974).—The authors' researches has shown that the composition of acridine is represented by the formula $C_{13}H_9N$, and not $C_{12}H_9N$, and its constitution thus: . Accordingly, hydroacridine, obtained by the action of reducing agents on acridine, will possess a constitution, $C_6H_4<{CH_2 \atop NH}>C_6H_4$.

The authors point out that the same soluble hydrophenylacridine is formed whether phenylacridine is reduced by sodium amalgam or by zinc and hydrochloric acid. Further, hydroacridine in alcoholic solution is decomposed by silver nitrate in accordance with the equation—



$$C_6H_4\left\langle{CH_2 \atop NH}\right\rangle C_6H_4 + 2AgNO_3 = C_6H_4\left\langle{CH \atop | \atop N-}\right\rangle C_6H_4,HNO_3 + 2HNO_3 + Ag_2.$$

Insoluble hydroacridine has the consitution, , which the authors propose to prove by the silver nitrate reaction. The relation of acridine to quinoline and pyridine is also discussed.



$$\begin{array}{c} C_6H_4<{CH_2 \atop N}>C_6H_4 \\ | \\ C_6H_4<{-N- \atop CH_2}>C_6H_4 \end{array}$$

V. H. V.

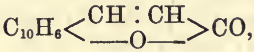
Methylnaphthalene. By P. BOESSNECK (*Ber.*, **16**, 1546—1547).—By the action of sodium on a mixture of α-bromonaphthalene and methyl iodide, Fittig and Remsen (*Annalen*, **155**, 112) obtained a small quantity of α-methylnaphthalene boiling at 231—232°, the chief product being naphthalene. The author finds that a much better yield is obtained by the distillation of a mixture of α-naphthylacetic acid with lime, 10 grams α-naphthylacetic acid yielding nearly 5 grams of hydrocarbon. A. K. M.

Phenylhydrazine-derivatives of the Quinones. (Preliminary Notice.) By T. ZINCKE (*Ber.*, **16**, 1563—1564).—When an aqueous solution of phenylhydrazine hydrochloride is added to β-naphthaquinone in alcohol or glacial acetic acid, a dark red solution is obtained, yielding red needles which, after recrystallisation from alcohol, melt at 138°. *β-Naphthaquinonephenylhydrazine*, $C_{16}H_{12}N_2O$, dissolves with moderate ease in hot alcohol and acetic acid, but is insoluble in water; it dissolves sparingly in dilute alkalis and acids, but does not form salts; concentrated sulphuric acid dissolves it, forming a violet-red solution from which water precipitates it unchanged. It forms a pale red *acetyl-derivative* melting at 120°. A second substance is obtained in the above reaction, which dissolves more readily and crystallises in white needles, the composition of which is unknown. *Phenanthraquinonehydrazine*, $C_{20}H_{14}N_2O$, is obtained by an analogous reaction, and forms bright red broad lustrous needles or scales melting at 165°, sparingly soluble in hot alcohol, more readily in hot acetic acid. It dissolves in concentrated sulphuric acid with a violet colour, and is precipitated unchanged on dilution with water. Acetic anhydride has no action on it. A. K. M.

β-Napthylaminesulphonic Acid. By L. LANDSHOFF (*Ber.*, **16**, 1931—1933).—Although phenol, even at a high temperature, is unaffected by ammonia, yet β-naphthol can be converted into β-naphthylamine by the action of this gas; the reaction is however far from complete. In the present paper the author points out that the sulphonic derivatives of β-naphthol can be converted readily into the corresponding β-naphthylaminesulphonic acid. In order to effect this change ammonia gas is slowly passed through the alkaline salts of the β-naphtholsulphonic acids heated at 250°. Dye-stuffs obtained from the β-naphthylaminemono-, di-, and tri-sulphonic acids are briefly noticed. V. H. V.

Naphtholtrisulphonic Acid. By L. Limpach (*Ber.*, **16**, 726).—Levinstein (*Ber.*, **16**, 462) called in question the correctness of the author's description of his method of preparation of β-naphtholtrisulphonic acid. The author now quotes the words of his German patent to show that his description was correct. He also says that, contrary to Levinstein's statement, only one trisulphonic acid is produced by his method. L. T. T.

β-Naphthacoumarin. By G. Kauffmann (*Ber.*, **16**, 683—686).—β-Naphthoxylaldehyde, already described by the author (Abstr., 1882, 1068), was mixed with anhydrous sodium acetate and acetic anhydride, and boiled for some time in a flask provided with a condensing tube. On treatment with water, a brown oil was obtained, which quickly solidified to a crystalline mass. Purified by repeated crystallisation from alcohol, this substance forms colourless plates, which melt at 124°. This substance was not the coumarin anticpiated, but the triacetyl compound of the aldehyde, $C_{10}H_6(O\overline{Ac}).CH(O\overline{Ac})_2$. It is insoluble in water, easily soluble in alcohol and acetic acid. It gives a dark brown coloration with ferric chloride. On boiling with sodium hydroxide, it is decomposed into the original aldehyde and acetic acid. On distilling the acetyl compound, acetic acid passes over, and a small quantity of the coumarin is obtained. The author then repeated his experiment, but heating in a sealed tube at 180° for 2½ hours. When cold the contents solidified to a brown crystalline mass, which on purification yielded fine, silky, and almost colourless needles of *naphthacoumarin.*

Naphthacoumarin,  $C_{10}H_6<\begin{array}{c}CH:CH\\ \text{—}O\text{—}\end{array}>CO$, is soluble in acetic acid, alcohol, ether, and chloroform, slightly so in boiling water, and the aqueous solution has a bluish fluorescence. Its melting point is 118°. When boiled with dilute potash, the naphthacoumarin is dissolved with a yellow coloration, but is reprecipitated unchanged on adding an acid. Heated to a higher temperature with very concentrated potash, a *nophthacoumaric acid* is produced. Naphthacoumarin thus shows the same reaction with alkalis as ordinary coumarin, and the author therefore concludes that in the dilute alkaline solution a salt of an isomeric naphthacoumaric acid exists corresponding to α-coumaric acid.

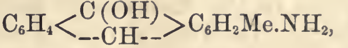
β-*Naphthacoumaric acid* is soluble in alcohol, from which it separates as a pale yellow crystalline powder, melting at 170°.

The formation of β-naphthacoumarin proves that the side groups in β-naphthoxyl aldehyde are in the ortho-position to one another. Its

formation from the acetyl-compound by direct distillation is also of interest as showing that the presence of a sodium salt is not essential to the coumarin-condensation.
L. T. T.

New Method of Forming Anthracene. By O. HENZOLD (*J. pr. Chem.* [2], **27**, 518—520).—When benzyl ethyl ether is heated with phosphoric anhydride, a violent reaction takes place. On distilling the product, a semi-solid mass is obtained, which, when re-crystallised from glacial acetic acid, forms glittering monoclinic plates of anthracene, melting at 208°. When treated with chromic acid, they yield anthraquinone. They are probably formed by the oxidation of stilbene, $C_2H_2Ph_2 + O = H_2O + C_2H_2(C_6H_4)_2$.
J. I. W.

Reduction in the Anthracene Series. By H. ROEMER (*Ber.*, **16**, 1631—1635).—The author showed (Abstr., 1882, 974) that metamidoanthraquinone is reduced when heated with hydriodic acid and amorphous phosphorus with formation of anthracylamine. Orthamidoanthraquinone (this vol., p. 72) is much less readily acted upon, and amidomethylanthraquinone with still greater difficulty. On boiling the latter for 1—2 hours with hydriodic acid of sp. gr. 1·96, amidomethylanthranol is obtained, whilst if the reduction is effected in sealed tubes at a temperature of 150°, the *hydriodide* of *amidomethylanthracenedihydride*, $C_{14}H_{10}Me.NH_2$, is formed. The *hydrochloride* forms lustrous needles melting at 245°, and the free *base* bright yellow lustrous scales, melting at 78—79°, and subliming at 130—140° with slight decomposition. It is almost insoluble in water, but dissolves very readily in alcohol and in ether, forming a yellow slightly fluorescent liquid, and also in chloroform, carbon bisulphide, benzene, xylene, and glacial acetic acid. With dilute nitric and sulphuric acids, it forms colourless solutions, from which the respective salts crystallise in white needles. It dissolves in concentrated sulphuric acid to a yellow solution, which however soon becomes green with evolution of sulphurous anhydride and formation of a sulphonic acid. Its solution in nitric acid is at first green, then yellow. On adding potassium nitrite to a solution of the hydrochloride, a green solution is obtained, from which ammonia throws down a red precipitate. It is insoluble in potash, and gives no coloured solution on boiling with zinc-dust and potash (distinctions from amidomethylanthranol). *Acetylamidomethylanthracenedihydride*, $C_{14}H_{10}Me.NH\overline{Ac}$, forms white lustrous needles (m. p. 198°), readily soluble in alcohol and in ether, with faint blue fluorescence. It is insoluble in hydrochloric acid, and is not decomposed if boiled with the latter or with potash, whilst at 150° hydrochloric acid converts it into the hydrochloride. When amidomethylanthracenedihydride is heated to 230° it remains unaltered in composition, its colour becomes somewhat darker, and its solution in ether more strongly fluorescent. With chromic acid, it yields a body insoluble in hydrochloric acid.
A. K. M.

Amidomethylanthranol. By H. ROEMER and W. LINK (*Ber.*, **16**, 703—706).—Roemer formerly (Abstr., 1882, 974) described the reduction of amidoanthraquinone (by hydriodic acid and amorphous phosphorus) to anthracylamine. The authors have now investigated the same subject with the amidomethylanthraquinone described in the next abstract. Using hydriodic acid of sp. gr. 1·7, an unstable compound, easily soluble in alcohol, hydrochloric acid, and alkalis is produced, which they have not further investigated. Using acid of sp. gr. 1·96, a precipitate insoluble in water was obtained. This dissolves in hot dilute hydrochloric acid, and its hydrochloride crystallises out on cooling in long needles. Washed with water, these needles lose hydrochloric acid, and leave the free base; this crystallises from alcohol in almost colourless needles, which darken on exposure to the air. It dissolves in alkalis, and the fluorescent solution deposits re-formed amidomethylanthraquinone. Its formula is $C_{15}H_{17}NO$, and it yields a diacetyl-derivative, showing that a hydroxyl-group must be present as well as the amido-group. These properties leave no doubt that it is an *amidomethylanthranol*,  $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{--CH--}>C_6H_2Me.NH_2$, but the position of the CH_3 and NH_2 groups, and whether they are in the same nucleus or not, is at present unknown. It melts at 183°, and at a slightly higher temperature sublimes with partial decomposition, in red needles. It is easily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid, very sparingly in water. Ferric chloride gives a green coloration in alkaline solution. Strong sulphuric acid produces a yellow solution, turning purple when heated; strong nitric acid (sp. gr. 1·48), a violet colour, slowly changing to orange. Its hydrochloride crystallises in glistening white needles containing $4H_2O$, which they lose at 80°. *Diacetylamidomethylanthranol* crystallises in white needles, melting at 170°. It is very unstable, is easily soluble in alcohol with a blue fluorescence, but its solution decomposes readily.

Traces of another body were also produced which remained behind with the phosphorus, after the extraction of the anthranol. It distils in steam, melts at 100°, and appears to be a *dihydride of methylanthracene.* L. T. T.

Nitro-, Amido-, and Hydroxy-methylanthraquinone. By H. Roemer and W. Link (*Ber.*, **16**, 695—703).—In crude anthracene, there is often present a methylanthracene which is very stable, and interferes with the preparation of alizarin. A mixture of methylanthraquinone and anthraquinone is formed, and the methyl-group is not eliminated by the subsequent processes, but contaminates the alizarin and damages its shade considerably. Messrs. Brönner have patented a process for getting rid of the methyl-compound by digesting the mixed quinones with benzene: methylanthraquinone is easily soluble; anthraquinone but very sparingly so. The authors have investigated the methylanthraquinone extracted by Messrs. Brönner, and prepared some derivatives. The crude extract was freed from resinous matter by washing with a very little benzene, crystallised from benzene, and finally from alcohol (in which anthraquinone is only very slightly soluble). *Methylanthraquinone* crystallises in pale yellow needles, soluble in acetic acid and benzene, sparingly in ether. Concentrated sulphuric acid dissolves it with blood-red coloration, which changes to violet on heating. It melts at 177° and sublimes in white needles. It appears to be identical with the methylanthraquinone of Wachendorf and Zincke (*Ber.*, **10**, 1485), and with that obtained from the same source by Börnstein (this vol., p. 70), but is isomeric with that of O. Fischer.

Nitromethyl-anthraquinone was obtained by treating the quinone with sulphuric acid and potassium nitrate; it melts at 269—270° when pure. It is sparingly soluble in alcohol, ether, benzene, chloroform, and acetic acid; easily in xylene, nitrobenzene, and aniline. It crystallises in pale yellow needles, which sublime in white needles. It dissolves in strong sulphuric acid with a yellow colour, which becomes yellowish-red, and finally brown on heating, sulphurous acid being produced at the same time. If the acid solution be poured into water, a purple colouring-matter is precipitated, which dissolves in alkalis to a fine violet-blue solution. *Amidomethylanthraquinone* was obtained by the reduction of the nitro-compound with alkaline stannous oxide solution. It crystallises from alcohol in red needles, fusing at 202°. It sublimes to long dark-red crystals. It is insoluble in water, soluble with a yellow coloration in ether, alcohol, benzene, acetic acid, and chloroform. Hot hydrochloric acid gives an almost colourless solution, from which the hydrochloride crystallises out on cooling in white scales, which are decomposed by water. *Acetylamidomethylanthraquinone* forms small bright red needles, melting at 176—177°.

Hydroxymethylanthraquinone was obtained from the amido-body by means of the diazo-reaction. It is sparingly soluble in alcohol and crystallises in orange needles, melting at 177—178°. It sublimes almost without charring, in long yellow needles. *Acetylhydroxymethylanthraquinone* crystallises from alcohol in orange-yellow scales, melting at 177°. L. T. T.

Derivatives of Anthramine. By A. Bollert (*Ber.*, **16**, 1635—1640).—When anthramine is boiled with glacial acetic acid, the solution obtained at once deposits small lustrous scales of very sparing solubility in the ordinary solvents. On boiling the precipitate with alcohol to separate acetylanthramine, pure *dianthramine*, $(C_{14}H_9)_2NH$, is obtained, closely resembling anthramine in appearance. It does not melt at 320°; it yields a blue-green solution with concentrated sulphuric acid, and on heating it with amyl nitrite, a red-coloured nitroso-derivative is produced. *Trimethylanthrammonium iodide*, $C_{14}H_9Me_3NI$, is readily obtained by the action of an excess of methyl iodide on anthramine at 100°. It is sparingly soluble in cold water, more readily in hot water, and almost insoluble in alcohol; a very dilute solution shows a faint blue fluorescence. It melts at 215° with decomposition. On treating its aqueous solution with freshly-precipitated silver oxide, a strongly alkaline liquid is obtained containing *trimethylanthrammonium hydroxide*, $C_{14}H_9Me_3N.OH$. The latter yields crystalline salts; the *hydrochloride* forms small lustrous crystals, readily soluble in cold water; the *platinochloride*, $(C_{14}H_9Me_3NCl)_2,PtCl_4$, is obtained as a yellowish crystalline precipitate. When a solution of the ammonium base is evaporated on a water-bath and the residue heated at 120—130°, *dimethylanthramine*, $C_{14}H_9NMe_2$, is produced, and on boiling the product with water and crystallising the residue from boiling alcohol, thin scales are obtained, melting at 155°. $C_{14}H_9Me_3N.OH = C_{14}H_9NMe_2 + MeOH$. This base is moderately soluble in hot alcohol, the solution showing a green fluorescence. It is much more readily soluble in hot dilute hydrochloric acid than anthramine, and from this solution the *hydrochloride* crystallises in colourless, lustrous scales. On boiling an alcoholic solution of anthramine with amyl nitrite, or on adding a very dilute solution of nitrous acid to a cold alcoholic solution of anthramine, a red crystalline precipitate, $C_{28}H_{21}ON_3$ (m. p. 250°), is obtained, sparingly soluble in alcohol, ether, and glacial acetic acid, more readily in amyl alcohol and carbon bisulphide. It is not acted on by potash or dilute acids, whilst concentrated sulphuric acid yields a blue solution. It is easily reduced by stannous chloride, with formation of anthramine. An attempt to prepare the isonitril of anthramine by the action of chloroform on its solution in alcoholic potash yielded a product which is probably *methenyldianthramineamidine*, $C_{14}H_9.N : CH.NH.C_{14}H_9$. It is readily soluble in hot alcohol, from which it separates on cooling as a brownish-yellow amorphous substance. *Formanthramine*, $C_{14}H_9NH.CHO$, is obtained as a yellow crystalline precipitate, by heating anthramine with an excess of concentrated formic acid (sp. gr. 1·22) at 100°. It melts at 242°, dissolves sparingly in hot alcohol, the solution showing a blue fluorescence. A. K. M.

Addition-products of some Terpenes. By P. MEISSEN (*Gazzetta*, **13**, 99—102).—From the results of Tonnies' experiments (Abstr., 1879, 35) it would seem that unsaturated hydrocarbons are capable of forming addition-products with nitrous anhydride. Nitrosyl chloride, as Tilden has shown, also has the property of uniting in a similar manner with most of the terpenes, and the author has succeeded in forming addition-products which, besides the terpene-group, contain a molecule of nitrosyl chloride, and one of nitric acid. The terpenes which yield these interesting compounds are those obtained from the essential oils of carroway (carvene), lemons, and orange. The purified terpene (50 grams) is saturated with dry hydrogen chloride, mixed with glacial acetic acid (30), and to this is added a mixture of amyl nitrite (70) with nitric acid (35), of sp. gr. 1·40, taking care to keep the whole well cooled. In this way a homogeneous greenish-blue liquid is obtained, which after some time deposits a white crystalline substance, the temperature rising somewhat at the same time. The crystals are insoluble in alcohol, but very soluble in chloroform, so that they may be purified by precipitating the chloroform solution with alcohol. The carvene compound, which forms small hard crystals, melts at 114—115° with decomposition and evolution of nitrous vapours. Analyses are given of the compounds formed with the three terpenes, and in all cases they agree with the formula

$$C_{10}H_{16}(HNO_3).NOCl.$$

When submitted to the action of different reagents, all three of the compounds decompose with the greatest ease, yielding dark-coloured resinous products. C. E. G.

Aldehydic Nature of Oxidation-products of Terebene. By H. Schiff (*Ber.*, **16**, 2010—2013).—The oxygen compound, formed on exposing turpentine-oil to the air, has attracted the attention of many chemists, but no satisfactory results have been obtained with it. The author shows that turpentine-oil, if not exposed for too long a time to the air in presence of diffuse sunlight, gives many of the reactions of an aldehyde, viz., a reduction of ammoniacal solutions of silver, a violet coloration with rosaniline sulphite, and an evolution of heat on addition of sodium hydrogen sulphite. After the oil is heated to its boiling point, the two former reactions can be observed, but not the latter, owing probably to a more intimate oxidation of the oil. The author endeavoured to separate the product of oxidation, and obtained a small quantity of a thick golden oil, which is altered readily by the air. It combines with ammonia and aniline, forming a crystalline compound with the latter. When oxidised by nitric acid, the oil gives a white solid acid melting at 50—60°, which appears to be neither camphoric nor abietic acid. When citron oil is exposed to sunlight, a similar violet coloration is produced by the addition of rosaniline sulphite. V. H. V.

Bitter Principle of Hymenodictyon Excelsum. By W. A. H. Naylor (*Pharm. J. Trans.* [3], **13**, 817—818).—The barks of two species of *Hymenodictyon*, *H. excelsum*, and *H. obovatum*, are bitter, and are used in India as tonics. Previous investigation of the bitter principle of the bark resulted in its being attributed to the presence of æsculin. The author has studied the behaviour of the bitter substance, and pronounces it to be an alkaloïd allied to paricine. The bitter substance may be extracted from a mixture of the bark with lime by percolation with alcohol; it is not crystalline, melts at 120°, is deliquescent, has an alkaline reaction, and a persistent bitter taste. It dissolves in and nearly neutralises acids. The hydrochloric acid solution gives amorphous precipitates of various colours with the following reagents,—phosphomolybdic, picric, and tannic acids; the double iodides of potassium with bismuth, mercury, and cadmium; mercuric chloride; potassium ferro- and ferri-cyanide; sodium phosphate, chloride, and nitrate; and ammonium chloride. The sulphate is precipitated by nitric acid. The platinochloride contained 20·08 per cent. platinum; a combustion yielded results 75·82 carbon, 9·8 hydrogen (paricine requires C 75·59, H 7·08). The alcoholic solution is optically inactive. The author intends to continue this investigation. D. A. L.

Solubility of the Colouring-matter of Wine in the various Constituents of Grape-juice. By F. Gantter (*Ber.*, **16**, 1701—1703).—The colouring-matter in the skin of the grape is soluble in a solution of tartaric acid or cream of tartar; the solubility increases with the temperature. It is only sparingly soluble in alcohol or in an aqueous solution of sugar. W. C. W.

Active Principle of the Root of Apocynum Cannabinum. By O. Schmiedeberg (*Pharm. J. Trans.* [3], **13**, 942).—This vegetable root contains two substances, one *apocynin*, an amorphous resinous substance, soluble in alcohol and in ether, almost insoluble in water; a very small quantity causes systolic pause in the heart of a frog. It does not seem to be a glucoside, although when boiled with moderately strong hydrochloric acid it produces a liquid which reduces alkaline cupric oxide, and itself becomes inert as regards the heart, &c. The second substance is *apocyneïn*, which is a glucoside, and in its properties agrees essentially with nereïn or digitaleïn, but, like apocynin, does not give any remarkable reaction with sulphuric acid and bromine. D. A. L.

Action of Nascent Hydrogen on Pyrroline. By G. L. CIAMICIAN and M. DENNSTEDT (*Ber.*, **16**, 1536—1544).—The pyrroline is heated with zinc-dust and acetic acid for 24 hours, and the product distilled on a water-bath under diminished pressure to expel the acetic acid and the unaltered pyrroline; on treating the residue with water, a green solution is obtained, leaving an insoluble residue of zinc-dust mixed with a resinous substance insoluble in alcohol. The solution is freed from zinc by means of hydrogen sulphide, acidulated with hydrochloric acid, evaporated, and the residue steam-distilled with an excess of potash, when a quantity of ammonia is given off. The distillate is acidulated with hydrochloric acid, evaporated, and the residue dissolved in a small quantity of water, and again distilled with potash. The purified oil boils at 90—91°; it is extremely soluble in water, and absorbs carbonic anhydride from the air, forming a solid deliquescent compound. It forms a *hydrochloride*, C_4H_7N,HCl, melting at 173—174°, readily soluble in boiling alcohol, from which it crystallises in prisms. From the formula of the hydrochloride, it is evident that the free *hydropyrroline* has the formula C_4H_7N. The *platinochloride*, $(C_4H_7N)_2,H_2PtCl_6$, is sparingly soluble in cold water, readily in boiling water; it crystallises in the triclinic system,

$$a : b : c = 1{\cdot}65801 : 1 : 1{\cdot}58370.$$

Methyl iodide acts very violently on hydropyrroline, with formation of the compound C_4H_6MeN,MeI; this crystallises from boiling alcohol in nacreous scales, melting at 286° with decomposition; it dissolves very readily in water, and its solution is not decomposed by potash. By the action of freshly precipitated silver chloride, the corresponding *chloride* is obtained. The *platinochloride*, $(C_6H_{12}N)_2,H_2PtCl_6$, crystallises in orange-coloured needles, with variable amounts of water. By the action of silver oxide on a solution of the methiodide, a strongly akaline liquid is obtained, which can be evaporated nearly to dryness without decomposition; on distilling the residue it decomposes, yielding a nearly colourless distillate, sparingly soluble in water, and having a penetrating odour resembling that of the isonitriles.

Nitrosohydropyrroline, $C_4H_6N.NO$, can be prepared by the action of potassium nitrite on a solution of the base in dilute sulphuric acid. It crystallises from light petroleum in needles melting at 37—38°; it dissolves very readily in water, alcohol, and ether, and gives the characteristic nitrosamine reaction with phenol and sulphuric acid.

The reactions with methyl iodide and nitrous acid show that hydropyrroline is a secondary base of the formula $C_4H_6 \vdots NH$.

A. K. M.

Tetrahydroquinoline. By L. Hoffmann and W. Königs (*Ber.*, 16, 727—740).—After a brief survey of the evidence now existing of the probability that the alkaloïds are hydrogenised pyridine-derivatives, the authors proceed to the careful investigation of tetrahydroquinoline and its derivatives as likely to throw some light on the quinine-alkaloïds.

Two secondary bases are formed by the reduction of quinoline, the one containing 4, the other 2 more atoms of hydrogen than quinoline. The latter melts at 161°, and does not distil, and is probably produced by the union of two molecules of quinoline. The present paper refers to the volatile hydride with four additional hydrogen-atoms. It was prepared by Wischnegradsky's method by reduction with tin and hydrochloric acid. *Tetrahydroquinoline* is liquid at ordinary temperatures, but solidifies, when pure, at very low temperatures to colourless needles. It boils at 244—246° (bar. 724 mm.), or 15° higher than quinoline. The *hydrochloride* crystallises in thin prisms melting at 180—181°, and is soluble in water and alcohol. The *platinochloride* forms reddish-yellow crystals melting at 200°. The *acid sulphate* crystallises from alcohol in prisms, from water (in which it is very soluble) in large monoclinic plates. The *tartrate* and *oxalate* are easily soluble; the *picrate* forms yellow sparingly soluble needles which melt when heated under water. Tetrahydroquinoline forms an easily soluble double salt with *zinc chloride*, and with *mercuric chloride*, a similar sparingly soluble compound: both compounds crystallise in white needles. Gold chloride produces in solutions of the hydrochloride, a yellow precipitate which is quickly reduced; silver is also reduced from an alcoholic solution of silver nitrate. Ferric chloride, or potassium dichromate and sulphuric acid, produce deep coloration in dilute, and an amorphous precipitate in concentrated solutions.

The addition of sodium nitrite to a slightly acid solution of tetrahydroquinoline precipitates *nitrosotetrahydroquinoline* as a yellowish oil showing Liebermann's reaction. On standing with excess of nitrous acid, or more quickly by shaking with nitric acid (1 vol. acid of sp. gr. 1·4 and 2 vols. water), it is converted into *nitronitrosotetrahydroquinoline*, $C_9H_9N(NO_2)NO$, crystallising from alcohol in yellow needles melting at 137—138°.

Tetrahydroquinolinehydrazine, $C_9H_9N.NH_2$, is obtained by the reduction of the nitroso-body in alcoholic solution with zinc-dust and glacial acetic acid. It separates from light petroleum in white crystals melting at 55—56°. It boils, with partial decomposition, at 255°. The neutral *sulphate* is sparingly soluble in water, and crystallises with 2 mols. H_2O. The *hydrochloride* is easily soluble in water, sparingly so in concentrated hydrochloric acid. The hydrazine reduces gold and platinum salts in the cold, Fehling's solution on boiling. Nitrous acid reconverts it into the nitroso-compound.

Tetrahydroquinolinetetrazone, $C_9H_9N.N_2.NC_9H_9$, is produced by shaking a cold etheric solution of the hydrazine with mercuric oxide. It resembles E. Fischer's aromatic tetrazones in possessing scarcely any basic properties. It is insoluble in water, sparingly soluble in alcohol and mineral acids, freely in chloroform, ether, carbon bisulphide, and benzene. It crystallises in needles melting at 160°. By long boiling with dilute hydrochloric or sulphuric acids, it is decomposed into quinoline and hydroquinoline, gas being at the same time evolved. Acetic acid produces this decomposition more readily, owing to its greater solvent power for the tetrazone.

Methyltetrahydroquinoline, $C_9H_{10}N.CH_3$, is obtained by the action of methyl iodide on tetrahydroquinoline. It is an oil which boils at 242—244° (bar. 720° mm.). The platinochloride forms red crystals melting, with evolution of gas, at 177°. The simple salts are mostly deliquescent, and scarcely crystallisable. The *acid sulphate* is obtained by the slow evaporation of its solution in absolute alcohol in crystals which deliquesce in the air. With sodium nitrite, an acid solution of methyltetraquinoline becomes of an intense orange colour, from the formation of a *nitroso-compound;* this body is precipitated as an oil by the addition of an alkali, but does not seem to be attacked by boiling therewith. The nitroso-compound is soluble in ether to a green solution, from which nitric acid precipitates a yellow solid, which is scarcely basic in properties, and is probably *nitromethyltetraquinoline.*

Simultaneously with methyltetrahydroquinoline, the *quaternary ammonium iodide*, $C_9H_{10}NMe.MeI$, is formed, and remains in the alkaline solution. It was isolated by E. Fischer's method (Abstr., 1878, 407). The chloride thus obtained forms short white prisms.

Tetrahydroquinoline-carbamide, $C_9H_{10}N.CO.NH_2$, is easily formed by mixing equivalent proportions of tetrahydroquinoline hydrochloride and potassium cyanate in aqueous solution. The liquid soon becomes filled with white needles which, when recrystallised from water, melt at 146·5°. This substance is sparingly soluble in cold water, almost insoluble in alcohol. Dilute acids have no action on it, boiling with alkalis regenerates tetrahydroquinoline. Carbon bisulphide which acts violently on piperidine, is without action on tetrahydroquinoline.

Benzoyl- and Acetyl-tetrahydroquinoline have both been already cursorily described by Wischnegradsky. The former crystallises from alcohol in plates belonging to the monosymmetric system, melting at 75°, and boiling undecomposed. The latter boils at 295°. Both have but very feeble basic properties, and are easily saponified by boiling with concentrated hydrochloric acid. By oxidation in the cold with a 4 per cent. solution of potassium permanganate, *oxalylanthranilic acid* was produced, together with acetic acid. The formation of this substance probably takes place in a manner similar to its formation from carbostyril already observed by Friedländer and Ostermaier (Abstr., 1882, 732).

Oxidation of Tetrahydroquinoline.—All attempts to obtain oxalylanthranilic acid by the direct oxidation of tetrahydroquinoline proved futile; the products formed were oxalic acid, quinoline, traces of anthranilic acid, and an amorphous feebly basic body resembling in properties the amorphous reduction-product obtained from quinoline. This amorphous body was always the principal product.

Some time ago König showed that by the action of sulphuric acid on piperidine, pyridine was produced, together with some sulphonic acids not then investigated. The authors have now isolated *barium pyridinedisulphonate*, $C_5H_3(SO_3)_2Ba$. It crystallises in white needles containing water of crystallisation. Part of the water goes off at 110°, but the last ½ mol. requires a temperature of 200°. Sulphuric acid acts on tetrahydroquinoline in a similar manner, but more readily, *quinoline* and *quinoline-sulphonic acids* being produced. Dilute nitric acid (1 : 6) does not attack tetrahydroquinoline; stronger acid (1 : 2) forms first nitroso- and nitronitroso-compounds, but after continued heating, the addition of water precipitates *quinolic acid*,

$$C_9H_4N(NO_2)(OH)_2.$$

Action of Bromine on Tetrahydroquinoline.—Excess of bromine yields tribromoquinoline already described by Lubavin. By using less bromine, the authors have obtained mono- and di-bromo-substitution products of the hydro-base. The two are separated by boiling with dilute hydrobromic acid: the monobromo-derivative being still strongly basic goes into solution, whilst the di-derivative is left behind as an oil. *Monobromotetrahydroquinoline hydrobromide*,

$$C_9H_{10}BrN,HBr,$$

crystallises from the above solution in white silky needles melting at about 192° with decomposition. *Dibromotetrahydroquinoline hydrochloride*, $C_9H_9Br_2N,HCl$, is obtained by boiling the above oil with moderately strong hydrochloric acid (1 : 2) : it melts at 162°, and is at the same time decomposed. With platinum chloride, it gives a crystalline platinochloride. The hydrochloride is decomposed by water, and is therefore different from the hydrochloride of the dibromohydroquinoline obtained by Claus and Istel by the reduction of tetrabromoquinoline, which may be crystallised from water, and melts at 74—75°.

Both the mono- and di-bromo-compounds form nitroso-bodies, showing Liebermann's reaction: they are both volatile in a current of steam; and are decomposed when heated, yielding hydrobromic acid, quinoline, and other products not investigated. The bromine therefore appears to be attached to a carbon-atom in the pyridine-ring. The free monobromo-body forms a crystalline mass melting below the temperature of the hand, and yields crystalline sulphates and chlorides. The dibromo-derivative is a thick oil, which solidifies in a freezing mixture. By passing tetrahydroquinoline over red hot pumice, quinoline and indole are obtained. An attempt to obtain skatole from methyl-tetrahydroquinoline was unsuccessful.

Physiological Action of Hydrogenised Pyridine Derivatives.—Professor Filehne has investigated this subject. Ethylpiperidine hydrochloride, $C_5H_{10}NEt,HCl$, is similar in its action to conine. Tetrahydroquinoline chloride is more energetic than quinoline, but causes injurious local action. Dimethyltetrahydroquinolium chloride,

$$C_9H_{10}NMe,MeCl,$$

is similar in its action to curare. For the action of "kairine" and "kairoline" see this vol., p. 1147. From Filehne's researches it appears probable that those derivatives of hydroquinoline (perhaps of hydrogenised diquinoline) will be of most medical value, in which the imido-hydrogen is replaced by an alcohol radical, and render it probable that this is the case in quinine. L. T. T.

Derivatives of Hydroxyquinoline. By O. Fischer (*Ber.*, 16, 712—721).—The author has continued his work on the hydroxyquinolines derived from the quinolinesulphonic acids. Both the α- and β-hydroxyquinolines are identical with those described by Skraup (this vol., 92), and in the present paper the author only gives those derivatives of the α-body which have not yet been described. The author upholds the correctness of the melting point (75—76°) of α-hydroxyquinoline given in his previous paper, against the lower one (73—74°) given by Skraup.

α-Hydroxyquinolinetetrahydride has been already described. The *tin* double salt is easily soluble in water, sparingly in hydrochloric acid. It crystallises in iridescent scales or yellowish prisms. The *zinc* double salt forms hexagonal plates, sparingly soluble in strong hydrochloric acid. Potassium ferrocyanide produces a white crystalline precipitate in acid solutions of the tetrahydride. The latter body gives an intense red coloration when boiled with acetic anhydride. α-Hydroxyquinolinetetrahydride can be converted into a tertiary base by methylating, ethylating, or benzylating.

α-Hydroxymethylhydroquinoline, $C_{10}H_{13}NO$, is obtained by treating the tetrahydride with methyl iodide (bromide or chloride). It is a strong base; dissolves easily in caustic alkalis, benzene, hot alcohol, and ether, and sparingly in water. The colourless rhombic crystals obtained from the alcoholic solution had the axis ratio: $a : b : c = 0·6309 : 1 : 1·5383$, and melted at 114°. A solution in dilute sulphuric acid gives an orange colour with sodium nitrite. Ferric chloride produces a deep brown colour in alcoholic solutions, a dark-brown flocculent precipitate being gradually deposited. The *hydrochloride* (*kairine*) is easily soluble in water, and gives, over sulphuric acid, monoclinic crystals containing 1 mol. H_2O, which they lose at 110°. The measurements of the crystals gave $a : b : c = 0·7180 : 1 : 0·3858$ and $\beta = 80° 17'$. The *sulphate* forms easily soluble flat prisms. The *picrate* crystallises from dilute alcohol (20—30 per cent.) in small yellowish-green plates sparingly soluble in water.

α-Hydroxyhydroethylquinoline is prepared in a manner similar to the methyl compound. It is easily soluble in benzene, alcohol, wood spirit, and ether, sparingly in water and light petroleum. The *hydrochloride* (*kairine* A) crystallises in white anhydrous prisms, easily soluble in water. Boiling with platinic chloride oxidises the solution.

Ethoxyquinoline, $C_{11}H_{11}NO$, was obtained by heating 1 mol. hydroxyquinoline in alcoholic solution with 1 mol. potassium hydroxide and 1 mol. ethyl bromide for an hour. It distils at 285—287° (bar. 718 mm.) as a thick oil which solidifies to a crystalline mass in the winter. Nitrous acid produces a yellow colour in dilute solutions.

Ethoxyhydroquinoline is obtained from the preceding by reduction with tin and hydrochloric acid. It distils at 275—276°, and remains liquid. The *nitroso*-derivative was obtained by adding it to a dilute sulphuric solution of sodium nitrite; the liquid becomes red, and, after a few seconds, deposits small yellow crystals; purified by solution in hot alcohol, the substance was obtained in pale yellow prisms. It shows Liebermann's reaction well. Concentrated hydrochloric acid dissolves the nitroso-body with deep-red coloration.

α-Ethoxyhydromethylquinoline was obtained from ethoxyhydroquinoline by treating it with methyl iodide. It forms a pale yellow oil, boiling at 269—270° (bar. 716 mm.). Its salts are easily soluble crystalline substances which are mostly deliquescent.

When 2 mols. of α-hydroxyhydroquinoline are heated in a sealed tube at 100—110° for an hour with 1 mol. monochloracetic acid, a body of the formula $C_{11}H_{11}NO_2$, which the author names *kairocoll*, crystallises out on cooling, whilst α-hydroxyhydroquinoline chloride remains in solution. The reaction takes place according to the equation:—

$$2C_9H_{11}NO + C_2H_3ClO_2 = C_{11}H_{11}NO_2 + C_9H_{11}NO,HCl + H_2O.$$

The author calls attention to this formation of an anhydride in the presence of water. *Kairocoll* is sparingly soluble in water, freely in alcohol, ether, and light petroleum, and crystallises from the latter in long thin white needles fusing at 66°.

The hydroxy-derivatives obtained from coal-tar quinoline and synthetic quinoline are identical, thus affording another proof of the identity of these two quinolines.

Physiological Effects of Hydroxyquinoline Derivatives.—Professor Filehne has investigated the physiological action of many of the foregoing substances. *α-Hydroxyquinoline* and *α-methoxyquinoline* and *their salts* possess poisonous properties. The *chlorides of α-hydroxyhydroquinoline* and *α-methoxyhydroquinoline* approach quinone in their action, but cause unpleasant secondary action, such as local decomposition of albumin, &c. *Hydroxymethylhydroquinoline hydrochloride* has exceedingly strong febrifuge properties unattended by any unpleasant secondary effects, and is now much used under the name of *kairine*. *Methyltetrahydroquinoline*, *β-hydroxyhydroquinoline*, and *α-ethoxymethylhydroquinoline*, all show similar action, varying, however, in the duration of the effect. The action of the sulphate of the last named is of longest duration, lasting about 15—16 hours.

L. T. T.

β-Hydroxyquinoline. By C. Riemerschmied (*Ber.*, **16**, 721—726).—β-Hydroxyquinoline was prepared as described by O. Fischer (this vol. 91). With Nordhausen acid below 200°, the α-sulphonic acid predominates, but if the heating is carried to 270° or a larger proportion of sulphuric anhydride used in the sulphuric acid, a much better yield of the β-acid is obtained. β-Hydroxyquinoline differs from the α-body in its non-volatility with steam, and its solubility in solution of sodium carbonate, from which it can be extracted by ether. β-Hydroxyquinoline is undoubtedly identical with that obtained by Skraup (this vol., 92) from metanitro- and metamido-phenol, but the author was not able to obtain Skraup's melting point (235—238°), his preparations always melting between 224—228°. An acid solution of potassium dichromate gives red needles of the chromate of this base. The platinochloride crystallises in orange-yellow plates with $4H_2O$ which it loses at 110°. Skraup gives orange-yellow needles with $2H_2O$.

β-Hydroxyhydroquinoline, $C_9H_{11}NO$, is obtained similarly to the α-body (see preceding Abstr.) by reduction with tin and hydrochloric acid. It is easily soluble in alcohol, ether, wood-spirit, water, &c., sparingly in light petroleum and cold benzene. It crystallises in stellate groups of needles and melts at 116—117°. It sublimes with scarcely any decomposition. Ferric chloride in aqueous solution gives a very deep-red coloration. The *nitroso*-derivative is almost insoluble in water and weak acids, easily soluble in alcohol or wood-spirit. It crystallises in almost colourless plates, and gives Liebermann's reaction.

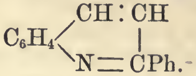
β-Hydroxyethylhydroquinoline forms striated crystals, melting at 73°. It is easily soluble in alcohol, ether, benzene, and wood-spirit, sparingly in water and light petroleum. Its *hydrochloride* contains 1 mol. H_2O, which it loses at 110°. It has a burning taste and bitter after-taste, and is, according to Filehne, similar in its physiological effects to kairine (see p. 1147). A white crystalline precipitate is produced by potassium ferrocyanide. An alkaline solution gives a dark brownish-red colour with ferric chloride: sodium nitrite gives an intense yellow.

β-Hydroxyquinolinesulphonic acid, $C_9H_6NO.SO_3H,H_2O$, is produced by treating β-hydroxyquinoline at low temperatures, with 8 times its weight of fuming sulphuric acid and allowing it to stand 48 hours. It is easily soluble in boiling water, crystallises with 1 mol. H_2O, and melts at 270°. It gives a dark-green coloration with ferric chloride. Its salts are yellow in colour: the potassium and sodium salts are easily soluble in water, the barium salt rather sparingly so. Fused with sodium hydroxide, it gives a brown mass from which ether extracts a new body, probably a dihydroxyquinoline.

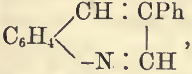
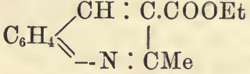
β-Amidoquinoline, $C_9H_8N_2$, is obtained by heating 1 part β-hydroxyquinoline with 3 parts ammonium zinc chloride. The mass softens at 160°, becomes liquid at 220°, but very little amide is formed, unless the mixture is heated for some hours at 300°. β-Amidohydroxyquinoline melts at 109—110°, and decomposes at a slightly higher temperature. If heated quickly, however, it sublimes, almost without decomposition. It is easily soluble in alcohol, ether, wood-spirit, and boiling water, sparingly so in cold water, light petroleum, and benzene. The picrate crystallises from alcohol in long red needles, insoluble in ether. Chloroform and caustic potash give the carbamine reaction. The *diazo-salts* of β-amidohydroxyquinoline produce, with phenols and tertiary bases, intense azo-dyes, as, for example, with β-sodium naphtholate a red, with dimethylaniline a yellowish-brown. L. T. T.

Preparation of Substituted Quinolines. By P. FRIEDLÄNDER and C. F. GOHRING (*Ber.*, **16**, 1833—1839). — α-Methylquinoline (quinaldine) can be prepared by the direct union of orthamidobenzaldehyde and acetone in the presence of an alkali. α-Phenylquinoline, formed on gently warming a solution of orthamidobenzaldehyde and excess of acetophenone in dilute alcohol with a few drops of soda solution, is identical with the γ-phenylquinoline of Grimaux (*Compt.

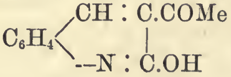
rend., 1883, 584), and the α-phenylquinoline of Döbner and v. Miller (*Ber.*, **16**, 1664). The formula for this compound is—



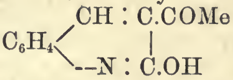
$$\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{CH:CH}\\ \qquad\;|\\ \mathrm{N{=}CPh.}\end{array}\right.$$

Phenylacetaldehyde unites with orthamidobenzaldehyde, forming β-phenylquinoline,  $\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{CH:CPh}\\ \qquad\;|\\ \mathrm{N:CH}\end{array}\right.$, which crystallises in needles melting at 93°. With an alkaline solution of ethyl acetoacetate, amidobenzaldehyde combines, producing the *ethyl salt of α-methylquinoline β-carboxylic acid*,  $\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{CH:C.COOEt}\\ \qquad\;|\\ \mathrm{N:CMe}\end{array}\right.$. This ethereal salt is deposited from an alcoholic solution in white needles (m. p. 71°), which are insoluble in water. It forms a crystalline platinochloride, $(C_{13}H_{13}NO_2)_2,H_2PtCl_6 + 2H_2O$. On saponification with alcoholic soda or hydrochloric acid, it yields α-lepidinecarboxylic acid (m. p. 234°).

If ethyl acetoacetate and amidobenzaldehyde are heated at 160° (without a solvent), *hydroxyquinolinemethylketone*,

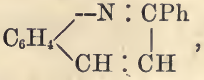


$$\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{CH:C.COMe}\\ \qquad\;|\\ \mathrm{N:C.OH}\end{array}\right.,$$

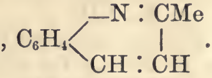
is obtained as a crystalline mass (m. p. 232°), soluble in hot water. The compound is precipitated by carbonic acid from its solution in alkalis. Amidobenzaldehyde acts on ethyl benzoylacetate, forming the compound,  $\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{CH:C.COMe}\\ \qquad\;|\\ \mathrm{N:C.OH}\end{array}\right.$. It melts above 270°, and is less soluble than the preceding substance, which it closely resembles in other respects. W. C. W.

α-Methylquinoline. By V. B. Drewsen (*Ber.*, **16**, 1955—1956).—Orthonitrobenzylidene-acetone is best prepared by the direct nitration of benzylidene-acetone; on reduction with stannous chloride in acid solution it is converted into *methylquinoline*, C_9H_6NMe, a heavy golden-yellow oil (b. p. 240°), combining with acids to form well characterised salts. Its platinochloride crystallises in golden needles. On oxidation with potassium permanganate, it yields a substance identical in its physical and chemical properties with the acetyl anthranilic acid, obtained by the oxidation of quinaldine under the same conditions. When lepidine is oxidised with potassium permanganate, it yields an acid of the composition, $C_9H_9NO_3$ crystallising in needles melting at 179°, soluble in alcohol and ether, sparingly soluble in cold water. V. H. V.

Phenylquinoline. By O. Doebner and W. v. Miller (*Ber.*, **16**, 1664—166).—The formation of quinaldine from a mixture of aniline, nitrobenzene, sulphuric acid, and aldehyde or glycol (Abstr., 1882, 868), was assumed by the authors to be due to the formation in the first case of crotonaldehyde. Experiments made with mixtures of acetaldehyde with higher homologues, *e.g.*, butyraldehyde and valeraldehyde, show that acetaldehyde alone yields this reaction. Cinnamic aldehyde should, however, yield *phenylquinoline*,



$$C_6H_4\left\langle\begin{array}{l}-N : CPh \\ | \\ CH : CH\end{array}\right. ,$$

corresponding to quinaldine,  $C_6H_4\left\langle\begin{array}{l}-N : CMe \\ | \\ CH : CH\end{array}\right.$. On warming a mixture of aniline and cinnamic aldehyde the compound $C_9H_8 : NC_6H_5$ is formed, crystallising in yellow scales melting at 109°. It is sparingly soluble in water, readily in ether and hot alcohol. Its *hydrochloride* crystallises in long yellow needles. *Phenylquinoline* is prepared by heating a mixture of 30 parts cinnamic acid, 20 parts aniline, and 20 parts hydrochloric acid, for two hours at 200—220°; the brown product is boiled with dilute hydrochloric acid, the cold filtered solution supersaturated with soda, and the phenylquinoline extracted with ether. It crystallises from dilute alcohol in long silky needles, melting at 83°, and it boils above 300° without decomposition. It dissolves sparingly in water, readily in ether and in boiling alcohol. The *hydrochloride*, *nitrate*, and *sulphate* are readily soluble in water; the *platinochloride*, $(C_{15}H_{11}N)_2,H_2PtCl_6$, forms yellow needles, sparingly soluble in water; the *chromate*, $C_{15}H_{11}N,Cr_2O_7H_2$, is a characteristic salt crystallising in gold-coloured scales. A. K. M.

Methylenediquinoïl Hydrochloride. By A. RHOUSSOPOULOS (*Ber.*, **16**, 2004—2005).—By gently heating methylenediquinoïl hydroxide and freshly precipitated silver chloride on a water-bath, a solution of methylenediquinoïl hydrochloride is obtained. On evaporation, this substance separates in white glistening tables melting at 160°, easily soluble in water, insoluble in ether. It is decomposed into quinoline and methylene chloride when boiled with potash. Its platinochloride, $CH_2(C_9H_6N)_2,H_2PtCl_6$, crystallises both in prismatic needles and octohedra, sparingly soluble in water, insoluble in alcohol.

V. H. V.

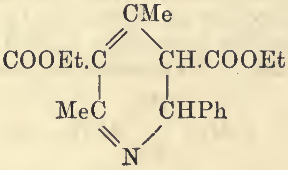
Colouring-matters from Coal-tar Quinoline. By W. SPALTEHOLZ (*Ber.*, **16**, 1847—1852).—After referring to the researches of Skraup (*Monatsh. Chem.*, 1881, 214) Hoogewerff and v. Dorp (*Rec. Trav. Chim.*, **2**, 28), and Jacobsen and Reimer (*Ber.*, **16**, 1082), on the identity of quinoline from different sources, the author points out that the colouring-matter which Williams obtained (*Roy. Soc. Edin. Trans.*, **31**, 377) by the action of alkalis on quinoline ethiodide, cannot be obtained if pure quinoline or pure quinaldine ethiodide is employed. It is best prepared by warming an aqueous solution of quinaldine ethiodide (1 part) and quinoline ethiodide (2 parts) with excess of potassium hydroxide. After the product has been digested in ether to remove resinous matter, the colouring matter remains in green crystals, which have the composition, $C_{23}H_{25}N_2I + \frac{1}{2}H_2O$, and are identical with those obtained from crude quinoline.

W. C. W.

Syntheses in the Pyridine Series. By A. Ladenburg (*Ber.*, 16, 1410—1411).—When pyridinethyl iodide is heated at the melting point of lead, a black mass is formed which, on distillation with excess of soda, yields water and an alkaline oil, insoluble in water. The oil (dried over potash) has not a constant boiling point, but distils between 130° and 170°. It appears to consist of a mixture of aromatic hydrocarbons (b. p. 80—140), pyridine, and ethylpyridine.

W. C. W.

Introduction of Hydrocarbon Radicles into the Pyridine-group. By R. Schiff and J. Puliti (*Ber.*, 16, 1607—1608).—Hantzsch obtained diethylic hydrocollidinedicarboxylate by the action of aldehydammonia on ethyl acetoacetate (this vol., p. 82). A similar reaction takes place when benzaldehyde (1 mol.) is mixed with ethyl acetoacetate (2 mols.), alcoholic ammonia added, and the mixture gently warmed. On crystallising the product from dilute alcohol *diethyl hydrophenyllutidinedicarboxylate*,



is obtained, melting at 156—157°. In the same way furfuraldehyde yields *diethylic hydrofurfuryllutidinedicarboxylate* melting at 164°:

$$2C_6H_{10}O_3 + C_4H_3O.COH + NH_3 = 3H_2O + C_{17}H_{21}NO_5.$$

By the action of nitrous acid on these products, the ethyl-derivatives of phenyl- and furfuryl-lutidinedicarboxylic acids are obtained. *Diethylic phenyllutidinedicarboxylate*, $C_{19}H_{21}NO_4$, melts at 66—67°. On distilling salts of these acids, substituted lutidines are formed.

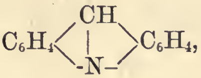
A. K. M.

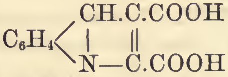
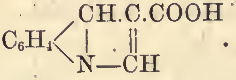
Synthesis of Ethylpyridine. By A. Ladenburg (*Ber.*, 16, 2059—2063).—The author in a former paper has noticed the formation of ethyl-γ-pyridine, when ethylpyridium iodide is heated, a change which involves an isomeric transformation thus: $C_5H_5N,EtI = C_5H_4EtN,HI$. In the present paper, this reaction is more fully investigated, and γ-ethylpyridine is described. When ethylpyridium iodide is heated in sealed tubes at 290°, there is formed, besides γ-ethylpyridine and traces of ammonia, ethylbenzene, which may be separated from the base by distillation after addition of hydrochloric acid to the crude product of the reaction. γ-*Ethylpyridine* is a colourless liquid (m. p. 152°, sp. gr. = 0·9553), sparingly soluble in water; its odour resembles that of pyridine. Its *platinochloride* crystallises in small six or eight-sided orange-coloured tables; its *aurochloride* in crystalline leaflets

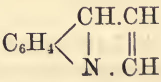
(m. p. 120°). By oxidation with potassium permanganate, γ-ethylpyridine is converted into γ-pyridinecarboxylic or isonicotic acid of Skraup and Weidel.

In conclusion, it is remarked that the formation of ethylbenzene from pyridine points to a somewhat similar arrangement of the atoms in pyridine and benzene. V. H. V.

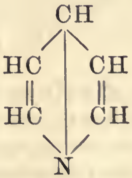
Quinoline- and Pyridine-carboxylic Acids. By C. RIEDEL (*Ber.*, **16**, 1609—1616).—Hoogewerff and van Dorp showed that when lepidine is oxidised by permanganate, the benzene ring is first attacked, with formation of methylpyridinedicarboxylic acid (*Ber.*, **13**, 1639). The author finds that by the oxidation of β-ethylquinoline (Abstr., 1880, 407), the ethyl-group is first oxidised, with formation of β-quinolinecarboxylic acid, and that by further oxidation the benzene ring is destroyed and pyridinetricarboxylic acid produced. This difference of behaviour between β-ethylquinoline and lepidine is explained by the presence of the ethyl-group in the former, β-methylquinoline behaving in the same way as lepidine. The above β-quinolinecarboxylic acid is identical with the acid which Graebe and Caro obtained by the action of heat on acridinic acid; but if their formula for acridine (Abstr., 1880, 398) were correct, this should be γ-quinolinecarboxylic acid. The author is of opinion that acridine is related to anthracene, and that its formula is $C_{13}H_9N$, and not $C_{12}H_9N$, as found by Graebe and Caro. Its constitution would then be



acridinic acid being , and β-quinolinecarboxylic acid, . For quinoline and pyridine he likewise suggests the formulæ:—

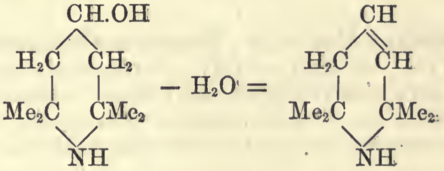


and



β-Quinolinecarboxylic acid is sparingly soluble in cold water, more readily in hot water and in hot alcohol; it melts at 271—272° with partial decomposition. It forms readily soluble salts with the mineral acids; the *hydrochloride* crystallising in long colourless needles. With picric acid, it forms a compound sparingly soluble in cold alcohol, and crystallising in long slender needles melting at 216° with decomposition. The *alkali-salts* are readily soluble in water, those of the alkaline-earths less so. The *copper* and *silver salts* are almost insoluble in cold water, the latter being, however, somewhat soluble in hot water. The *platinochloride*, $(C_{10}H_7NO_2)_2,H_2PtCl_6$, crystallises in yellow concentrically-grouped needles, readily soluble in water. Pyridinetricarboxylic acid, [1, 2, 3, 5 : N = 1], obtained by the oxidation of β-quinolinecarboxylic acid, appears to be different from all three known acids. It is readily soluble in water and in alcohol; its solution is coloured reddish-yellow by ferrous sulphate. When heated, it softens at 145—150° with evolution of carbonic anhydride, then solidifies, and does not again melt even at 275°; the product (γ-pyridinecarboxylic acid [N : COOH = 1 : 3 or 1 : 2]), is sparingly soluble in cold water, moderately in hot. A. K. M.

Triacetonalkamine. By E. FISCHER (*Ber.*, **16**, 1604—1607).—The author previously showed (this vol., p. 790) that this compound obtained by the reduction of triacetoneamine, is a hydroxytetramethylpiperidine. On heating it with concentrated sulphuric acid at 100° (160° as previously stated is too high), it loses water, with formation of the base $C_9H_{17}N$ (*triacetonine*), closely resembling piperidine; the reaction probably takes place thus:



similar to the formation of tropidine from tropine.

Triacetonine is readily volatile in steam, forming a crystalline hydrate, from which the free base is obtained by digestion with solid potash. It is a colourless, mobile liquid, having an odour resembling that of piperidine. The *hydrochloride*, $C_9H_{17}N,HCl$, is readily soluble in water and in alcohol, almost insoluble in ether; the *hydrobromide* forms characteristic white prisms, readily soluble in hot water, sparingly in cold water. Triacetonine is a secondary base, yielding a nitrosamine with nitrous acid. *Triacetonemethylalkamine*, $C_9H_{18}NOMe$, is readily obtained by heating triacetonealkamine (1 part), with methyl iodide (2 parts), and methyl alcohol (3 parts), for 8 hours at 100°. It melts at 74°, dissolves readily in luke-warm water, and shows a strongly alkaline reaction. The *hydrochloride* and *sulphate* are readily soluble in water; the *aurochloride* crystallises from hot water in splendid yellow needles. Triacetonemethylalkamine forms a compound with mandelic acid which has a mydriatic action on the eye. A. K. M.

Compounds of the Creatinine-group. By E. DUVILLIER (*Compt. rend.*, **96**, 1583—1585).—*Methylamido-α-caprocyamidine*, $C_8H_{15}N_3O$, is obtained by mixing cold concentrated solutions of methylamido-α-caproic acid and cyanamide in equivalent proportions, adding a few drops of ammonia, and allowing the liquid to stand. After some weeks the liquid becomes converted into a mass of white crystals, and these are purified by crystallisation from water. This caproic creatinine forms an unctuous powder, only slightly soluble in cold water, but more soluble in hot water, and very soluble in hot or cold alcohol.

Ethylamido-α-caprocyamidine is obtained by the action of cyanamide on ethylamido-α-caproic acid. It crystallises in long needles, which are somewhat soluble in cold water, much more soluble in hot water, and very soluble in alcohol.

As in the case of methylamido-α-butyric and methylamidoisovaleric acids (this vol., p. 220) the action of cyanamide on methylamido-α-caproic and ethylamido-α-caproic acids yields creatinines without any intermediate formation of creatines.

α-Oxybutyrocyamine hydrochloride, $C_5H_{11}N_3O_2,HCl$, obtained by dissolving α-oxybutyrocyamine in hydrochloric acid, forms an uncrystallisable syrup, soluble in all proportions in absolute alcohol. The *sulphate*, $(C_5H_{11}N_3O_2)_2,H_2SO_4 + H_2O$, forms crystals resembling those of potassium sulphate. They are somewhat soluble in water, and slightly soluble in alcohol. Mercuric chloride and mercuric nitrate give no precipitate with solutions of α-oxybutyrocyamine, but a white precipitate is formed on adding a drop of potassium hydroxide solution.

C. H. B.

Action of Methyl Alcohol on Piperidine Hydrochloride.

By A. LADENBURG (*Ber.*, **16**, 2057—2059).—If piperidine hydrochloride is heated at 200° with methyl alcohol, the hydrochlorides of methyl- and dimethyl-piperidine are formed together with methyl ether. These changes may be represented by the following equations:—

$$\text{(I)}\ 2MeOH + C_5H_{11}N,HCl = Me_2O + C_5H_{11}N,HCl + H_2O;$$
$$\text{(II)}\ MeOH + C_5H_{11}N,HCl = C_5H_{10}NMe,HCl + H_2O;$$
$$\text{and (III)}\ 2MeOH + C_5H_{11}N,HCl = C_5H_9NMe_2,HCl + 2H_2O.$$

The author offers some remarks on the constitution of the piperidine derivatives. Dimethylpiperidine hydrochloride, C_5H_9NMe,HCl, which behaves generally as a substituted ammonium chloride, forms methylpiperidine when distilled, but dimethylpiperidine if heated with potash. Hofmann explains this change by supposing a transformation of a methyl-group from a nitrogen to a carbon-atom, similar to that which takes place in the conversion of methylaniline into toluidine. The author objects to this explanation, and points out that dimethylpiperidine by the action of hydrochloric acid is converted into methyl chloride and methylpiperidine; a change which is without parallel in the benzene derivatives. The author puts forward another view, in supposing that in the formation of dimethylpiperidine an affinity between the carbon- and nitrogen-atoms is broken up, and then the second methyl-group attaches itself to the nitrogen-atom. Dimethylpiperidine will then have the constitution

$$CH_2\colon CH.CH_2.CH_2.CH_2.NMe_2,$$

and on treatment with hydrochloric acid will yield a base isomeric with piperidine, $CH_2\colon CH.CH_2.CH_2.CH_2.NMe_2$, which is converted into methylpiperidine. Several other observations agree with this explanation; first, the formation of trimethylamine and not trimethyl-piperidine, by the action of methyl iodide on dimethylpiperidine; secondly, the fact that piperylene takes up four and not two atoms of bromine; thirdly, the decomposition of the base obtained from dimethylpiperidine by the action of methyl iodide and silver oxide into piperylene and trimethylamine, thus:—

$$CH_2 : CH.(CH_2)_3.NMe_2,MeOH = CH_2 : CH.CH_2.CH_2 : CH_2 + NMe_3 + H_2O.$$

V. H. V.

Hydrotropidine. By A. LADENBURG (*Ber.*, **16**, 1408—1410).—The sparingly soluble compound which is produced by the action of amorphous phosphorus and fuming hydriodic acid on tropine (*Ber.*, **14**, 227) is *tropine iodide*, $C_8H_{15}NI_2$.

Hydrotropidine, $C_8H_{15}N$, is formed when tropidine iodide is subjected to the action of zinc-dust and hydrochloric acid. The crude product is distilled with excess of soda, dried over sticks of potash, and redistilled. Hydrotropidine is only slightly soluble in water, and is less soluble in warm than in cold water, so that dilute solutions are rendered turbid by the heat of the hand. It is a powerful base, forming crystalline salts. The base boils at 167—169°, and has the sp. gr. 0·9366 at 0° and 0·9259 at 15°. The *hydrochloride*, $C_8H_{15}N,HCl$, forms white deliquescent crystals. The *platinochloride*,

$$(C_8H_{15}N)_2,H_2PtCl_6,$$

crystallises in orange-coloured plates, which are moderately soluble in water. The *aurochloride* forms yellow crystals, soluble in warm water. The picrate is deposited from a hot aqueous solution in slender needles.

The author regards hydrotropidine as a methyl derivative of tetrahydroethylpyridine, and assigns it the formula C_5H_7NMeEt.

W. C. W.

New Alkaloïd in Cannabis Indica or Indian Hemp. By M. HAY (*Pharm. J. Trans.* [3], **13**, 998—999).—The alkaloïd is obtained in the following manner:—The aqueous extract of powdered *Cannabis indica* is treated with lead subacetate, filtered, and the filtrate precipitated with ammonia. The filtered ammoniacal solution is acidified with sulphuric acid, and the alkaloïds precipitated from it by phosphotungstic acid. The precipitate is washed, treated with barium hydroxide, and filtered. After the removal of the excess of barium by means of a current of carbonic anhydride, the filtrate is evaporated almost to dryness, acidified with sulphuric acid, and treated with absolute alcohol, in which the sulphate of the alkaloïd is soluble. The sulphate in solution is converted into chloride by first adding barium hydroxide, and subsequently treating it with hydrochloric acid. The chloride is evaporated, taken up with absolute alcohol, and the alcoholic solution treated with sodium carbonate, and extracted with ether; the alkaloïd is deposited from the ethereal extract in colourless needles, which are readily soluble in water and alcohol, and moderately so in ether and chloroform. The aqueous solution is precipitated by the various precipitants of alkaloïds. It does not give a violet colour with sulphuric acid and potassium dichromate, but like strychnine causes tetanus in frogs. The author proposes the name *tetano-cannabine* for this alkaloïd. The quantity of alkaloïd obtained from 1 kilo. was insufficient for an analysis. D. A. L.

Existence of a Basic Substance in Maize. By O. Luxardo (*Gazzetta*, **13**, 94—97).—Maize flour was extracted with dilute sulphuric acid, the extract treated with basic lead acetate, filtered, and slowly evaporated; the residue was then exhausted with absolute alcohol, and the alcohol removed by distillation; the substance thus obtained was examined for alkaloïds by the methods detailed in the paper. From the results, the author infers that in sound maize seeds there may be nitrogenous substances analogous to alkaloïds and ptomaïnes in their behaviour with reagents. He notices, however, that the methods of Dragendorff and Stas and Otto, based as they are on the treatment of the substance with dilute acids, may give rise to basic substances by the action of the acids on the albuminoïd substances present in the seeds, especially if warmed with them, and therefore they do not afford certain evidence that the basic substances were originally present as such. C. E. G.

Ptomaïnes. By J. Guareschi and A. Mosso (*J. pr. Chem.* [2], **27**, 425—432).—140 kilos. of well washed fibrin from ox-blood was placed in two glazed earthenware vessels, covered with a large zinc bell, whose edges dipped about 15 cm. deep into water, and allowed to stand for five months. The fibrin had at the end of that time been converted into a thick dark-red homogeneous liquid. This was acidulated with sulphuric acid, evaporated at 60° to a thick paste, baryta-water added to alkaline reaction, filtered after 24 hours, and the filtrate and wash-waters shaken for a long time with chloroform. (The extraction with chloroform was repeated 12 times; all the extracts contained the same ptomaïne.) The chloroform extract was evaporated, and the resulting dark golden-yellow oily residue mixed with tartaric acid; a resin that then separated was removed by shaking with ether, and the now colourless liquid mixed with excess of 50 per cent. potash, and the liberated oil extracted with ether. On evaporating the ethereal solution, a strongly alkaline brown oil of faint pyridine or conine-like odour was obtained. It is sparingly soluble in water, and resinifies very readily. The *hydrochloride* crystallises in somewhat deliquescent, colourless, cholesterin-like plates. The *platinochloride*, $C_{10}H_{15}N,H_2PtCl_6$, forms a light flesh-coloured crystalline precipitate, insoluble in water, alcohol, and ether; it is not decomposed at 100°. (The platinochloride from each chloroform extract was analysed, and showed that only the one ptomaïne was present.) The hydrochloride gave a crystalline yellow precipitate with auric chloride; white precipitates with Mayer's reagent, mercuric chloride, or tannin; a yellow precipitate with phosphomolybdic acid, sparingly soluble in ammonia without blue coloration; and a whitish-yellow precipitate with phosphotungstic acid. The physiological action of the ptomaïne is similar to that of curare, but it is much less active than the latter. A. J. G.

Putrefaction Alkaloïds. By A. Poehl (*Ber.*, **16**, 1975—1981).—Epidemics caused by unsound bread have long been recognised, and it has been observed that they are preceded by long-continued rains and floods, which cause an abundance of ergot (*Claviceps purpurea*) in the following harvests. These epidemics take two forms, viz., *Ergotismus convulsivus*, more common in France, Switzerland, and this country, and *Ergotismus gangrœnosus*, which prevails in Russia, Germany, and Sweden. In Russia there were two remarkable outbreaks of the latter in the years 1832 and 1837, which caused a mortality among children attacked of 1 : 1·75 to 1 : 4, and of the former in 1824. In the course of the rainy summer of 1881 Russia was threatened with another outbreak of ergotismus; accordingly the Minister of the Interior instituted a Commission, of which the author was a member, to investigate this phenomenon of ergot.

Eichwald, in his history of ergotismus epidemics, has shown (1) that the appearance of the epidemic stands in no direct relation to the proportion of blight in the grain; (2) that animals cannot be so inoculated as to produce in them similar symptoms; (3) that the putrefaction of the corn is a necessary condition of the ergotismus; (4) that the poisonous results are produced only in certain stages of the decomposition; (5) that the various forms of ergotismus cannot be explained by the quantity of ergot introduced within the system or its time of action.

In the present paper, the author elucidates the following conditions of the putrefaction alkaloïds in blighted rye meal: (1) the conversion of the starch into glucose; (2) fermentation of the glucose with formation of lactic acid; (3) peptonisation of the albumins by the peptic action of the mycelium of *Claviceps purpurea;* (4) conversion of the peptone into ptomopeptone, and its decomposition with formation of putrefaction alkaloïds.

Firstly. In the year 1873, the author recognised that damp caused in the meal a large proportion of glucose, by the action of a ferment contained in the endocarp and perisperm of the grain. The experiments of Hammarsten have also proved that the starches of maize, rye, and oats are more easily converted into glucose by diastatic action than the starches of potatoes, pease, and wheat (comp. Bell's recent researches, this vol., p. 1160). In this connection it may be mentioned that the inhabitants of Lombardy suffer from an epidemic caused by maize. A form of mildew has been observed on maize, and this has the power of peptonising albumins, with formation of putrefaction alkaloïds.

Secondly. In presence of a ferment the glucose would further decompose into butyric and lactic acids.

The author further observed that rye grain, even if not attacked by the claviceps, yet when merely exposed to damp, evolved trimethylamine when heated with alkalis, and it is well known that albumins at the moment of putrefaction evolve ammonia or amines under the action of alkalis.

Thirdly. One of the most important phenomena of the change of the albumin of meal is the formation of peptones; it has also been noticed that lactic acid is a better test for peptonisation than other acids, as phosphoric, acetic, oxalic, or tartaric. The author has frequently observed the formation of peptone from the albumin of meal, caused by the action of *Penicillium glaucum* and the fungus of *Claviceps purpurea*, the latter of which produces the most marked effects.

Fourthly. The author exposed pure and tainted rye meal to a damp atmosphere, and found that the latter more readily entered into decomposition, with formation of the putrefaction alkaloïds or ptomaïnes. Further large quantities of pure and tainted meal were allowed to rot, and the putrefying mass examined from time to time by Stas-Otto's process. From alkaline and from acid ethereal extracts of the mass, substances were obtained of various degrees of consistence and of various odours. These products gave all the general reactions for alkaloïds, and differed from one another towards precipitants and colour reagents according as they had been obtained at various stages of the decomposition. By shaking the alkali solution with chloroform, benzene, and amyl alcohol, an alkaloïd was obtained, which gave precipitates with potassio-mercuric iodide, phosphomolybdic and tungstic acids, potassio-bismuth and -cadmium iodides, platinum and gold chlorides, &c. It also gave a beautiful violet coloration with Fröhde's reagent (sulphuric acid and sodium molybdate), resembling that produced by morphine; the absorption-spectra, however, of the two alkaloïds differ most markedly. The author was only able to observe the formation of the above alkaloïd during summer time.

Starting from the view that peptones on further putrefaction are converted into ptomopeptones which yield nitrogen when heated with sodium hypobromite, then the quantity of nitrogen so evolved may be taken as a measure of this conversion. Accordingly the author made comparative experiments with samples of damp rye-meal and meal mixed with peptic ferment, with 5 per cent. ergot, and with blight. The results are given in the table below.

Time of action.	Percentage of nitrogen given off from			
	Pure meal.	Meal with blight.	Meal with ergot.	Meal with peptic ferment.
3 days	0·1316	0·1671	0·1933	0·3762
4 ,, ...	0·1527	0·2592	0·2909	0·3949
8 ,, ...	0·1989	0·2842	0·3157	0·4210
13 ,, ...	0·2196	0·3415	0·4269	—
20 ,, ...	0·5259	—	0·5662	—

From these results it follows—(1) that ergot and mould have a peptonising action on the albumins and favour their decomposition; (2) the degree of putrefaction of the albumins is directly proportional to their peptonisation; (3) in the first stages of putrefaction, the decomposition of the albumins is greater in ergot meal than in mouldy or pure meal, but in the more advanced stages these differences are not so marked. Further researches on the decomposition of albumins by the *Claviceps purpurea*, and the part played by various genera of fungi are promised. V. H. V.

Putrefaction Alkaloïds. By L. BRIEGER (*Ber.*, **16**, 1405—1407).—The gelatinous product which the author obtained (this vol., p. 924) by treating the hydrochloride $C_5H_{14}N_2H_2Cl_2$ of the base contained in putrefying flesh with moist silver oxide, is the free base, and not an oxidation product, as the author formerly believed. The salts do not possess the characteristic, disgusting smell of the free base; this has not yet been obtained in a crystalline state. It is sparingly soluble in amyl alcohol, freely soluble in water, insoluble in ether and in absolute alcohol. It gives white precipitates with mercuric chloride and lead acetate, a yellow precipitate with potassium cadmium iodide, and a red precipitate with potassium bismuth iodide. It does not exhibit any reaction with the other reagents for alkaloïds.

The poisonous base $C_5H_{11}N$, formed by the putrefaction of flesh, is precipitated by mercuric chloride and by basic lead acetate. It is readily soluble in ether and alcohol. A subcutaneous injection of this poison causes increased activity of the heart, rapid respiration, and a copious secretion of saliva exhibiting an alkaline reaction. Under the influence of this alkaloïd, cats perspire freely at the paws, and their sweat has an alkaline reaction. W. C. W.

Putrefaction Alkaloïds. By E. and H. SALKOWSKI (*Ber.*, **16**, 1798—1802).—Reply to L. Brieger.

Colouring Matter of Bile of Invertebrates and Vertebrates and Unusual Urine Pigments. By C. A. MCMUNN (*Proc. Roy. Soc.*, **35**, 132—134).—The author has observed the existence of chlorophyll colouring matter in the bile and various extracts of the livers of Mollusca and Anthropoda, and of the pyloric or radial cæca of the Echinodermata: for this the name *enterochlorophyll* is proposed. The slight differences observable in various cases are shown to be due to the probable greater or less amount of chlorophyll constituents, viz., blue and yellow chlorophyll, chlorofucine, xanthophyll, and luteine. The bile of the crayfish and pulmonate mollusca contains hæmochromogen associated with enterochlorophyll. The so-called liver of the invertebrates is not only a digestive, but a pigment producing and storing organ.

The identity of stercobilin and hydrobilin produced by the action of nascent hydrogen on bilirubin is established, and a difference between them and fibrile urobilin is shown to exist. V. H. V.

Physiological Chemistry.

Chemistry of Food. By J. Bell (*Proc. Roy. Soc.*, 35, 161—162). —The author has carried out a series of researches on butter, cheese, milk, the cereal foods, bread, and lentil flour.

Butter.—It is indicated that the soluble and insoluble fatty acids in butter fat do not exist as simple, but as complex glycerides, palmitic and oleïc acids being combined in the same molecule with butyric acid.

Cheese.—The ratio of soluble to insoluble fatty acids in the fat extracted from cheese is the same as that in milk fat. This result is at variance with the view maintained by some chemists that albuminoïds are slowly converted into fat.

Milk.—The changes occurring in sour milk have been investigated, and the diminution in the proportion of fats not solid has been determined.

Cereals.—The author suggests that the saccharine matter appears to have been developed or determined only in aqueous extract, without regard to the transformations effected by the soluble albuminoïds on the saccharoses and carbohydrates. These albuminoïds are shown to possess a varying diastatic action on starch, that of rye being the most, that of rice the least active. V. H. V.

Physiology of Carbohydrates in the Animal System. By F. W. Pavy (*Proc. Roy. Soc.*, 35, 145—147).—The most complex members of the carbohydrates and saccharose groups are transformed generally by ferments, chemical reagents, or heat into less complex substances; for example, starch into the dextrins and finally into maltose, cane-sugar into dextrose. In this note, the author shows that there exists in the alimentary canal, the circulatory system, and the liver, a ferment which effects a reverse transformation, converting both glucose and cane-sugar into maltose, but starch either into maltose or a dextrin of low cupric oxide reducing power.

V. H. V.

Filtration of Albumin Solutions through Animal Membranes. By J. W. Runeberg (*Zeitschr. Physiol. Chem.*, 6, 508—527). —The author's earlier experiments on the filtration of solutions of albumin through animal membranes have already been described (*Arch. f. Heilkunde*, 18). He has there shown that the permeability of a membrane towards albuminous fluids and emulsions diminishes under the influence of increasing pressure, and *vice versâ*, whereby the proportion of albumin in the resulting filtrate is less under high pressures than under low ones. His results, carefully controlled and repeated, were constant and unambiguous. It may be, however, that the behaviour of membranes other than those then employed may be different. In these instances, sheep intestine preserved in alcohol, was commonly used, only exceptionally the fresh intestine of sheep and rabbit. Last year, Gottwald, of Moscow, described the results of an investigation carried on in Hoppe-Seyler's laboratory at Strassburg, wherein he used the human ureter, as freshly obtained as possible, for the filter membrane, and from which he concludes that the influence of pressure is diametrically opposite to that stated by the author, who has accordingly instituted a fresh series of experiments, with a view of determining the source of this discrepancy.

He gives details of seven experiments in which the filter membranes were in two, human ureters; in one, fresh intestine of a sheep; and in the remaining four surface membranes, the membrane from a condonia being employed in three of these, and fresh costal pleura from an ox in the seventh. The albuminous fluids employed in these experiments were various pleuritic effusions, containing 2·88 per cent., 3·40 per cent., 5·34 per cent., and 6·44 per cent. of albumin; ascitic fluids removed from patients suffering from peritoneal cancer, and containing respectively 2·70 per cent. and 3·72 per cent. of albumin; and lastly, a solution of dried serum albumin with a percentage of 2·46. The apparatus used by the author is fully described in the earlier publication alluded to, and the present paper is accompanied by a sketch of its arrangement during experiments. The experiments, for the sake of simplicity, were made under two conditions of pressure, a higher pressure of 100 cm. and a lower one of 40 cm.

The results of the experiments wherein the human ureter was employed show that the permeability of this form of membrane also increases with diminished pressure and *vice versâ*, so that for each degree of pressure a pretty constant ratio is observed.

The experiments with surface membranes yielded precisely similar results. The author consequently assumes it to be proved that on filtration of albuminous fluids through compound animal membranes outside the organism, their permeability is inversely proportional to the pressure exerted. It cannot be at once concluded from this that the same relation exists within the living organism—a problem requiring pathological and physiological investigation. But the author has made certain observations and experiments in regard to the question of transudation of albumin from the kidneys in cases of albuminuria, which go to establish the identity of the process with that which is known to take place outside the body. And it may with a high degree of probability be assumed that those forms of albuminuria, which are so frequently met with unaccompanied by any inflammatory or degenerative process in the kidneys, find an explanation in an exalted permeability of the filtering membrane, brought about by changed conditions of pressure in the glomeruli.

D. P.

Acetonuria. By R. v. JAKSCH (*Zeitschr. Physiol. Chem.*, 6, 541—556).—Little is yet known of the occurrence and elimination of acetone in the human body. Kaulich has established its presence in the case of diabetic urine, and has concluded on insufficient grounds, however (from the odour of the distillate), that it makes its appearance in the urine in the course of certain acute diseases.

The discovery by the author in an instance of diabetic coma when sugar was absent from the urine that the ferric chloride reaction first described by Gerhardt was obtained, caused him to similarly test the urine in a large number of cases. Further investigation has shown that urine giving a distinct ferric chloride reaction will likewise yield a distillate which shows Lieben's iodoform reaction (iodoform produced with iodine, potassium iodide, and soda solution). But he also obtained the same result with the distillates of urine which gave no reaction with ferric chloride, and especially with the urine of fever patients. Deichmüller has confirmed these results in the instance of scarlet fever.

Since a number of volatile substances furnish the iodoform reaction, the problem was to determine the particular volatile constituents of fever urine upon which it depended, especially whether upon acetone. With this object the urine of fever patients was subjected to examination with positive results. The quantitative estimation of the small quantities of acetone occurring in urine was made by a photometric method, for details of which, as also those relating to the examination of urine, the reader is referred to the author's paper. He also showed that putrefaction does not interfere with the presence of acetone, and urine containing a known amount of it was found to yield the same amount unchanged three weeks after spontaneous fermentation had occurred. Acetone was found in the urine of healthy individuals, in quantities varying from a mere undeterminable trace up to 0·01 gram in the excretion for the 24 hours. Hence the author concludes that there is a condition of physiological acetonuria, acetone being a normal and constant product of tissue change, becoming under certain pathological conditions excessively produced and eliminated. The pathological states in which this excess is exceptionally well shown are in high continued fever, when the quantity amounts as a rule to several decigrams, keeping approximately parallel to the height of the fever. The kind of fever and the presence of complications are without influence. In diseases unaccompanied by fever, the elimination of acetone is, as a rule, not augmented; but there are exceptions met with, and which the author has noted in some cases of cancer, in the so-called acetonuria, and in certain cases of diabetes mellitus.

In diabetes, the quantity of acetone may be increased or remain normal without any clinical indications of this difference. In some rare cases of diabetes, the urine yields much acetone on distillation, and gives at the same time Gerhardt's ferric chloride reaction. This reaction the author refers to the presence of acetoacetic acid in the urine, and as this affords acetone on distillation, the richness of such urine in acetone is simply explained. This augmented acetonuria and the ferric chloride reaction are not alone found coincident with certain cases of diabetes, but in other diseases, as measles, scarlatina, and pneumonia, although rarely. Both may stand in a certain interdependence, but increased acetonuria and the occurrence of acetoacetic acid in the urine are certainly not identical. On the contrary, the association of the two is exceptional. D. P.

Hemialbumosuria. By Ter-Grigoriantz (*Zeitschr. Physiol. Chem.*, **6**, 537—540).—Hemialbumose was first found by Bence Jones in the urine of a patient suffering from osteomalacia. Kühne also found it in a similar case, and as a product of the peptic and tryptic digestion of albuminates. Albumin peptone is changed into hemialbumose when heated to 140°. In a case described by the author, and forming the subject of this paper, the hemialbumose disappeared from the urine, and was replaced by peptone, hemialbumosuria thus becoming peptonuria.

The patient, a man of 24 years of age, was admitted to hospital with syphilitic ulcer, and there underwent treatment by inunction with mercurial ointment. In three weeks an acute generally diffused eruption spread over his whole body, at first resembling that of measles, but becoming confluent, and running the course of an intense dermatitis accompanied by fever. At the end of 14 days, it terminated with profuse lamellar desquamation of the entire epidermis. The urine of this subject on examination gave the recognised reaction of hemialbumose as described by H. Huppert, and later those of peptone. This transformation also was observed to occur simultaneously in urine which had been kept for three days.

D. P.

Further Contributions to the Distribution and Elimination of Lead. By V. Lehmann (*Zeitschr. Physiol. Chem.*, 6, 528—536).—In regard to the modes whereby lead is extracted from the body, most diverse statements are met with as to its presence in the urine, which of all media has been the most frequently examined; whilst its excretion by the bile, milk and saliva has been established by various authors. So far as Lehmann is aware, the fæces have hitherto escaped examination.

In this new series of experiments he employed rabbits, in which plumbic nitrate was injected in quantities varying from 16 mgr. to 0·5 gram. The separation and quantitative determination of the lead were effected by electrolysis and the colorimetric method, using hydrogen sulphide in presence of alkali (this vol., p. 687).

The results show that the liver, an organ which in cases of metallic poisoning almost always holds the first place in order of examination, contains relatively to the weight very little lead. The bile, on the other hand, contains a large proportion, confirming the previous observations of Annaschat, and the bones likewise show a high proportion, a result which is in harmony also with the statements of Gusserow and Heubel.

As much lead was found to be excreted in the fæces as in the urine: the lead thus got rid of must have been eliminated in the bile, and not reabsorbed by the intestines, a circumstance which serves to explain the lesser proportion found in the liver, from which elimination by the bile would naturally occur.

The author investigated the changes which are brought about in the elimination of lead in the urine under the action of various therapeutic agents, especially potassium iodide, a salt which has long been given in cases of metallic poisoning, particularly in chronic mercury and lead poisoning, for the purpose of promoting elimination from the system.

He found that the action of this salt is to promote the elimination of lead, exciting it when this has ceased to take place naturally by bringing again into circulation that which so far as his investigations tend to show, had become deposited in the bones. He further found that potassium bromide, and probably also potassium chloride, have analogous effects in promoting elimination, a result of some therapeutic importance, for potassium iodide cannot always be administered with safety, and these salts may in such cases serve as substitutes. Sodium chloride did not appear to exert any influence on the process. D. P.

Chemistry of Vegetable Physiology and Agriculture.

Submersion of Vineyards. By P. DE GASPARIN (*Compt. rend.*, **96**, 1552—1555).—One of the best methods of preventing the ravages of the phylloxera is to keep the soil of the vineyard continually moist, and in the south-east of France this is effected by submerging the vineyard during winter. The soils which are thus treated are compact argillo-calcareous soils which, with one or two exceptions, contain more than 30 per cent. of impalpable constituents, and more than 30 per cent. of calcium carbonate. Soils of this character are sufficiently pervious to allow the water to diffuse through them by capillary action, and yet are sufficiently impervious to prevent the water passing through them rapidly. In those cases where the surface soil is sandy, the subsoil is found to be compact, calcareous, and argillaceous. The same method of treatment is, however, applied successfully to the dunes of Aigues Mortes and to other sandy soils.

C. H. B.

Sap. By J. ATTFIELD (*Pharm. J. Trans.* [3], **13**, 819—820).—The present paper contains an account of observations made on sap exuding from a wounded silver birch tree. A branch had been lopped off a birch tree 39 feet high, and 7 inches in diameter about 10 feet from the ground, before the leaves had expanded, leaving a wound about an inch in diameter, from which sap dropped. A bottle was suspended so as to catch the sap, and from observations taken, it was found that the flow was apparently faster in sunshine than in the shade, and by day than by night; and altogether amounted to about 4 litres a day, this had been running for 15 days, but how long it would continue is uncertain. The sap was clear and bright, sp. gr. 1·005, had a faintly sweet taste and a slightly aromatic odour. After 12 hours it deposited a trace of a sediment which, when examined microscopically, was found to consist of parenchymatous cells and a few so-called sphere-crystals. The liquid contained 99 per cent. water and 1 per cent. solid matter, which was composed mainly of sugar 91 per cent., the other constituents being ammonium salts; albuminoïds; nitrates; phosphates, and organic salts of calcium and magnesium; mucilage, and traces of nitrites and potassium salts. It had calcium and magnesium salts in solution equal to 25 degrees of total permanent hardness. It con-

tained a ferment capable of converting starch into sugar, and when exposed to the air, it soon teemed with bacteria, the sugar being changed into alcohol.
D. A. L.

Effect of Altitude on the Alkaloïds of the Bark of Cinchona Succirubra. By J. E. HOWARD (*Pharm. J. Trans.*, **13**, 1013—1015).—After some remarks on the growth and cultivation of cinchonas in general, in which the author makes special reference to the physical relationship existing between quinine and cinchonidine (both lævogyrate), and between quinidine and cinchonine (both dextrogyrate); attention is drawn to the results of the analyses of two specimens of red bark (*C. succirubra*) from two trees of common origin; they were also of the same age, 19 years old, and had grown up under fairly similar conditions, climatic excepted,—the one, A, being cultivated at Hakgala, 5,500 feet elevation, being the larger of the two trees, yielding 25 lbs. of dry bark, with a "brown coat;" the other, B, yielding 7 lbs. of dry bark "with a grey coat," was cultivated at Peradeniya, 1,500 feet elevation.

	Quinine.	Cinchonidine.	Cinchonine.	Quinidine.	Amorphous.	Total alkaloïds.
A.	2·06	3·47	0·61	trace	0·66	6·80
B.	0·47	0·05	1·67	0·30	1·06	3·55

From these results it would seem that altitude has a beneficial influence, not only on the quantity but also on the quality of the alkaloïds. The quantity from the tree grown at the greater elevation is nearly double, whilst the quality is also much superior to that of the tree grown in the low-lying district. Quinine and cinchonidine in the former seem to have replaced the quinidine and cinchonine of the latter.
D. A. L.

Cinchona Bark grown in Jamaica. By B. H. PAUL (*Pharm. J. Trans.* [3], **13**, 897).—The author has examined samples of the bark produced for sale in Jamaica; the results are tabulated below:—

Variety of plant.	Bark from	Quinine.	Quinidine.	Cinchonidine.	Cinchonine.	Amorphous.	Total alkaloïd.
Cinchona officinalis...	Trunk	3·74	0·04	1·77	0·23	0·30	6·08
	Twig	1·08	trace	0·37	0·60	0·20	2·25
	Root	2·90	1·01	0·67	4·60	0·58	9·76
,, *succirubra*..	Trunk	2·04	0·13	2·58	2·45	0·50	7·70
	Twig	0·78	—	0·47	0·23	0·29	1·77
	Root	1·76	0·34	1·39	4·40	0·90	8·79
,, *calisaya* ...	Trunk	0·34	0·23	0·82	0·82	1·80	4·01
	Twig	—	—	—	—	—	1·30
	Root	trace	4·07	0·45	1·80	0·65	6 97
,, *micrantha*..	Trunk	1·13	0·30	0·67	3·24	0·68	6·02
	Twig	0·43	—	0·28	0·60	0·50	1·81

The large proportion of quinidine in the root-bark of the *Calisaya* plant is exceptional, and coupled with the small quantity of quinine, may be evidence of unhealthy growth, or perhaps the plants sent to Jamaica were not *Calisaya*, but really *Cinchona micrantha.* The amount of quinine in the *succirubra* sample shows that there is a good type of this cinchona being cultivated in Jamaica. Comparing these results with analyses made some few years back, it is inferred that in most cases the quality of the bark has improved. The reverse, however, is the case with the "calisaya" plants; perhaps for the reason given above. D. A. L.

Seeds of Camellia oleifera. By H. McCallum (*Pharm. J. Trans.* [3], **14**, 21).—The *Camellia oleifera* grows abundantly in China, where the seeds are gathered and the oil pressed out and used for hair dressing and illuminating. The residue is made into cakes or powdered, the powder being used for washing purposes, especially for extracting grease spots; an infusion of it is also made for killing worms, grubs, &c., and even fish. The cakes are used with water as a hair wash. The seeds contain a glucoside, *saponin*, as well as the oil. 44 per cent. of oil may be extracted by means of ether, using a Soxhlet's tube, and 10 per cent. of saponin from the residue by treatment with 84 per cent. alcohol; even after this treatment it is soapy.

The oil is viscid, yellowish, scentless, with an unpleasant after taste, and is not soluble in 84 per cent. alcohol. The saponin is not quite pure, as it leaves 0·9 per cent. ash. It is a friable amorphous white powder, which irritates the nostrils; when dry it is almost odourless, but its aqueous solution has a disagreeable odour. Its taste is at first sweetish, then bitter and disagreeable, causing a biting sensation in the throat. It is hygroscopic, very soluble in water, freely in 84 per cent. alcohol, sparingly in absolute alcohol, and insoluble in ether. An aqueous solution is precipitated by barium hydroxide, by Fehling's solution, by basic lead acetate in the cold, and by normal lead acetate and dilute hydrochloric acid when warmed; in the last case a glucose remains in solution. When the aqueous solution is boiled with Fehling's solution, a slight reduction takes place. It forms emulsions with oils and chloroform; and when it is shaken with mercury, the metal is reduced to a fine grey powder.

D. A. L.

Occurrence of Nucleïn in Moulds and in Yeast. By A. Stutzer (*Zeitschr. Physiol. Chem.*, **6**, 572—574).—The author placed a solution containing a percentage of 1·05 potassium chloride, 1·0 calcium nitrate, 0·25 magnesium sulphate, 0·5 potassium phosphate, and 5·0 tartaric acid in open saucers in a locality tolerably free from dust. Moulds were soon developed which, after forming in sufficient quantity, were washed with distilled water, pressed between filter-paper, and dried over sulphuric acid.

The dried mean contained 3·776 per cent of nitrogen.

As proteïn N 3·026
As nucleïn N 1·539.

100 parts of nitrogen consisted of—

19·86 N as amides, peptones, &c.
39·39 albumin N.
40·75 nucleïn N.

The moulds are consequently able to form, besides albumin, a tolerably large amount of nucleïn. Hoppe-Seyler had already observed that yeast likewise contains nucleïn.

In these experiments, fresh beer yeast was left for some days with alcohol of 95 per cent., then pressed between filter-paper, several times extracted with alcohol in the cold, and finally dried over sulphuric acid.

Two sets of analyses yielded like results:—

Total nitrogen	8·648 per cent.
Proteïn N	7·773 ,,
Nucleïn N	2·257 ,,

It contained in 100 parts nitrogen—

10·11 N as amides and peptones, &c.
63·80 N as albumin.
26·09 N as nucleïn.

D. P.

Analytical Chemistry.

Experiments on the Small Scale in Sealed Tubes. By E. Drechsel (*J. pr. Chem.* [2], **27**, 422—423).—Preliminary experiments on reactions in sealed tubes can be readily effected with the use of only a few milligrams of substance by employing tubes (made of ordinary tubing) 5—6 c.m. long and 3—4 mm. wide, sealed at one end and drawn out at the other to a thick-walled capillary tube of 10—15 c.m. long. This tube is then fixed by means of a split cork in a test tube containing a liquid boiling at the temperature required.

A. J. G.

Alkalimetric Indicators. By J. Wieland (*Ber.*, **16**, 1989—1991).—The author has examined the relative sensitiveness of various azo dye-stuffs proposed as indicators for alkalimetry. Of substances not affected by carbonic acid, ethyl-orange is the most delicate; 2 drops of a 0·05 per cent. solution is sufficient for 50 c.c. to obtain a sharp change of colour. The analytical results are compared in the original memoir in a tabular form.

V. H. V.

Separation of Chlorine, Bromine, and Iodine. By J. B. Barnes, Junr. (*Pharm. J. Trans.* [3], **13**, 940—942).—The author has tried a few experiments on the efficiency of Vortmann's process, already described (this vol., 119), for qualitative purposes. He remarks that practically iodine is wholly expelled from a solution of an iodide by evaporating almost to dryness four times with either lead or manganese dioxide and 3 per cent. acetic acid; on the other hand, bromine is only expelled from bromides when strong acid (33 per cent. or above) is used; whilst chlorides treated in a similar manner are but very slightly decomposed, or not at all. In this manner also the iodine and bromine are readily expelled from a mixed solution of iodides and bromides; provided the lead oxide is added little by little, while the acidified solutions are in a state of ebullition, thus preventing the formation of iodic acid (*ibid*). In a mixture of chlorides, bromides, and iodides, chlorine alone could be detected after the fourth evaporatoin with 33 per cent. acetic acid and lead dioxide. Another experiment proved that iodine could be removed from a similar mixture by treatment with manganese dioxide, whilst the bromine could be separated from the chlorine by subsequent treatment with lead oxide. The last experiment can be utilised to advantage for testing for these substances;—The mass to be tested is put into a dish, and ordinary acetic acid and manganic oxide are added to it; the appearance of a brown colour indicates iodine, if it is present, the whole is boiled vigorously until the vapour ceases to "blue" starch-paste, showing that the iodine is removed. Now test for bromine (or in case there is no iodine, test at once previous to boiling), and if it is present boil with acetic acid and lead oxide until the vapour does not turn starch-paste and potassium iodide blue, showing the total expulsion of bromine. The residue is filtered and tested for chlorine. An objection to the use of manganic oxide is, that solutions containing it are very liable to spurt during evaporation.

D. A. L.

Detection of Free Sulphuric Acid in Presence of Aluminium Sulphate. By O. MILLER (*Ber.*, **16**, 1991—1992).—In the paper manufactory the detection and estimation of sulphuric acid is of great practical importance. The experiments of the author prove that of the indicators hitherto proposed, methyl-orange is the most delicate for the detection of free sulphuric acid in presence of aluminium sulphate. The degree of dissociation on boiling an aqueous solution of this salt can be determined by the use of methyl-orange. For the quantitative estimation of the free acid in aluminium sulphate, its solution is precipitated by alcohol, and the filtrate evaporated over a small flame, and then titrated. Experiments are quoted to prove the accuracy of the process. Ethyl-orange, although the most sensitive indicator towards free acid, yet is coloured a rose tint by neutral aluminium sulphate, which prevents the observation of the neutral point.

V. H. V.

Estimation of Iron by means of Permanganate Solution. By J. KRUTWIG and A. COCHETEUX (*Ber.*, **16**, 1534—1536).—The authors find that the inaccuracy due to the presence of hydrochloric acid may be avoided if the following conditions are observed:—The ore should be dissolved in the smallest possible quantity of hydrochloric acid, reduced by means of zinc, sulphuric acid added in quantity double that of the hydrochloric acid, the solution diluted to 300 c.c. and titrated with a dilute solution of potassium permanganate.

A. K. M.

Precipitation of Iron by Hydrogen Sulphide. By L. Storch (*Ber.*, **16**, 2014—2015).—If hydrogen sulphide be passed into a solution of tin chloride or ammonium tin chloride mixed with an excess of an iron salt, a dirty yellow or greyish-green precipitate is formed, containing tin and iron in the proportion of 100 to 4. This precipitate is soluble in hydrochloric acid, and hydrogen sulphide precipitates from the solution tin sulphide only; warm potash, ammonia, or sodium hydrosulphide dissolves the tin precipitate, and the solutions, when allowed to stand, deposit the iron as hydroxide or sulphide. Ammonium sulphide dissolves the tin, leaving the iron sulphide.
V. H. V.

Solubility of Metallic Sulphides in Thio-acids. By L. Storch (*Ber.*, **16**, 2015—2016).—The precipitation of copper as sulphide is prevented in a most marked way, not only by thio-molybdates, (Debray), -arsenates, and -stannates (Berzelius), but also by thiotungstates and -vanadates. This phenomenon is also more noticeable with cuprous than cupric salts. Similarly the precipitation of iron, mercury, and cadmium sulphides is prevented by the above-named acids, especially thiostannates. The resultant solution is either clear or contains the thio-salt of the precipitable metal in the colloïdal state. Thus, for example, on adding ammonium sulphide to ferric chloride, in presence of ammonium molybdate, a green solution is obtained, which after a time deposits the iron thiomolybdate of Berzelius.
V. H. V.

Detection of Mercury in Animal Tissues. By H. Paschkis (*Zeitschr. Physiol. Chem.*, **6**, 495—503).—Until a few years ago, electrolysis was almost exclusively employed in the examination of animal tissues for mercury. Schneider's method left little to be desired in point of delicacy and accuracy, but was tedious in detail, and the apparatus somewhat complicated. E. Ludwig's method for the separation of mercury from the tissues is, however, easier of application, and needs much less time, whilst equal in other respects to the former. By it the mercury is separated from the largely diluted solution by means of finely divided zinc or copper, from which, by simple heating, the metal is obtained directly. Originally Ludwig distilled the mercury from the washed and dried zinc-dust in a slow current of air, passing it over a layer of red-hot oxide of copper, to complete the combustion of other products of distillation, and condensing mercury and water in a quill-sized capillary tube. Subsequently he has so far modified the process as to dispense with the airstream, heating the zinc amalgam in a tube closed at one end, and getting rid of the aqueous vapour by passing the products over a layer of ignited zinc-dust before their entrance into the capillary tube.

Fürbringer has proposed a modification of Ludwig's process, in so far that he substitutes the so-called brass-wool for the zinc, which after removal from the mercurial solution is washed in water, alcohol, and ether, dried and heated in a tube drawn out at both ends in which the mercury becomes condensed (*Berlin. Klin. Wochenschr.*, 1878,

p. 332). Recently V. Lehmann has adversely criticised Ludwig's method, and concludes that it is neither accurate nor simple and expeditious. This opinion is quite contrary to the experience of the author of this paper as well as of Güntz, O. Hassenstein, and Oberländer, whose results are likewise confirmatory of the accuracy of Ludwig's process.

The fact that Lehmann's criticism called in question the validity of certain investigations made by the author conjointly with L. v. Vajda, induced him to repeat a series of experiments with this process and its modifications.

1. *Ludwig's Method.*—About 400 c.c. of normal urine, containing a known amount of mercuric chloride, were warmed to 60—70°, acidified with hydrochloric acid, about 3 grams of zinc-dust added, and after agitation for some time the clear solution poured off, and the resulting amalgam washed several times, first with pure water and then with water to which a few drops of potash solution had been added. After drying upon the water-bath, this amalgam was introduced into a tube of hard glass of about 8 mm. diameter, closed at one end with successive layers of asbestos, coarse cupric oxide, and zinc-dust in front: the tube being then drawn out to a capillary bore of the thickness of an ordinary straw, was placed in a small combustion furnace, the cupric oxide first raised to a low red heat, the zinc-dust moderately heated, and at last the amalgam is strongly ignited. In 10—15 minutes the mercury is found in the capillary portion of the tube, which is then cut off, a small fragment of iodine inserted in the widest part, and gently heated. In five such experiments, in which the quantities of mercuric chloride used were respectively 0·005, 0·002, 0·001, 0·0005, and 0·0002 gram, distinct iodide sublimates were obtained. In a sixth experiment, in which 0·0002 gram of mercuric chloride was added to 400 c.c. of urine, also containing albumin, the result was equally decided.

2. *Fürbringer's Method.*—400 c.c. of the same urine, as prepared for the above experiments, was similarly treated, brass-wool being substituted for the zinc-dust. The wool, after washing with hot water, alcohol, and ether, was introduced into a tube of 8 mm. diameter, drawn out in capillary fashion at both ends, heated over a Bunsen lamp, and a fragment of iodine introduced into the still warm tube. In three experiments in which 0·001, 0·0005, and 0·0002 gram of mercuric chloride were employed, a distinct reaction was obtained in both of the capillary extremities of the tube. In a fourth instance, the reaction was also distinctly given by 50 c.c. of urine taken from the body of a man who had poisoned himself with corrosive sublimate.

3. *Modification of Ludwig's Method.*—The advantage shown in washing the zinc-amalgam with a weak alkaline solution, whereby organic matters, especially uric acid, are removed, and empyreumatic products avoided in the subsequent distillation, induced the author to dispense with the layers of cupric oxide and zinc-dust in the combustion tube. The latter containing only the zinc-amalgam, was heated over a Bunsen lamp, as already described, and distinct reactions were yielded by similar quantities of mercuric chloride.

4. *Experiments with Leaf-gold.*—The process was the same as in the previous experiments, the leaf-gold washed with ether, dried on a watch-glass in the water-bath, and after kneading into a pellet introduced into a thick glass tube of 3 mm. diameter, closed at one end and drawn out at the other. The sublimate of mercury obtained upon heating in the capillary portion, gave a distinct reaction with iodine in each of the four experiments in which the quantities of mercuric chloride employed were respectively 0·002, 0·001, 0·0005, and 0·0002 gram. The author concludes that Ludwig's process, in skilful hands, is neither complicated nor tedious, whilst in point of delicacy it is at least equal to its several modifications. Fürbringer's process is undoubtedly somewhat quicker and more simple in its details, but it must be borne in mind that the same intimate contact of solution and metal attainable in the case of zinc-dust, is hardly to be expected when brass-wool is employed. The process is most simplified by the substitution of leaf-gold. The destruction of the urine by potassium chlorate and hydrochloric acid, as proposed by Lehmann (this vol., p. 687), is in no case necessary. Lastly, an objection lately urged against Ludwig's method by Schuster, that the simultaneous distillation of the zinc itself may conceal the mercurial sublimate, is possible only when excessive ignition has been resorted to. That the iodides of arsenic or bismuth should be mistaken for mercuric iodide is, as already shown by Ludwig, only conceivable in inexperienced hands. D. P.

Determination of Organic Matter in Potable Water. By J. W. Mallet (*Chem. News*, **47**, 218—220 and 232—233).—Apparatus is described, whereby the water to be examined may be evaporated under greatly reduced pressure and at a correspondingly low temperature, out of contact with the air. Under such conditions the organic matter is altered much less than in the apparatus generally made use of. As test materials, leucine and tyrosine were selected, as representing the more stable products of putrefaction liable to occur in natural water, and for which the combustion process in its usual form had been found to give results far from satisfactory. Sixteen experiments were made; from leucine 95·77 per cent. of the total carbon was obtained (97·24 to 91·40), and 93·32 per cent. of the total nitrogen (95·64 to 88·27); whilst from tyrosine 97·04 per cent. of the carbon (98·13—92·65), and 95·72 per cent. of the nitrogen (97·29 to 90·45) were obtained. These numbers show a marked improvement on results previously obtained, and the error in the determination of the two elements is in one direction, viz., a partial loss. It has been proposed to remove nitrogen existing as ammoniacal salts, by treatment with magnesia, before estimating the organic nitrogen, but it is found that at 40° to 45°, urea in a very short time begins to evolve ammonia; still in waters containing relatively very large quantities of ammoniacal salts the error due to the decomposition of urea, &c., would be perhaps less than that attributable to the dissociation of these salts during the evaporation, to an extent not accurately determinable. It has been proposed to remove nitrates and nitrites by the reducing action of phosphorous or hypophosphorous acid; solutions of tyrosine and potassium nitrate were evaporated with addition of phosphorous acid, the residue just neutralised with magnesia, and then brought to a suitable condition by the addition of pure silica and drying in the previously described vacuum apparatus. On combustion, results were obtained for the carbon and nitrogen of the tyrosine as good as those obtained from solutions of this substance in pure water. A series of experiments under different conditions showed that on distilling a very dilute solution of ammonia a not inconsiderable amount is lost; thus under ordinary conditions it amounts to about 14 per cent. of the whole. In this case the temperature of the distillate was about 28°, but by reducing this to 6°, the average loss became only 2 per cent. If a current of air be drawn through or over a dilute solution of ammonia—0·5 mgrm. in 500 c.c. —the ammonia is very slowly removed, but at a temperature of 50—60°, the whole of the ammonia may be removed in about 16 hours. A solution of urea when boiled or kept at a high temperature is decomposed gradually with evolution of ammonia, but at lower temperatures, *i.e.*, 50—60°, this decomposition is much less rapid. A few experiments were also made to test the modification of the permanganate process proposed by Tidy, viz., the maintenance of an approximately constant excess of permanganate; the modification seems to be an improvement, but further experiments are required.

H. B.

Coefficients of Solubility of some Silver Salts, and Systematic Method of Testing for Hydrocyanic, Hydrochloric, Hydrobromic, Hydriodic, Chloric, Bromic, Iodic, Hydroferrocyanic, and Hydroferricyanic Acids. By A. LONGI (*Gazzetta*, **13**, 87—89).— The author has carefully determined the coefficients of solubility of certain silver salts in various solvents, as in the subjoined table, and

Solvent.	Temp.	Silver Salt.	A.	B.
Ammonia, 5 p. c.; sp. gr. 0·998	12°	Cyanide	433·17	431·73
	,,	Chloride	430·20	428·64
	,,	Bromide	8805·55	8779·37
	25°	Iodide	∞	∞
	,,	Bromate	28·49	28·14
	,,	Iodate	42·73	42·39
Ammonia, 10 p. c.; sp. gr. 0·96	18°	Cyanide	192·52	184·59
	,,	Chloride	13·46	12·76
	12°	Bromide	300·33	288·46
	,,	Iodide	27,420·35	26,327·54
	25°	Bromate	2·254	2·162
	,,	Iodate	2·383	2·202
Water	,,	Bromate	597·73	595·31
	,,	Iodate	27,821·88	27,728·94
Nitric acid, 35 p. c.; sp. gr. 1·21	,,	Bromate	262·83	320·36
	,,	Iodate	859·81	1044·32

A is the number of cubic centimeters of the solvent required to dissolve 1 gram of the salt.

B is the number of grams of solvent required to dissolve 1 gram of the salt.

on the results has based a method for testing for the acids mentioned above.

In order to test the substance, if insoluble in water, it is boiled with sodium carbonate, and the filtrate acidified with acetic acid; if soluble, the aqueous solution is rendered acid in the same way; the solution is then precipitated with silver nitrate in slight excess and a little nitric acid is added; but if hydrogen sulphide is present it must first be heated until the gas is entirely dispelled.

The solution may contain chlorate and some bromate of silver and also mercuric cyanide; it is treated with zinc and a little sulphuric acid; this precipitates the mercury and silver, and reduces the chloric and bromic to hydrochloric and hydrobromic acids. When the reduction is complete, the liquid is divided into three parts; in one hydrocyanic acid is tested for by a ferrosoferric salt; another is tested for bromine indicating bromic acid; and the third for chlorine by precipitating with silver nitrate and digesting with ammonia (0·998); if a white precipitate insoluble in boiling nitric acid is formed on adding nitric acid to the filtrate, it indicates that a chlorate was present.

The original precipitate, which may contain cyanide, bromide, iodide, bromate, iodate, ferrocyanide, and ferricyanide of silver, is carefully washed and digested with ammonia (0·998).* This leaves undissolved the silver bromide, iodide, and ferrocyanide, which is carefully washed and treated with hydrogen sulphide solution and a little hydrochloric acid; after removal of the excess of hydrogen sulphide the solution is tested for hydroferrocyanic acid in the usual way with a ferrosoferric salt, and the filtrate from the prussian blue precipitate is then examined for iodine and bromine with carbon bisulphide, &c.

Into the ammoniacal solution containing the cyanide, chloride, bromate, iodate, and ferricyanide, an excess of sulphurous acid solution is poured; this precipitates the silver cyanide and chloride, and reduces the other acids, precipitating them as bromide, iodide, and ferrocyanide of silver. On treating the washed precipitate with ammonia (0·998) the three last are left undissolved and are tested in the manner described above, showing the presence in the original solution of bromic, iodic, and hydroferricyanic acids. The silver chloride and cyanide dissolved by the ammonia are reprecipitated by nitric acid, and the precipitate divided into two parts; one is treated with a little dilute hydrochloric acid and the solution tested for hydrocyanic acid, whilst the presence of chloride in the other is indicated by its leaving an insoluble residue when boiled with nitric acid. C. E. G.

Method of Determining Hydrochloric, Hydrocyanic, and Thiocyanic Acids when Simultaneously Present. By W. Borchers (*Chem. News*, **47**, 218).—A portion of the solution is titrated with silver solution. The quantity of silver thus found, required to combine with the three acids is added to another portion of the solution and the precipitate filtered quickly; it need not be washed unless sulphates are also present. The precipitate is washed

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* The quantity of ammonia required is relatively large, and the treatment of the precipitate must be continued until nothing appreciable passes into solution.

into a flask with nitric acid of 1·37 sp. gr., and boiled until complete oxidation has taken place. There then remains silver chloride, which separated and weighed gives the chlorine present; the solution contains silver nitrate corresponding with the silver cyanide, and also silver sulphate corresponding with the silver thiocyanide. The sulphuric acid is determined by precipitation with barium nitrate, and in the partially neutralised filtrate, the silver is determined by titration. If a ferrocyanide is also present, it is precipitated by an acid ferric salt free from chlorine, and in the filtrate the three acids are determined as before. If the titration with silver is made before removing the ferrocyanide, an excess of silver must be added before the addition of the ferric salt used as indicator. H. B.

Estimation of Hydrocyanic Acid. By R. A. CRIPPS (*Pharm. J. Trans.* [3], **13**, 917—918).—In the directions for the estimation of hydrocyanic acid in the United States Pharmacopœia, it is stated that 13·5 grams of dilute hydrocyanic acid mixed with magnesia, when titrated, using potassium chromate as indicator, should require 50 c.c. standard silver nitrate, representing 2 per cent. absolute hydrocyanic acid. The author points out that this quantity would be correct provided a double cyanide of magnesium and silver were formed and the completion of the formation indicated by the chromate. It happens that a magnesium silver cyanide, $MgCy_2,2AgCy$, does exist, and can be obtained in crystals by dissolving silver cyanide in magnesium cyanide, but potassium chromate cannot be used as an indicator of the completion of its formation. The author is of opinion therefore that 100° of standard silver nitrate would be required instead of 50 c.c., and that the British Pharmacopœia process is preferable to that recommended in the United States Pharmacopœia.

D. A. L.

Milk. By H. STRUVE (*J. pr. Chem.* [2], **27**, 249—256).—In opposition to the results of Biedent and Badenhausen as to the nature and condition of the caseïn of both cow's and human milk, it is contended that there is no difference in the quality of the albuminoïds contained in both kinds of milk, but that human milk contains a smaller proportion of nitrogenous matters, and specially of caseïn than cow's milk does. All dissolved albuminoïds are separable from the insoluble caseïn and fat by means of dialysis into an aqueous solution of chloroform; most of the insoluble caseïn forming the coverings of the fat-globules separating together with the caseïn. By agitating milk with ether, the fat-globules become much distended, the coverings burst, and the fat passes into solution. Only very few fat-globules are in a free condition. O. H.

Ether Test for Quinine. By A. J. COWNLEY (*Pharm J. Trans.* [3], **13**, 917); (compare *ibid.*, **7**, 653, and this vol., 1018).—The author remarks on the inefficiency of the test for the detection of cinchonidine, even when Byassin's improvement of adding ammonia and using small quantities of ether is resorted to: as much as 10 per cent. cinchonidine may be overlooked in a sample of quinine sulphate. D. A. L.

Use of Bromine in Testing for Alkaloïds. By C. L. Bloxam (*Chem. News*, **47**, 215).—If the alkaloïd be dissolved in dilute hydrochloric acid, and bromine-water added drop by drop, the following reactions are obtained:—Brucine gives a violet colour, strychnine the same on boiling, narcotine a rose-pink, and the same with quinine. With excess of bromine, strychnine, brucine, and narcotine readily give yellow precipitates, whilst quinine, morphine, and cinchonine are only precipitated with difficulty or from strong solutions. If ammonia be added to the quinine and bromine solution, the characteristic green colour is produced. If the morphine solution containing excess of bromine-water be boiled, zinc added and again boiled, cooled and dilute ammonia added, a pink colour is produced. H. B.

Bromine as a Test for Strychnine. By H. Jackson (*Chem. News*, **48**, 11).—The author finds that acidifying with a few drops of concentrated sulphuric acid greatly intensifies and hastens the production of the violet coloration with bromine in solutions of strychnine. A distinct rose-pink coloration is produced in a solution containing $\frac{1}{2000}$ of a grain of strychnine. The author suggests a plan for the estimation of strychnine, using a standard solution of strychnine and then comparing colours in a manner similar to the Nesslerising method. D. A. L.

Analysis of Nux Vomica. By W. R. Dunstan and F. W. Short (*Pharm. J. Trans.* [3], **13**, 1053—1055).—The authors have analysed samples of nux vomica beans from different localities. The process employed is substantially that described at p. 689 of this volume, the percolate, however, is acidified with 5 per cent. sulphuric acid, and 10 c.c. of it only are taken for the second agitation; the liquid having been rendered alkaline with ammonia, the extraction is effected by two successive treatments with 15 c.c. of chloroform. The beans varied in size and appearance; all the cotyledons were seven-veined; the analytical results were as follow:—

Percentage of Strychnine and Brucine.

Variety.	Madras.	Cochin.	Bombay ordinary.	Bombay fine.
Collected 1877	2·74	3·04	3·14	3·46
„ 1883	3·15	3·60	3·90	

When the nux vomica seeds are exposed to a temperature above 100° decomposition takes place, and then the chloroform alcoholic percolate is discoloured. If the colour is deep or brown, it is advisable to remove it; this can be readily effected by shaking the percolate with a 5 per cent. solution of sodium carbonate.

The authors have made several experiments to test the efficiency of various precipitants for ascertaining the purity of alkaloïdal residues. They now test by dissolving the residue in dilute sulphuric acid, exactly neutralising with ammonia, and precipitating with ammonium tannate solution; the precipitate is dissolved in a saturated solution of sodium carbonate, the alkaloïd extracted with chloroform, and the chloroform evaporated. D. A. L.

Picric Acid as a Test for Albumin and Sugar in Urine. By G. Johnson (*Pharm J. Trans.* [3], **13**, 1015—1019).—To test for albumin, add to the urine either a small quantity of solid picric acid, or an equal volume of a saturated solution of picric acid, or pour some of the solution on the urine so as to form a layer; in all cases the presence of albumin is indicated by the immediate appearance of a coagulum; in the last case, the coagulum forms a horizontal ring at the junction of the liquids. This coagulum is soluble in alkalis; if therefore the urine is very alkaline it must be acidified before testing; this precaution is seldom necessary, as the picric acid is sufficient to effect the required neutralisation. This test is more delicate than the old nitric acid one. Any turbidity of the urine must be got rid of previously to testing with picric acid.

To test for, and determine the amount of glucose in a saccharine solution or urine, the author makes use of the reduction of picric to picramic acid by glucose in the presence of potash. This change, as is well known, is accompanied by a change of colour from yellow to deep red; now the author has found by experiment that the depth of the red colour produced depends entirely on the amount of glucose present, and is, moreover, invariably proportionate to the dilution of the solution. Thus, if one solution contained a certain quantity of sugar, and another solution contained four times as much, then the colour produced by the latter, diluted to four times its own bulk, would be of the same depth as the colour produced by the former. Therefore a certain colour-strength is settled upon as a standard, and all solutions are very carefully and accurately diluted down to this standard; the dilution is conveniently conducted in a graduated vessel alongside of which the tube containing the standard is attached; then the quantity of glucose in the standard, multiplied into the degree of dilution, will give the quantity of glucose in the solution under examination. The author's standard colour is that produced by a quarter-grain of sugar to the fluid ounce, and is thus obtained:—A fluid drachm of a solution of sugar containing 1 grain to the ounce, is mixed with half a drachm of potash solution (B.P.) and 10 minims of a saturated solution of picric acid, and made up to 4 drachms with distilled water. This mixture is now boiled for one minute, cooled, and, if necessary, made up to 4 drachms. The picramic colour is very fugitive, therefore the 4-grain colour is imitated by the following mixture: all solutions are B.P. preparations, strong ferric chloride solution (1 drachm), ammonium acetate solution (4 drachms), glacial acetic (4 drachms), distilled water ($2\frac{1}{2}$ ozs.), which produces a much more stable colour. All quantitative experiments with saccharine solutions or urine, are conducted in the same way as the standard is produced. It is not necessary to alter the quantity of potash, the amount of picric acid must however vary with the quantity of sugar present; it is always better to have a slight excess, as the yellow colour does not interfere with the red. The colour is not affected by pure albumin; the colouring-matter, however, of egg-albumin has a reducing action on picric acid: this colouring-matter is easily removed by filtration through animal charcoal. Results obtained by this process compared with those by Pavy's ammonio-cupric method, show rather lower figures; this the author attributes to something not saccharine reducing the copper solution, but not the picric acid; and he finds that normal urine contains two cupric-oxide-reducing substances:—1. Those not destroyed by potash, such as uric acid, &c. 2. Those destroyed by potash. Those of class 1 do not reduce picric acid, hence it happens that if the cupric oxide reduction obtained from a urine which has been boiled for some time with dilute potash be deducted from the cupric oxide reduction effected by the original urine, the reduction thus obtained is equal to that given by the picric acid with the original urine. This reducing substance only differs from glucose in not being fermentable by yeast; there are some sugars which behave in a similar manner, namely, sorbite and eucalin; it is therefore very probable that this saccharoïd ingredient of normal human urine may be a true sugar, although its identity with glucose is incomplete. D. A. L.

Dialysis of Putrescible Substances. By H. STRUVE (*J. pr. Chem.* [2], **27**, 231—249).—The author recommends suspending a bladder filled with the fluid to be dialysed in a saturated solution of chloroform in water, or in pure ether, and details the results thus obtained in the case of white of egg, and of milk both cows' and human. He finds that the whole of the albumin and soluble caseïn, as well as all crystalline constituents, pass through the bladder, leaving behind the cell-walls and the fat. He contends that these results show the distinction between colloïds and crystalloïds to be without foundation. O. H.

Use of Phosphoric Acid in Pettenkofer's Reaction for Bile Acids. By E. DRECHSEL (*J. pr. Chem.* [2], **27**, 424).—The failure in obtaining Pettenkofer's reaction when phosphoric acid is used in place of sulphuric acid is due to the employment of too large a quantity or too concentrated an acid. A few drops of a mixture of 5 vols. of commercial syrupy phosphoric acid with 1 vol. of water, should be used. A. J. G.

Technical Chemistry.

Marsh-gas Fermentation in the Mud of Ditches, Swamps, and Sewers. By H. TAPPEINER (*Ber.*, **16**, 1740—1744).—The fermentation produced by the addition of mud to a sterilised 1 per cent. solution of meat extract containing cotton wool and Nägeli's salts, yields a gaseous mixture containing 48·05 per cent. CO_2 and SH_2 and 51·68 per cent. of H. The gases evolved by the action of mud on the meat extract solution and cotton wool consist of CO_2 and SH_2 81·81,

CH_4 13·07, and H 4·89 per cent. Butyric and acetic acids were produced in each case. The relative amounts of CO_2 and CH_4, produced by the action of mud on meat extract alone, are in the ratio of 1 : 3·1—3·6. Similar results are obtained if vegetable albumin or peptone is substituted for meat extract. Small quantities of these bodies give rise to an evolution of gas which lasts for weeks.

W. C. W.

New Properties of Ferric Sulphate. By ROHART (*Compt. rend.*, **96**, 1705—1708).—Ferric sulphate, as neutral as possible and free from any appreciable quantity of ferrous sulphate or ferric chloride, combines with animal and vegetable substances, precipitating them from solution, and forming definite and highly stable compounds, which undergo no alteration when exposed to air. A solution of ferric sulphate of 50° B. containing 26 per cent. of ferric oxide, added to urine in the proportion of 2 per cent., instantly precipitates urea, mucus, and urinary phosphates, and the urine thus treated undergoes no change on exposure to air. Similar results are obtained with sewage. Different parts of animals, and entire fish and small animals, when suspended for a few days in a solution containing 1 per cent. of ferric sulphate, are rendered non-putrescible, and may be dried without undergoing change. There is actual combination between the ferric sulphate and the organic matter, the former appearing to take the place of some of the water contained in the latter. An adder weighing 59 grams was dried completely: it weighed 19 grams. It was then immersed for six days in the ferric sulphate solution, and again dried; it now weighed 25 grams, or an increase of 32 per cent. on its weight in the dry state. The ferric sulphate which thus combines with the organic matter cannot be dissolved out by hydrochloric acid, and is not decomposed by boiling with barium chloride solution. Meat treated with this reagent retains its red colour, but becomes so hard that it can scarcely be scratched with the nail. Experiments with eggs show that the ferric sulphate solution penetrates into the organisms by endosmosis.

C. H. B.

Employment of Boric Acid for Preserving Food. By J. FORSTER (*Ber.*, **16**, 1754—1759).—The author considers the use of boric acid for preserving articles of food to be a questionable practice. Boric acid increases the secretion of bile and the amount of albuminous matters excreted.

W. C. W.

Manufacture of Tartaric Acid. By L. H. FRIEDBURG (*Pharm. J. Trans.* [3], **13**, 992—1000).—In the process described, the finely powdered argol, sablons, or lees, is added gradually to milk of lime and boiled with constant stirring for two hours; in this way potassium hydroxide and calcium tartrate are formed, and the nitrogenous organic matter decomposed, ammonia going off with the steam. When the boiling is complete, the mass is diluted, and the potash neutralised with hydrochloric or sulphuric acid, more cold water is now added, and the whole well stirred for some considerable time (all night). The liquor containing potassium salts, &c., is filtered off, concentrated, and otherwise made marketable. The impure calcium tartrate, which is very prone to putrefaction, is speedily decomposed with sulphuric acid in the cold, methyl-violet paper being used to indicate when the required quantity of sulphuric acid has been added. From this brown solution, the tartaric acid is carefully reprecipitated as calcium tartrate, lime being used at first, but chalk towards the end, using litmus as indicator of the complete neutralisation. The precipitate is filtered and slightly washed; the calcium tartrate forms light greenish-yellow crystals, which may be kept for any length of time without decomposing. This is also decomposed by sulphuric acid in the cold, again using methyl-violet paper. The precipitated gypsum is filtered off and well washed, and the tartaric acid solution evaporated at 80° until the gypsum in solution is deposited; it is then run into crystallising boxes. The brown crystals thus obtained are dissolved to a liquor density of 25° B., treated with animal charcoal (which has been washed with hydrochloric acid), filtered, evaporated to 39° to 40° B., and either run into lead boxes to crystallise slowly, or delivered into a tank fitted with a stirrer, where it is stirred for several hours, and a crop of small crystals formed directly. The crystals are washed and dried in centrifugals, steam being used for washing. The liquid from the first crystallisation deposits another crop of white crystals; it then becomes brown mother-liquor, from which crops of crystals are obtained until the predomination of sulphuric acid and other impurities does not allow further crystallisation. They are then diluted, the greater part of sulphuric acid removed by lime; and iron and aluminium phosphates got rid of by further treatment with lime, when acid calcium tartrate is left in solution; this is filtered hot, and decomposed by sulphuric acid, when it yields a very pure solution of tartaric acid.

For the preparation of potassium hydrogen tartrate, the acid solution is divided into two equal parts, the one is neutralised with potassium carbonate, the two are then mixed, and the potassium hydrogen tartrate is precipitated. D. A. L.

Chemistry of Fish. By W. O. Atwater (*Ber.*, **16**, 1839—1846).—The author gives the results of the analyses of the flesh of 64 kinds of fresh and preserved fish, which are used for food.

W. C. W.

Fermentation of Bread. By Moussette (*Compt. rend.*, **96**, 1865).—The liquid obtained by condensing the vapours from a bread oven contained 1·6 per cent. by volume of alcohol, and 0·06 per cent. by weight of acetic acid, together with a small quantity of ferric acetate (from the walls of the oven), and a very small quantity of ammonia. This experiment, which was made in 1854, proves that alcohol is one of the products of the fermentation of bread (see next Abstract).

C. H. B.

Fermentation of Bread. By G. Chicandard (*Compt. rend.*, **96**, 1585—1588).—It is generally supposed that in the fermentation of flour paste the starch is converted into maltose under the influence of diastases existing in the flour, the maltose being eventually converted into glucoses, which undergo alcoholic fermentation. But the diastases existing in flour act only on starch altered by heat, and have no action on unaltered starch; moreover, the presence of alcohol in the paste has never been proved. The author has analysed filtered infusions of flour, paste with leaven, paste with yeast, and bread, and he finds that there is no soluble starch in flour, or in the two pastes, but that a considerable quantity exists in bread. The four substances contain equivalent quantities of glucose, from which it follows that the glucose originally existing in the flour is not decomposed. Flour contains albumin which is coagulated by heat and is precipitated by nitric acid and by potassium ferrocyanide and acetic acid. The two pastes contain no albumin coagulable by heat, but they contain albuminoïds precipitable by nitric acid and by potassium ferrocyanide and acetic acid, together with peptones not precipitated by these reagents, but precipitated by tannin. Bread contains no albuminoïds, but it contains peptones precipitated by tannin, corrosive sublimate, &c. Microscopic examination shows that the paste with leaven contains no *saccharomyces*, and that the cells of *saccharomyces cerevisiæ* introduced into the paste with yeast gradually diminish in number. Both pastes contain a number of moving microbes, of very varying length, which appear to be bacteria. These bacteria develop very rapidly in paste with yeast, and they can be cultivated in water holding yeast in suspension, from which it would appear that yeast is favourable to their development. The gas evolved during fermentation is a mixture of carbonic anhydride, hydrogen, and nitrogen, and is analogous in composition to the gas evolved in the putrefaction of albuminoïds.

The author concludes that the fermentation of bread is not due to a *saccharomyces*, and that it consists, not in hydration of the starch followed by alcoholic fermentation, but consists in the conversion of a portion of the insoluble albuminoïds of the gluten into soluble albuminoïds, and eventually into peptones. The starch is modified by the heat only, a considerable quantity of soluble starch and a small quantity of dextrin being formed. The agent of fermentation is a bacterium which develops normally in paste, the development being accelerated by the presence of yeast.

These remarks do not apply to the English process, in which fermentation is produced by a mixture of yeast with potato-starch altered by heat. C. H. B.

Italian Petroleums. By B. Porro (*Gazzetta*, **13**, 77—85).—The author has examined four specimens of petroleum found in Italy at Petralio Montanaro near Piacenza, at Rivanazzuno near Voghera, at Tocco Casanria, and at San Giovanni Incarico.

The first had a sp. gr. of 0·7849 at 15°, and when distilled gave 44·7 per cent. light petroleum; 19·8 distilling between 127° and 150°; 22 between 150° and 203°; 14·4 above 203°, and left 6·9 per cent. residue.

The second of sp. gr. 0·9132, gave 22 distilling below 230°; 33 between 230° and 270°; 37 above 270°, and 7·7 residue.

The third and fourth of sp. gr. 0·951 and 0·974, gave respectively 63·5 and 69·6 per cent. oil; 32·2 and 28·3 of pitch, and about 12 and 20 of gas. C. E. G.

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ERRATA IN VOL. XLIV.

Page	Line	
100	21 from top	*for* insoluble *read* soluble.
—	— „ „	*for* rose-red *read* bright blue.
—	22 „ „	*for* bright blue *read* rose-red.
116	24 „ bottom	*for* The analyses of drainage of fallows at a depth of 27 inches show a loss of, *read* The analyses of fallows show that the uppermost 27 inches contain.
116	10 „ bottom	*for* sand and flint, *read* sand and gravel, such as form the soil of the plain of Gennevilliers.
432	4 „ top	*for* Amberger *read* Amberg.
541	20 „ bottom	*for* Lutherite *read* Witherite.
589	24 „ bottom	*for* pseudocumol *read* pseudocumene.
693	7 „ bottom	*for* Caul *read* Paul.
769	2 „ top	*for* J. Probert and A. W. Poward, *read* I. Probert and A. W. Soward.
814	4 and 8 from bottom..	*for* Klingenberg *read* Klinkenberg.
815	1 at top	
917	13 from top	*for* acetamide *read* acetanilide.
—	12 „ bottom	*for* melting at 212·5°, *read* which explode on heating.
943	11 and 12 from bottom	*for* Laminaria vesiculosus. Fucus stenophylla. *read* Laminaria stenophylla. Fucus vesiculosus.
1159	3 from bottom	*for* hydrobilin *read* hydrobilirubin.
—	Last line	*for* fibrile *read* febrile.
1174	18 from bottom	*for* Badenhausen *read* Radenhausen.

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