BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1926.

General, Physical, and Inorganic Chemistry.

Fine structure of Balmer lines. G. Hansen (Ann. Physik, 1925, [iv], **78**, 558—600).—An examination of the fine structure of the Balmer lines of hydrogen with the aid of a Lummer–Gehrcke plate and the measurement of the intensities by means of a recording microphotometer. The sources of error in the apparatus are discussed and the necessary corrections effected. The ratio of the relative intensities of the long and short wave-length components of the doublets varies more with the pressure of the gas than with the current density. The frequency separations determined for the doublets H_α, H_β, H_γ, H_δ, H_ϵ are 0·316, 0·317, 0·328, 0·322, and 0·324 cm.$^{-1}$, respectively, for a pressure of 0·22 mm. The Sommerfeld–Kramers theory requires that the frequency separation of H_α should be 0·329 cm.$^{-1}$ for the field-free doublet. When the current density is maintained constant at 0·04 amp./cm.^{2} and the pressure is varied from 0·23 to 0·015 mm., the frequency separation of H_α increases from 0·316 cm.$^{-1}$, passes through the maximum of 0·320 cm.$^{-1}$ at a pressure of 0·09 mm., and falls again to 0·313 cm.$^{-1}$. This maximum is thus within 3% of that demanded by the theory. The general effects of varying the conditions of the discharge are discussed.

A. E. Mitchell.

Measurement of the fine structure of hydrogen lines with the Lummer–Gehrcke plate. E. Gehrcke (Ann. Physik, 1925, [iv], **78**, 461—464).—The work of van Cittert on this subject (A., 1925, ii, 909) is criticised.

R. A. Morton.

Interpretation of the hydrogen and helium spectra. J. C. Slater (Proc. Nat. Acad. Sci., 1925, **11**, 732—738).—The anomalous Zeeman effect and the multiplicity of spectral terms may be due either to interaction between the valency electrons and the electrons of the core, or to peculiarities in the valency electrons themselves, the double levels in atoms having one electron being due to an assumed duality in the quantum laws. If so, the spectrum of hydrogen should resemble that of the alkalis, and that of helium the alkaline-earths. The evidence obtained from observations on the multiplicity of the lines and from the Zeeman effect is discussed in detail and is not unfavourable to the second alternative.

E. B. Ludlam.

Absorption and resonance radiation of excited helium. W. H. McCurdy (Nature, 1926, **117**, 122).—Absorption was observed of the lines 5875, 4471, 4026, 3889, 3187, 5016, 3964, 3614, 6676, and 4921 Å. in excited helium, and the possibility of obtaining resonance of the line 3889 Å. has been demonstrated.

A. A. Eldridge.

Spectrum of ionised lithium. Y. Sugiura (J. Phys. Radium, 1925, [vi], **6**, 323—333).—The spark spectrum of lithium has been examined using a perforated cathode in a platinum tube coated with lithium chloride, the accuracy obtained being about 0·5 Å. Rays due to ionised lithium, Li II, have been identified and compared with those of helium; the two spectra are in good agreement with the law of spectroscopic displacement for the series *mD—nF* and *md—nf*, but less strictly for the remaining series. The classification of the different series is discussed, and the lines 2924 and 5485 Å. are ascribed to the doublet and simple ray spectra, respectively, in contradiction to the conclusion of Mohler (A., 1925, ii, 615). The quantum defects corresponding with each term of the series are deduced from the observations and are in agreement with theoretical calculations, whilst the critical potentials calculated from the spectroscopic data agree with the direct measurements of Mohler (*loc. cit.*). The ionisation potential of ionised lithium, the term 1*S*, is calculated to be 67·5 volts.

W. Hume-Rothery.

Life-periods of the metastable s_3 and s_5 states of neon. H. B. Dorgelo (Z. Physik, 1925, **34**, 766—774).—The neon lines $2s_3—2p$ and $2s_5—2p$, under suitable excitation conditions, exhibit self-reversal and other absorption phenomena. This behaviour shows that the s_3 and s_5 states must be metastable. Their life-periods have now been measured by observing the time interval, after the cessation of excitation, during which neon is still able to absorb the $2s_3—2p$ and $2s_5—2p$ lines. The intervals were determined by two procedures, one involving a toothed-wheel device, and the other depending on the control of the exciting currents. The period of the s_3 state is given as 5×10^{-4} sec., and that of the s_5 state as $4{\cdot}2\times10^{-3}$ sec. The s_4 state also has a period sufficiently long to produce similar absorption phenomena. The metastable states of neon are compared with those of mercury.

S. Barratt.

Maximum intensity and width of lines of the principal series of sodium. B. Trumpy (Z. Physik, 1925, **34**, 715—721).—The intensity and width of the lines of the principal series of sodium, of term numbers 3—12, have been studied in absorption. The maximum absorption coefficient of the lines, and also their physical half widths, were determined by the usual methods of photographic spectrophotometry. The absorption coefficient is given as $8 \cdot 55 \times 10^{-7}$ for the line $1s-4p$, and as $2 \cdot 30 \times 10^{-7}$ for $1s-13p$, the intervening lines having intermediate values. The numbers are only approximate, as the length of the absorbing column could not be accurately fixed. The half width of $1s-4p$ is about seven times that of $1s-13p$, under identical observation conditions. The width of the lines is nearly independent of temperature and of the total gas pressure, but is very sensitive to the density of the sodium vapour. The Lorentz broadening due to "impact damping" cannot cope with the phenomena; the observed widths of the lines are far too great.

S. Barratt.

Absorption of sodium vapour. J. Holtsmark (Z. Physik, 1925, **34**, 722—729; cf. preceding abstract).—Theoretical. An attempt is made to account for the very great increase in width of the absorption lines of sodium when the density of the vapour is increased. The atoms are treated as resonators of the "classical" type, and these do not vibrate freely, but are coupled together. This coupling causes the broadening. The theory leads to widths of the observed order. For small concentrations, the width of the lines should be proportional to the square root of the concentration of sodium vapour, in agreement with Trumpy's experiments.

S. Barratt.

Wave-lengths and pressure-shifts in the spectrum of magnesium. M. Petersen and J. B. Green (Astrophys. J., 1925, **62**, 49—60).—Tabulated results are given of wave-length measurements of magnesium lines in an arc in air, and in an arc in a vacuum. Pressure shifts observed were less in magnitude than existing data, and increase with the series term. A. A. Eldridge.

Spectrum of ionised calcium (Ca II). F. A. Saunders and H. N. Russell (Astrophys. J., 1925, **62**, 1—7).—Results are given of measurements in nearly all parts of the spectrum of Ca II from a large variety of sources; there exists a system of combination series similar to those of Mg II. The second and third members of the principal series have been found, and series of the types $2\pi-m\sigma$, $2\pi-m\delta$, and $3\varphi-m\varphi'$ detected, as well as other combinations.

A. A. Eldridge.

Interpretation of the spectra of the alkaline-earths. G. Wentzel (Z. Physik, 1925, **34**, 730—735).—Theoretical. Existing data are reviewed and discussed. L. F. Gilbert.

Regularity in the distribution of spectral lines of iron and intra-atomic magnetic field. H. Nagaoka and Y. Sugiura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1924, **1**, 155—206).—If an iron arc is kept vertical, and there is a sufficiently high potential difference, *e.g.*, 56,000 volts/cm., between the electrodes, the Stark effect is observed. By examining the ultra-violet portion of the spectrum, between 2400 and 3000 Å., more than 200 lines showing the simplest of the Stark phenomena, namely, increase in intensity of the lines with slight displacement towards shorter wave-lengths, have been measured. On mapping out these lines according to the frequency, it has been shown that they form a number of triplets, quadruplets, and sextuplets, and also doublets which probably form part of more complex and anomalous separations. From the average separation in the quadruplets, on the assumption that it is due to the Zeeman effect produced by the atomic magnetic field acting on the electrons emitting light, this field has been calculated to be $7 \cdot 6 \times 10^6$ gauss, which is in accordance with the value found by Weiss (J. Physique, 1907, [iv], 6, 661) from experiments on the magnetism of iron at high temperatures. From triplets with symmetrical distribution of intensity, the same agreement is not obtained, which is attributed to the possibility that the external magnetic field may produce an effect on lines already affected by the internal field when the plane of the electron orbit is oblique to the direction of the atomic field. It is suggested that the intricate nature of the spectral lines in ferromagnetic metals may perhaps be traced to the existence of an intra-atomic field, and it may ultimately be possible, by a combined study of the Zeeman and Stark effects, to arrange them in a spectral series. M. S. Burr.

Intensity measurements in the iron spectrum. J. B. van Milaan (Z. Physik, 1925, **34**, 921—923).—The intensities in the multiplet $\bar{f}-\bar{d}$ were measured and satisfactory agreement was obtained with the Burger–Dorgelo summation rule. The ratio of the intensities indicates, however, that the formulæ hitherto suggested are only approximations.

E. B. Ludlam.

Principal series of the copper arc spectrum. F. Simeon and E. S. Dreblow (Nature, 1926, **117**, 17).—The copper arc, examined with a large quartz spectrograph, shows the line 2024 Å. (reversed) only when the middle of the arc is projected on the slit of the instrument, the line 2025 Å. appearing at the poles only. The spark spectrum showed only the line 2025 Å. The observed wave-lengths of the two lines are 2024·19 and 2025·34 Å., giving $\Delta\nu$ 28·1 ($\pm 1 \cdot 0$), Randall's calculated value being 32·7. It is concluded that the line 2024 Å. is a true arc line, and 2025 Å. a spark line, so that they do not constitute the second pair of the principal series.

A. A. Eldridge.

Radiation emitted by optically excited zinc vapour. J. G. Winans (Proc. Nat. Acad. Sci., 1925, **11**, 738—742).—Light from a water-cooled zinc arc was concentrated on zinc vapour in a silica tube and the resonance spectrum photographed. A scheme is given showing the change in energy levels of the electrons corresponding with each line. Also four bands were obtained, three of which formed a band system, but the fourth—the furthest in the ultra-violet—differed in character and in relative intensity compared with the lines. When the zinc vapour was illuminated by a water-cooled mercury arc, in addition to resonance lines of mercury (impurity in the zinc tube), lines due to zinc were observed, which are due to collision between an excited mercury atom and a normal zinc atom. The strong cadmium line, 3261, also appeared, excited in the same way by impact, and showing that cadmium was present as an impurity. E. B. LUDLAM.

***pp'*-Group in the arc spectrum of zinc.** R. A. SAWYER and N. C. BEESE (Nature, 1925, **116**, 936—937).—The rule that, in two-valency system spectra, the frequency of the first *pp'*-group is nearly a mean between the frequency of the first line of the principal series of singlets in the spectrum and that of the first line of the principal series of doublets of the once more ionised atom, is applied to cadmium and extended to zinc. The precise classification of the zinc line 2070·11 Å. is considered.

A. A. ELDRIDGE.

New lines between 3100 and 2200 Å. in the arc spectrum of lanthanum. S. PIÑA DE RUBIES (Anal. Fís. Quím., 1925, 23, 444—449).—See A., 1925, ii, 612.

Wave-lengths and relative intensities in the molybdenum *K*-series *X*-ray spectrum. S. K. ALLISON and A. H. ARMSTRONG (Physical Rev., 1925, [ii], 26, 701—713).—See A., 1925, ii, 1015.

Relative intensities of some *X*-ray lines in the *L*-spectrum of tungsten and the *K*-spectrum of copper. S. K. ALLISON and A. H. ARMSTRONG (Physical Rev., 1925, [ii], 26, 714—723).—See A., 1925, ii, 1015.

Apparent shape of *X*-ray lines and absorption limits. F. K. RICHTMYER (Physical Rev., 1925, [ii], 26, 724—735).—The effect of instrumental factors on the observed intensity distribution of *X*-ray lines and at absorption limits has been investigated as regards the height and width of the slit and the uniformity of energy distribution over the focal spot. When the results are corrected for the width of slit used, the *K* absorption limit of silver is sharp, its width falling within the limit of experimental error, 2×10^{-4} Å. The curves of the energy distribution in the $K\alpha$ doublet of molybdenum correspond with monochromatic lines of width $<0·0003$ Å. and relative intensity 2. A. A. ELDRIDGE.

Relative intensity of *X*-ray lines. Y. NISHINA and B. B. RAY (Nature, 1926, **117**, 120—121).—A preliminary account of the method employed to obtain sensitivity curves applicable to measurements of the relative intensities of *L*- and *M*-series, in particular the *L*-series of tungsten. A. A. ELDRIDGE.

Regular relation between chemical elements with respect to the effect of an electric field on series lines. J. STARK (Ann. Physik, 1925 [iv], **78**, 425—433).—The Balmer series of hydrogen may be expressed by $\nu=2w-mw$. For heavy elements, instead of the single *mw* series, there are at least five series, *ms*, *mp*, *md*, *mf*, mf_2. The difference between the quantum number of a series line of an element and that of the hydrogen line having the same integer is called the hydrogen-difference of the line considered, *e.g.*, *ms—mw*, *mp—mw*. For lines of the sharp, intermediate, and diffuse series in the heavy elements, the Stark effect ($\Delta\lambda$) has the same sign as the hydrogen-difference, and within a series-type $\Delta\lambda$ is smaller for different elements as the hydrogen-difference is greater. For a single element within a series, the hydrogen-difference decreases with increasing term-number and $\Delta\lambda$ decreases. For equal hydrogen-differences, $\Delta\lambda$ is greater for the sharp than for the intermediate series, and again for this series greater than for the diffuse series. The same results are probably true for the other series. The important implications of these considerations are pointed out. R. A. MORTON.

Experimental basis of the Zeeman effect. E. BACK (Physikal. Z., 1925, 26, 833—841).—A lecture reviewing the development of the Zeeman effect, and the interpretation of the experimental data.

F. G. TRYHORN.

Stark effect in hydrogen. M. KIUTI (Japan J. Phys., 1925, 4, 13—38; cf. A., 1923, ii, 273).—The *s*-components of H_α, $\Delta\pm5$ and ±6, predicted by Kramers, have been found. The *p*-components, $\Delta\pm8$, seem to exist, but are very faint. The results for H_β also agree with Kramers' theory. Apparent central components on the red side of H_β belong to the many-lined spectrum. The second order effect for H_γ is only roughly in accord with the theory. In the many-lined spectrum, three pairs of line showed a strong effect, each line being accompanied by an isolated component; the effect of this spectrum on other lines and on the Fulcher bands is described.

E. B. LUDLAM.

Compton effect. G. HAGEN (Ann. Physik, 1925, [iv], 78, 407—420).—The Compton–Debye theory of the change of wave-length occurring in the scattering of *X*-radiations requires that the change of wave-length should be dependent on the angle of scattering, but independent of the origin of the primary radiation and of the scattering medium. These relationships have been verified by determining the change of wave-length, for various angles of scattering, of *X*-rays from molybdenum, rhodium, silver, tungsten, and tantalum, when scattered by paraffin, magnesium, and lithium. The Compton effect was not observed in the scattering of *X*-rays from tantalum or tungsten by paraffin. F. G. TRYHORN.

[Compton effect.] F. KIRCHNER (Ann. Physik, 1925, [iv], **78**, 421—422; cf. preceding abstract).—The failure of Hagen to obtain the Compton effect in the scattering by paraffin of short-wave *X*-radiations from tantalum and tungsten may possibly be due to a confusion of the $K\alpha$ and $K\beta$ lines, as a result of inaccurate focussing of the apparatus.

F. G. TRYHORN.

Device for the study of the Compton effect. J. W. M. DU MOND (Nature, 1925, **116**, 937).—By the use of an *X*-ray tube in which both the scattering substance and the analysing crystal are contained in a small metal box mounted on the end of the anti-cathode, a photographic spectrogram of the Compton effect can be obtained with less than one-thousandth of the usual exposure. Very little evidence has been obtained for any intensification of the Compton modified lines greater than that which a strict proportionality to the incident intensity would require. A. A. ELDRIDGE.

Influence of self-inductance and dilution on the persistence of spectral lines, the ultimate lines, and the quantum theory of optical spectra. A. T. WILLIAMS (Anal. Soc. cient. Argentina, 1924, **97**, 15—53).—The condensed spark spectra of solutions containing calcium, barium, strontium, magnesium, zinc, cadmium, manganese, or copper were examined. For the first three, weak lines which are unaffected by additional self-inductance appear only when the concentration is $>1\%$. When self-inductance decreases the intensity of a line to that obtained with a non-condensed spark, the line persists at a dilution of 1—0·01%; strong lines persist in 0·001% solutions. For magnesium, zinc, and cadmium, there is practically no parallelism between the effect of self-inductance and that of dilution. Manganese lines markedly decreased in intensity by self-inductance disappear at a concentration $<1{\cdot}0\%$. Copper lines which disappear by the action of self-inductance usually disappear below 1% or 0·1%; these lines are absent if the non-condensed spark is employed. The typical ultimate lines of copper, magnesium, calcium, strontium, and manganese, but not those of barium, are but slightly affected by a change in the polarity of the solution. The series relations of the ultimate lines of the elements of the first and second columns of the periodic table are tabulated. The ultimate lines (doublets of the ionised atom) of magnesium, calcium, strontium, and barium correspond, respectively, with the ultimate lines (doublets of the neutral atom) of sodium, potassium, rubidium, and cæsium. The quotients V_i/V_r and $\boldsymbol{V}_i/\boldsymbol{V}_r$ (where $\boldsymbol{V}_i$ is the potential necessary to displace completely a second electron after the first has been displaced by the potential V_i, and $\boldsymbol{V}_r$ the potential sufficient to translate inter-orbitally a second electron after the first has been completely displaced by the potential V_r) are constant for the corresponding lines of the similar series in the alkali metal group, in the sub-group magnesium, zinc, and cadmium, and in the sub-group calcium, strontium, and barium; they decrease when the temperature of thermal ionisation of the element rises. The ultimate lines in the arc and in the spark appear when the atoms are excited to a potential less than the corresponding ionisation potential. CHEMICAL ABSTRACTS.

Energy levels of the nitrogen molecule. R. T. BIRGE (Nature, 1926, **117**, 81).—A discussion. A. A. ELDRIDGE.

Critical potential of the *K* level of neon. F. HOLWECK (Compt. rend., 1926, **182**, 53—54).—The critical potential for the *K* level of neon, measured by the absorption method (cf. A., 1925, ii, 336), is 862 ± 3 volts; this is probably more correct than the value given by the spectroscopic method, viz., 856 volts. S. K. TWEEDY.

Soft *X*-rays from iron, cobalt, nickel, and copper. C. H. THOMAS (Physical Rev., 1925, [ii], **26**, 739—748).—Up to 1500 volts, 46 critical potentials have been found for nickel, 48 for cobalt, and 46 for iron; in each case nine of these are designated ionisation potentials, the remainder being radiation potentials. For copper at 0—90 and 700—1200 volts, 25 critical potentials were found. General correspondence exists between the critical potentials of iron, nickel, and cobalt. A. A. ELDRIDGE.

Ionisation of hydrogen by slow electrons. H. KALLMANN and M. BREDIG (Z. Physik, 1925, **34**, 736—750).—The nature of the ions formed during the collision of hydrogen molecules with electrons moving under a potential difference of 15—30 volts was studied by the magnetic deviation method. H^+, H_2^+, and H_3^+ ions were detected, the H^+ and H_3^+ ions being probably formed secondarily from the H_2^+ ions, although some H_3^+ ions may be formed by the reaction of H^+ ions with molecular hydrogen. An effect corresponding with ions of the formula $H_{\frac{1}{2}}^+$ was also observed; this effect can be explained as a result of the decomposition of some H_2^+ to H^+ ions. L. F. GILBERT.

Ionisation of nitrogen by electron impact as interpreted by positive ray analysis. T. R. HOGNESS and E. G. LUNN (Physical Rev., 1925, [ii], **25**, 786—793).—At pressures below 10^{-5} mm., only N_2^+ ions were observed; with increase of pressure, the percentage of N^+ ions increased, reaching 60% at 0·006 mm. N_2^+ ions were formed by the impact of electrons of energy >17 volts; N^+ ions, by disruption of N_2^+ ions, above 24 volts. Thus, the critical potentials 16·95 and 24·6 volts correspond with the formation respectively of stable and unstable N_2^+ ions. Over the range 2·7—27 volts, the dissociation of an unstable N_2^+ ion is independent of its speed. N^{++} ions do not appear below 500 volts; N_2^- ions were observed. Helium increases the formation of N^+ ions. Apparently the negative bands are emitted by the stable ions. A. A. ELDRIDGE.

Action of visible light on electrodes. R. AUDUBERT (J. Phys. Radium, 1925, [vi], **6**, 313—322).—*E.M.F.* measurements have been made with cells containing aqueous electrolytes and two identical electrodes, one of which was illuminated by an arc or tungsten lamp. With pure metals when no contaminating surface films are present, the effect is instantaneous, and the illuminated electrode is anodic with platinum, copper, and mercury, and cathodic with gold or silver, but platinum is greatly influenced by the exact method of preparation. The photo-voltaic effect is diminished by an increase in the solution pressure of the cation of the electrolyte, and increases with the frequency of the exciting radiation. No effect is produced below a limiting frequency, which increases as the metal becomes more electro-positive, but platinum forms an exception to both rules. A positive polarisation of the electrode diminishes the photo-voltaic effect of platinum, copper, and mercury, and increases that of gold and silver. A negative polarisation acts oppositely, and by artificial polarisation the sign of the photo-effect may be reversed. Electrodes covered by thin films such as copper oxide or bromide, and silver sulphide or chloride, show complex results differing from those for pure metals. The theory of Athanasiu (A., 1924, ii, 239) is criticised, and the results are ascribed to the existence of an electrical double layer at the liquid–metal surface, and to a photo-electric effect causing dissociation into free ions and electrons. According to the relative sign of the charge on the metal, either electrons or free ions leave the latter, and both positive and negative photo-voltaic effects are thus accounted for. W. Hume-Rothery.

Secondary emission from a nickel surface due to slow positive ion bombardment. A. L. Klein (Physical Rev., 1925, [ii], **26**, 800—806).—When positive ions from heated aluminium phosphate are accelerated on to a nickel target, the percentage saturated secondary electron emission increases approximately as the square of the primary ion energy. There are many reflected positive ions of energy 0—2 volts, and a group having about 0·9 of the primary energy. A. A. Eldridge.

Peculiar effect in the bombardment of platinum with slow electrons. E. Rudberg (Medd. k. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 12, 1—9).—Illumination of a platinum plate which is being bombarded with slow electrons results in a small decrease in the secondary emission, the magnitude of which is not influenced to any marked extent by the speed of the primary electrons. If the platinum has been previously heated at a fairly high temperature, the illumination effect is at first not perceptible, but gradually returns. The effect is not confined to any particular radiation and appears to be thermal in character.

J. S. Carter.

Attempt to excite a mercury surface by electron bombardment. H. R. Moore (J. Amer. Chem. Soc., 1925, **47**, 2932—2933).—The effects of a *P.D.* of 240 volts between a hot-wire filament (*e.g.*, platinum, tungsten) and a mercury surface in an evacuated vessel were observed (cf. Moore and Noyes, A., 1924, ii, 748), oxygen being admitted a fraction of a second before the filament current was turned off. Crinkling of the surface occurred when the oxygen was at pressures of 7—30 cm., even when admission was made 5 min. after stopping the filament current. This is probably due to the formation of a unimolecular layer of mercuric oxide which retains mechanically electrons received from the filament. Removal of the oxygen caused restoration of the surface; with readmission, the crinkling reappeared, often more pronounced. The surface layer of atoms probably suffers local alteration during the process, since the spilling of one drop of mercury renews the surface completely. Reversal of the field often produced positive results with oxide-coated platinum and thoriated tungsten filaments, showing that the phenomenon is "composite" and does not differentiate sharply between activation of the gas and excitation of the surface.

S. K. Tweedy.

Equilibrium of the calcium chromosphere. E. A. Milne (Month. Not. Roy. Astr. Soc., 1925, **86**, 8—28).—In an earlier paper (A., 1925, ii, 628), the equilibrium of the high-level calcium atoms in the sun has been discussed on the assumption that they are supported against gravity by radiation pressure and that the calcium with one positive charge possessed only two stationary states of equal statistical weight. The discussion is extended without these restrictions. The value for the mean life in the excited state is now found to be $1·8 \times 10^{-8}$ sec. if there are only two stationary states, but if one of these states is double a further correction leads to the value $1·3 \times 10^{-8}$ sec. The calculated value of the residual intensity in the infra-red lines is about ten times that in the hydrogen and potassium lines, and they ought to be ten times brighter than the hydrogen and potassium lines in the flash spectrum at low levels. E. B. Ludlam.

Mobility of negative ions in petroleum, hydrogen, and hydrogen–chlorine flames. P. E. Boucher (Physical Rev., 1925, [ii], **26**, 807—819).—The mobility of negative ions in a hydrogen flame increases, and in a petroleum flame decreases, with rise of temperature. The mobility is decreased, to a progressively less extent, by the addition to the flame of chlorine, bromine, chloroform, carbon tetrachloride, ammonium chloride, or iodine. The mobility in a hydrogen–chlorine flame is increased by addition of sodium chloride, sodium carbonate, or potassium chloride. Temperature and potential changes probably affect the mobility of the ion by influencing the formation of clusters. A. A. Eldridge.

Life-period of ionium. O. Koblic (Chem. Listy, 1925, **19**, 389—391).—The average life-period of ionium has been found to be 29,000 years from comparison of the intensity of a saturated current from the ionium of a sample of pitchblende containing 63—65% of uranium with that of a saturated current from ionium–thorium oxide, if the ratio of ionium to thorium in the latter is assumed to be 3 : 7 (Hönigschmidt). A. R. Powell.

Absorption of β-rays by matter. (Mme.) J.-S. Lattès and G. Fournier (Compt. rend., 1925, **181**, 1135—1136; cf. A., 1925, ii, 176, 622; this vol., 5).—The primary β-rays emitted by radium in equilibrium with its degradation products, like the secondary rays previously examined, obey the general law $\mu/\rho = a + bN$, where N is the atomic number of the absorbing element, and a and b are constants varying with the character of the rays. Values of a and b are given for three principal groups of the primary β-rays now examined. The ratio a/b is found to be constant for all cases examined, and is equal to 105. The general law may therefore be written $\mu/\rho = b(105 + N)$. S. I. Levy.

β-Ray spectra of radioactinium and its disintegration products. O. Hahn and (Frl.) L. Meitner (Z. Physik, 1925, **34**, 795—806).—Radioactinium was separated from its decomposition products and its β-ray spectrum obtained. The spectrum was then obtained after successive intervals of time and thus the lines were determined which were due to the products, actinium-*X* and the active deposit. These lines were compared with those obtained from pure actinium-*X* with the active deposit, and finally compared with those for the active deposit alone. The numbers of lines measured were, for radioactinium 49, for actinium-X 21, for the deposit 9, the investigation of the last being incomplete.

E. B. LUDLAM.

γ-Radiation of the actinium series and evidence that the γ-radiation emission follows the disintegration of the atom. (FRL.) L. MEITNER (Z. Physik, 1925, **34**, 807—818; cf. preceding abstract).—It is maintained that the γ-radiation does not come from the original nucleus, but results from the disturbance caused by the loss of an α- or a β-particle. The energies and the wave-lengths of the γ-rays from radioactinium, actinium-X, and actinium-C'' are calculated and show agreement with the values to be expected from the resultant atom, and not from the original atom. For γ-rays of great energy, the photo-electric emission of an electron takes place only in the level from which the work of emission is greatest, as from the L to the L_1 level. The calculation of the probability of absorption of K-radiation inside the atom, as estimated from the visual intensities of the lines, gives a value of the order of 10%.

E. B. LUDLAM.

Continuous spectrum and the γ-ray spectrograph of J. Thibaud. A. PICCARD (J. Phys. Radium, 1925, [vi], **6**, 334; cf. Thibaud, *ibid.*, 1925, **6**, 82; A., 1925, ii, 257).—The continuous background observed by Thibaud (*loc. cit.*) in the spectra of secondary β-radiation may be due to absorption of the radiation by the secondary radiator, consisting of a strip of metal. The use of a very thin strip of metal might overcome this defect.

W. HUME-ROTHERY.

Secondary γ-ray spectra: the origin of the continuous background and the variation of the relative intensity of rays. J. THIBAUD (J. Phys. Radium, 1925, [vi], **6**, 334—336; cf. preceding abstract).—The retardation of β-rays of known velocity by thin sheets of aluminium has been studied, and may be expressed by the equation $\Delta(RH)/RH=-0{\cdot}5x$, where x is the thickness of the sheet in mm. ($x<0{\cdot}08$) and RH is in cm. gauss. The continuous background in the spectra of secondary β-radiation cannot be ascribed solely to retardation by the secondary radiator as suggested by Piccard (*loc. cit.*), but is due to a continuous γ-radiation of which the origin may be nuclear, but is probably due to degradation of the quantum by the Compton effect. With radium-C, the relative intensity of neighbouring γ-rays in the natural β-radiation is quite different from that in the artificially excited β-radiation.

W. HUME-ROTHERY.

Transmutation of elements. Lead. A. SMITS (Nature, 1926, **117**, 13—15).—The silica-lead lamp used is described and illustrated; in the lead employed, mercury or thallium could not be detected analytically, neither could either of these metals be detected spectroscopically in the various parts of the lamp. A comparison of the initial spectrum of the lead, the spectrum of mercury, and the spectrum of the lead after burning the lamp at 40 amp. and 80 volts for 10 hrs., indicated a transmutation of lead into mercury and thallium. Spectra showing a much stronger transmutation were obtained, all the mercury lines being present, when sparking was employed to obtain high current densities. Extended observation was difficult on account of the formation of a film of lead silicate, blackened by silicon, but the difficulty was overcome by modification of the apparatus.

In another method, lead was dispersed by sparking in a liquid dielectric; the lead in colloidal solution was converted into nitrate, the fine deposit of metallic lead being collected separately. The dispersed lead, but not the lead electrodes, gave a reaction for mercury when material volatile in air was heated in iodine vapour.

A. A. ELDRIDGE.

Absorption by scattering of hydrogen positive rays by passage through hydrogen and helium. R. CONRAD (Z. Physik, 1925, **34**, 73—99).—The absorption of hydrogen positive rays by passage through hydrogen and helium at a pressure of 0·05 mm. and for velocities of about 2×10^8 cm./sec., is chiefly caused by scattering. The coefficient of scattering is directly proportional to the pressure and inversely proportional to the fourth power of the velocity, for pressures below 2×10^{-4} mm.

E. B. LUDLAM.

Structure of tin. H. COLLINS (Chem. News, 1925, **131**, 403—405).—Speculative.

Magnetic evidence of the distribution of electrons in the inner M_{32} and M_{33} levels in atoms of the elements of the first transition group. D. M. BOSE (Z. Physik, 1925, **35**, 213—218).—From magnetic evidence, it is deduced that in the elements from scandium to iron the M_{33} level fills up and from cobalt to copper the M_{32} sub-group is formed. With the exception of cobalt and nickel, the calculated values agree with spectroscopic data.

E. B. LUDLAM.

Application of the correspondence principle to relative intensities in series spectra. F. C. HOYT (Physical Rev., 1925, [ii], **26**, 749—760).—A discussion of the representation of intensities in emission and absorption in terms of the probabilities of transition and of the estimation of the probability of spontaneous transition based on the correspondence principle. The relative probabilities of the transitions involved in the principal series of sodium are computed, and compared with experimental determinations.

A. A. ELDRIDGE.

Interpretation from the correspondence principle of the spontaneous appearance of spectral lines of the type *ms–md*. G. JOOS (Physikal. Z., 1925, **26**, 729—730).—Theoretical. An explanation of the appearance of the forbidden lines $1s$—$3d$ of potassium is put forward. The fact that the changes of k, the azimuthal quantum number, are not equal to ±1 is connected with the assumption that the angular velocity of rotation of the perihelion depends on the angle made by the axis of the orbital ellipse and a fixed direction in the core. This idea implies that the core is not spherical.

R. A. MORTON.

Forces due to radiation. L. BRILLOUIN (Ann. Physique, 1925, [x], **4**, 528—586).—The mathematical theory of the forces exerted by a wave on a surface on which it is incident has been developed. These forces are given by the mean values of the tensor of the elastic forces and the flux of the "quantity of movement." Expressions for these as functions of the energy density in the medium and the wave velocity have been deduced for waves of compression in a fluid, and for longitudinal and transverse waves in an elastic solid. It is possible to base a theory of the solid state on these expressions, by regarding the thermal agitation in a solid as composed of a system of elastic waves passing in all directions, and exerting pressure on the walls. A. B. MANNING.

Relative sizes of atoms and ions. RITA BRUNETTI (Atti R. Accad. Lincei, 1925, [vi], **2**, 410—415).—It follows from the assumptions previously made to explain the displacement of the limit of the *X*-ray lines which occurs when an atom passes from the free state into the combined state, that the relative size of the atom and its ion should be related to the changes in the number of electrons in the shell as a result of combination. The formula which was derived for these changes has been tested by the insertion of experimental data for the spectral displacements and the lattice potentials for a number of alkali halides and the alkaline-earth sulphides. The results indicate that the ions of the alkali metals have smaller volumes than the free atoms, and that the volumes of the negative ions of the halogens and of metalloids are greater than those of the atoms. It is further shown that the explanation of the displacement of the limit of the *X*-ray lines as the result of ion formation followed by the introduction of the ion into the crystal lattice accounts for the regularities shown in Lothar Meyer's curve of atomic volumes, and for Grimm's curve illustrating the periodicity of ionic radii (A., 1922, ii, 635). F. G. TRYHORN.

Radii of atoms and ions. W. P. DAVEY (Chem. Reviews, 1925, **2**, 349—368).

Striated discharge in hydrogen. A. BRAMLEY (Physical Rev., 1925, [ii], **25**, 794—799).—The potential distribution, electron concentration, and mean electron energy at eleven points were determined at pressures of 0·625, 0·20, 0·09, and 0·02 mm. A. A. ELDRIDGE.

Critical potential of the negative band spectrum of nitrogen. E. E. WITMER (Physical Rev., 1925, [ii], **26**, 780—785).—The experimental results indicate that the negative band spectrum appears as a whole at the ionisation potential of nitrogen, or between that and 18 volts. A. A. ELDRIDGE.

Infra-red spectra of certain elements. J. C. MCLENNAN, H. G. SMITH, and C. S. PETERS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 39—50).—The spectra of nitrogen and carbon monoxide have been investigated in the region 6000—9000 Å., but no evidence was obtained in support of Nagaoka's suggestion (A., 1923, ii, 594) that these spectra should be approximately the same. New lines have been found in the arc spectrum of mercury in the near infra-red. A number of new lines have been observed in the arc spectrum of gold and tellurium in the red and near infra-red regions. J. S. CARTER.

Band spectra and electronic configuration of nitrogen and carbon monoxide molecules. H. NAGAOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1923, **1**, 125—133).—The data obtained by different investigators for the band spectra of nitrogen and carbon monoxide have been compared and show a close resemblance. Since the band spectra are probably due to molecules, this confirms the similarity of electronic configuration of the molecules of the two gases suggested by their striking resemblance in other physical properties. The line spectra, which are due to atoms, differ from one another. The possibility that the electrons of the molecule may be arranged as a space lattice, forming a face-centred cube with the two nuclei in the centre, is discussed. This arrangement, and also Langmuir's arrangement, would probably result in a ratio of specific heats of 1·67, instead of 1·40 as is actually the case. An arrangement of two cubes with a common edge, allowing the possibility of rotation of the molecule as a whole, is therefore suggested. M. S. BURR.

Flashing of certain types of argon–nitrogen discharge tubes. W. CLARKSON (Proc. Physical Soc., 1925, **38**, 10—15; cf. *ibid.*, 1924, **37**, 130).—The discharge tubes were filled with argon–nitrogen mixtures to pressures of 0·2—45·0 mm., and since the electrodes were only 1—2 mm. apart, the positive column was absent, and only the negative glow apparent. The observations are in general agreement with those obtained previously on neon and air discharge tubes. At pressures below 20 mm., the flash was the normal glow discharge, but at higher pressures the discharge was an arc. For a constant pressure, both the upper and low critical voltages for steady discharge, and the apparent critical voltages for continuous flashing, were constant for any one tube. Minor differences between tubes are discussed. C. J. SMITHELLS.

Band spectra of aluminium. G. ERIKSSON and E. HULTHÉN (Z. Physik, 1925, **34**, 775—787).—The spectrum of the aluminium arc in air and in hydrogen has been photographed under high dispersion. The arc in air shows intensive bands, degraded to the red, which are probably to be assigned to an AlO dipole molecule. In hydrogen, a weaker hydride band spectrum appears, degraded towards the red, with heads at 4067, 4241, 4354, and 4568 Å. This spectrum has been fully measured and analysed into a band system (ν_0=23,477). The moment of inertia of the unexcited AlH molecule is given as $1{\cdot}54\times10^{-40}$ g./cm.^{2}, and the distance between the atomic centres as $0{\cdot}984\times10^{-8}$ cm. S. BARRATT.

Absorption spectrum of manganese vapour in the visible and ultra-violet. R. V. ZUMSTEIN (Physical Rev., 1925, [ii], **26**, 765—770).—Thirty-one manganese absorption lines between 5394·07 and 1995·1 Å. are tabulated, with their intensities. The relatively small number of intense lines, and the occurrence of groups consisting of one, two, or three lines, indicate that all the absorptions are from manganese in the normal state (1^6s term); $1^6s—{}^6d'$, $1^6s—{}^8p$, $1^6s—{}^6p$, and possibly $1^6s—4p$ and $1^6s—2p$, combinations are represented. A. A. Eldridge.

Band spectra of mercury. H. Nagaoka (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1922, **1**, 1—6).—A new form of lamp for exciting the mercury band spectra is described, and various methods of analysis of the fine structure of the bands are discussed. M. S. Burr.

Change in the infra-red absorption spectrum of water with temperature. J. R. Collins (Physical Rev., 1925, [ii], **26**, 771—779).—Maximum absorption of the bands was observed for 0° at 0·775, —, 0·985, 1·21, 1·45, and 1·96 μ; for 95° at 0·74, 0·845, 0·97, 1·17, 1·43, and 1·94 μ, rise of temperature being accompanied by an increase in the maximum absorption for the bands at 0·77, 0·98, and 1·21 μ. The results are in conformity with the supposed presence of molecules $(H_2O)_2$ and $(H_2O)_3$. A. A. Eldridge.

Infra-red absorption spectra. Solutions of nitrogen pentoxide and nitrogen tetroxide in organic liquids. F. Daniels (J. Amer. Chem. Soc., 1925, **47**, 2856—2866).—The absorption bands of nitrogen pentoxide between 2 and 7 μ are not shifted by the process of dissolution in organic liquids (*e.g.*, chloroform, dichloroethane). Slight shifts (0·05 μ) in the maxima may be attributed to concentration effects. Dissolution of nitrogen tetroxide in organic liquids, however, causes the absorption maxima to shift from 5·65 to 5·45—5·30 μ. The results do not support the radiation hypothesis of chemical action. It is considered that the relative position of the electron pair between the atoms of a molecule determines the infra-red absorption spectra of the latter. S. K. Tweedy.

Infra-red spectra of solutions. O. Reinkober (Z. Physik, 1925, **35**, 179—192).—The substances examined were water, methyl, ethyl, and propyl alcohols, glycerol, and concentrated solutions of ammonium chloride in these solvents. The region was from 2 to 9·5 μ. The reflexion spectra of the aqueous solution of ammonium chloride and of potassium nitrate were also examined in the same region. The frequency of internal vibration of the cation increases in solution, the opposite of the effect for the anion. The effect was the same in the different solvents. E. B. Ludlam.

Light absorption and emission phenomena in anthracene. N. S. Capper and J. K. Marsh (J. Amer. Chem. Soc., 1925, **47**, 2847—2850).—Whereas pure, white, sublimed anthracene exhibits no selective absorption in phenetole and in chloroform solutions, recrystallised anthracene slightly tinted yellow by chrysogen exhibits absorption bands at 475, 445, 418, and 397 μμ, the last two being very weak (cf. Morton, Chem. News, 1872, **26**, 199). The bands at 475 and 445 μμ are, therefore, due to chrysogen, and Taylor and Lewis' deduction that dianthracene should absorb light at 707 μμ becomes erroneous (cf. A., 1924, ii, 580). The absorption observed by these authors at this wave-length may be due to the solvent, phenetole, since many benzenoid substances show well-marked absorption at this wave-length (Russell and Lapraik, J.C.S., 1881, **39**, 168) and fluorene and phenanthrene lose all visible fluorescence on careful purification. Pure anthracene polymerises as readily as the yellow-tinted specimens. This is due to absorption of light in the region of the four most characteristic bands (310—375 μμ) and not of light of wave-length 445 and 475 μμ (Taylor and Lewis, *loc. cit.*). The absorption and fluorescence spectra of chrysogen are similar to those of anthracene, but occur at higher wave-lengths. Apparently the green fluorescence of chrysogen depends for its stimulation on the potential emission of fluorescent light by anthracene. The fourth fluorescence band of pure anthracene in the red region, found by Morton, was not observed. S. K. Tweedy.

Influence of different nuclei on the absorption spectra of substances. J. E. Purvis (J.C.S., 1925, **127**, 2771—2776; cf. *ibid.*, 1914, **105**, 590, 1372).—The ultra-violet absorption spectra of a number of substances containing benzene nuclei have been examined in alcoholic solution. The bands of phenyl, benzyl, thymol, and camphor salicylates are comparable with those of salicylic acid, differing chiefly in position and strength, *i.e.*, only one of the nuclei shows specific absorption. The salicylates of theobromine, caffeine, phenazone, and quinine show much larger variations, but least in the quinine compound. *o*-Acetoxybenzoic acid approaches the behaviour of benzoic acid, showing that the replacement of the hydrogen of hydroxyl by another radical not possessing any specific absorption tends to nullify the effect of the hydroxyl group. The same influence is observed in the *o*-acetoxybenzoates of theobromine and quinine. In the specific absorption of the benzoate, citrate, and hydrochloride of caffeine, the basic nucleus is the chief agent. The results indicate that the specific and general absorption depend on the nature of the base, the nature of the acid, and the presence of hydrogen in hydroxyl, the vibration of the hydrogen evidently being an important factor in the absorption. M. S. Burr.

Absorption of light by hæmatoporphyrin. III. L. Kajdi (Biochem. Z., 1925, **165**, 475—496).—The change of the position of the absorption bands of acid hæmatoporphyrin does not depend on the concentration of acid if alcohol is present in fairly large concentration. The absorption bands of alkaline hæmatoporphyrin also change their position with changing concentration of solvent. If hæmatoporphyrin is dissolved in aqueous alkali, ethyl or amyl alcohols, ether, alcoholic acid or alkali, and the solutions are placed in sunlight, a new band (sometimes two) appears in the red. Solutions in aqueous acid do not give new bands under these conditions. By contact with rubber, the many-banded spectrum of hæmatoporphyrin, whether dissolved in pure alcohol, in acetic acid and alcohol, or in aqueous alkali, changes into a two-banded spectrum, with or without exclusion of air, in dark or in light. The substance contained in the rubber causing this change can be extracted by alcohol. Hæmatoporphyrin solutions in which new bands have appeared by the action of sunlight, on contact with rubber give a two-banded spectrum which cannot be reverted to its original form by re-exposure to sunlight.

P. W. Clutterbuck.

Photographic spectrophotometry. H. B. Dorgelo (Physikal. Z., 1925, **26**, 756—794).—A summary of recent work with bibliography. The following matters, amongst others, are discussed: the laws of darkening of photographic plates, intensity measurements in groups of lines, light sources and distribution of energy throughout the spectrum, photomicrometric apparatus. R. A. Morton.

Spectro-chemistry of compounds containing nitrogen. K. von Auwers and R. Kraul (Z. physikal. Chem., 1925, **118**, 304).—Corrigenda to a previous paper (A., 1925, ii, 847).

L. F. Gilbert.

Three-dimensional method of representing quantum transitions in band spectra. H. B. Lemon and C. M. Blackburn (Astrophys. J., 1925, **62**, 61—64).—A three-dimensional representation of transitions corresponding with radiations in band spectra constructed for the case of the first negative Deslandres system associated with carbon is described.

A. A. Eldridge.

Fluorescence of cadmium vapour. A. D. Power (Physical Rev., 1925, [ii], **26**, 761—764).—The freshness of the vapour primarily determines the intensity of the lines 3262 Å. ($1S-2p_2$), 4678 Å. ($2p_3-1s$), 4800 Å. ($2p_2-1s$), 5086 Å. ($2p_1-1s$), and 2289 Å. ($1S-2P$), when excited by light of wavelength<3300 Å. The presence of thallium and indium as impurities was revealed by fluorescence lines, but not by the spark. A. A. Eldridge.

Polarisation of fluorescent light from solutions of dyes. P. Fröhlich (Z. Physik, 1925, **35**, 193—206).—The degree of polarisation is considerable only for liquids of high viscosity, but it is not the same for different solutions of the same viscosity. Freezing the solution does not alter the degree of polarisation. In some cases, the solvent also fluoresces and the light emitted is polarised. In all cases examined, the degree of polarisation was different for different wavelengths of the exciting light. E. B. Ludlam.

Luminescence spectra of Geissler tubes. A. Bjelopolski (Bull. Acad. Sci. Russie, 1918, [6], 1033—1046; from Chem. Zentr., 1925, II, 266—267).—The spectrum obtained in the wide portions of a Geissler tube is so weak that it cannot be photographed unless the tube be heated by long-continued passage of a current. The discharge may, however, be deflected electromagnetically and concentrated on a screen. Spectra are thereby obtained which can be photographed. The spectra obtained in this way from tubes containing hydrogen resemble those obtained in the capillary portions of tubes filled with methane or benzene. Their lines coincide with those of the second hydrogen spectrum of Frost (Astrophys. J., 1902, **16**, 100), Watson, and Hasselberg (Mem. Acad. St. Pétersbourg, [8], **31**, Nr. 14). The hydrogen tubes used were 10—24 yrs. old.

G. W. Robinson.

Excitation of spectra of gases by chemical reaction. H. Fränz and H. Kallmann (Z. Physik, 1925, **34**, 924—950).—The mechanism and energetics of the production of luminosity in chemical reactions between gases are discussed, in particular the excitation of the mercury resonance line by the action of chlorine on sodium in the presence of mercury and its non-appearance when bromine is used. The work of Haber and Zisch (A., 1922, ii, 461) is confirmed and extended. The action of all three halogens respectively on mercury vapour produces only band spectra; the bands with chlorine are the same as those observed in the electrical discharge through mercuric chloride; those with bromine and iodine are different from the spectra excited electrically in the bromide and iodide. Traces of impurity in the sodium affect the spectra in a marked manner when very little chlorine is present. E. B. Ludlam.

Utilisation of luminescent and catalytic substances [*e.g.*, for *X*-ray screens]. P. L. G. Marcotte.—See B., 1926, 29.

Apparatus for direct registration of transparency curves of absorbing substances and of spectral effects. C. Müller (Z. Physik, 1925, **34**, 824—832).—The apparatus consists of a monochromator, photo-electric cell, and string galvanometer combined with a special sliding form of rotating sector. The special advantage of the arrangement is that points on the curves of absorption, sensitivity, intensity, and the zero point can be obtained in any desired order. Thus four transparency curves with five comparison lines for 50 wave-lengths can be registered in 30 min. With appropriate changes, the method can be extended to measurements in the infra-red and to *X*-rays. E. B. Ludlam.

Effect of ultra-violet light and *X*-rays on the stability of matter. A. L. Foley (Proc. Indiana Acad. Sci., 1925, **34**, 185—193).—Silica tubes containing carbon monoxide, krypton, neon, argon, bromine, chlorine, carbon monoxide, helium, hydrogen, iodine, nitrogen, oxygen, sulphur dioxide, water, or xenon, also glass tubes containing the above substances (with the exception of the first three), or the following elements in an atmosphere of nitrogen: aluminium, antimony, arsenic, barium, bismuth, cadmium, copper, magnesium, manganese, selenium, sulphur, or tin, in addition to control tubes, were exposed to ultra-violet light (silica tubes) or *X*-rays (glass tubes), the contents being periodically observed with the aid of an electrodeless discharge and photographs of the spectra. The results demonstrate the inadequacy of present knowledge of spectra; the electrodeless discharge gives results differing from those obtained in tubes containing electrodes. Mercury lines were usually present, but diminished in the presence of aluminium, arsenic, copper, or tin. Exposure of metals to *X*-rays liberates little or no gas. With continued discharge, changes in the spectra were observed similar to those previously ascribed to phenomena connected with the presence of electrodes. CHEMICAL ABSTRACTS.

Energy levels of the nitric oxide molecule. H. SPONER (Nature, 1926, **117**, 81).—Evidence is adduced showing that the third positive group of nitrogen bands belongs to the nitric oxide molecule. The excitation potentials of the levels of the nitric oxide molecule are 5·44 and 13·96 volts; hence the ionisation potential must be greater than 14 volts. A. A. ELDRIDGE.

Dielectric constants of liquids. I. Measurement of dielectric constants of liquids. Y. MATSUIKE (Sci. Rep. Tohôku Imp. Univ., 1925, **14**, 445—452).—An apparatus is described for the measurement of dielectric constants of liquids by means of the resonance of two high-frequency oscillating circuits in one of which the liquid under examination forms the dielectric of a fixed condenser. The dielectric constants of six liquids have been determined at 25° and the results are in fair agreement with those of other observers. A. E. MITCHELL.

Molecular volume and molecular refraction of mixtures of liquids. W. HERZ (Z. anorg. Chem., 1925, **149**, 270—272).—The rule formulated by Lorenz and Herz (A., 1925, ii, 356) connecting the molecular volume at absolute zero and the molecular refraction, also the generalisation V_0p_k/T_k=constant, where V_0 is the molecular volume at 0° Abs., T_k the critical temperature on the absolute scale, and p_k the critical pressure, have been extended to mixtures of liquids. R. CUTHILL.

Molecular and atomic volumes. VIII. Metaheulandites. W. BILTZ and F. SPECHT (Z. anorg. Chem., 1925, **150**, 10—19; cf. A., 1925, ii, 1141).—For measuring the volumes of partly dehydrated zeolites, a liquid is necessary which cannot replace the zeolithic water or enter the lattice, but which, nevertheless, wets the particles. Mercury was found suitable and a pyknometer was used which had a swan neck to prevent the solid rising to the open mouth. With a natural heulandite, the volume found was the same as when petroleum was used. When the heulandite was dehydrated, no change in volume occurred until the water content had fallen from 5·5 to 3 mol.; further dehydration caused at first a slow, and then a rapid, fall in volume. Zeolithic water thus causes no expansion of the lattice. When the volume was measured in petroleum, the decrease began with the beginning of dehydration, because this liquid can partly or wholly replace the zeolithic water. A. GEAKE.

Molecular and atomic volumes. IX. Hexahydrates of chromic and chromous chlorides. E. BIRK and W. BILTZ (Z. anorg. Chem., 1925, **150**, 20—25; cf. preceding abstract).—The molecular volumes of the three hexahydrates of chromic chloride and of chromous chloride hexahydrate were measured in petroleum. The molecular volume of the most stable of the chromic salts, the dark green dichlorotetra-aquochromic chloride dihydrate,

$$[CrCl_2(H_2O)_4]Cl,2H_2O,$$

is 145·2, that of the grey hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, is 148·1, and that of the least stable, the light green monochloropenta-aquochromic chloride monohydrate, $[CrCl(H_2O)_5]Cl_2,H_2O$, is 151·4. The molecular volume thus falls with increasing stability, as for organic isomerides, the difference for each pair being 2%. The molecular volume of chromous chloride hexahydrate is 129·6, and this corresponds with a volume of 14·5 for each mol. of water. The molecular volumes of the water in the chromic chloride hexahydrates are 14·7, 15·2, and 15·7, respectively, and the chromous chloride thus corresponds with the dark green chromic salt and may be formulated $[CrCl_2(H_2O)_4],2H_2O$. A. GEAKE.

Mechanically-enforced double refraction of amorphous liquids in relation to molecular configuration. D. VORLÄNDER and R. WALTER (Z. physikal. Chem., 1925, **118**, 1—30).—Experiments in which a large number of organic liquids and a number of aqueous solutions, principally of salts of organic acids, were subjected to mechanical forces by being placed inside a stationary metal cylinder in which a coaxial solid metallic cylinder of slightly smaller dimensions was rotated at a high speed, show that the organic liquids acquire a normal, and the aqueous solutions an anomalous, double refraction. The values of the specific double refraction, $[D]=D/\mu\eta$, where D is the observed double refraction, μ the rotational velocity, and η the viscosity, are tabulated. In general, when η is less than 5 no double refraction is induced. Consideration of the $[D]$ values for a series of fatty acids and their triglycerides shows that there is some connexion between the optical properties and length of carbon chain. With increasing number of carbon atoms, the $[D]$ values increase at first slowly, then rapidly, and finally attain what is apparently an upper limiting value. Introduction of side chains or lengthening of those already present causes a diminution in $[D]$. With benzene compounds, the $[D]$ values increase in passing from *o*- to *m*- to *p*-compounds.

The double refraction is greater for those substances possessing an ethenoid linking than for the corresponding saturated compounds. The mechanically produced double refraction of colloidal solutions is discussed, and it is shown that there is some connexion between $[D]$ and size of particles. J. S. CARTER.

Rotatory dispersion of nicotine. T. M. LOWRY and B. K. SINGH (Compt. rend., 1925, **181**, 909—911).—The rotatory dispersions of nicotine over the range 4046—6708 Å. are given by the formula $\alpha/\alpha_1=0{\cdot}2379/(\lambda^2-0{\cdot}06)$, where α_1 is the rotation for the mercury line 5461 Å., and are therefore "simple" (cf. Lowry and Dickson, A., 1914, ii, 786). S. K. TWEEDY.

Diamagnetic and paramagnetic rotation of the plane of polarisation. R. LADENBURG (Z. Physik, 1925, **34**, 898—906).—As a result of thermal agitation, the number of electrons rotating in opposite directions in the magnetic field is not equal; the consequent rotation of the plane of polarisation is calculated from the dispersion theory and from Langevin's theory of paramagnetism. E. B. LUDLAM.

Optical rotation of arabic acid and the alkali arabates. M. A. Rakusin (Biochem. Z., 1925, **160**, 285—287).—Arabic acid, prepared from gum arabic of $[\alpha]_D-24\cdot8^\circ$, had $[\alpha]_D-27\cdot86^\circ$; lithium arabate $[\alpha]_D-17\cdot81^\circ$; ammonium arabate $[\alpha]_D-19\cdot81^\circ$; sodium arabate $[\alpha]_D-21\cdot67^\circ$; potassium arabate $[\alpha]_D-23\cdot06^\circ$. E. C. Smith.

Relationship between optical rotatory powers and relative configurations of optically active compounds. II. Relative configurations of optically active mandelic acids and β-phenyl-lactic acids. G. W. Clough (J.C.S., 1925, **127**, 2808—2813).—On the basis of the rule previously deduced (A., 1918, ii. 255) that the introduction of the same substituent into similarly constituted, optically active compounds possessing the same relative configurations produces alterations of the same character in their optical rotatory powers, the configurations of the optically active forms of mandelic and β-phenyl-lactic acids have been investigated. The molecular rotations of the following compounds have been determined: *l*-mandelic acid and its ethyl ester, methyl *l*-phenylbenzoyloxyacetate, methyl *l*-β-phenyl-lactate, methyl *d*-α-acetoxy-β-phenylpropionate, and methyl *l*-α-benzoyloxy-β-phenylpropionate. These results, combined with those of other investigators, indicate that *l*-hexahydromandelic acid and *l*-mandelic acid belong to the "*d*"-series (*loc. cit.*) of α-hydroxy-acids. The configurations of *l*-benzoin, the related optically active glycols, and amygdalin can thus be confirmed with reference to that of *d*-tartaric acid. *d*-β-Phenyl-lactic acid may also be classed with the "*d*"-series of α-hydroxy-acids. It is therefore possible to assign configurations to the glycols from this acid, and also to the four optically active phenylglyceric acids, provided it is assumed that *cis*-addition of hydroxyl occurs on oxidation of the cinnamic acids. M. S. Burr.

Calculation of Verdet's constant in the molecular theory of magnetic rotatory polarisation. R. de Mallemann (Compt. rend., 1925, **181**, 1139—1141).—The constant Λ in its simplest form is expressed by $15\cdot82\times10^{-7}M(n-1)^2/dn$ for the sodium D-line. The calculated values show very good agreement with the values obtained experimentally by Perkin for a number of aliphatic compounds. The values of p, the number of effective electrons, assumed for the calculation, are for every case examined less by 4 than the accepted values of n, the number of valency electrons; hence the compounds examined appear to contain one atom of carbon less than they do in fact, and the free atom of carbon would have a zero value. S. I. Levy.

Valency theories and the magnetic properties of complex salts. D. M. Bose (Nature, 1926, **117**, 84).—If Z is the atomic number of the inert gas which terminates any transition group of elements, all those co-ordination compounds in which $Z=Z'(=N-E+2P$, where N is the atomic number of the co-ordinating atom, E its primary valency in the given compound, and P is 4, 6, etc., according as the complex compound is fourfold, sixfold, etc.) are diamagnetic, whilst the others are paramagnetic; the result is in agreement with that of Baudisch and Welo (A., 1925, ii, 943, 1031). Further, the number of Bohr's magnetons contained in any co-ordination compound of the first transition group of elements is $Z-Z'$, so far as magnetic properties have been studied. A. A. Eldridge.

Elements with anomalous valencies. M. Gomberg (Chem. Reviews, 1925, 2, 301—314).

Co-ordination and co-valency. J. A. V. Butler (Trans. Faraday Soc., Dec., 1925, advance proof).—Co-ordination as an effect associated with compound formation is to be distinguished from co-valency; it consists in the congregation around an ion of a number of units with unshared electron pairs forming a new and distinct group of electrons outside the filled or partly filled groups in the simple ion. The attachment of the co-ordinated group is not due to the tendency of the simple ion to attain the configuration of the next higher inert gas. The maximum number of co-ordination valencies are deduced on the basis of the Main-Smith and Stoner sub-groups and agree with those given by the Sidgwick rule. Using this definition of co-ordination, it is shown that orthophosphoric, sulphuric, and chloric acids are true co-valent compounds, whilst the oxy-acids of the transitional elements, vanadic, chromic, and manganic acids, are co-ordinated. These co-ordinated acids give reversible oxidation potentials, indicating that the processess of oxidation and reduction involve the simple gain and loss of electrons. This behaviour is quite different from that of the oxy-acids of the non-metals. F. G. Soper.

Nature of the chemical linking. Structure of silicon tetrachloride. G. Joos (Physikal. Z., 1925, **26**, 734—737).—Silicon tetrachloride may be regarded as four chlorine ions disposed tetrahedrally about a central silicon atom bearing four charges. The distance of each chlorine ion from the centre is taken from crystal data as 2·59 Å., and on this basis a value of 2847 cal./mol. is computed from electrostatic forces for the free energy. Spectroscopic and thermochemical data lead to a value of 2301 cal./mol. Accurate agreement requires the sphere including the four chlorine ions to be 7% greater than the value assumed from crystal data. The degree of agreement is regarded as justifying the idea of polar binding in this compound. R. A. Morton.

Regularity in the rare earths. G. von Hevesy (Z. anorg. Chem., 1925, **150**, 68; cf. A., 1925, ii, 938).—A numerical correction. A. Geake.

***X*-Ray analysis.** P. Günther and I. N. Stranski (Z. physikal. Chem., 1925, **118**, 257—275).—To test the possibility of the quantitative determination of alloys by means of the intensity of their *X*-ray spectrum, the influence of cobalt on the emission spectrum of nickel was investigated. It is shown that the ratio intensity Ni$K\alpha$/intensity Ni$K\beta$ is scarcely changed in the presence of cobalt and that the ratio intensity Co$K\alpha$/intensity Ni$K\alpha$ for a 50% alloy is nearly 1. Owing to the absorption of the Ni$K\beta_1$ line, the ratio intensity Co$K\beta_1$/intensity Ni$K\beta_1$ is greater than 1. It is deduced that where the presence of a second element strengthens or weakens the radiation in an approximately equal manner, quantitative data on the composition can be obtained from the emission spectrum. H. Terrey.

Discovery of eka-manganese elements. (Frl.) I. Tacke (Z. angew. Chem., 1925, **38**, 1157—1160; cf. A., 1925, ii, 939).—A description of the chemical separation of the elements masurium and rhenium in the work previously described. W. T. K. Braunholtz.

X-Ray examination of the inner structure of strained metals. IV. α-Iron plastically strained in extension, compression, and torsion. A. Ono (Mem. Coll. Eng. Kyushu, 1925, **3**, 267—286; cf. A., 1925, ii, 746).—The *X*-ray diffraction pattern of α-iron strained plastically in extension, compression, or torsion is in every case a series of rings having regularly oriented bright spots decreasing in intensity from the inner ring to the outer. The position of these spots has been analysed and shown to be due to the existence of two different kinds of symmetry in the strained crystal lattices. In the first kind, the rotation of the lattice during strain takes place about one of the axes in a definite direction, and in the second kind the lattice rotates about an axis which may occupy any position in a definite plane. In α-iron strained in extension, the symmetry is of the second kind, with the axis (110) more or less parallel to the direction of extension, whereas in the same metal strained by compression the symmetry may be of the first kind with the axis (111) in the direction of compression, or of the second kind with the axis of rotation (011) lying in the cross-sectional plane. In twisted α-iron, the second kind of symmetry exists with the plane (110), and probably also the plane (211), in the horizontal position. A. R. Powell.

X-Ray examination of the inner structure of strained metals. V. Mechanism of crystal rearrangement and the cause of strain-hardening. A. Ono (Mem. Coll. Eng. Kyushu, 1925, **3**, 287—305).—Mathematical. The mechanism of the crystal rearrangement of a strained metal is investigated by assuming that slip and rotation are the causes of distortion and that the direction of slip is constant for each kind of lattice. The calculated results agree closely with those deduced from *X*-ray diffraction patterns. The resistance to slip of a metal increases with a diminution in the grain size, and this agrees with the fact that fine-grained metals are usually much harder and stronger than those in which the crystals are relatively large. A. R. Powell.

Constitution of iron. F. Wever.—See B., 1926, 15.

Allotropy of chromium. A. J. Bradley and E. F. Ollard (Nature, 1926, **117**, 122).—A sample of chromium was found by *X*-ray examination to be a mixture of two allotropes. In the predominating form the atoms are arranged on two hexagonal lattices, giving an almost hexagonal close-packed structure, the axial ratio *c*/*a* being 1·625 instead of 1·633, and the distance between neighbouring atomic centres 2·714 and 2·705 Å. A. A. Eldridge.

X-Ray determination of arrangement of atoms in the gold–copper and palladium–copper mixed-crystal series. C. H. Johansson and J. O. Linde (Ann. Physik, 1925, [iv], **78**, 439—460).—The lattice structures of the compounds Cu_3Au and CuAu have been ascertained. Tammann's view (A., 1919, ii, 398) that slowly cooled mixed-crystal series always exhibit regular structure has been criticised by Masing (A., 1922, ii, 37) and others. It is now confirmed that regular arrangement of atoms does not normally occur in mixed-crystal series. In the gold–copper series, the quickly cooled alloys show the normal conductivity–composition curve with a minimum at 50% (Mathiesen). With the slowly cooled alloys, the conductivity reaches maximum values at points corresponding with the compounds CuAu and Cu_3Au. *X*-Ray photographs show that near the maxima there are superimposed structure effects, whilst in regions removed from the maxima these lines do not occur. Højendahl's theory of conductivity in mixed crystals (A., 1924, ii, 647) as extended by Borelius (A., 1925, ii, 749) is supported. An increase in electrical conductivity is not necessarily due to a change in the lattice type, but it is always bound up with an increase in regular arrangement of atoms. R. A. Morton.

Lattice parameter and density of tungsten. W. P. Davey (Physical Rev., 1925, [ii], **26**, 736—738).—Earlier values for the lattice parameter ($a=3·155\pm0·001$) and *d* ($19·32\pm0·02$) of tungsten (99·999% pure) have been confirmed. A. A. Eldridge.

Arrangement of micro-crystals in rolled platinum plate. S. Tanaka (Mem. Coll. Sci. Kyōtō, 1925, **9**, 197—217; cf. *ibid.*, 1925, **8**, 319).—The examination by means of *X*-rays of platinum foil rolled in one direction only shows that the normal to the trapezohedral face of the micro-crystals is inclined about 10° to the direction of rolling, in the plane containing the direction of rolling and the normal to the rolled surface. E. B. Ludlam.

X-Ray examination of some ammonia catalysts. R. W. G. Wyckoff and E. D. Crittenden (J. Amer. Chem. Soc., 1925, **47**, 2866—2876).—Various iron oxides and catalysts have been investigated by the *X*-ray powder method. The unit cube of magnetite has an edge of 8·37 Å.; if excess of ferrous iron is present, it appears as a separate phase, which disappears when an equivalent amount of alumina, silica, or zirconia (promoters) is added. With alumina, ferrous aluminate is formed and enters into solid solution, whilst the composition of the oxide tends towards that of ferroso-ferric oxide. The unit cube of magnetite containing potassium aluminate differs but little in size from the unit cube of ferroso-ferric oxide, and it is impossible to say whether or not solid solution occurs. Promoters maintain a large surface of iron in catalysts by inhibiting sintering of the reduced metal, so that the crystals of the latter grow only very slowly. α-Iron obtained by the reduction of magnetite has a unit cube of edge 2·859 Å.; if promoters are added before reduction, iron is obtained with unit cells differing in size by less than 0·1% from those of pure iron.

S. K. TWEEDY.

Crystal structures of sodium and potassium trinitrides and potassium cyanate and the nature of the trinitride group. S. B. HENDRICKS and L. PAULING (J. Amer. Chem. Soc., 1925, **47**, 2904—2920).—The rhombohedral unit of sodium trinitride (d 1·853) contains 1 mol. and has $\alpha=38° 43'$ and $a=5·481$ Å.; the sodium atom is at (0, 0, 0) and the nitrogen atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, (u, u, u), and $(\bar{u}, \bar{u}, \bar{u})$, where $u=0·423$. The tetragonal unit of potassium trinitride (d 2·038) contains 4 mol. and has $a=6·094$ and $c=7·056$ Å.; the potassium atoms are at $(0, 0, \frac{1}{4})$, $(0, 0, \frac{3}{4})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$, whilst the nitrogen atoms are at $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$; $(u, \frac{1}{2}+u, 0)$, $(\frac{1}{2}-u, u, 0)$, $(\bar{u}, \frac{1}{2}-u, 0)$, $(\frac{1}{2}+u, \bar{u}, 0)$; $(\frac{1}{2}+u, u, \frac{1}{2})$, $(u, \frac{1}{2}-u, \frac{1}{2})$, $(\frac{1}{2}-u, \bar{u}, \frac{1}{2})$, and $(\bar{u}, \frac{1}{2}+u, \frac{1}{2})$, where $u=0·135$. The unit for potassium cyanate, which is very similar in structure to potassium trinitride, has $a=6·070$ and $c=7·030$ Å.; the true structure was not deduced. The trinitride ion consists of a linear arrangement of three nitrogen atoms; two alternative electronic configurations are given. The azide group probably has the same collinear structure. The acid fluoride ion has a structure similar to that of the trinitride and cyanate ions.

S. K. TWEEDY.

Preparation and crystal structure of ferrous oxide. R. W. G. WYCKOFF and E. D. CRITTENDEN (J. Amer. Chem. Soc., 1925, **47**, 2876—2882).—A ferrous oxide was prepared by saturating electrically fused magnetic oxide with iron, the uniform interior product being freed from excess of iron by electromagnetic separation. The oxide, which is free from ferric iron, is practically non-magnetic (susceptibility=0·00052 per g.). The crystal unit, which is a cube of edge 4·29 Å., contains four molecules and has the sodium chloride structure giving a calculated d of 5·99. When much magnetite is present, the unit cube is slightly larger, but there is no evidence of solid solutions being formed at the ordinary temperature.

S. K. TWEEDY.

Hydroxides of aluminium and iron. I. J. BÖHM (Z. anorg. Chem., 1925, **149**, 203—216; cf. A., 1924, ii, 310).—The naturally-occurring hydroxides have been compared with artificially prepared hydroxides by the X-ray method of Debye and Scherrer (A., 1917, ii, 437). Bonsdorff's aluminium hydroxide (Ann. Phys. Chem., 1833, **27**, 275) is identical with hydrargillite. Aluminium hydroxide gels precipitated from cold solutions give no interference effects, but those from hot solutions give the same figure as bauxite, especially if allowed to age under boiling water. Bauxite gives a characteristic figure, which from its analogy to that of ruby mica indicates the formula of bauxite to be Al_2O_3,H_2O, and this hydrate has been prepared artificially. Sols of aluminium hydroxide give the bauxite figure after long boiling.

All the naturally-occurring hydroxides of iron except ruby mica consist of impure göthite. Ferric hydroxide gels appear to contain no crystalline hydroxide, unless they are heated with $2N$-potassium hydroxide at 150°, when the göthite figure appears. Ferric hydroxide sols give a figure corresponding with a basic salt, but the deposit from old sols consists of göthite.

R. CUTHILL.

Incandescence of certain metallic oxides. J. BÖHM (Z. anorg. Chem., 1925, **149**, 217—222).—The change undergone by the oxides Sc_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2, Nb_2O_5, and Ta_2O_5 when they are ignited, which is apparent as sudden incandescence and results in the oxides becoming insoluble in acids, is shown by X-ray methods to be accompanied by a change in structure from amorphous to crystalline. The behaviour of explosive antimony is due to the same cause.

R. CUTHILL.

X-Ray analysis of some mixed crystals of the silver halides. R. B. WILSEY (J. Franklin Inst., 1925, **200**, 739—746).—An X-ray analysis has been made, using the Hull powdered crystal method, of the series of mixed crystals of silver chloride with silver bromide, and of silver bromide with silver iodide. The silver chloride–silver bromide mixtures showed the simple cubic structure (sodium chloride type) characteristic of the pure components, with a lattice spacing lying between those of the two components, and showing a linear relationship to the molar composition of the mixed crystals. Most of the silver bromide–silver iodide mixtures showed the existence of two mixed crystals, one the simple cubic type characteristic of pure silver bromide, but with an enlarged lattice spacing, and the other the diamond cubic or hexagonal type of the silver iodide crystal, with a slightly diminished lattice constant. In mixtures up to and including 70 mol.% of silver iodide, the simple cubic structure predominated, its lattice spacing increasing with the percentage of silver iodide fused in the mixture. Silver iodide appears to go quite readily into the silver bromide lattice, the calculations indicating that the largest simple cubic structure observed contained as much iodide as bromide. Judging by the effect on the lattice constant of the silver iodide structure, very little silver bromide entered the silver iodide lattice. Beyond 70 mol.% of silver iodide its own structure predominated in the mixture, and the lattice spacing of the simple cubic structure diminished, owing to a smaller fraction of the silver iodide entering the silver bromide lattice. The prediction of Trivelli (Rec. trav. chim., 1923, **42**, 714) that the incorporation of silver iodide would be found to enlarge the silver bromide lattice was verified. It seems likely that this enlargement is connected in some way with the increased speed obtainable in photographic emulsions of silver bromide containing small percentages of silver iodide.

F. G. TRYHORN.

Isomorphism of the molybdates of the rare-earth metals with those of calcium, strontium, barium, and lead. F. ZAMBONINI (Atti R. Accad. Lincei, 1925, [vi], **2**, 377—383; cf. A., 1925, ii, 1133).—Values of the angles and intensities of X-ray reflexions from crystals of the molybdates of lanthanum, cerium, praseodymium, neodymium, and samarium are tabulated.

F. G. TRYHORN.

Influence of the lanthanide contraction on the lattice dimensions of the cubical platinum metals. T. Barth and G. Lunde (Z. physikal. Chem., 1925, **117**, 478—490).—Precision measurements of the lattice constants of rhodium, iridium, palladium, and platinum were made by Wyckoff's method (Z. Kryst., 1923, **59**, 55). The increase in the lattice constants in passing from rhodium to iridium and from palladium to platinum only partly compensates for the decrease in the lattice constants of the rare earths in the same vertical series.

The length of the side of the unit gold cell, as determined by the Debye–Scherrer method, is 4·05 Å.

L. F. Gilbert.

***X*-Ray reflexions from mercuric iodide.** R. J. Havighurst (Amer. J. Sci., 1925, [vi], **10**, 556—558; cf. A., 1925, ii, 17).—From measurements by the powder method, and by the reflexion of the tungsten *K*-series from single crystal faces, the values $c=12·34$, $a=6·16$ Å. are computed for the dimensions of the elementary cell, containing 4 mols. of mercuric iodide. A smaller unit cell, containing 2 mols., is obtained by the rotation of the x and y axes of the crystal through 45°. For this cell, $c=12·34$, $a=4·356$ Å. All the lines obtained by the powder method are accounted for by this cell. Calculated for this unit d is 6·405, as compared with the experimental value of 6·30. F. G. Tryhorn.

Arrangement of atoms in tetragonal crystals of the mercurous halides, and the calculation of the optical double refraction of mercurous chloride. E. Hylleras (Physikal. Z., 1925, **26**, 811—814).—A determination of the crystal structure of the mercurous halides by the Debye–Scherrer method gave the following results for the cell dimensions: mercurous chloride, $a=6·30$, $c=10·88$; bromide, $a=6·61$, $c=11·16$; iodide, $a=6·95$, $c=11·57$ Å. The elementary cells contain eight mercury and eight halogen atoms. The crystal lattice of these substances may be regarded as similar to that of sodium chloride in which each sodium atom is replaced by two mercury atoms, so oriented that the line joining them coincides with the c-axis, and its midpoint takes the place of the sodium atom. Each chlorine atom in the sodium chloride lattice is replaced in the mercurous halide lattice in an analogous manner by two halogen atoms, The parameters α and β were determined from measurements of the intensities of the *X*-ray reflexions. For all three compounds, α is between 42° and 45°, and β between 54° and 60°. The optical double refraction of mercurous chloride was calculated by applying the Born theory to the above crystal structure. The values of the parameters $\alpha=45°$, $\beta=60°$ gave satisfactory values for the principal refractive index, but values about 20% too low for the secondary index. Complete agreement between calculated and observed figures was obtained when $\alpha=45°$ and $\beta=54·30°$.

F. G. Tryhorn.

Varieties of thorium oxide and their catalytic action in the dehydration of alcohol. G. R. Levi (Atti R. Accad. Lincei, 1925, [vi], **2**, 419—422).—An *X*-ray examination has been made of specimens of thorium oxide prepared by different methods. The hydroxide precipitated and dried at temperatures up to 120° is amorphous, as is the oxide prepared by heating the hydroxide to 340°. By heating the hydroxide to 1050°, or the nitrate or oxalate to 750°, the oxides obtained are crystalline and identical in structure. The formation of the so-called "meta" oxide as a distinct variety by heating the nitrate or oxalate is disproved. The catalytic activity of thorium oxide in dehydrating alcohol is approximately equal for the crystalline and the amorphous forms.

F. G. Tryhorn.

Measurement of the four magnetic transverse effects. E. H. Hall (Physical Rev., 1925, [ii], **26**, 820—840).—A detailed description is given of the measurement of the Hall, Ettingshausen, Nernst, and Leduc effects, together with tabulated results for gold, palladium, nickel, and cobalt at various temperatures between 17° and 86°. A. A. Eldridge.

The magneton. W. Gerlach (Physikal. Z., 1925, **26**, 816—824).—A lecture summarising the present state and the theoretical and experimental development of the magneton theory.

F. G. Tryhorn.

Magneton number in complex compounds of some paramagnetic elements. D. M. Bose (Z. Physik, 1925, **35**, 219—223).—The number of Bohr magnetons in complex compounds of ferric iron, chromium, nickel, and copper is found to be equal to the difference between the atomic number of the noble gas at the end of the series, krypton, 36, and the "effective" atomic number of the central atom as defined by Sidgwick. E. B. Ludlam.

Magnetic properties of phosphors. E. Rüpp (Ann. Physik, 1925, [iv], **78**, 505—557).—An examination of the susceptibilities of a number of phosphors with partly diamagnetic and partly paramagnetic heavy metal atoms has been made, and the susceptibilities are co-ordinated with the central molecules and phosphorescent centres, the metal content, the phosphorescence bands, the temperature range of the phosphorescence, the susceptibility at low temperatures, the variation of susceptibility with the field strength, and the atomic magnetism of the heavy metal atoms. It is found that the central molecules of the mass (–CaS–, –CaO–) are more paramagnetic than the simple molecules (CaS, CaO) and that the central molecules are associated with a partly diamagnetic, as in the bismuth, copper, and silver phosphors, and a partly paramagnetic, as in the manganese, nickel, and tin phosphors, constituent. In the sulphur phosphors, it is likely that this constituent is the sulphide of the heavy metal. Various bands of one and the same heavy metal phosphor correspond with various sulphur compounds of the same metal, and lead to the conclusion that the same metal may be uni-, bi-, or ter-valent in the same phosphor. A method for the determination of the susceptibility of a finely divided substance has been developed, and depends on the observation of its Brownian movement, when dispersed in a suitable medium, with and without a magnetic field. The magnetic moment of an individual centre of phosphorescence has been measured.

A. E. MITCHELL.

Influence of grain size on the magnetic properties of silicon-iron sheet. O. VON AUWERS.—See B., 1926, 15.

Comparison of a new ferro-nickel [permax] of remarkable magnetic properties with permalloy. H. TSCHERNING.—See B., 1926, 58.

Permanent magnets. F. STÄBLEIN.—See B., 1926, 57.

Electrical symmetry of nickel molecules. A. PERRIER and E. BOREL (Arch. Sci. phys. nat., 1925, [v], 7, 289—298; cf. *ibid.*, 1923, 5, 333).—A preliminary account of the technique of the determination of the longitudinal magnetic effects of electric currents in nickel at the ordinary temperature. Determinations are made by the ballistic method of the variations in magnetisation of a long tube of thin nickel as a result of the sudden passage of a heavy current. Details are given of the method of overcoming the simultaneous effects of the transverse magnetic field arising from the passage of the current through the nickel tube. The chief difficulties in the measurements are due to the deformability of the nickel tube, and to the magnetic properties of the nickel, which cause a lag in the action of the transverse magnetic field.

F. G. TRYHORN.

Contact rectification by metallic germanium. E. MERRITT (Proc. Nat. Acad. Sci., 1925, **11**, 743—748).—Germanium possesses high thermo-electric power and resembles silicon chemically and in crystal form; consequently germanium may be expected to act as a rectifier for alternating currents, silicon being one of the best rectifiers known. This has been found to be the case, although the rectifying action is less marked than with many other materials; on the other hand, the contacts are quite stable and the action is uniform over the surface. Characteristic curves for several typical contacts are given, bismuth presenting a contrast to most other metals, the rectifying contacts being inferior. The effect of temperature was examined and curves are given.

E. B. LUDLAM.

Unipolarity phenomena in compressed powders. F. TREY (Physikal Z., 1925, **26**, 849—862).—Theories of the rectifying action of certain crystals are discussed in the light of experiments whereby artificial detectors, mainly consisting of precipitated and compressed metallic sulphides, have been compared with their natural analogues. The natural and artificial sulphides of silver, cobalt, and tin, and also silver iodide, conduct electrolytically. When silver sulphide is pressed between equal electrodes, the current is transmitted equally well in either direction. If, however, unequal electrodes are used, *e.g.*, one is a point of wire positively charged, the negative ions will only be able to render up their charges by contact. The smallness of point of contact will cause an accumulation of ions; a polarisation and hence unipolarity effects will be observed. The investigation of the natural and compressed lead sulphides gave complicated results. A definite polarisation of a surface layer of moisture was observed, but the detector action could not be explained in this way.

The precipitated and compressed lead sulphide and also powdered lead glance transmit the current equally well in either direction and obey Ohm's law. On heating these preparations to 150°, a strong unipolarity effect is observed. It is shown that although lead sulphate and lead oxide exhibit polarisation, the real detector mechanism of lead sulphide is not bound up with surface effects. A possible explanation is based on an analogy with alloys of copper and silver. The pure metals show no rectifying action, whilst alloys may do so. Lead sulphide may function as a heterogeneous system. Iron sulphides behave similarly to lead sulphides. Compressed powders and ores of copper sulphide obey Ohm's law. The sulphides of bismuth have resistances too great to be amenable to investigation.

R. A. MORTON.

Optical properties of amethyst quartz. C. V. RAMAN and K. BANERJI (Trans. Opt. Soc., 1924—5, **26**, 289—292).—Diffraction fringes are produced by the passage of unpolarised light through a section-plate of amethyst quartz cut normally to the optic axis, the plate, because of sectional repeated twinning, acting as a phase-changing diffraction grating.

A. COUSEN.

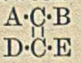
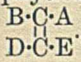
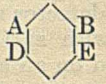
Bending of crystals. C. H. BOSANQUET (Proc. Physical Soc., 1925, **38**, 88—91).—Crystals of rock salt, 15×5×1—2 mm., can be bent into a semicircle in hot water or brine. Three alternative mechanisms are suggested for the deformation, (*a*) irrotational slip along cleavage planes, (*b*) alteration in the lattice spacing, (*c*) break up of the crystal into undistorted fragments with different orientations. These theories are tested by obtaining *X*-ray reflexions from the surface of a bent crystal rocked through a small angle. The reflected lines were curved and drawn out, showing that the orientation of the lattice varies in the crystal, but no change in lattice spacing could be detected within the accuracy of measurement (±1%). It is concluded that the third is the true explanation, and that the spaces between the crystal fragments are filled with amorphous sodium chloride.

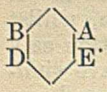
C. J. SMITHELLS.

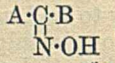
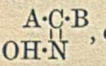
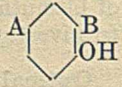
Influence of strain on the Thomson effect. H. E. SMITH (Proc. Physical Soc., 1925, **38**, 1—9).—The influence of strain on the Thomson effect in wires was investigated by Nettleton's method (*ibid.*, 1916, **29**, 16). For pianoforte steel, charcoal iron, constantan, and nickel, the Thomson coefficient decreases with tension (becomes less negative) until the elastic limit is reached, after which it increases. Thereafter the removal and re-application of tension produce a cyclic variation in the coefficient, even in wires stressed beyond the elastic limit. The coefficient for tungsten was determined within the elastic limit, and has a positive value, increasing with tension, and also following a cycle. Brass and German silver showed no change in the Thomson effect with variation in tension.

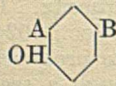
C. J. SMITHELLS.

Endurance properties of non-ferrous metals. D. J. MCADAM, JUN.—See B., 1926, 16.

Determination of the configuration of geometrically isomeric carbon compounds. A. Langseth (Z. physikal. Chem., 1925, **118**, 49—64).—The data for a large number of structural isomerides show that there is a close correspondence in the relation between the physical properties of the isomerides,  $\begin{array}{c}A\cdot C\cdot B\\ \|\\ D\cdot C\cdot E\end{array}$ and  $\begin{array}{c}B\cdot C\cdot A\\ \|\\ D\cdot C\cdot E\end{array}$, and that shown by the corresponding benzene derivatives, 

and 

. In a similar way, the relations between the physical properties of the oximes,  $\begin{array}{c}A\cdot C\cdot B\\ \|\\ N\cdot OH\end{array}$ and  $\begin{array}{c}A\cdot C\cdot B\\ \|\\ OH\cdot N\end{array}$, correspond with those exhibited by 

and 

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J. S. Carter.

Influence of temperature on the mol. wt. of copper. A. Jouniaux (Bull. Soc. chim., 1925, [iv], **37**, 1525—1533).—The molecular condition of copper at various temperatures is deduced by the cryoscopic method from results of Sahmen, Heycock and Neville, and others, appropriate corrections being introduced where mixed crystals are formed. Between 400° and 650° Abs., the molecule is complex, association diminishing until the normal mol. wt. is reached. The metal is monatomic between 650° and 1356°, the m. p. Above the m. p., complexity increases very rapidly, until at 2583°, the b. p., the molecule is octoatomic. The latter conclusion is reached from the results of Ruff and Bergdahl and of Greenwood on the vapour pressure of copper at temperatures approaching the b. p., the constants in Dupré's relation being thereby evaluated and used in connexion with Clapeyron's equation. The mol. wt. given by the quotient of the mol. latent heat, calculated by Trouton's rule, and the atomic latent heat of vaporisation is approximately eight times the atomic weight. A point of inflexion is found on the dilatation curve of copper at 1600° Abs., in the region where marked association occurs.

C. H. D. Clark.

Quantitative relationship between the mol. wt. of metals and their density in the liquid state. —A. Jouniaux (Bull. Soc. chim., 1925, [iv], **37**, 1534—1536; cf. preceding abstract).—From a survey of the results obtained with different metals, it is concluded that a relationship between mol. wt. and liquid density exists. When the specific volume of a liquid metal is a linear function of the temperature over a specified range, the degree of association is constant within the limits in question. A study of cases where the relationship is not a linear one indicates that the second differential coefficient of the specific volume with respect to temperature is positive or negative, according as the molecule is monatomic or polyatomic, respectively.

C. H. D. Clark.

Electrical conductivity of certain light aluminium alloys and copper conductors as affected by atmospheric exposure. E. Wilson.—See B., 1926, 16.

Influence of an electrostatic charge on the surface conductivity of a plate of rock salt. P. Vaillant (Compt. rend., 1925, **181**, 915—917).—The superficial conductivity of a plate of rock salt increases when positively charged and decreases when negatively charged. The positive ions thus have greater mobilities than the negative ions, indicating that the conducting ions are H˙ and OH′ and not those of sodium chloride. The influence of the electrostatic charge decreases as the humidity of the atmosphere increases. The conductivity is very small in a dry atmosphere, but increases greatly when the plate is charged. (Cf. Perkins, J. Phys. Radium, 1923, [vi], **4**, 246.)

S. K. Tweedy.

Relationship between hardness and the thermal and optical properties of elements. P. Lasarev (Bull. Acad. Sci. Russie, 1918, [6], 1259—1260; from Chem. Zentr., 1925, II, 259; cf. A., 1924, ii, 517).—The proportionality between hardness and atomic concentration (*i.e.*, the reciprocal of atomic volume) follows from the assumption that the mutual attractive force of the atoms of different elements is the same function of the distance between them.

G. W. Robinson.

Influence of admixtures on the pyrophoric properties of finely divided metals. II. N. I. Nikitin (J. Russ. Phys. Chem. Soc., 1925, **56**, 120—127; cf. A., 1924, ii, 556).—The loss of pyrophoric properties occurring when finely divided metals are heated is due to incipient recrystallisation of the metal. In the case of reduced iron, the presence of 2% (20%) of alumina in intimate admixture enables the metal to resist the tendency to crystallise and thus to retain its pyrophoric property even after being heated to 650° (700°). A mixture of finely divided metallic cobalt with manganese oxide, prepared by reducing the mixed oxalates of the two metals, undergoes crystallisation only with difficulty; even when less than 1% of manganese is present, maintenance of a temperature of 365° for 45 min. fails to destroy the pyrophoric properties of the cobalt, whilst a mixture containing 48% of manganese inflames in the air after being heated at 410°. Recrystallisation of copper and lead appears to take place at very low temperatures, since preparation of these metals by reduction at 125° results in non-pyrophoric powders.

T. H. Pope.

Heat of combustion of salicyclic acid. E. Berner (J.C.S., 1925, **127**, 2747—2750).—The heat of combustion of carefully purified salicylic acid determined in a bomb calorimeter is 5233·8 cal. (15°) per g. (vac.) at constant volume, or 5237·4 cal./g. when weighed in air against brass weights. The ratio of the heats of combustion of benzoic acid and salicylic acid is 1·2073 (vac.).

M. S. Burr.

Heats of combustion of standard substances. W. Swientoslawski (J. Chim. phys., 1925, **22**, 583—588).—Polemical against Jaeger and Steinwehr (A., 1925, ii, 126). The value of the heat of combustion of benzoic acid calculated from the data of

Fischer and Wrede is nearly 0·2% below that found by Dickinson and others. The benzoic acid used by the former, and by Swientoslawski and Popov (A., 1915, ii, 315), was impure. The determination of the calorific value of Fischer's apparatus by Jaeger and Steinwehr (Ann. Physik, 1906, [iv], **21**, 23) contained a systematic error which raised the value for benzoic acid by approximately 0·3%. L. S. THEOBALD.

Freezing points. H. FOOTE and G. LEOPOLD (Amer. J. Sci., 1926, [v], **11**, 42—46).—F. p. determined at atmospheric pressure have usually been obtained under conditions tending to saturation with air, and methods proposed to eliminate the effects of variable amounts of air disregard the experimental fact that saturation may be rapidly accomplished. It appears preferable to regard the f. p. as the temperature at which solid and liquid are in equilibrium with dry air under a pressure of 1 atm. The effect due to the solubility of air on the m. p. of ice is 0·0023°, which, with the lowering due to pressure alone (0·0075°), makes the f. p. of air-saturated water 0·0098° below the temperature of the triple point. The f. p. of organic liquids are in general affected to a greater degree by the presence of dissolved air than is the f. p. of water. A. COUSEN.

Allotropy of zinc. D. STOCKDALE (J.C.S., 1925, **127**, 2951—2956).—Measurements have been made of the difference in *E.M.F.* between two zinc electrodes immersed in a fused mixture of zinc chloride, oxychloride, and bromide, at temperatures from 300° to 330°, a difference of temperature of about 10° being maintained between them. After allowing for lag, the breaks in the *E.M.F.*-temperature (or time) curve indicate that zinc undergoes an allotropic change at 315°, but the experiments are not entirely conclusive. This result, however, is in agreement with the observations that certain of the physical properties of zinc are discontinuous between 310° and 330°. M. S. BURR.

Densities at the absolute zero and the total expansion of the liquid state of organic compounds. W. HERZ (Z. anorg. Chem., 1925, **149**, 230—234).—The equation of van Laar ("Die Zustandsgleichung von Gasen und Flüssigkeiten," Leipzig, 1924, p. 140) $d_0/d_k=2(1+\gamma)$, where d_0 is the density at 0° Abs., d_k is the density at the m. p., b. p., or critical point, and $2\gamma=1+0{\cdot}038\sqrt{T_k}$, T_k being the (absolute) critical temperature, is used to determine the densities of a number of organic compounds at 0° Abs. The difference between the molar volumes at 0° Abs. and the critical point represents the total expansion of the liquid state lying between these temperatures. Its value increases in ascending a homologous series, or when one element in a compound is replaced by a heavier one. It is nearly the same for isomeric compounds of similar character. R. CUTHILL.

Vapour-pressure measurements on pure ozone. E. H. RIESENFELD and M. BEJA (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 7, 1—27; cf. A., 1922, ii, 637, 761).—The vapour pressure of ozone over the temperature interval −169° to −108·5° is satisfactorily represented by the equation $\log p=-\lambda_0/4{\cdot}571T+1{\cdot}75\log T-\varepsilon T/4{\cdot}571+C$, p being the pressure in mm. of mercury, T the absolute temperature, $\lambda_0=3500$, $\varepsilon=0{\cdot}05797$, and $C=5{\cdot}783$. At −169° and −108·5°, the vapour pressures are 4·8 and 840·8 mm., respectively. The b. p. of ozone is $-115{\cdot}5\pm0{\cdot}5°$. The heat of vaporisation varies with the temperature according to the equation $\lambda=\lambda_0+3{\cdot}499T-0{\cdot}05817T^2$, the values at 0° Abs. and the b. p. being 3500 and 2547 cal./mol., respectively. The value of the conventional chemical constant, pressure being measured in atm., is 2·9 (oxygen 2·8). J. S. CARTER.

Vapour pressures of metals; new experimental method. W. H. RODEBUSH and A. L. DIXON (Physical Rev., 1925, [ii], **26**, 851—858).—By the use of a quasi-static method, the vapour pressure of mercury at seven temperatures, from 170·4° (6·29 mm. of mercury) to 202·8° (18·90 mm.), has been determined, and that of lead at eight temperatures, from 1391° Abs. (5·70 mm. of mercury) to 1508° Abs. (19·70 mm.). The latter results are in agreement with the equation $\log p(\text{mm.})=-10372/T-\log T-11{\cdot}35$. The heat of vaporisation of lead at the m. p. is calculated to be 46,300 cal., and the chemical constant C_0 is −1·40, in agreement with the value −1·588 required by the quantum theory of monatomic gases. A. A. ELDRIDGE.

Mercury vapour pressure at low temperatures. F. E. POINDEXTER (Physical Rev., 1925, [ii], **26**, 859—868).—By the use of a modified form of Buckley ionisation gauge, the vapour pressure of mercury between $1{\cdot}210\times10^{-3}$ mm. at 19·73° and $3{\cdot}00\times10^{-9}$ mm. at −79·61° has been determined and tabulated for twenty-seven temperatures; the results correspond with the equations: $\log p(\text{liquid})=8{\cdot}86-3{\cdot}44(10^3/T)$; $\log p\,(\text{solid})=9{\cdot}35-3{\cdot}55(10^3/T)$. The heat of vaporisation of mercury is computed for sixteen temperatures from the vapour-pressure curve. The heat of fusion is calculated to be 600 cal. A. A. ELDRIDGE.

Vapour pressures of solid and liquid cyanogen. J. H. PERRY and D. C. BARDWELL (J. Amer. Chem. Soc., 1925, **47**, 2629—2632).—Vapour pressures of solid cyanogen have been measured from −93° to the triple point, and of liquid cyanogen from the triple point to −7°; the derived equations for the pressures in mm. are $\log P=(-1695{\cdot}122/T)+9{\cdot}65530$ for the solid, and $\log P=(-1818{\cdot}554/T)-5{\cdot}0813\log T+22{\cdot}30083$ for the liquid. The triple point is at −27·90° and 552·2 mm., and the normal b. p. is −21·17°. The latent heats of sublimation, vaporisation, and fusion are 7750, $8331-10{\cdot}133T$, and 1904 (triple point) cal./mol., respectively. A. GEAKE.

Cause of change of physical properties of highly dried liquids, and influence of temperature on rate of drying. S. B. MALI (Z. anorg. Chem., 1925, **149**, 150—156; cf. Baker, J.C.S., 1922, **121**, 568).—Drying reduces the vapour pressures of carbon disulphide, toluene, benzene, and carbon tetrachloride by an amount which is the greater the higher the temperature at which the drying has been carried out. The refractive index also appears to change at the same time. R. CUTHILL.

New statistical definition of entropy. M. PLANCK (Z. Physik, 1925, **35**, 155—169).—The new definition based on quantum considerations is: entropy $S=k \log P$, where P is the number of stationary states of the system the energy of which does not exceed a definite value E. The equation is not derived from considerations of probability, and is applicable to systems of few degrees of freedom. For systems of several degrees of freedom it leads to the formula for the free energy, $F=-kT \log P+E$. E. B. LUDLAM.

Viscosity of ammonia gas. R. S. EDWARDS and B. WORSWICK (Proc. Physical Soc., 1925, **38**, 16—23).—The viscosity of ammonia was determined at 15°, 100°, and 184° by transpiring the gas through a capillary tube previously calibrated with air. By extrapolation, the values of η_0 and η_{100} were found to be $94{\cdot}4\times10^{-6}$ and $129{\cdot}5\times10^{-6}$ C.G.S. units, respectively. The value of Sutherland's constant C, in the equation $\eta=KT^{3/2}/(C+T)$ was found to be 377. The mean collision area of the ammonia molecule calculated from this value is $6{\cdot}33\times10^{-16}$ cm.^{2} The results agree closely with those of Rankine and Smith. C. J. SMITHELLS.

Kinetic theory of compressibility of solutions and binary liquid mixtures. II. K. C. KAR (Physikal. Z., 1925, **26**, 737—739).—The author's equation (A., 1925, ii, 970) is in agreement with the empirical equation of Gilbaut (A., 1898, ii, 111). The equation is verified for a large number of salt solutions; *e.g.*, a 3·51% solution of ammonium chloride in water at 18° under 8 atm. pressure has an observed compressibility of $43{\cdot}6\times10^{-6}$, whereas the calculated value is $42{\cdot}8\times10^{-6}$. The compressibility of chloroform and carbon disulphide mixtures (not miscible) is given accurately by the equation, but for acetic acid–water mixtures the theoretical and observed curves differ, owing to the fact that the deduction of the formula demands dilute solutions as a necessary condition. R. A. MORTON.

Viscosity of sulphur dioxide, and of mixtures of it with hydrogen. M. TRAUTZ and W. WEIZEL (Ann. Physik, 1925, [iv], **78**, 305—369).—A simple apparatus is described for the rapid and accurate determination of the viscosities of gases at various temperatures. By determining the rate of flow of air, hydrogen, and carbon dioxide through tubes of various lengths and diameters, it was found that rim effects in these tubes are directly proportional to the rate of flow and to the density of the gas, and indirectly proportional to the fourth power of the radius. It is further shown that these relationships correspond with the Hagenbach correction (*ibid.*, 1860, **109**, 385). The independence of the rim effect on the length of the tube permits the use of quite short lengths in the measurements of gas viscosities. A detailed consideration is given of various corrections which must be applied to viscosity measurements. The chief of these are those for expansion of the capillary tube, barometric fluctuations, and for the deviation of the gas under measurement from the ideal state. Appendices are given containing mathematical discussions of the theory of the transpiration method of measurement, and of the above corrections. Measurements were made of the viscosities of sulphur dioxide, and of numerous mixtures of it with hydrogen, at a series of temperatures between 17° and 199°. The viscosity of sulphur dioxide changes from 1221×10^{-7} at 14° to 2071×10^{-7} at 199°, the temperature coefficient being practically constant over this range. The Sutherland formula (Phil. Mag., 1893, [v], **36**, 507) does not apply to this gas. The viscosity curve of mixtures of sulphur dioxide and hydrogen exhibits a maximum, which, as the temperature increases, flattens, and is displaced towards mixtures richer in sulphur dioxide. At 17°, a mixture containing approximately 70 molar % of hydrogen has a maximum viscosity, whilst at 199° the maximum occurs with the mixture containing 50 molar % of hydrogen. The increase of viscosity of mixtures on the addition of hydrogen is roughly proportional, up to the maximum, to the mole fraction of hydrogen. The temperature coefficient of the viscosity of these mixtures approximates to that of pure sulphur dioxide, until sufficient hydrogen has been added to give a maximum viscosity. Beyond this maximum, the addition of further hydrogen slowly reduces the temperature coefficient to that of pure hydrogen. A comparison of these results with those for other gas mixtures suggests that the appearance of a maximum in the viscosity curve is dependent on the critical temperatures of both gases. F. G. TRYHORN.

Theory of atmolysis. J. SAMESHIMA (Japanese J. Chem., 1925, **2**, 33—44).—The rate of separation of the components of an ideal gas mixture when atmolysed under ideal conditions has been calculated. In the case of a two-component system, the following relations are deduced: $t=c(1/a-1/b)+1/b-x/a-(1-c)/b\,.\,c^{-b/a}.\,x^{b/a}$, or $t=(1-c)(1/b-1/a)+1/a-y/b-c/a(1-c)^{-a/b}.\,y^{a/b}$, and $y=(1-c)c^{-b/a}.\,x^{b/a}$, where a and b are the volumes of the pure gases which pass through a porous plate in unit time, c is the volume of the first gas in unit volume of the gas mixture, t the time from the beginning of atmolysis, and x and y are the volumes of the two gases in the remainder after time t.

For a system of n components: $t=(c_1/a_1+c_2/a_2+c_3/a_3+\ .\ .\ .\ +c_n/a_n)-(x_1/a_1+1/a_2\,.\,c_2c_1^{-a_2/a_1}.\,x_1^{a_2/a_1}+1/a_3\,.\,c_3c_1^{-a_3/a_1}.\,x_1^{a_3/a_1}+\ .\ .\ .\ 1/a_n\,.\,c_nc_1^{-a_n/a_1}.\,x_1^{a_n/a_1})$ etc., and $x_2=c_2c_1^{-a_2/a_1}.\,x_1^{a_2/a_1}$, $x_3=c_3c_1^{-a_3/a_1}.\,x_1^{a_3/a_1}$, . . . $x_n=c_nc_1^{a_n/a_1}.\,x_1^{a_n/a_1}$, where a is the volume of each pure gas that flows through a porous plate in unit time, c is the initial volume of each component of the mixture, and x is the volume of each component in the remaining gas after time t, different components being shown by different suffixes. The relation between the composition of the gases and t and those between the composition and volume of the gases are shown diagrammatically. L. L. BIRCUMSHAW.

Elastic properties of alloys. P. CHEVENARD and A. PORTEVIN.—See B., 1926, 59.

Boron–aluminium alloys. P. HAENNI.—See B., 1926, 58.

Artificial ferronickels and meteoric iron containing nickel. M. PESCHARD.—See B., 1926, 58.

Compounds and alloys of titanium and aluminium. W. Manchot and A. Leber (Z. anorg. Chem., 1925, **150**, 26—34; cf. A., 1908, ii, 40; 1910, ii, 302).—Alloys of titanium and aluminium containing up to 37·3% of titanium were prepared by heating potassium titanifluoride with aluminium; uniform alloys containing more titanium could not be obtained. Titanium was determined by dissolving in hydrochloric acid and titrating with methylene-blue or bromine; aluminium was determined by difference, qualitative analysis showing that the alloys were pure, except for slight traces of iron and silicon. Cooling curves were followed by melting the alloys in a crucible completely surrounded with aluminium oxide powder, this being found preferable to an atmosphere of an inert gas. In general, the curves showed two halts, one corresponding with the compound Al_3Ti and the other with aluminium; the former increased with increasing titanium content, whilst the latter diminished and disappeared when the alloy contained 37·3% of titanium, corresponding with the compound Al_3Ti. No depression of the m. p. of aluminium was found, the m. p. rising with increasing titanium content from that of aluminium (658°) to a maximum of 1355° for the compound. Microscopical examination of the alloys revealed only two components, the compound usually appearing as needles. By dissolving the aluminium in cold 5% hydrochloric acid or sodium hydroxide the pure compound remains, *d* 2·74; the composition was confirmed both volumetrically as above and by gravimetric determination of titanium and aluminium.

A. Geake.

Distillation of amalgams. A. Miethe and H. Stammreich (Z. anorg. Chem., 1925, **149**, 263—269).—The amount of foreign metal carried over in the distillation of dilute amalgams under reduced pressure is shown to be negligible provided that care is taken to prevent local overheating and to keep back spray. Distillation of a mixture of colloidal gold and mercury gave a distillate which showed no trace of gold.

R. Cuthill.

Solubility of cetyl alcohol in liquid sulphur dioxide. W. F. Seyer and R. W. Ball (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 149—151).—Saturated solutions of cetyl alcohol in liquid sulphur dioxide contain 0·42% of the alcohol at 5·3°, 7·70% at 22·2°, 31·18% at 23·5°, 57·46% at 25·5°, and 78·93% at 30·9°.

J. S. Carter.

Derivation of adsorption isotherms. A. Gorbatschev (Z. physikal. Chem., 1925, **118**, 357—360).—An addendum to a previous paper (A., 1925, ii, 959).

L. F. Gilbert.

Transformation of water of hydration into water of adsorption by mechanical disintegration of crystal hydrates. T. Hagiwara (Japanese J. Chem., 1925, **2**, 27—32).—By triturating microcrystalline aluminium hydroxide with quartz, heating the crystals at varying stages of disintegration in the electric furnace, and measuring the loss of weight of water, it is found that the greater the degree of disintegration the more easily is the water of hydration given up, and that with very fine particles the water takes on the characteristics of water of adsorption. This is in direct agreement with von Weimarn's theory (J. Russ. Chem. Soc., 1907, **39**, 651; Kolloid-Z., 1909, **4**, 198). Analogous results have also been obtained with göthite crystals.

L. L. Bircumshaw.

Adsorption of barium chloride by colloidal hydrated manganese dioxide in aqueous solutions. W. Chlopin and A. Balandin (Z. anorg. Chem., 1925, **149**, 157—166).—This adsorption is not in agreement with the Freundlich isotherm, but appears to be due to the reaction, $MnO_2,H_2O+BaCl_2=BaMnO_3+2HCl$, accompanied by adsorption of one of the resultants by the manganese dioxide. At high salt concentrations, the former effect predominates, at low salt concentrations the latter. The enrichment of radium in barium may be explained in terms of adsorption by manganese dioxide (cf. Ebler and Bender, A., 1913, ii, 546; 1914, ii, 18).

R. Cuthill.

Negative adsorption. VIII. Behaviour of kaolin towards aqueous solutions of alcohol and salts. M. A. Rakuzin and A. N. Nesmejanov (Biochem. Z., 1925, **160**, 288—290; cf. A., 1924, ii, 853).—Kaolin causes no increase of concentration by the removal of water from aqueous solutions of ethyl alcohol and metallic chlorides.

E. C. Smith.

Influence of thin surface films on the evaporation of water. E. K. Rideal (J. Physical Chem., 1925, **29**, 1585—1588).—Contrary to the results obtained by Hedestrand (A., 1925, ii, 102), it is found that the rate of evaporation of water from a surface is considerably diminished by the presence of a unimolecular film of fatty acid on the surface, and that an increase in surface concentration or film pressure retards the rate of evaporation. In Hedestrand's air-streaming method, it was assumed that the concentration gradient of water vapour in the stagnant layer is always small enough for any real change in the rate of evaporation of water from the liquid surface to be detected by a change in the rate at which water vapour is swept from the surface of the stagnant layer by the air stream. This is shown to be incorrect. An apparatus is described by means of which the rate of removal of water vapour from the neighbourhood of the water surface is increased, so that the ratio between the rate of removal and true rate of evaporation is increased, and thus any effect due to the presence of a thin film on the water becomes apparent. Rates of evaporation for water surfaces covered by unimolecular films of lauric, stearic, and oleic acids at various pressures are given. Different acids retard the rate of evaporation to different extents, and both condensed and expanded films behave similarly in this respect.

L. L. Bircumshaw.

Phenomena of capillary chemistry. R. Dubrisay (Compt. rend., 1925, **181**, 1142—1143; cf. A., 1923, ii, 741; 1924, ii, 731; 1925, ii, 961).—Ten drops of benzene solutions of various fatty acids were allowed to flow from burettes into water and alkaline solutions at various temperatures, the volumes occupied in each case being recorded. With water, the volumes increased with falling temperature; with alkaline solutions, the reverse was the case. This agrees with the author's view that the influence of fatty acids on the tension at a benzene–water interface is greater as the alkali salts become less soluble in water, since soaps are more soluble in hot than in cold water. S. I. Levy.

Superficial solutions. A. Marcelin (Ann. Physique, 1925, [x], 4, 460—527).—A full account of work already published (cf. A., 1924, ii, 390, 594; 1925, ii, 772).

Kinetic phenomena at liquid surfaces. L. Karczag and P. Roboz (Biochem. Z., 1925, **162**, 22—27).—The Brownian movement, in water and various liquids, of a series of substances including powdered metals and metalloids, inorganic and organic compounds, has been examined. Two types of motion are recognised, viz.: (1) the kinetic type without definite arrangement; (2) the static type in which definite forms are recognisable. Organic substances, *e.g.*, benzoic acid, acetylphenylhydrazine, and leucine, exhibit movements of the first type, which may be further subdivided into two groups distinguished as centrifugal and centripetal. Inorganic compounds are chiefly precipitated, whilst metals and metalloids exhibit centripetal motion. Inorganic compounds have no influence on the kinetic motion, but organic compounds, especially those which belong to the centrifugal type, exert a pronounced retarding effect. Kinetic phenomena at the inner boundary surface of two liquids are not controlled by hydrostatic pressure. The motion is largely governed by the dielectric constant of the medium; when the dielectric constant is less than that of water a marked restraining influence is evident. H. G. Reeves.

Electric phenomena and ionic permeability of membranes. V. Membranes of amphoteric character. A. Fujita (Biochem. Z., 1925, **162**, 245—257).—If two solutions of an electrolyte of different concentrations are separated by a gelatin (or coagulated egg-white) membrane, the potential difference is the same as when the liquids are freely in contact only if the gelatin is isoelectric. If the gelatin is negatively charged, the more dilute solution is more positively charged than where there is free contact, whereas if the gelatin is positively charged, the reverse is the case. With agar membranes, the more dilute solution is always a little more positively charged than when there is free contact. The influence of the membrane disappears only in presence of considerable amount of hydrochloric acid. P. W. Clutterbuck.

Comparison of methods of measuring polarity of surfaces. N. K. Adam, R. S. Morrell, and R. G. W. Norrish (J.C.S., 1925, **127**, 2793—2795).—The polarities of glass, stearic acid, paraffin wax, two non-veiling varnishes, and one veiling varnish, have been compared by reference to (1) the catalytic activity of the surface for the combination of ethylene and bromine or ethylene and chlorine (Norrish, *ibid.*, 1923, **123**, 3006), (2) the measurement of the work W required to separate the surface from water in contact with it, W being related to the angle of contact θ of water with the solid surface by the relation $W=T(1+\cos\theta)$, where T is the surface energy of water (Adam and Jessop, A., 1925, ii, 962). There is a considerable difference between the results obtained by the two methods. Glass has less catalytic activity than either stearic acid or the veiling varnishes, but very much greater attraction for water; and stearic acid, which has only a slightly greater attraction for water than paraffin wax, has a very much greater catalytic activity. It is supposed that in certain cases, *e.g.*, with veiling varnishes, the reacting gases may penetrate some distance inwards, so that more catalytically active groups are reached. In the case of paraffin wax, no polar or catalytically active groups can be reached by penetration. M. S. Burr.

Comparison between dialysis and ultrafiltration, electrodialysis and electroultrafiltration. E. Heymann (Kolloid-Z., 1926, **38**, 58—59).—See this vol., 31.

Mechanism of ultrafiltration. J. Duclaux and J. Errera (Kolloid-Z., 1926, **38**, 54—57).—See A., 1925, ii, 530.

Dialysis and ultrafiltration. H. Reinboldt (Kolloid-Z., 1925, **37**, 387—397).—A comprehensive treatment of the uses and technique of, and the apparatus employed for, dialysis and ultrafiltration. N. H. Hartshorne.

Electric phenomena and ionic permeability of membranes. VI. Membranes of paraffin, wax, mastic, and rubber. L. Michaelis and S. Dokan (Biochem. Z., 1925, **162**, 258—265).—Paraffin, wax, mastic, and rubber membranes generally cause the more dilute solution of a diffusion cell to become positively charged. A smaller effect is obtained with multivalent than with univalent ions, especially when the cations are multivalent. If the cation is the hydrogen ion or a ter- or quadri-valent cation, the influence of the membrane almost disappears. An inversion of the effect is observed in the case of the mastic cell in presence of thorium when the more dilute solution became negatively charged. P. W. Clutterbuck.

Electrical properties and ionic permeability of membranes. IV. Potential differences and permeability of collodion membranes. L. Michaelis and A. Fujita (Biochem. Z., 1925, **161**, 47—60).—A completely dried collodion membrane is practically impermeable, but a slight permeability still exists for cations. Two methods are available for the detection of permeability: measurements of potential difference and diffusion experiments of long duration. Such a membrane is to be found in the skin of an apple. The theory involving the contact potential between two phases is scarcely applicable here, however, and a theory based on capillarity is preferred. C. Rimington.

Osmotic pressure of solutions. M. Levalt-Ezerski (J. Russ. Phys. Chem. Soc., 1925, **56**, 249—264; cf. *ibid.*, 1924, **55**, 160).—The osmotic pressure of aqueous sucrose solutions at 0° is directly proportional to the depression of the f. p. and amounts to $12{\cdot}04\Delta t$ atm.; this rule is applicable to all values of Δt not exceeding 10°, and holds for electrolytes as well as non-electrolytes and for mixed as well as single solutes. The osmotic pressures of solutions at 100° are given by the expression $58{\cdot}89\Delta t$, where Δt represents the elevation of b. p. and should not exceed 2·8°. As regards their change with temperature, osmotic pressures follow Gay-Lussac's law, the limitations as to range of temperature being as above.

The concentration of the solution, expressed in molecular quantities of solute taken, is a characteristic magnitude only for highly dilute solutions of non-electrolytes and in no way characterises the properties of solutions of high concentrations. For the latter solutions, a very useful characteristic is the magnitude Δt, expressing either the depression of the f. p. or the elevation of the b. p.

For different solutions of all concentrations, the results available are in conformity with the modification of Raoult's equation, $(p-p')/p=in/(N+in)$ or $(p-p')/p=1/[1+EN/\Delta t(\text{obs.})]$; this equation agrees completely with the figures for both 0° and 100° given in the published tables. The equation $(p-p')/p=in/(N+in)$ furnishes a new and convincing proof of the hydrate theory, and in the case of solutions of non-electrolytes permits of the calculation of the fraction of the total quantity of water which takes part in the formation of hydrates. T. H. Pope.

Osmotic pressure of aqueous solutions of cerous chloride. A. Chistoni (Arch. Farm. sperim. Sci. aff., 1925, **40**, 161—163).—Cryoscopic measurements with solutions containing between 0·5% and 4·0% of cerous chloride indicate that a solution containing 2·57% of this salt is isotonic with one containing 0·75% of sodium chloride. The ionisation of the cerous chloride is considerably less than that of sodium chloride in these isotonic solutions, the ionisation coefficients being 0·487 and 0·991, respectively. F. G. Tryhorn.

Electrolyte-free, water-soluble proteins. V. Acid proteins. II. Donnan equilibrium and colloidal behaviour of proteins. J. Frisch, W. Pauli, and E. Valkó (Biochem. Z., 1925, **164**, 401—436; cf. A., 1925, ii, 518).—The authors have investigated the alterations in conductivity, anion activity, and viscosity of solutions of pure electrolyte-free ovalbumin and serum-albumin after the addition of increasing amounts of hydrochloric, sulphuric, and phosphoric acids. The conductivity coefficient, f_μ, and activity coefficient, f_a, differ considerably in the presence of excess of hydrochloric acid. On the assumption that the protein salt behaves as a completely ionised electrolyte, and taking Sørensen's value for the mol. wt., the value 40 has been obtained for the maximum acidity of ovalbumin. This corresponds closely with the value 39 for the free amino-groups of the diamino-acids in the protein molecule, deduced from the results of Osborne and Harris and of Hausmann (A., 1899, i, 653), The curves of conductivity, activity, and viscosity of the protein solution with increasing concentration of acid follow one another closely, each rising to a maximum. Since there can be no question of Donnan equilibria in a system of freely diffusible ions, these results support the Pauli theory of the imbibition of gelatin rather than that advocated by Loeb. E. C. Smith.

Quantitative studies in dispersoid synthesis by von Weimarn's mechanical method. S. Utzino (Japanese J. Chem., 1925, **2**, 21—26).—Von Weimarn's method has been applied to the following substances, all of which have thereby been obtained in the dispersoid condition: "metallic" selenium, "metallic" tellurium, rhombic sulphur, microcrystalline aluminium hydroxide, microcrystalline barium sulphate, crystalline antimony trisulphide, silver (thin foil), mercury, gold, and denatured egg-albumin. The substances were triturated with anhydrous dextrose at the ordinary temperature, except in the case of mercury and gold, where satisfactory results could only be obtained by trituration at the temperature of liquid air, and denatured albumin, which was triturated with ice at a low temperature, The dispersive medium was distilled water, except for barium sulphate, where 55% of alcohol was used. The average size of the dispersoid particles was about 52 μμ, and in some cases (*e.g.*, selenium and tellurium), the colloidal solutions remained stable for more than a year. A table is given to show that the stability of colloidal selenium solutions decreases with increasing degree of dispersion of the particles. Possible explanations for this are suggested. L. L. Bircumshaw.

Colloidal bismuth. A. Gutbier, T. Kautter, and R. Gentner (Z. anorg. Chem., 1925, **149**, 167—180; cf. Gutbier and Hofmeier, A., 1905, ii, 327; Gutbier and Huber, A., 1916, ii, 556).—A warm glycerol solution of bismuth nitrate made alkaline with sodium hydroxide is reduced by formaldehyde. The resulting sol oxidises very readily unless dialysed and neutral. By carrying out the reduction in presence of a protective colloid such as gum arabic, completely reversible sols can be obtained. The colloid particles are negatively charged. R. Cuthill.

Colloidal rhodium. A. Gutbier and E. Leutheusser (Z. anorg. Chem., 1925, **149**, 181—190; cf. Gutbier and Hofmeier, A., 1905, ii, 533).—A solution, which must not be too dilute, of sodium hexachlororhodate containing 1% of gum arabic (in absence of which the resulting sol is very unstable) is reduced at 90° with hydrazine hydrate. The product shows considerable resistance to coagulation by electrolytes, and, if dialysed, is not immediately coagulated by boiling. Chloride ion is always present, apparently being adsorbed by the gum. The colloid particles are negatively charged. A new method of preparing pure rhodium is described. R. Cuthill.

Colloidal tellurium. A. Gutbier and B. Ottenstein (Z. anorg. Chem., 1925, **149**, 223—229).—Telluric acid is reduced with dextrose in presence of ammonia. The sol formed contains, even after dialysis, adsorbed dextrose (and often tellurous acid), and to this it probably owes its remarkable stability. A method of determining the adsorbed substances is described. The colloid particles are negatively charged. R. Cuthill.

Colloidal sugar. P. P. von Weimarn (Japanese J. Chem., 1925, **2**, 63—72).—The author's theory of the colloidal stage of crystallisation is summarised, and it is shown that the method previously used for the synthesis of colloidal solutions of potassium hydroxide (cf. "Kolloides und kristalloides Lösen und Niederschlagen," 153, 410) can be applied to the preparation of colloidal sugar solutions. The sugar must be dissolved in one organic liquid, which is miscible with another organic liquid in which the sugar is practically insoluble. Results are given of preliminary experiments with solutions of dextrose in acetone and ethyl alcohol, precipitated by pouring into ethyl ether at 20—21°. By this means, the colloidal stage of crystallisation of dextrose can be observed over a period of several hours. Microscopical measurement of the crystals formed 48 hrs. after pouring into ethyl ether showed that larger crystals were formed from the more dilute solutions than from the less dilute.

Acetone solutions of dextrose, sucrose, and lactose, poured into aromatic hydrocarbons (xylene, toluene, or benzene), gave dispersoid sugar solutions, characterised by various well-defined colours.

L. L. Bircumshaw.

Colloid chemistry of humic acid and peat. Wo. Ostwald and A. Steiner.—See B., 1926, 34.

Determination of size of colloidal particles by means of alternating electric fields. E. F. Burton and (Miss) B. M. Reid (Phil. Mag., 1925, [vi], **50**, 1221—1226).—The limiting velocity of settling under gravity of colloidal particles of such a size that the gravitational settling is ordinarily masked by the Brownian movement has been measured. The U-tube used was only slightly modified from that ordinarily used in cataphoresis measurements. An electric field was applied for a short time in one direction, then for an equal time in the reverse direction. The total movement was thus due only to gravitational settling and was measured after a suitable time. An 80-volt storage battery supplied the *E.M.F.*, and a mechanical device reversed the potential every 1½ min. The method was applied to a series of copper sols prepared by forming the arc under water containing increasingly larger traces of potassium hydroxide. The rate of settling increased from $0{\cdot}89\times10^{-5}$ cm./sec. for the copper sol in water alone to $1{\cdot}29\times10^{-5}$ cm./sec. with 24 drops of $0{\cdot}01N$-potassium hydroxide in 200 c.c. of water. The corresponding radii of the particles, calculated by assuming Stokes' law, are $7{\cdot}14\times10^{-6}$ cm. and $8{\cdot}60\times10^{-6}$ cm., respectively. A. B. Manning.

Diffusion analysis. R. Auerbach (Kolloid-Z., 1925, **37**, 379—387).—A description of the determination of the degree of dispersion from diffusion measurements. The theory, practice, and range of applicability of the method are discussed.

N. H. Hartshorne.

Measurement of particle size. A. Kuhn (Kolloid-Z., 1925, **37**, 365—377).—A review is given of methods for determining the size of colloid particles, based on measurements of velocity of movement under gravity or centrifugal force, diffusion constants, sedimentation equilibria, Brownian movement, osmotic pressure, ultrafiltration, dialysis, and viscosity, and of optical methods involving the counting under the microscope of the chemically enlarged particles or direct counting under the ultramicroscope, measurement of the mean distance between particles, the application of Rayleigh's theory, and X-ray interference. N. H. Hartshorne.

Mechanical analysis of sediments. J. R. H. Coutts and E. M. Crowther.—See B., 1926, 31.

Size distribution of particles. D. Werner.—See B., 1926, 31.

Measurement of the charge on colloidal particles. H. R. Kruyt (Kolloid-Z., 1925, **37**, 358—365).—A review of the methods for the measurement of the charge on colloid particles. The paper embraces the cataphoresis of coloured and colourless sols, and transport measurements.

N. H. Hartshorne.

Application of Röntgenspectrography to the study of colloidal systems. R. O. Herzog (Kolloid-Z., 1925, **37**, 355—358).—The author summarises the results obtained by the application of Röntgenspectrography to colloidal systems, under the headings: (i) transition from the liquid (amorphous) state and *vice versa*; (ii) determination of the crystal type; (iii) determination of crystal size and form, and (iv) the crystallite arrangement in gels.

N. H. Hartshorne.

Röntgenoscopy of colloidal systems. H. Mark (Kolloid-Z., 1925, **37**, 351—355).—A treatment of the theory and practice of the Röntgenographic investigation of colloids. In particular, the production of a suitable source of X-rays, and the interpretation of the results are dealt with.

N. H. Hartshorne.

Optical methods for the investigation of anisotropy in colloids. H. Zocher (Kolloid-Z., 1925, **37**, 336—351).—The methods available for the detection and measurement of anisotropy in colloids are described and discussed. N. H. Hartshorne.

Viscosity of soap solutions. B. L. Clarke (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 1, 1—9).—Soap solutions undergo change in viscosity with age, the change proceeding faster the lower the temperature and the more dilute the solution. Solutions may be brought to reproducible viscosities by merely boiling them for a short time and taking precautions to prevent the absorption of carbon dioxide. Determinations of the viscosities of sodium oleate solutions at 18° over the concentration range $0{\cdot}04$—$0{\cdot}10N$ and of sodium stearate solutions at 98·3° over the range $0{\cdot}015$—$0{\cdot}12N$ show that the viscosities conform to the requirements of the formula $\log \eta/\eta_0=\theta c$, where η_0 and η are the viscosities of pure water and of a soap solution of concentration c, θ being a constant. The data of Farrow (J.C.S., 1912, **101**, 347) on the viscosities of solutions of sodium palmitate at 70° are also in accordance with this equation. J. S. Carter.

Stability of colloidal solutions. IV. Antagonistic effect of electrolytes on concentrated and dilute sols and a general theory of ion antagonism. K. C. Sen (Z. anorg. Chem., 1925, **149**, 139—149; cf. A., 1925, ii, 664).—The antagonistic effect of the chlorides of sodium and calcium, potassium and calcium, sodium and barium, and potassium and barium in the coagulation of suspensions of arsenious sulphide (cf. Mukherjee and Ghosh, A., 1925, ii, 394; Weiser, A., 1924, ii, 309) is more pronounced with dilute sols than with more concentrated sols. It is suggested that, in general, if any ion with the same sign of charge as the colloid particle is more strongly adsorbed or concentrated at the interface, then it will oppose the action of the oppositely charged coagulating ion. If the concentration of the latter increases sufficiently, coagulation, or change in sign of the charge, or (in emulsions) inversion of the phases may occur. R. CUTHILL.

Constitution of the system sodium stearate–water. A. VON BUZAGH (Chem. Rundschau Mitteleuropa Balk., 1925, 2, 52—54, 72—73; from Chem. Zentr., 1925, II, 271—272).—The author has studied the conductivity and hydroxyl-ion concentrations of sodium stearate gels below 60°. With falling temperature, the conductivity approaches a limiting value which is reached more slowly with more concentrated solutions. The water in soap gels is apparently mechanically bound, since the composition of the liquid phase expressed from gels several weeks old is inconstant, the amount of stearate in solution decreasing with increase of the solid phase. The conductivity of the ultrafiltrate is less than that of the original system. This is attributed to adsorption of stearate molecules by stearic acid liberated by hydrolysis, in agreement with the fact that the system becomes more basic as the quantity of solid phase increases. G. W. ROBINSON.

Viscosity of colloids in presence of electrolytes. N. R. DHAR (J. Physical Chem., 1925, 29, 1556—1567).—A theoretical paper, in which it is shown that previous experimental results on the viscosity of colloids, especially of the hydrophobe type, support the assumptions that (1) other things being equal, the uncharged substance is more hydrated than the sol; (2) the greater the hydration of a substance, the greater is its viscosity; (3) when a sol adsorbs an ion carrying the same charge as the sol, the charge on the sol is increased and the viscosity decreases, and (4) when a sol adsorbs more of the ion carrying the opposite charge than the ion carrying the same charge, the charge on the sol is decreased, further hydration takes place, and the viscosity increases (cf. Sen, Ganguly, and Dhar, A., 1924, ii, 394; Sen and Dhar, *ibid.*, 733; Ghosh and Dhar, A., 1925, ii, 386, 778). Support is also afforded for the view that sols which behave abnormally on dilution and towards mixtures of electrolytes of different valencies, and further which show positive acclimatisation, should also show a greater decrease of viscosity when small quantities of a coagulating electrolyte are added to them, than sols which behave normally on dilution and towards mixtures of electrolytes, and which show negative acclimatisation. The behaviour of hydrophile colloids as regards viscosity is discussed, and the results obtained by Pauli, Loeb, and others with substances like gelatin, albumin, etc., are explained qualitatively on the basis of the views expressed above. An alternative, and more satisfactory, explanation is based on the assumption that particles of gelatin or albumin have a natural tendency to disintegrate. In the case of isoelectric gelatin, the suspended particles disintegrate, these smaller particles adsorb more water, and consequently the viscosity of the system increases. When acids or alkalis are added, the charge on the sol is increased by preferential adsorption of hydrogen or hydroxyl ions, and hence the tendency to disintegrate, the degree of hydration, and the viscosity will also increase. L. L. BIRCUMSHAW.

Coagulation of complex negative sols by electrolytes. N. A. YAJNIK and S. L. BHATIA (J. Chim. phys., 1925, 22, 589—594).—The coagulating effect of many electrolytes on Turnbull's-blue and Prussian-blue sols has been studied. The electrolytes included halides, nitrates, sulphates, etc. of the alkali metals; chlorides of barium, mercury, nickel, cobalt, and aluminium; nitrates of lead and cadmium; and sulphates of zinc, nickel, cobalt, aluminium, and chromium. The concentrations of electrolyte which completely coagulated, but did not precipitate, the sol in 2 hrs. at 17—18° were compared. With Turnbull's-blue, the order is chromium > aluminium > nickel > cobalt > zinc > barium > lead > mercury > rubidium > potassium > sodium > lithium. The Schultze–Hardy law holds for complete coagulation, but not when sedimentation is involved (cf. Ganguli and Dhar, A., 1923, ii, 58; Burton and MacInnes, A., 1922, ii, 130). The coagulating power of rubidium bromide is less than that of potassium chloride in the case of Prussian-blue sols. L. S. THEOBALD.

Influence of hydrogen-ion concentration on the speed of flocculation of negative colloids. A. BOUTARIC and (MME.) Y. MANIÈRE (Compt. rend., 1925, 181, 913—915).—Observations on the flocculation of some negative colloids (*e.g.*, arsenic sulphide) with various acids indicate that the most important factor is the actual hydrogen-ion concentration and not the normality of the acid. The speed of flocculation is not always independent of the nature of the acid; this may be because the speed of adsorption of hydrogen ions varies for the different acid media, or because the acid radical itself undergoes adsorption. The latter explanation would also account for the protection phenomena previously observed (cf. A., 1925, ii, 526, 778). S. K. TWEEDY.

Supposed influence of lævulose and the action of magnesium salts on the coagulation of citrate- and phosphate-blood. (MISS) E. SLUITER (Proc. K. Akad. Wetensch. Amsterdam, 1925, 28, 636—639).—Blood or plasma, which has been rendered non-coagulable by the addition of sodium citrate or metaphosphate, is coagulated by 1 c.c. of a 10% solution of commercial lævulose, but not by a specimen of pure lævulose prepared from inulin. The coagulating action of the former is due to the presence of a quantity of magnesium chloride (0·62 g. $MgCl_2$ per 100 g. sugar) sufficient in itself to produce the observed effects. J. W. BAKER.

Action of electrolytes on clays. S. KONDO.—See B., 1926, 14.

Theory of peptisation. K. C. Sen (J. Physical Chem., 1925, **29**, 1533—1547; cf. A., 1925, ii, 666).—By means of examples, it is shown that a high degree of adsorption and a suitable concentration of the electrolyte are necessary for peptisation, and that with the same electrolyte and the same peptisable substance, peptisation depends to a certain extent on the amount of adsorption. When different peptisable substances are used, peptisation is specific and depends on the nature of the adsorbent and on that of the peptising agent. The agglomeration of a precipitate decreases its power of adsorption, and hence its peptisability. With different acids and the same adsorbent, the amount of adsorption and ease of peptisation are not necessarily proportional. Peptisation is markedly retarded by the presence of bi- and ter-valent negative ions, although the corresponding acids are usually the most highly adsorbed. Univalent acids in general follow the rule that the greater the adsorption, the greater is the peptising power. The stability relations of peptised substances are considered at some length. L. L. Bircumshaw.

Velocities of chemical reactions in presence of organic colloids. N. A. Izgaryschev and M. I. Bogomolova.—See this vol., 132.

Structure of gelatin gels. E. O. Kraemer (J. Physical Chem., 1925, **29**, 1523—1527).—A rough calculation shows that the gelatin sol unit (considered as a compact impenetrable cube) must measure about 5 $\mu\mu$, and if the gelatin gel consists of chains of sol units loosely knit together, then the average interval between such chains will be about 100 $\mu\mu$. With such a loose structure, the water phase in the interstices would be expected to exhibit the properties of water in mass. In an attempt to demonstrate the heterogeneity of gelatin gels, mercury particles, about 200—250 $\mu\mu$ in radius, were mixed with dilute gelatin systems before gelation, and cinematographic records of the Brownian motion of these particles were made with an apparatus previously described ("Colloid Symposium Monograph," 1924, **2**, 57). In gels of 0·5% and above, the Brownian movement was practically prevented, but gradually appeared on warming, whilst in gels of about 0·3% a measurable Brownian motion persisted. The distribution of the displacement magnitudes was normal, indicating that the structure of such weak gels is still considerably finer than the indicating mercury particles and their displacements. These experiments, whilst giving no evidence as to the heterogeneity of gelatin gels, must not be taken to support the view that the structure is molecular in magnitude. L. L. Bircumshaw.

Hydrates of antimony trioxide. A. Simon and H. Poehlmann (Z. anorg. Chem., 1925, **149**, 101—124; cf. Lea and Wood, J.C.S., 1923, **123**, 259; Jander and Simon, A., 1923, ii, 772).—Hydrated antimony trioxide prepared by the decomposition of tartar emetic with hydrochloric acid cannot be freed from all traces of electrolytes without becoming crystalline and anhydrous. The amount of water in the product varies with the temperature of precipitation, and desiccation curves give no indication of the presence of definite hydrates, but rather suggest that the hydrated oxides are merely colloidal modifications of antimony trioxide differing primarily in fineness of division. This view is supported by experiments on their adsorptive power for potassium hydroxide (cf. Jander and Simon, *loc. cit.*). The water in the gels can be replaced by alcohol, and the vapour-pressure isotherms of both hydrogels and alcogels show that the liquids in them are contained in a system of capillary cavities, the gels being constant in volume. The colloid particles are negatively charged. No hydrates can be isolated by Willstätter's acetone method (A., 1924, ii, 615). R. Cuthill.

Kinetics of the swelling and shrinking of gels. S. Liepatov (Biochem. Z., 1925, **166**, 220—233).—See A., 1925, ii, 685, 968.

Measurement of swelling. P. A. Thiessen (Kolloid-Z., 1925, **37**, 406—411).—A description of the methods and apparatus used for the measurement of swelling. N. H. Hartshorne.

Diffusion. Free path of water molecules. Influence of a field of force. Statistical equilibrium. N. V. Karpen (Bull. Acad. Sci. Roumaine, 1925, 9, [9—10], 2—7).—Theoretical and mathematical. Formulæ for the diffusion of dissolved substances are derived. The diffusion coefficient K is related to the free path λ_0 of the molecules between two consecutive collisions with molecules of the solvent, the mol. wt., M, and the temperature, T, by the equation $K=\lambda_0/\sqrt{12}\,.\,\sqrt{RT/M}$. Assuming λ_0 to have approximately the same value, the values of $K\sqrt{M}$ at constant temperature for certain non-electrolytes have been calculated, the mean value being 8·2. From this, the value of λ_0 is $2{\cdot}12\times10^{-9}$ cm. at 17°. This is also the free path of the water molecules. The influence of a field of force and the conditions for equilibrium are considered. J. S. Carter.

Kinetic activation as a factor in gas reactions. W. Taylor (Trans. Faraday Soc., Jan., 1926, advance proof).—Theoretical, in which it is shown that the expression deduced by Franck and also by Rice (cf. A., 1925, ii, 1076) for the velocity coefficient of a unimolecular reaction in a single gas can be generalised for the case of a mixture of gases with any number of components. L. S. Theobald.

Thermal formation of ozone. E. H. Riesenfeld and M. Beja (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, 6, No. 8, 1—20).—The ozone–oxygen equilibrium has been investigated by exploding different mixtures of ozone and oxygen and determining the concentration of ozone in the residual gas by means of starch–iodide paper. Using mixtures containing up to 37% by volume of ozone, no ozone could be detected by this method after explosion, and hence the amount of ozone present is less than corresponds with a partial pressure of 2×10^{-8} atm. The maximum temperature attained by explosion of a 37% ozone mixture is 2130° Abs. Using mixtures containing 45—94% ozone by volume, the partial pressure of ozone in the gas after explosion lies between 2 and 4×10^{-8} atm., independent of the initial composition of the gas mixture. By these explosions, maximum temperatures of 2300° to 2850° Abs. are obtained. According to the Nernst theorem, the maximum pressure of the ozone formed from pure oxygen at atmospheric pressure is $1{\cdot}3\times10^{-7}$ atm., this pressure being obtained at 3500° Abs. Within the limits of error, which are very wide, the experimentally determined ozone concentrations are in fairly good agreement with those calculated. J. S. CARTER.

Ionisation of weak electrolytes in water–alcohol solutions. III. Relations between the chemical constitution and alcohol-sensitivity of dibasic acids in ethyl alcohol. M. MIZUTANI (Z. physikal. Chem., 1925, **118**, 318—326; cf. A., 1925, ii, 793, 867).—The ionisation of oxalic, malonic, succinic, glutaric, malic, fumaric, maleic, and phthalic acids dissolved in ethyl alcohol has been investigated. The sensitivities to alcohol of the two ionisation constants when the carboxyl groups in a dibasic acid are far apart are about the same, but this rule does not hold when these groups are near to each other. The ionisation of solutions of glycollic and monochloroacetic acids, phenol, *p*-chlorophenol, and resorcinol in ethyl alcohol was also studied.

L. F. GILBERT.

Ionisation of weak electrolytes in water–alcohol solutions. IV. Ionisation in methyl alcohol solutions. M. MIZUTANI (Z. physikal. Chem., 1925, **118**, 327—341; cf. preceding abstract).—The same experimental (potentiometric) method was used as with the ethyl alcohol solutions. Results are given of measurements with solutions of formic, acetic, propionic, butyric, *iso*valeric, lactic, glycollic, salicylic, benzoic, and monochloroacetic acids, phenol, resorcinol, and *p*-chlorophenol, malonic, succinic, phthalic, malic, fumaric, and maleic acids, ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, aniline, methylaniline, dimethylaniline, pyridine, and *o*-toluidine. The observed effects are correlated with differences between the solubilities of the substances in water and the alcohols. L. F. GILBERT.

Hydrogen-ion concentration and "electropy." M. BÁLINT (Biochem. Z., 1925, **165**, 465—472).—The p_H range of "electropic" dyes is determined. Electropic colour changes are due to change of the p_H of the dye solution, and not of electrostatic charge (cf. A., 1924, i, 688). The action of the usual decolorising substances is prevented if the solution be suitably buffered. Regeneration of colour is only effected either by acids or acid buffers and decolorisation by bases, basic buffers, and substances which adsorb hydrogen ions. P. W. CLUTTERBUCK.

Expression for the true reaction of solutions. D. GIRIBALDO (Biochem. Z., 1925, **163**, 8—12).—An expression $lr=\log[\mathrm{H}^{\cdot}]/[\mathrm{OH}']$ is proposed as an alternative to p_H. It has zero value at neutrality, becomes positive on the acid side, and negative on the alkaline side of neutrality. E. C. SMITH.

Dissociation constants, solubility products, and the titratability of alkaloids. I. M. KOLTHOFF (Biochem. Z., 1925, **162**, 289—353).—Those alkaloids which are monacid bases and have a dissociation constant greater than 5×10^{-7} give a sharp end-point with methyl-red. When the constant is smaller, dimethyl-yellow, methyl-orange, or bromophenol-blue must be used, and the titration carried to the correct p_H by comparison with a standard of p_H calculable from the dissociation constant. In presence of 50% alcohol, the end-point with methyl-red is not sharp and bromophenol-blue should be used. A table is given showing the dissociation constants, solubilities, and solubility products of 49 alkaloids and related substances. P. W. CLUTTERBUCK.

Solubility product of dicalcium phosphate. M. K. DOMONTOVITSCH and O. V. SARUBINA (Biochem. Z., 1925, **163**, 464—469).—From direct determinations, in saturated solutions, of the concentrations of calcium, phosphate, and hydrogen ions, the solubility product, $(\overset{++}{\mathrm{Ca}})(\overset{--}{\mathrm{HPO_4}})$, was found to be $10^{-6{\cdot}25}$ at 19—22° in distilled water. In various electrolyte solutions of total ion concentration equal to $M/10$, the value was $10^{-5{\cdot}75}$. R. K. CANNAN.

Neutral salt effect in the acetochloroanilide ⟶ *p*-chloroacetanilide rearrangement as a function of hydrogen-ion activity. G. ÅKERLÖF (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 2, 1—15).—The velocity measurements of Rivett (A., 1913, ii, 202, 1041) have been extended so as to include the effect of addition of aluminium chloride and the influence of lithium, sodium, potassium, magnesium, calcium, barium, zinc, and aluminium chlorides at concentrations up to about $3N$ on the activity of the hydrogen ion from $0{\cdot}2485N$-hydrochloric acid, as determined by *E.M.F.* measurements on the cell, Pt $\mathrm{H_2}|0{\cdot}2485N\text{-HCl}+\text{salt}|\text{Sat.KCl}|\text{Sat.KCl}\ \mathrm{Hg_2Cl_2}|\mathrm{Hg}$, at 20° have been investigated. Addition of neutral salt results in an increased activity of the hydrogen ion, *e.g.*, in presence of $2{\cdot}75N$-potassium chloride, $2{\cdot}81N$-lithium chloride, and $2{\cdot}70N$-calcium chloride the hydrogen-ion activities are 0·446, 0·981, and 0·838, respectively, as compared with the value 0·208 for the salt-free solution. The values of $K-K_0/C$ for the various salts, where K_0 and K are the velocity constants in the absence of and in presence of neutral salt and C is the salt concentration expressed as a normality, are all of the same order of magnitude and increase somewhat with increasing salt concentration. The experimental numbers are in fair agreement with the equation $K/K_0=(\alpha/\alpha_0)^{\mathrm{D}/\sqrt[3]{\mathrm{C}^2}}$, where α_0 and α are the hydrogen-ion activities in the salt-free solution and in a salt solution of concentration C, and D is a constant the mean value of which is 0·65. The equation is in fair agreement with the data of Harned (A., 1918, ii, 436) and the author (A., 1922, ii, 134) on the influence of neutral salts on the rate of ester hydrolysis in acid media.

J. S. CARTER.

Water of hydration of crystalline compounds. Tensimetric analysis of the system anhydride–water. I. A. G. BERGMAN (J. Russ. Phys. Chem. Soc., 1925, **56**, 177—232).—The theory of the vapour pressure of hydrated compounds, the various methods proposed for its measurement, and the results obtained by previous investigators are discussed.

Observations on the efflorescence of hydrated salts lead to the conclusion that crystallohydrates exhibit two vapour pressures: the one for damaged crystals, this being what is usually observed and measured, and the other for undamaged crystals, this being of considerably lower magnitude. For cadmium sulphate, the former vapour pressure is seventy times the latter. By means of van Bemmelen's method, measurements have been made of the hydration and dehydration isotherms for a series of sixteen solid systems of the type, anhydride–water. These vapour-pressure isotherms are of all possible types, ranging from the ideal stepped form to the continuous zeolite form. The water of hydration of bi-complex salts of the type $[X3en][X(C_2O_4)_3]$, in which X=Co or Cr, exhibits certain peculiar characteristics not observed in other hydrated compounds. T. H. Pope.

Influence of pressure on equilibria in binary systems. I. N. A. Pushin and J. V. Grebenshchikov (Z. physikal. Chem., 1925, **118**, 276—294).—The influence of pressure on conditions of equilibrium on the systems urethane and diphenylamine, urethane and *p*-nitroanisole, and sodium and mercury has been investigated. The results are in accordance with theoretical considerations (cf. A., 1912, ii, 331). L. F. Gilbert.

The system water and the nitrates and sulphates of ammonium and potassium at 25°. Y. Osaka and R. Inouye (Japanese J. Chem., 1925, **2**, 87—98).—The system has been studied by analysis of the solid and liquid phases existing in equilibrium at 25°. The following five series of solid solutions appear as solid phases: $(NH_4,K)_2SO_4$, a complete series with no gap; $(NH_4,K)_2(NO_3)_2\alpha$ and

$$(NH_4,K)_2(NO_3)_2\beta,$$

two series with a gap from 15·6 to 65 molal % of ammonium nitrate; $(NH_4K)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$, which extends from the double salt

$$(NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$$

to the solid solution of the approximate formula $(0{\cdot}6NH_4,0{\cdot}4K)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$; and

$$(NH_4,K)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2,$$

which extends from the double salt

$$(NH_4)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2,$$

to the solid solution of the approximate formula $(0{\cdot}865NH_4,0{\cdot}135K)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$. The relations are represented by a space model, and by its projection on the plane of the four radicals. The compositions of the solutions characteristic of the ternary and quaternary systems represented in terms of the formula

$$100mH_2O,xK_2,(100-x)(NH_4)_2,ySO_4,(100-y)(NO_3)_2,$$

are as follows: solid phases $K_2SO_4+K_2(NO_3)_2$, x=100, y=14·89, m=26·49; $0{\cdot}844K_2,0{\cdot}156(NH_4)_2,(NO_3)_2+0{\cdot}35K_2,0{\cdot}65(NH_4)_2(NO_3)_2$, x=20·52, y=0, m=4·15; $(NH_4)_2SO_4,(NH_4)_2(NO_3)_2+(NH_4)_2SO_4$, x=0, y=27·28, m=5·26; $(NH_4)_2SO_4,(NH_4)_2(NO_3)_2+2(NH_4)_2SO_4,3(NH_4)_2(NO_3)_2$, x=0, y=16·68, m=4·90; $(NH_4)_2(NO_3)_2+2(NH_4)_2SO_4,3(NH_4)_2(NO_3)_2$, $x = 0$, y=6·99, m=3·96; $(K,NH_4)_2SO_4+$

$$(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\beta,$$

x=23·51, y=18·53, m=6·03;

$$(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\beta+(K,NH_4)_2(NO_3)_2\alpha,$$

x=18·4, y=5·9, m=3·5; $(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\alpha+(K,NH_4)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$, x=10, y=8, m=4. L. L. Bircumshaw.

Complex formation in lead nitrate solutions. II. Quaternary system potassium nitrate–lead nitrate–barium nitrate–water. S. Glasstone and E. J. Riggs (J.C.S., 1925, **127**, 2846—2854; cf. Glasstone and Saunders, *ibid.*, 1923, **123**, 2134).—The measurements of Foote (A., 1904, ii, 658) on the system KNO_3–$Ba(NO_3)_2$–H_2O at 25° have been extended, and the isotherms determined both for this system and for the system $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°. The quaternary system was investigated both at 25° and at 50°. It appears that lead nitrate can exist in some form isomorphous with either potassium nitrate or the double salt $2KNO_3,Ba(NO_3)_2$, but the experimental results permit of no definite conclusion being reached. R. Cuthill.

New mass action law. I. Treatment of the new formula. R. Lorenz (Z. anorg. Chem., 1925, **150**, 99—104; cf. A., 1924, ii, 761; 1925, ii, 536, 537, 866, 870).—In a reversible reaction in a condensed system of the type $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ at equilibrium $\mu_{Cd}+\mu_{PbCl_2}-\mu_{Pb}-\mu_{CdCl_2}=0$, in which μ is the molar thermodynamic potential. The values of the thermodynamic potentials of the reacting substances are given by equations of the type $\mu=K+\alpha x^2/(1+rx)^2+RT\log_e(1-x)$, from which is derived the new equation for the law of mass action in condensed systems $x(1-y)/y(1-x)=Ke^u$, in which x, y, $(1-x)$, and $(1-y)$ are molar fractions. u has the value

$$u=(\alpha/RT)\,.\,\{x^2-(1-x)^2/(1+r)\}/(1+rx)^2-(\alpha'/RT)\,.\,\{y^2-(1-y)^2/(1+r')\}/(1+r'y).$$

α, α', r, and r' are constants which are related to the values a and b in van der Waals' equation: $\alpha=(b_2{}^2a_1-2b_1b_2a_{12}+b_1{}^2a_2)/b_1{}^3$; $\alpha'=(b_4{}^2a_3-2b_3b_4a_{34}+b_3{}^2a_4)/b_3{}^3$; $r=(b_2-b_1)/b_1$, and $r'=(b_4-b_3)/b_3$, in which 1, 2, 3, and 4 refer to the four reacting substances. When the reacting substances are in corresponding states, $r'=(b_4-b_3)/b_3=(v_4-v_3)/v_3$, in which v is the molar volume. In condensed molten systems, this is usually sufficiently nearly true, and a table of corrections is given for reduced temperatures of 0·4—0·7°. If more than 1 mol. of a reactant takes part in the reaction, the thermodynamic potential becomes $\nu\mu=\nu k+\alpha\nu x^2/(1+rx)^2+RT\log_e(1-x)^\nu$, where ν is the number of molecules, and in general at equilibrium $\Sigma(\nu\mu)=0$ (cf. van Laar, "Sechs Vorträge ü. d. thermodynamische Potential," Braunschweig, 1906). A. Geake.

Fractional precipitation. II. Topochemical influence, and the separation of manganese and zinc with sodium sulphide. O. Ruff and B. Hirsch (Z. anorg. Chem., 1925, **150**, 84—98; cf. A., 1925, ii, 992).—The solubility product of manganese sulphide ($1{\cdot}4\times10^{-15}$) is much greater than that of zinc sulphide ($1{\cdot}2\times10^{-23}$), but, if sodium sulphide is added to a solution containing both metals, the zinc sulphide is not precipitated in pure condition owing to the mechanical inclusion of manganese sulphide. The two sulphides have similar crystal forms and lattice parameters, and it is probable that, on this account, zinc sulphide forms such a compact layer round manganese sulphide that zinc ions from the solution cannot penetrate it to the manganese sulphide nuclei. When a solution of a zinc salt is added to precipitated manganese sulphide, completion of the reaction is favoured by freshness of precipitation, low temperature, and fine division, but is independent of the concentration of zinc; it is concluded that zinc sulphide skins of similar thickness are always formed. When mixtures of zinc and manganese are fractionally precipitated with sodium sulphide, separation is improved by increasing the ratio $Zn^{\cdot\cdot}:Mn^{\cdot\cdot}$, by diluting the sodium sulphide, by rapid stirring, and by low temperature; under suitable conditions, the precipitate contains less than 0·2% of manganese. The addition of neutral salts has little effect, but increasing hydrogen-ion concentration improves the separation, and manganese sulphide cannot be precipitated from a normal solution when this is greater than 89×10^{-6}.

A. Geake.

Determination of transition points in non-aqueous solutions by the electromotive force method. R. B. Mason and J. H. Mathews (J. Physical Chem., 1925, 29, 1507—1516).—The *E.M.F.* method has been used for the determination of transition points in anhydrous pyridine solutions. There is a sharp break in the temperature–*E.M.F.* curve at 55° for the half cell Cu-Hg|$CuCl_2,2C_5H_5N$ when connected to either the half cell $HgCl_2,2C_5H_5N$|Hg or $CdCl_2,2C_5H_5N$|Cd-Hg. This break is evidently due to the transition of $CuCl_2,2C_5H_5N$ to $2CuCl_2,3C_5H_5N$. On account of several secondary chemical reactions, the *E.M.F.* of the cupric chloride cell gradually changes. The temperature–conductance curve shows a break at approximately 56°. The Cd-Hg|$CdCl_2,2C_5H_5N$|sat. solution of $ZnCl_2$|$ZnCl_2,2C_5H_5N$|Zn-Hg cells were the most satisfactory of all the cells tried as regards conductance, stability, and reproducibility. The temperature–*E.M.F.* curve shows a sharp break at 9·3°, at which the compounds $CdCl_2,6C_5H_5N$ and $CdCl_2,2C_5H_5N$ are in equilibrium. This value is in good agreement with the temperature obtained by the solubility method (9°). On heating the cell Pb-Hg|$PbCl_2,2C_5H_5N$|sat. solution of $PbCl_2$|$CdCl_2,2C_5H_5N$|Cd-Hg, the cadmium and zinc amalgams change polarity. This reversal is apparently an irreversible change, although there is some indication of a transition point at 53°.

L. L. Bircumshaw.

Decomposition of metallic sulphates by heat. (Mlle.) G. Marchal (J. Chim. phys., 1925, 22, 559—582; cf. Hofman and Wanjulow, Trans. Amer. Inst. Min. Eng., 1913, 43, 563).—Results in greater detail are given for the sulphates already mentioned (A., 1925, ii, 1162). The anhydrous sulphates of gallium, beryllium, nickel, cobalt (violet form), manganese, cadmium, silver (yellow form), and magnesium, respectively, afford evidence of decomposition at 500°, 565°, 690°, 690°, 720°, 780°, 850°, and 880°. The total equilibrium pressures become equal to atmospheric at 690°, 788°, 883°, 958°, 1028°, 1060°, 1108°, and 1150°, respectively. Curves showing the logarithm of the total pressure and the total pressure itself, each against temperature, as well as the data for the measured total pressure, and for the calculated partial pressures of the resulting sulphur oxides and oxygen, are given. Equilibrium is quickly established once a given suitable temperature is reached. The mean value of the calculated heat of reaction for nickel sulphate between 800° and 900° is 62·8 cal.; for cobalt sulphate between 820° and 950°, 50·6 cal.; and for gallium sulphate between 600° and 650°, 52·6 cal. With the cadmium salt, the results were confined to the dissociation represented by $5CdSO_4 \rightleftharpoons CdSO_4,4CdO+4SO_3$. At the same temperature, the total equilibrium pressure for nickel sulphate is greater than that for cobalt sulphate, for zinc sulphate much greater than for the cadmium salt, and for gallium sulphate greater than for aluminium sulphate, and hence the separation of the metals from their respective pairs by selective decomposition is possible.

The order found above agrees with that predicted from a knowledge of the heats of reaction at the ordinary temperature.

L. S. Theobald.

Suggestion for a second thermochemical standard. P. E. Verkade and J. Coops, jun. (Bull. Soc. chim., 1925, [iv], 37, 1536—1540).—Polemical, in reply to Swientoslawski (A., 1925, ii, 540). Since it is admitted that salicylic acid is suitable as an auxiliary substance to benzoic acid, it is urged that salicylic acid should be recognised as a second standard, as previously suggested by the authors (A., 1925, ii, 39).

C. H. D. Clark.

Thermal properties of viscous sulphur. P. Mondain-Monval (Compt. rend., 1926, 182, 58—60).—Calorimetric experiments with sulphur are described. The transition S(liq.) ⟶ S(viscous), which occurs above 160°, absorbs 2·8 cal./g., and the transition $S_\alpha \longrightarrow S_\beta$ absorbs 2·7 cal./g. The mean specific heat of S_α is 0·176, of liquid sulphur, 0·220, and of viscous sulphur, 0·290 (cf. Lewis and Randall, A., 1911, ii, 371).

S. K. Tweedy.

Heat of adsorption and surface tension. H. Cassel (Physikal. Z., 1925, 26, 862—864).—Theoretical. Iljin's method of treatment (A., 1925, ii, 958) is extended and the connexion between various expressions for heat of adsorption is explained.

R. A. Morton.

Vapour pressure and heat of dilution of aqueous solutions [of carbamide]. E. P. Perman and T. Lovett (Trans. Faraday Soc., Jan., 1926, advance proof; cf. Perman and Price, A., 1913, ii, 20).—The vapour pressures of aqueous solutions of carbamide have been determined by a statical method (Trans. Faraday Soc., 1923, 19, 112—116) over a wide range of concentrations at 40·02°, 49·99°, 60·28°, 70·39°, and 80·10°. The smooth curves obtained by plotting the lowering of vapour pressure against the weight of carbamide per 100 c.c. of solution meet, on extrapolation, in a point representing a vanishingly small vapour pressure and a concentration of 132 g./100 c.c. of solution. The proportionality between $\log p_0/p$ and n/N holds fairly well for all concentrations and temperatures, but the agreement is improved by adding to N a small fraction of n. Since the introduction of a hydration factor, as in Callendar's formula, lessens agreement, it is concluded that there is no hydration of the carbamide, and that the mol. wt. is normal. The vapour pressure–temperature curves for solutions of the same concentration are shown and are named "isosthens." Van Babo's law does not hold for aqueous solutions of carbamide. The densities for solutions up to a concentration nearly approaching saturation are given for the above temperatures. The curves form a regular series. The derived density–temperature curves for equal concentrations appear to be linear, their slopes decreasing slightly with increasing concentration.

For determining the heats of dilution of concentrated solutions of carbamide in water, a new method, involving the measurement, by electrical means, of the heat change occurring, was employed. The heat lost by radiation was compensated by the use of a heating coil, whilst a second coil exactly counterbalanced the heat absorbed on dilution. The amounts of heat absorbed by the saturated solutions when 1 mol. of water is added are small compared with the values for metallic salt solutions. The curves heat absorbed–concentration are for the most part almost linear, but alter sharply at the ends. They overlap at the lower concentrations and their slope becomes less at higher temperatures. Data at temperatures 40·02°, 49·99°, 60·28°, 70·39°, and 80·1° are given. At the lower temperatures, the calculated affinity of water for various solutions is roughly proportional to the heat of dilution, but at the higher temperatures it increases more rapidly with increasing concentration, and finally becomes greater. The observed values of H, the heat of dilution defined by Kirchhoff's equation, agree well with those calculated from the equation $H=RT^2\partial(\log_e p_0/p)_c/\partial T$. In general, the heat of dilution was observed to fall as the temperature increased.

The results of Tucker (A., 1915, ii, 674) are discussed, and a new method for determining solubility is suggested. L. S. THEOBALD.

Conductivity of mixtures of strong electrolytes. H. EGNÉR (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 5, 1—8; cf. Bray and Hunt, A., 1911, ii, 688; Kraus, A., 1922, ii, 269).—Measurements have been made of the electrical conductivities at 25° of solutions of hydrogen, lithium, sodium, potassium, magnesium, and calcium chlorides and of mixtures of hydrogen chloride with lithium, sodium, and calcium chlorides, of magnesium chloride with sodium and calcium chlorides, and of potassium chloride with lithium chloride in the concentration range 0·002—0·1N. The conductivities of the mixed solutions as calculated by the aid of the isohydric principle from the data for the single salts are always slightly greater than those experimentally determined. For the mixtures which contain hydrogen chloride the differences (2·2—0·3%) are decidedly in excess of the errors of experiment, but even in this case the difference tends to disappear with dilution. The viscosity correction changes the calculated values only slightly and in a favourable direction. A small difference in the value of λ_0 has very little influence on the value of the computed conductivity. J. S. CARTER.

Influence of iodine on the conductivity of aqueous solutions of cadmium iodide and potassium iodide. H. BRUNS (Z. Physik, 1925, **34**, 751—765).—The solubility of cadmium iodide in water has been determined between 21° and 87°. Little change in the conductivity of 5% cadmium iodide solution is caused by addition of iodine; the conductivity of more concentrated cadmium iodide solutions is, however, definitely increased. Addition of iodine decreases the conductivity of potassium iodide solutions, owing to the formation of the comparatively slow I_3 ions. These ions are also formed in the cadmium iodide solutions, but their effect is said to be more than compensated by the splitting up of $(CdI_2)_n$ aggregates. The results of f. p. determinations agree with the above theory. The effect of iodine on the emission of ions from the heated salts is correlated with conductivity observations (cf. Schmidt, A., 1925, ii, 251). L. F. GILBERT.

Mobility of ions in solid cuprous and silver sulphides. H. BRAUNE (Z. Elektrochem., 1925, **31**, 576—581).—The rate of migration of the anions in solid cuprous and silver sulphides is known to be very much less than that of the cations. Approximate data for the mobility of both ions have been obtained by measuring the diffusion which takes place between a cast cylinder of pure sulphide and one of a dilute solid solution of the one sulphide in the other, or of selenides in sulphides. The temperature of the experiments ranged from 100° to more than 800°. For the silver ion, the diffusion coefficient is given by $D_T=113e^{-2285/T}$, for the cuprous ion by $D_T=40{\cdot}3e^{-1893/T}$, and for the sulphide ion by $D_T=89{\cdot}3e^{-10120/T}$, confirming the great difference in the temperature coefficients of cations and anions. The transport numbers of sulphide ion in silver sulphide have been calculated: they range from $0{\cdot}9\times10^{-8}$ at 177° to $0{\cdot}7\times10^{-3}$ at 836°. W. A. CASPARI.

The hydrate problem. III. Electroendosmose and the electrolytic transport of water. H. REMY (Z. physikal. Chem., 1925, **118**, 161—192; cf. A., 1915, ii, 310).—The movement of liquids under the action of applied potential differences has been studied with pure water and solutions of electrolytes of concentration 0·001N to N and with diaphragms of powdered sulphur, animal charcoal, clay, the Zsigmondy–Bachmann membrane, gelatin, and parchment paper. With parchment and gelatin diaphragms, the effect of increasing the concentration of electrolyte is to accelerate the shift of liquid. At the concentrations used, this effect is not truly endosmotic, *i.e.*, is not due to increase of anion adsorption on the diaphragm, and must be ascribed to transport of water attached to the ions. L. F. GILBERT.

Oxidation potentials and equilibria in the system: chlorine–iodine–hydrochloric acid–water. G. S. FORBES, S. W. GLASS, and R. M. FUOSS (J. Amer. Chem. Soc., 1925, **47**, 2892—2903).—The oxidation potentials of chlorine and of chlorine plus iodine in 4, 5, and 6N-hydrochloric acid have been measured at 25°. For iodine trichloride, the results are given by $E=E_0+0{\cdot}0124\log[ICl_3]$, and for the monochloride by $E=E_0+0{\cdot}0154\log[ICl]$, where E_0 is the extrapolated $E.M.F.$ for solutions containing 1 g.-equiv. of iodine and 3 or 1 g.-equiv. of chlorine, respectively, per litre. These equations indicate a valency change twice as great as that actually occurring; this may be explained by the assumption that the electrochemical change is $Cl_2+2e \rightleftharpoons 2Cl'$, and not $ICl \rightleftharpoons I^{\cdot}+Cl'$.

The above solutions may be accurately titrated electrometrically, providing escape of chlorine is avoided and platinum–iridium electrodes are used. The following equilibrium constants, which are independent of the acid concentrations, are calculated: $[ICl][Cl_2]/[ICl_3]=7{\cdot}2\times10^{-4}$; $[I_2][Cl_2]/[ICl]^2=7{\cdot}8\times10^{-15}$; $[I_2][ICl_3]/[ICl]^3=1{\cdot}1\times10^{-11}$. Oxidation-potential measurements form a sensitive test for the presence in iodine of impurities of higher oxidation potential. S. K. Tweedy.

Effect of electrode material on oxidation potentials. J. A. V. Butler, W. E. Hugh, and D. H. Hey (Trans. Faraday Soc., Jan., 1926, advance proof).—A comparison of the oxidation potentials of various metals has been made. At 25°, in the cells $Hg|Hg_2Cl_2|N/200$¦$K_3Fe(CN)_6$ or $K_4Fe(CN)_6|$metal and $Hg|N$-KCl¦N-KCl|metal, platinum (platinised and plain), palladium, iridium, osmium, gold, rhodium, and ruthenium gave a constant potential (0·1905±0·0001 volt) within an hour. Molybdenum, tungsten, nickel, silver, and mercury did not give constant potentials. The system, cuprous–cupric chlorides in aqueous ammonia allowed a wider range of metals to be compared directly with two platinised platinum electrodes as standards. Palladium, iridium, gold, osmium, rhodium, ruthenium, silver, nickel, and mercury as electrodes quickly reached the potential of the standards (to within ±0·0001 volt). Metallic selenium and graphite gave constant values differing from that of platinum by 0·3 and 0·6 millivolt, respectively. Electrodes of molybdenum, tungsten, tantalum, arsenic, and antimony did not give constant potentials. The independence of oxidation potentials of the electrode material, when this takes no appreciable part in the cell reaction, is thus confirmed.

L. S. Theobald.

Oxidation–reduction potentials of organic substances. H. von Euler and A. Ölander (Z. anorg. Chem., 1925, **149**, 1—17).—By means of the oxygen and hydrogen electrodes, *E.M.F.* measurements have been made with buffered solutions of quinol, quinone, acetaldehyde, ethyl alcohol+acetic acid (or acetate), ethyl alcohol+acetaldehyde+acetic acid, lactic acid, sodium lactate, dextrose, lævulose, sodium benzoate, and potassium cinnamate.

R. Cuthill.

Does radium exert an influence on the potential of the hydrogen electrode? M. Centnerszwer and M. Straumanis (Z. physikal. Chem., 1925, **118**, 240—250).—Calculations of the degree of dissociation of molecular hydrogen at 20° and 760 mm. give values ranging from $2{\cdot}3\times10^{-32}$ to $2{\cdot}01\times10^{-34}$. Experiments in which the degree of dissociation of the hydrogen was changed by subjecting it to the action of radium bromide showed no measurable change in the potential of the hydrogen electrode. L. F. Gilbert.

Mixed electrodes of the second type. P. Gross and O. Halpern (Z. physikal. Chem., 1925, **118**, 255—256; cf. A., 1925, ii, 405).—A reply to Horovitz's criticism (A., 1925, ii, 673). L. F. Gilbert.

Thermodynamic potential difference at the boundary of two liquid phases. III. S. Vossnessenski and K. Astachov (Z. physikal. Chem., 1925, **118**, 295—300; cf. A., 1925, ii, 673; this vol., 30).—The cells N-calomel electrode|HCl in water|HCl in phenol|N-calomel electrode; Hg|HgCl,N-KCl in water|HCl in water|HCl in phenol|KCl in phenol, HgCl|Hg; N-calomel electrode|H_2SO_4 in water|H_2SO_4 in phenol|N-calomel electrode; and N-calomel electrode|H_3PO_4 in water|H_3PO_4 in phenol|N-calomel electrode were studied. Measurements were also made of the distribution of hydrogen chloride and sulphuric acid between water and phenol. The results are discussed theoretically. L. F. Gilbert.

Potential difference and equilibrium across a semipermeable collodion membrane in the case of sodium chloride and Congo-red. R. Azuma and N. Kameyama (Phil. Mag., 1925, [vi], **50**, 1264—1276).—The potential differences and ionic equilibria across a collodion membrane separating solutions of sodium chloride and sodium chloride plus Congo-red have been measured. If the Congo-red be assumed to ionise as a uni-univalent electrolyte ($Na_2R=Na^++NaR^-$) in the range of concentrations measured (2·0—6·0 millimol. per litre), and if the ionic-strength principle of G. N. Lewis be assumed to hold good for the mixtures of sodium chloride and Gongo-red used (sodium chloride from 6 to 50 millimol. per litre), the experimental results are in general agreement with the thermodynamical requirement of the equality of the activities of sodium chloride on either side of the membrane. The potentials of the following cells were measured: $N.E.|N$-KCl$|B|$C.R.+NaCl$(c_1)||$NaCl$(c_2)|B|N$-KCl$|N.E.$, and $N.E.|N$-KCl$|B|$NaCl$(c_1)||$NaCl$(c_2)|B|N$-KCl$|N.E.$, where $N.E.$ is a normal calomel electrode, B is a gelatin-salt bridge (0·05—0·1N-sodium chloride in 10% gelatin), $||$ is the membrane, and C.R. is Congo-red. It was hoped thus to obtain the potential difference across the membrane, but owing to the difficulty of eliminating liquid–liquid potentials in solutions containing Congo-red, it was not possible to prove that this potential difference agreed with that predicted thermodynamically.

A. B. Manning.

Potential of fluorine from measurements of the decomposition voltages of fused fluorides. O. Ruff and W. Busch (Z. Elektrochem., 1925, **31**, 614—615).—Investigations on the electrodeposition of magnesium from fused mixtures of magnesium fluoride with the fluorides of the alkali and alkaline-earth metals (A., 1925, ii, 569) led the authors to arrange these metals in a deposition series. Neumann and Richter (A., 1925, ii, 1164) are wrong in identifying this with a potential series. Neumann and Richter's data are criticised on the grounds that there is not sufficient proof that the measured potentials correspond with decomposition voltages and that the values differ considerably from those of Arndt and Willner (A., 1908, ii, 457) for the fused alkaline-earth chlorides. The identification of the potentials with normal potentials is open to criticism and the linear extrapolation from 800° to the ordinary temperature is thermodynamically unsound. J. S. Carter.

Electromotive behaviour of cupric oxide. R. E. W. Maddison (Trans. Faraday Soc., Jan., 1926, advance proof; cf. Allmand, J.C.S., 1910, **97**, 603).—The behaviour of the electrode

$Pt|CuO,Cu_2O,N\text{-}NaOH$

has been re-examined at 25°±0·1°. Smooth platinum foil with mercury contacts, and a standard element $Hg|HgO,N\text{-}NaOH$ as auxiliary electrode, were used. Initially, the electrodes gave a relatively high value, which became more negative in the course of a few weeks, and the final values were not the same in every case. The fall in *P.D.* varied up to 40 millivolts. In the final stages, many electrodes seemed to show a certain periodicity with regard to values of *P.D.* In order to examine the effect of temperature, copper oxide was prepared by heating the carbonate for 30 min. at temperatures from 245° to 760°, in air and in a vacuum. Both the initial and final *P.D.* of the electrode vary with the temperature of preparation of the oxide and the duration of heating. Higher initial values were obtained after vacuum treatment, but the final *P.D.* was scarcely affected. Storage of the oxide during a year produced no change in its electromotive behaviour; the effect of chilling the oxide gave contradictory results. The polymerisation hypothesis of Allmand (*loc. cit.*) was tested, but without definite results.

The appearance and specific gravity of the cupric oxide specimens varied considerably.

L. S. Theobald.

Improved salt bridge. H. S. Stern (J. Physical Chem., 1925, **29**, 1583—1584).—A modification of Müller's salt bridge is described, in which the rubber tube is replaced by a stop-cock, one of the paper stoppers being omitted. The advantages of the apparatus and the method of using it are discussed.

L. L. Bircumshaw.

Theory of static and dynamic displacement. D. Reichinstein (Z. Elektrochem., 1925, **31**, 593—613).—Largely retrospective. The author's hypothesis relative to the constant sum of equilibrium concentrations is applied to passivity, to adsorption, and to processes taking place at electrodes. In the last-mentioned case the summation constancy refers, not to concentrations, but to thicknesses of layers.

W. A. Caspari.

Method of measuring the relative surface charges of electrolytes. A. Garrison (J. Physical Chem., 1925, **29**, 1517—1522).—The principle of the electric condenser has been used to measure the potentials of the surfaces of a number of electrolytes relative to the surface of water. The apparatus consists essentially of the electrolyte contained in a shallow glass dish, connected to a $0 \cdot 1N$-calomel electrode, the mercury of which is connected to a quadrant electrometer and a horizontal metal plate which can be raised or lowered and charged to a definite potential. The surface of the electrolyte and the metal plate form the two plates of a condenser. The metal plate is given different potentials until no charge is induced in the electrometer when the plate is moved. By comparing the potentiometer readings for no deflection of the electrometer needle, using different electrolytes, the surface charges of the electrolytes relative to water may be measured to 0·005 volt. Measurements with a number of salts and acids showed that the first traces of a substance added to water have the largest effect on its surface charge, whilst subsequent additions as a general rule have a small effect, often decreasing the charge and sometimes reversing the sign.

The general relations between concentration and surface charge are similar to the relations between concentration and adsorption. L. L. Bircumshaw.

Overvoltage. F. Meunier (J. Chim. phys., 1925, **22**, 595—632).—A review, with bibliography, of the whole subject, in which definitions of overvoltage and methods of measurement are discussed. The influence of time, current density, nature, and concentration of the electrolyte, added substances, and other factors is described in detail.

L. S. Theobald.

Electrolysis of acid solution of copper sulphate. L. V. Redman (J. Physical Chem., 1925, **29**, 1548—1555).—The relative merits of Siegrist's "kinetic theory" (Z. anorg. Chem., 1901, **26**, 273) and the "mathematical theory" of Rosebrugh and Miller (cf. A., 1911, ii, 181) are discussed, and experiments with solutions of copper sulphate in sulphuric acid are described which were made with the object of deciding between the two theories. If the liberation of hydrogen first occurs when the rate of deposition of copper called for by Faraday's law exceeds the maximum rate at which copper can be chemically reduced from a given solution, then periodic interruptions of the current will be without effect, and a current which when uninterrupted will liberate hydrogen, will also liberate it if periodically interrupted. If, on the other hand, the liberation of hydrogen is due to the exhaustion of copper salt in the solution at the cathode, then with an interrupted current nothing but copper may be deposited, although the same current uninterrupted would bring about liberation of hydrogen. Measurements with interrupted current showed that the limiting current rises continuously with the number of interruptions per second, and when the interruptions are frequent enough, the limiting current is about double that with uninterrupted current. This result disposes of Siegrist's kinetic theory, and shows that the assumptions made by the mathematical theory are applicable to the case in question.

The voltage–time curve during the first few seconds of electrolysis was studied in more detail by means of an oscillograph. L. L. Bircumshaw.

Amphoteric ionisation of polonium and bismuth. F. Paneth (Z. Elektrochem., 1925, **31**, 572—576).—The electrolytic dissolution of thin deposits on gold electrodes in dilute solutions of potassium hydroxide has been examined by the method of Le Blanc (A., 1906, ii, 67). Polonium goes into solution both at the cathode and the anode; the ratio of the rates is 1 : 1·4 in $0 \cdot 1N$-electrolyte and 1 : 10 in $0 \cdot 005N$-electrolyte. Bismuth (thorium-*C*) behaves similarly, the ratio of the rates of cathodic to anodic dissolution being 1 : 1·2 and 1 : 3·0 for 0·004*N*- and 0·001*N*-electrolytes, respectively.

W. A. Caspari.

Catalytic phenomena when zinc is dissolved in acids. M. Centnerszwer and M. Straumanis (Z. physikal. Chem., 1925, **118**, 415—437).—The addition of salts of iron, silver, antimony, bismuth, copper, arsenic, cobalt, gold, nickel, and the consequent precipitation of these metals accelerates the dissolution of zinc by acids, the effect increasing from left to right of the series. Retardation is produced by salts of thallium, cadmium, tin, and lead. Highly oxygenated compounds, *e.g.*, ammonium molybdate and potassium permanganate, accelerate the process. The velocity of dissolution increases in proportion to the concentration of the catalyst when the concentration is small, but at higher concentrations a limiting value is approached. An induction period is ascribed to the time occupied in the separation of the catalysing metal. Theoretical considerations suggest that the induction period should be inversely proportional to the zinc surface and should diminish as the concentration of catalyst is increased; actual observations are in qualitative agreement with this prediction. The addition of colloidal substances retards the precipitation of the catalyst, thus causing an increase of the induction period and a decrease in the rate of dissolution.

L. F. Gilbert.

Overpotential of hydrogen on finely divided metals and its connexion with the catalytic influence of metals on the solution of zinc. M. Centnerszwer and M. Straumanis (Z. physikal. Chem., 1925, **118**, 438—446; cf. preceding abstract).—Measurements have been made of the potential difference which must be applied to effect the dissolution of metals nobler than zinc, usually in *N*/2-hydrochloric and sulphuric acids. The overpotential of hydrogen is much greater on smooth crystalline surfaces than on finely divided metallic precipitates; this behaviour is correlated with the observation that large bubbles of hydrogen are evolved from smooth surfaces and much smaller bubbles when the overpotential is low. At a given current density, hydrogen has a definite overpotential which depends on the chemical nature of the metal. The velocity of dissolution of zinc in the presence of other metals cannot yet be interpreted in the light of a quantitative theory.

L. F. Gilbert.

Theory of the velocity of chemical reactions. II. N. Bjerrum (Z. physikal. Chem., 1925, **118**, 251—254; cf. A., 1924, ii, 240; 1925, ii, 681).—The author maintains the correctness of his deduction of Brönsted's formula (A., 1922, ii, 699). The hypotheses underlying this deduction are more fully explained.

L. F. Gilbert.

Molecular attraction and velocity of reactions. O. Maass and C. Sivertz (J. Amer. Chem. Soc., 1925, **47**, 2883—2891).—The reaction between dry propylene and liquid hydrogen chloride, yielding *iso*propyl chloride, and a chlorohexane as side product, was examined at 0° and 20° by the method described previously (A., 1925, ii, 214). With equimolar quantities, 75% of the acid reacts with all the propylene at 20°; when 2 mols. of acid to 1 mol. of propylene are used, the reaction velocity is increased fourteen-fold. Mercury has no influence on the reaction in the liquid state; 1—2% of water has only a slight effect, but large quantities cause the formation of two distinct liquid phases and the reaction velocity is greatly increased. The rate with hydrogen bromide is 200 times as great as that with hydrogen chloride. The acid acts as a catalyst probably because of regional orientation in the liquid phase caused by its polar nature. No perceptible reaction occurs in the gaseous phase, even at 100°. It is considered that the translational and rotational energies of molecules hinder chemical combination, whereas vibrational energy promotes it; on this basis, the effects of pressure and temperature may be qualitatively explained, increased pressure causing closer proximity of the molecules and so aiding regional orientation and consequently affecting the reaction velocity.

S. K. Tweedy.

Behaviour of cyanamide in acid and alkaline solution. G. Grube and G. Motz (Z. physikal. Chem., 1925, **118**, 145—160; cf. A., 1914, i, 152).—The reaction $2CN{\cdot}NH_2 \rightleftharpoons (CN{\cdot}NH_2)_2$ goes practically completely from left to right at low temperatures and in weakly alkaline solutions; rise of temperature and increase in alkalinity shift the equilibrium point towards the left. The hydrolysis of cyanamide to carbamide is a first order reaction when cyanamide and acid concentrations are low, the velocity being approximately proportional to the concentration of the acid when this is less than 0·1*N*. With higher acid and smaller cyanamide concentrations, constants corresponding with a unimolecular reaction are still obtained, but increase more rapidly with rising acid concentration than is demanded by proportionality. The reaction is of a higher order with concentrated cyanamide solutions containing low concentrations of acid; this is due to salt formation between part of the acid and the carbamide.

L. F. Gilbert.

Chemical reactions in powdered mixtures of two kinds of crystals. G. Tammann [with F. Westerhold, B. Garre, E. Kordes, and H. Kalsing] (Z. anorg. Chem., 1925, **149**, 21—98; cf. Hedvall and Heuberger, A., 1923, ii, 860; 1924, ii, 484).—If in the plane of contact of compressed pastilles of two powdered crystalline substances a layer of a third substance be formed on heating, the rate of isothermal growth of the layer is given by $l=b\log_e t+$ constant, where l is the thickness of the layer after heating for a time t, and b is a constant depending on the temperature. A similar law holds for the rate of reaction in powdered mixtures, which is in every case increased by stirring, so that in many cases the reaction goes almost to completion. The rate of interpenetration of the different crystals is determined more by the movement of the molecules within the crystal, *i.e.*, recrystallisation, than by the movement of the lattices themselves. At the temperature at which this effect becomes appreciable, the powdered mass commences to cake, and it is found empirically that the ratio of this temperature (Abs.) to the temperature (Abs.) at which reaction becomes appreciable is about 0·57, unless one of the reactants has a transition point above the former temperature. The actual temperature range over which reaction occurs and also the approximate heat of reaction are determined from heating curves. Where neither reactants nor resultants conduct metallically, conductivity measurements will detect traces of liquid formed in the reaction. In many reactions no liquid could be detected in this way, but adsorbed films of liquid may have played a part in bringing about reaction.

Investigation of the reaction between tungsten trioxide or molybdenum trioxide and basic oxides and carbonates has shown that if the radius of the particles of the reactants exceeds the thickness of the layer of resultant formed on their surface, the rate of transformation decreases with increasing size of grain. The temperature at which reaction commences between basic oxides and sulphates and nitrates is much affected by the salt having a transition point. With this proviso, it is the same for a given basic oxide reacting with any sulphate. Experiments on the reaction between carbonates and sulphates have failed to confirm many of Spring's results (cf. A., 1888, 1243), *e.g.*, no reaction occurs between sodium carbonate and barium sulphate below 500° (cf. Balareff, A., 1924, ii, 483). The reaction of silver carbonate with sodium halides has been examined. Silica is more reactive as glass than as quartz. In the reaction between oxides and sulphides, the rate of heating and compression of the reactants have a varying effect on the rate of the reaction and the temperature of its commencement. The reactivity of silicon, titanium, and zirconium dioxides with basic oxides decreases in this order. Experiments have also been made on the reaction between vanadium pentoxide, antimony trioxide, and arsenic trioxide, and a series of basic oxides. Of the latter, calcium and lead oxides were the most reactive, whilst ferric oxide and alumina did not react at all. Some new vapour-pressure determinations have been made for arsenic trioxide, and the influence of foreign substances on the vapour pressure has been examined.

The reaction between powdered mixtures of crystals has been investigated thermodynamically.

R. Cuthill.

Corrosion of cast iron in sulphuric acid of varying concentration. G. Delbart.—See B., 1926, 56.

Action of silica on electrolytes. A. F. Joseph (Nature, 1926, **117**, 17).—Taking into consideration the retention of water by silica prepared as described by Mukherjee (A., 1925, ii, 962), the author still fails to detect the slightest adsorbing power for hydrochloric acid.

A. A. Eldridge.

Action of silica on electrolytes. II. A. F. Joseph and H. B. Oakley (J.C.S., 1925, **127**, 2813—2818).—The investigation of Joseph and Hancock (J.C.S., 1923, **123**, 2022) has been extended to the action of silica on bases. The titration curve of silica with sodium hydroxide is typical of the combination of a strong base with a weak dibasic acid. In the action of sodium or potassium hydroxide on silica, the main factor determining the extent of reaction is an equilibrium between the solid silica, the layer of solid silicate formed on its surface, and the liquid phase. With bases forming no readily soluble silicate, the main factor is an ordinary solubility relationship between solid and soluble silicates. Addition of a neutral salt increases the amount of solid silicate formed.

R. Cuthill.

Velocities of chemical reactions in presence of organic colloids. N. A. Izgaryschev and M. I. Bogomolova (J. Russ. Phys. Chem. Soc., 1925, **56**, 61—66).—The authors have investigated (1) the influence of egg-albumin and globulin on the hydrolysis of ethyl acetate in $0 \cdot 2N$-concentration by $0 \cdot 1N$-sulphuric acid, (2) that of egg-albumin and edestin on the hydrolysis of this ester by $0 \cdot 1N$-hydrochloric acid, and (3) that of gelatin, egg-albumin, and globulin on the inversion of sucrose by $0 \cdot 1N$-hydrochloric acid. Increase in the concentration of egg-albumin, globulin, or edestin causes increasing retardation of both reactions, and determination of the hydrogen-ion concentration of the solutions shows that the retardation is the result of the formation of compounds between the acid and the proteins. Increasing proportions of gelatin cause increase to a maximum and then progressive diminution in the velocity of inversion of sucrose; possibly the colloidal–capillary properties of the gelatin molecules play a part in this case.

T. H. Pope.

Kinetics of ester hydrolysis by liver lipase. E. Knaffl-Lenz (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, 6, No. 3, 1—18).—The rate of hydrolysis of ethyl butyrate by the glycerol extract from liver is proportional to the concentration of enzyme and inversely proportional to that of the substrate. In alkaline solution at constant p_H, the velocity coefficient calculated on the assumption of a unimolecular process increases as the reaction proceeds, but in more acid media (p_H 5·45) remains constant. In alkaline solution, the quotient x/t, where x is the amount of ester hydrolysed in time t, has a constant value. The rate of reaction diminishes continuously if the acid formed as a result of hydrolysis is not neutralised. It is suggested that the ester itself has an arresting action on the activity of lipase, the magnitude of which is proportional to the substrate concentration. Although sodium butyrate has very little influence on the rate of hydrolysis in alkaline solution, in more acid media (p_H 5·7) it has a considerable retarding effect, the rate of reaction decreasing as the reaction proceeds. Under the experimental conditions, a synthesis of ester from alcohol and acid by lipase is not possible. The equilibrium point reached depends on the initial concentration of ester, the enzyme completely losing its activity at p_H 5·2; hence by increasing the substrate concentration the equilibrium is displaced towards the ester side. The rate of hydrolysis of mono- and tri-butyrin even in alkaline media continually diminishes. The optimum for hydrolysis of ethyl butyrate by lipase is in the p_H region 7·8—8·8 and that for butyrin about p_H 9·7.

J. S. Carter.

Kinetics of lipase reactions. S. ARRHENIUS (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 4, 1—33).—The data of Knaffl-Lenz (A., 1923, i, 621, and preceding abstract) are discussed. Under the conditions where the rate of hydrolysis of ethyl butyrate conforms to the requirements of the unimolecular law (p_H 5·45) there is a progressive destruction of enzyme. In alkaline solution where the rate of destruction of enzyme is extremely slow, the deviations from constancy of the value of x/t are due to errors in the determination of the initial time t_0. The continual decrease in the value of x/t for propyl propionate and butyrin is due to a relatively rapid destruction of lipase. Lipase is held to be a mixture of enzymes which are inactivated at varying rates, the more active varieties being most rapidly destroyed. The inversion of sucrose by invertase (Michaelis and Menten, A., 1913, i, 540) is discussed and the equation put forward by the above authors is shown to hold only over a limited range of sucrose concentration. Constant rate of hydrolysis is probably the normal course of lipase reactions, gradual inactivation of enzyme and the influence of reaction products being responsible for the observed deviations.

J. S. CARTER.

Precipitation of calcium sulphite. R. G. W. FARNELL.—See B., 1926, 72.

Passivity, catalytic action, and other phenomena. A. S. RUSSELL (Nature, 1925, **117**, 47—48).—An extension of the author's view of passivity (A., 1925, ii, 406) and its correlation with the recent work of Taylor, Armstrong and Hilditch, Heyrovský, and Lowry; in chromium, manganese, iron, cobalt, and nickel, the number of electrons in the outermost orbit is "ideally" between 1 and 2, and the state is regarded as passive or active, respectively, when one or two electrons are in the outer orbit. When passive, chromium and iron lie between copper and bismuth in their susceptibility to attack by acids, although when active they are more reactive than cadmium. Probably both iron and chromium when in true solution in a second metal become passive; in solution in each other, the passive "stainless" steel is produced. If metallic atoms may conduct an electron from one reacting molecule to another, adsorption and catalytic action may be related with passivity. Such metals, which may exist normally in either the active or the passive form, are, it is considered, best able to adsorb gases and to act as catalysts when in the passive form, passing in so doing into the active form. The theory explains why the metals which exhibit passivity alone have very low overvoltages, and suggests an explanation of the fact that gases adsorbed on nickel, platinum, palladium, etc. are sometimes in the atomic condition.

A. A. ELDRIDGE.

Case of mutarotation, and its application to the study of the hydrolysis of ethyl oxalate by water and dilute acids. E. DARMOIS (Compt. rend., 1925, **181**, 1137—1138).—Whilst the depression in rotatory power of ammonium dimolybdomalate produced by the addition of oxalic acid is immediate, addition of ethyl oxalate brings about a depression which increases with the time, finally reaching the value obtained directly by addition of oxalic acid. This effect is ascribed to the hydrolysis of the ester, which may thus be followed in neutral and acid solution. The hydrolysis is catalysed by hydrogen ions, and is thus autocatalytic when no foreign acid is present. Ethyl hydrogen oxalate acts very much more rapidly on the complex salt than the neutral ester.

S. I. LEVY.

Autocatalysis with varying catalyst. Biperiodic febrile reactions. A. QUARTAROLI (Gazzetta, 1925, **55**, 619—638).—The results of further experiments (cf. A., 1925, ii, 53) show that, under the influence of hydrogen peroxide in alkaline solution, iron, cobalt, and nickel undergo only an oxidising action, which results in products capable of decomposing hydrogen peroxide. In the case of copper, however, there exists for any definite degree of alkalinity a critical zone of hydrogen peroxide concentration, the action being either oxidising or reducing, according as this concentration is exceeded or the reverse. Hence, if a relatively concentrated hydrogen peroxide solution is used, its decomposition exhibits two successive and distinct febrile periods, the first and weaker one being due to copper peroxides, and the second, violent one to suboxides; these periods are separated by a period of minimum activity due to the normal oxide.

With silver, and especially with gold and mercury, the action of alkaline hydrogen peroxide solution is solely a reducing action which increases in intensity with the alkalinity. An excessive reducing action here leads to formation of the free metal in a pulverulent, non-colloidal form of only slight activity. Thus, when the concentration of the alkali is at least 1·66%, intense but ephemeral febrile periods occur, diminution of the ratio of the concentration of the hydrogen peroxide to that of the alkali below a certain limit resulting in reduction to the free metal and consequently to rapid fall in the velocity of the reaction. If the concentration of the alkali is continuously lowered, the intense febrile period undergoes amplification until it comprises almost the whole reaction. With lead, there arises an analogous phenomenon due, however, to different causes. When the alkalinity and hence the reducing action is low, a highly active lead peroxide is formed, whilst a greater alkalinity and a sufficient concentration of hydrogen peroxide lead to a brief febrile period, followed, when the ratio between hydrogen peroxide and alkali falls below a certain limiting value, by a sudden slackening of the reaction owing to the formation of ordinary lead oxide. The behaviour of thallium in this respect is similar to that of lead.

T. H. POPE.

Relation of homogeneous to catalysed reactions. Catalytic decomposition of hydrogen iodide on the surface of platinum. C. N. HINSHELWOOD and R. E. BURK (J.C.S., 1925, **127**, 2896—2900; cf. Hinshelwood and Prichard, A., 1925, ii, 310, 981, 983).—This reaction occurs in a unimolecular manner in accordance with the equation $HI=H+I$. Hydrogen has a slight retarding influence.

R. CUTHILL.

Catalytic activity of contact substances. III. Catalysis of detonating gas at high temperatures by metals inactive at the ordinary temperature and binary alloys from group 8 of the periodic system. H. Remy and H. Gönningen (Z. anorg. Chem., 1925, **149**, 283—296; cf. A., 1925, ii, 1176).—The metals of the iron group, ruthenium, and the alloys of these metals with the platinum metals were used as catalysts. The temperature at which catalytic action commences can be accurately determined from the temperature–volume curve. If the catalysts are first charged with hydrogen, the alloys rhodium–iron and iridium–iron are the most active, nickel alloys except that with iron are rather less active, and iron and the alloys osmium–iron and nickel–iron are the least active. Previously charging with oxygen reduces the activities of most of the pure metals, but has a varying effect on the alloys. The effect of the rate of heating and of diluting the detonating gas with hydrogen has been studied. Contact masses prepared by reduction of the oxides are more active than those obtained by reduction of the chlorides. R. Cuthill.

Mechanism of catalysis by aluminium oxide. M. C. Boswell and H. M. Dilworth (J. Physical Chem., 1925, **29**, 1489—1506; cf. A., 1923, ii, 231; 1925, ii, 215, 805).—It is suggested that the catalytic power of aluminium oxide is due to a very stable surface film of hydrogen ions and hydroxyl ions in a state of great tension, surrounding the particles of oxide. In support of this theory, it is found that aluminium oxide catalyses the following reactions, involving, simultaneously, hydrogen and oxygen: (1) the dehydration of ethyl alcohol to ethylene; (2) the combination of acetylene and water to form acetaldehyde; (3) the combination of ethylene and water to form ethyl alcohol; (4) the union of hydrogen and oxygen to form water. The dehydrogenation of ethyl alcohol at 350° has been studied quantitatively. In addition to the formation of ethylene, the following reactions occur: (1) $2C_2H_4 \longrightarrow C_2H_6+C_2H_2$ and (2) $C_2H_4 \longrightarrow 2C+2H_2$. The acetylene from (1) is polymerised and adsorbed by the aluminium oxide along with the carbon from (2). The combination of free hydrogen and ethylene to form ethane does not occur, since the dissociation is a much faster reaction. Further support for the theory is obtained by measurements of the adsorption of ethylene and acetylene on aluminium oxide for several partial pressures, and of the variation of adsorption of ethylene on aluminium oxide with variation of temperature and variation of water content. A mechanism is suggested for the adsorption of electrolytes from aqueous solution on aluminium oxide. L. L. Bircumshaw.

Catalytic hydrogenation of organic substances. O. Schmidt (Z. physikal. Chem., 1925, **118**, 193—239).—Elements suitable for hydrogenation catalysis have small ionic radii and a large number of electrons in the outer shell; they take up hydrogen, which is converted into an active dissociated form. It is known that electrically neutral atomic hydrogen is capable, in many cases, of effecting reduction, but the dissociated hydrogen here formed probably consists of ions. Quantitative theoretical considerations show that the ease of ionisation depends on the effective sphere of action of the metallic ions formed in the solid catalyst, *i.e.*, with constant valency those ions with the smallest radii are the most effective catalysts. Rise of temperature increases catalytic activity. These conclusions are borne out by a study of the reduction of ethylene to ethane using finely divided iron, cobalt, nickel, copper, silver, gold, zinc, and lead as catalysts. It is considered that the catalytic hydrogenation of carbon compounds is an ionic reaction (cf. Thomas, A., 1923, ii, 64). Measurements were made of the surfaces of various nickel catalysts. Methods of determining the hydrogen taken up by catalysts are described: systematic measurements were made in the case of nickel. The hydrogen taken up by finely divided nickel at constant temperature and pressure is proportional to the surface, but is affected by the presence of impurities. At low temperatures, part of the hydrogen is present in the form of loose compounds with the catalyst. The reactivity is proportional to the surface and sorbed hydrogen, but is modified by the solubility of the other reactants in the catalyst. L. F. Gilbert.

Formation and growth of silver nuclei in the decomposition of silver oxalate. J. Y. Macdonald and C. N. Hinshelwood (J.C.S., 1925, **127**, 2764—2771).—A new method of following chemical changes in which gas is evolved has been applied to the study of the thermal decomposition of silver oxalate, which is found to occur in accordance with the equation $Ag_2C_2O_4=2Ag+2CO_2$. The reaction appears to be autocatalytic, this being shown to be due to the formation of silver nuclei on the surface of the oxalate crystals at a rate which governs the rate of reaction, so that the simple equation for homogeneous autocatalysis does not apply. Oxygen retards the reaction. R. Cuthill.

Catalytic oxidation of ammonia. W. J. Maliarevski and N. A. Maliarevskaja.—See B., 1926, 50.

[Catalytic] oxidation of ammonia. C. Ellis.—See B., 1926, 51.

Catalytic effect of lead and manganese on the drying of China-wood (tung) oil. G. E. Ludwig.—See B., 1926, 67.

Toxicity of thiophen for nickel catalyst: action of the copper catalyst. B. Kubota and K. Yoshikawa (Japanese J. Chem., 1925, **2**, 45—62).—See A., 1925, ii, 805.

Composition of reduced nickel as catalyst. B. Kubota and K. Yoshikawa (Japanese J. Chem., 1925, **2**, 99—107).—See A., 1925, ii, 1174.

Production of sulphuric acid by electrolysis. R. Saxon (Chem. News, 1925, 385).—Electrolysis of a solution of an equimolar mixture of copper sulphate and ammonium aluminium sulphate yields a solution of sulphuric acid which may reach a concentration of 17% in 7 hrs. Simultaneously copper is deposited on the cathode and aluminium hydroxide in the catholyte. A. R. Powell.

Electrometric study of the reactions between alkalis and silver nitrate solutions. H. T. S. Britton (J.C.S., 1925, **127**, 2956—2970).—The precipitation of silver oxide by sodium hydroxide has been followed electrometrically, and the values of the solubility product $[\mathrm{Ag}^{\cdot}][\mathrm{OH}']$ have been calculated. From the results, the *E.M.F.* of the cell $\mathrm{Ag}|\mathrm{Ag_2O},\mathrm{NaOH}|\mathrm{H_2}$ and of the oxygen–hydrogen cell have been deduced. The average value of the former lies between the extreme values obtained by Rørdam (A., 1922, i, 338), thus making it appear likely that the variability of the silver electrode in presence of silver oxide in alkaline solutions is due to reduction, rather than to the existence of two forms of the oxide (cf. Luther and Pokorný, A., 1908, ii, 277). Lewis' value for the *E.M.F.* of the oxygen–hydrogen cell (A., 1906, ii, 262) seems to be too low, because a low value was taken for $[\mathrm{Ag}^{\cdot}][\mathrm{OH}']$.

The titration of silver nitrate with ammonia has been examined by means of both the silver and oxygen electrodes. Precipitation is incomplete even when the amount of ammonia required by the equation $\mathrm{AgNO_3+NH_4OH=AgOH+NH_4NO_3}$ has been added, apparently owing to complex formation: $\mathrm{AgNO_3+2NH_3 \rightleftharpoons Ag(NH_3)_2NO_3}$ proceeding at the same time as this reaction, and to the dissolution of some of the silver oxide in the ammonium nitrate formed. Calculation of the equilibrium constant for complex formation, assuming the above equation, leads to a fairly constant value, which agrees with the value deduced from the *E.M.F.* data of Bruni and Levi (A., 1917, ii, 470). Very nearly the same figure is obtained from the measurements of these authors for ammoniacal solutions of silver nitrite, indicating that the dissociation constant of the diammino–silver complex is independent of the anion. R. Cuthill.

Electrolytic deposition of nickel. R. Saxon (Chem. News, 1926, **132**, 4).—Electrolysis of a mixture of equal volumes of saturated solutions of nickel and potassium sulphates yields first a precipitate of nickel hydroxide, then a deposit of metallic nickel on the cathode, whilst sulphuric acid concentrates round the anode. The yield of nickel is increased if a sheet of zinc is placed between the electrodes, the zinc dissolving with evolution of hydrogen.
A. R. Powell.

Photochemical kinetics. R. Wegscheider (Rec. trav. chim., 1925, **44**, 1118—1120).—Polemical against Plotnikov (cf. A., 1925, ii, 838; Langedijk, *ibid.*, 1116). L. L. Bircumshaw.

Reactions caused by light-excited bromine. J. Eggert [with F. Wachholtz and R. Schmidt] (Physikal. Z., 1925, **26**, 865—868).—Ethyl maleate is converted into the corresponding fumarate by illumination of the liquid (or a solution in carbon tetrachloride) provided bromine is present. The reaction is exothermic and the bromine acts as a sensitiser. A second photochemical reaction also occurs simultaneously in the bromination of ethyl maleate to ethyl dibromosuccinate. The first change has been followed thermally and the second by titration. The absorption of a single quantum $h\nu$ at 436 $\mu\mu$ by a $0{\cdot}1N$-solution of bromine in liquid ethyl maleate results in the stereochemical change of 295 mols. and the addition of 8 mols. of bromine. These values are independent within fairly wide limits of (*a*) light intensity, (*b*) dilution up to 1 : 70 with carbon tetrachloride. The quantum equivalents vary with temperature; for the first reaction, the efficiency is doubled in going from 19·5° to 23°, and for the second from 17° to 25°. Between the limits 0·03—$0{\cdot}3N$-solutions of bromine, the quantum efficiency of the stereochemical change does not vary, whilst that of the additive process varies directly as the halogen concentration. When mixtures of ethyl maleate and fumarate undergo similar treatment, the quantum equivalent of the first change depends on the ratio of the two esters, whilst that of the second reaction is unaltered. Both changes depend on the size of the quantum employed, the quantum efficiency at 436 $\mu\mu$ being about twice that observed at 546 $\mu\mu$.

Excited bromine molecules appear to have a relatively long life-period. Collisions of activated bromine molecules with ethyl maleate molecules are inelastic; collisions with inactive bromine molecules or carbon tetrachloride molecules are elastic. After collision, the ester molecules are activated. Those which collide during the activation period with inactive bromine molecules react by addition, those which collide only with the solvent suffer stereoisomeric change. These views are supported by the fact that ethyl fumarate brominates with the same quantum efficiency as ethyl maleate. The interpretation involves the assumptions of a life period of 10^{-5}—10^{-6} sec. for activated bromine, and of a capacity to hand on its activation energy in small amounts to 300 mols.

The first assumption is supported by the demonstration that when bromine is activated in the vapour phase it retains its energy long enough to hand it on after penetrating the liquid surface. For the second assumption, no evidence is adduced.
R. A. Morton.

Selective action of polarised light on starch grains. (Lord) Rayleigh (Nature, 1926, **117**, 15).—*A priori* reasoning indicates that polarisation of light should diminish chemical action in the case of starch grains, if these are oriented at random (cf. this vol., 34). A. A. Eldridge.

[Selective action of polarised light on starch grains]. W. N. Jones (Nature, 1926, **117**, 15—16; cf. preceding abstract).—Polemical.
A. A. Eldridge.

Measurement of radiation intensities by photographic methods. F. C. Toy (Nature, 1926, **117**, 83—84).—In the method preferred, the intensity of the stronger beam is reduced by means of a "neutral" absorbing screen, so that the intensities are equal; the function of the plate is then solely to detect equal intensities of the same kind of radiation, and the accuracy is dependent only on the constancy of emulsion characteristics over a small portion of any single plate. A. A. Eldridge.

Ozone formation through electronic impact. F. Krüger and O. Utesch (Ann. Physik, 1925, [iv], 78, 113—156).—An extensive investigation has been made of the conditions and extent of ozone formation by the action of cathode rays on oxygen and air. The cathode rays emerged from a hot cathode tube through a window of thin aluminium foil into a small vessel, which was fitted with charged plates in order that the ionisation current, due to the rays, might be measured. The effects of varying the current strength in the cathode tube, the primary voltage, the thickness of the aluminium foil, and the rate of passage of the oxygen or air current were investigated. An estimation and comparison of the number of ions and of ozone molecules formed per unit of time showed that the latter were from 20 to 40 times as numerous as the former. Although the ratio of these quantities was not constant for different experimental conditions, they are to be regarded as approximately proportional, the discrepancies being attributed to fluctuations in the strength of the cathode ray stream. The equivalence found by Moeller (Diss., Danzig, 1912) between the number of ions formed in nitrogen and the number of ozone molecules formed in oxygen by cathode rays of equal intensity is thus not confirmed. A comparison of the action of cathode rays on air, oxygen, and nitrogen indicated that the secondary radiation produced is, in accordance with Lenard's rule, proportional to their densities, and that it is therefore unnecessary to postulate any influence of a chemical reaction on the production of the secondary radiation. As a result of these experiments, it is concluded that the formation of ozone is unconnected with the ionisation process, but is the result of collision of normal oxygen molecules with oxygen molecules excited by electronic impacts. Such a mechanism is to be anticipated from the photochemical formation of ozone. The yield of ozone was determined under various conditions, the maximum value being 150 g. per amp.-hr. expended in the cathode tube. This is very much smaller than the yield from technical ozonisers. The low yield is due to the absorption of energy in the passage of the cathode rays through the foil window, the energy of the emergent rays being computed as 3—5% of the electrical energy expended in the tube. The distribution of the cathode-ray energy in the process of ozone formation was determined by measuring the secondary ionisation, the yield of ozone, and the increase of pressure in the irradiated gas. From the latter, the heat generated in the process was calculated. The results show that of the total energy of the cathode rays incident on the gas, 2—4% is used in the ionisation process, 5—11% for ozonisation, and the residue dissipated as heat.

F. G. Tryhorn.

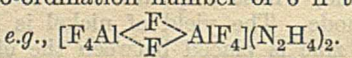
Action of silica on barium and magnesium sulphates. G. Marchal.—See B., 1926, 51.

Decomposition of the alkaline-earth phosphates by alkali carbonates. D. Raquet (Bull. Soc. chim., 1925, [iv], 37, 1548—1549; cf. Colani, A., 1925, ii, 1001).—The decomposition of calcium, barium, or strontium phosphate by potassium carbonate solution (incomplete in the first case) is impeded by the presence of sodium hydroxide; with sodium carbonate, it is incomplete and also so impeded. The decomposition of magnesium ammonium phosphate is accelerated by sodium hydroxide.

C. H. D. Clark.

Reduction of heavy metal sulphides by barium oxide. W. Biltz and E. von Mühlendahl (Z. anorg. Chem., 1925, 150, 1—9).—When heated with barium oxide, cupric sulphide is partly reduced to the metal, according to the equations: $CuS+BaO=CuO+BaS$, $4CuO+BaS=4Cu+BaSO_4$. Lead sulphide is similarly reduced, but neither cupric nor lead sulphide is reduced by calcium oxide, as these reactions would be endothermic. The reaction between cupric sulphide and barium oxide was followed thermally, and the product was examined chemically and microscopically. Reaction begins between 200° and 400° and the largest yield of metal is obtained when double the theoretical amount of barium oxide is taken; after 1 hr. at 1150°, the reaction had gone completely to the first stage and 72% to the second, and varying the conditions did not further increase the yield. The reaction with lead sulphide also begins between 200° and 400°, but some sulphide remains unreduced at 1150°, the highest temperature used.

A. Geake.

Fluoro-salts of aluminium and of tervalent iron and chromium. R. Weinland, I. Lang, and H. Fikentscher (Z. anorg. Chem., 1925, 150, 47—67).—Except in the case of prosopite, aluminium has the co-ordination number 6 in all its known fluoro-salts, both natural and artificial; these compounds contain either a hexafluoro- or an aquopentafluoro-anion. Prosopite has the formula $[Al(F,OH)_4]_2Ca$, and in it aluminium has the co-ordination number 4. The following organic *fluoroaluminates* have been prepared and analysed: $AlF_3,N_2H_4,2HF$; $AlF_3,2C_5H_5N,2HF,H_2O$; $AlF_3,C_2H_4(NH_2)_2,2HF,H_2O$; AlF_3,CH_5N_3,HF,H_2O; $AlF_3,2CH_5N_3,2HF$; $AlF_3,3CH_5N_3,3HF$. Only one of these contains the hexafluoro-anion and two the aquofluoro-anion; the other three can be represented with a co-ordination number of 6 if the nucleus is doubled, *e.g.*,  $[F_4Al{<}\genfrac{}{}{0pt}{}{F}{F}{>}AlF_4](N_2H_4)_2$. A *potassium aluminium fluoride*, $AlF_3,2KF,2H_2O$, obtained by the addition of acid potassium fluoride to aluminium chloride, is similarly formulated. Tervalent iron also forms hexafluoro- and aquopentafluoro-anions with the co-ordination number 6; the following organic *fluoro*-compounds were prepared: $[Fe,F_5,H_2O]H_2,2CH_5N_3$; $[Fe,F_5,H_2O]H_2,C_2H_4(NH_2)_2$; $[Fe,F_5,H_2O]H_2,2C_5H_5N,2H_2O$; $[FeF_4]H,C_5H_5N,H_2O$. In the last compound, it is probable that the water is not in the anion and that the co-ordination number is 4; this is also the case for the *alkali* salts, $[FeF_4]K$ and $[FeF_4]NH_4$, which contain no water. The heavy metals, on the other hand, form *salts* in which the iron has the co-ordination number 6: $[Fe,F_5,H_2O]Ag_2,2H_2O$; $[Fe,F_5,H_2O]Tl_2,2H_2O$; $[Fe,F_5,H_2O][Cd(H_2O)_6]$; $[FeF_6]_2[Cu(H_2O)_6]_3$. No fluoro-salts of chromium could be obtained having a co-ordination number other than 6; the only organic salt that could be prepared was the *guanidine* salt, $[CrF_6]H_3,3CH_5N_3$. The compound formulated $2FeF_3,FeF_2,10H_2O$ (A., 1907, ii, 265) contains no ferrous iron and no fluorine ions. Its conductivity is low and it is therefore formulated as the non-electrolyte

$$[Fe,F_3,(H_2O)_3],1{\cdot}5H_2O.$$

A. GEAKE.

Double sulphates of the rare-earth and alkali metals. III. Double sulphates of lanthanum and sodium. F. ZAMBONINI and G. CAROBBI (Atti R. Accad. Lincei, 1925, [vi], **2**, 300—302; cf. A., 1925, ii, 222, 579).—A determination of a portion of the 25° isotherm of the system $La_2(SO_4)_3$–Na_2SO_4–H_2O confirms the existence of the compound $La_2(SO_4)_3,Na_2SO_4,2H_2O$. It is obtained as minute white crystals by the slow evaporation of very dilute solutions of the two simple sulphates, and is stable in contact with solutions containing from 0·13% to 16·28% of sodium sulphate, and up to 0·19% of lanthanum sulphate. The water of crystallisation is not lost below 150°. F. G. TRYHORN.

Black oxides of praseodymium. W. PRANDTL and K. HUTTNER (Z. anorg. Chem., 1925, **149**, 235—262).—The formula of the brownish-black powder obtained by heating praseodymium hydroxide or its salts with volatile acids in air is Pr_6O_{11}, the conflicting results of other authors being due to the presence of impurities. This oxide does not dissociate below 900°, forms no definite hydrates with water, and has d^{20} 6·61. It is to be regarded as a salt-like compound of Pr_2O_3 with some higher oxide.

The substances claimed by Meyer (A., 1904, ii, 734) and Brauner (Proc. C. S., 1898, 70) to be PrO_2 appear to be hydrated Pr_6O_{11}. The oxide PrO_2 has, however, been prepared by oxidation of Pr_2O_3, or from Pr_6O_{11} by fusion with sodium chlorate or treatment with acetic acid. Admixture of various metallic oxides with the oxide Pr_2O_3 prevents its complete oxidation (cf. Meyer and Koss, A., 1903, ii, 45), some lanthanum praseodymate being formed in the presence of lanthanum oxide (cf. Marc, A., 1902, ii, 503). The oxide PrO_2 is a black powder, d^{20} 6·82, which above 350° loses oxygen and forms Pr_6O_{11}. It has neither acidic nor basic properties. Both oxides have similar chemical properties, which are those of higher oxides rather than of peroxides. No corresponding salts have been obtained.

R. CUTHILL.

Colour imparted to glass by fluorine, sulphur, and selenium compounds. K. FUWA.—See B., 1926, 13, 14.

Colouring glass with phosphates, arsenious oxide, and carbon. K. FUWA.—See B., 1926, 53, 54.

Separation of hafnium and zirconium. N. V. PHILIPS GLOEILAMPENFABR.—See B., 1926, 12.

Lead dihydride and lead tetrahydride. E. J. WEEKS (J.C.S., 1925, **127**, 2845—2846).—Lead dihydride, Pb_2H_2, is formed as a grey deposit when aluminium foil is added to a solution of an alkali plumbite. It appears to form the tetrahydride when heated in hydrogen. R. CUTHILL.

Reaction between gaseous ammonia and the chlorides of phosphorus.—H. PERPÉROT (Bull. Soc. chim., 1925, [iv], **37**, 1540—1548; cf. A., 1925, ii, 1186).—Further investigation of the reaction between ammonia and the chlorides of phosphorus in carbon tetrachloride solution suggests that the primary products of reaction are the compounds $PCl_5,10NH_3$, $PCl_3,6NH_3$, and $POCl_3,6NH_3$. The decomposition curve of the compound $PCl_5,10NH_3$ with time shows a sharp break at about 310°. Since ammonium chloride mixed with sand shows a similar break at about the same temperature, it is concluded that the substance is partly a mixture of the amine $P(NH_2)_5$ and ammonium chloride, this result being confirmed by the action of liquid ammonia. The intermediate tervalent compound, $PCl_3,6NH_3$, is found to be somewhat more stable than the quinquevalent compounds, and has a break in the time–decomposition curve at about 200°.

C. H. D. CLARK.

Pyrophoric bismuth. L. VANINO and A. MENZEL (Z. anorg. Chem., 1925, **149**, 18—20; cf. Thibault, A., 1904, i, 247).—A co-precipitated mixture of bismuth and aluminium hydroxides is reduced by hydrogen at 170—210°. The product is spontaneously inflammable at the ordinary temperature, its activity being dependent on the presence of the aluminium hydroxide and to some extent on its amount. R. CUTHILL.

Reaction between bismuth trisulphide and hydrochloric acid. S. RAMACHANDRAN (Chem. News, 1925, **131**, 386).—Bismuth trisulphide is slightly soluble even in 1 : 16-hydrochloric acid at 29°; its solubility increases rapidly with the temperature, and hydrogen sulphide begins to be evolved at 70° (cf. A., 1925, ii, 1208). A. R. POWELL.

Tellurium nitride. W. STRECKER and W. EBERT (Ber., 1925, **58**, [*B*], 2527—2539; cf. Strecker and Claus, A., 1923, **11**, 152).—The action of ammonia, dried over potassium hydroxide, on a solution of tellurium tetrachloride or tetrabromide in ether gives mixtures of tellurium dioxide or trioxide with ammonium salt. An explosive product is not obtained when the ammonia is condensed over sodium and the gas from the evaporating liquid is led into the ethereal solution. If dry ammonia is passed over tellurium tetrachloride at 0°, the *compound* (?) $TeCl_4,6NH_3$ is obtained, which becomes white and absorbs moisture when exposed to air. If the halide is cooled to −80° and ammonia condensed thereon, a mixture is produced which detonates when heated; it cannot, however, be freed from admixed ammonium salts by treatment with water, which causes it to become white and lose its explosive properties. The action of ammonia on tellurium halides is therefore investigated in an apparatus which allows the dry halide to be treated with liquid ammonia with exclusion of water and the pasty product of the reaction to be washed with liquid ammonia and thus to achieve as complete as possible an extraction of the ammonium salts produced in the reaction. A highly explosive compound is thereby obtained which contains tellurium, halogen, and nitrogen. It appears unlikely that this is the nitride, TeN, described by Metzner and by Damiens (A., 1923, ii, 316) contaminated with ammonium salts. Action probably occurs in accordance with the scheme $3TeBr_4+16NH_3=Te_3N_4+12NH_4Br$. This conception is in harmony with the quantitative observation that the explosive compound and ammonium salt are the sole products of the change. The reaction is therefore to be regarded as ammonolysis in accordance with the equations $3TeBr_4+4NH_3=Te_3Br_9N+3NH_4Br$, $3TeBr_4+8NH_3=Te_3Br_6N_2+6NH_4Br$, $TeBr_4+4NH_3=TeBrN+3NH_4Br$, thus explaining the presence of halogen in the product. The primary action consists in the addition of ammonia to the tetrahalide, and this is followed by gradual replacement of the halogen atom by the amino-group and then by loss of ammonia into imino-compounds and ultimately nitride and ammine salts which do not contain eliminable ammonia.

H. WREN.

[Hypochlorous acid and the alkali perchlorides.] O. VON DEINES (Z. anorg. Chem., 1925, **149**, 99—100).—The conclusions of Dietzel and Schlemmer (A., 1925, ii, 892) on the course of the reaction between chlorine and sodium hydroxide are shown to be vitiated by numerical errors. The reaction in the cold occurs according to the equation: $2NaOH+Cl_2=NaOCl+NaCl+H_2O$. R. CUTHILL.

Potentiometric indication in the action of halogens on ferrocyanides. C. DEL FRESNO (Z. Elektrochem., 1925, **31**, 617—621).—See A., 1925, ii, 1192.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. J. HEYROVSKÝ (Nature, 1926, **117**, 16).—A reply to Campbell's criticisms (this vol., 37) and a more detailed explanation of the nature of the author's polarographic electro-analytical method with the dropping mercury cathode. Besides showing good agreement with the deposition potentials at the dropping mercury cathode expected for the triad 25, 43, and 75, the "75" hump in the curve, when specially prominent, is accompanied by appearance of the *L*-lines of the element 75 in the *X*-ray spectra. A. A. ELDRIDGE.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. G. DRUCE (Nature, 1926, **117**, 16; cf. Campbell, this vol., 37, and preceding abstract).—Explanatory. A. A. ELDRIDGE.

Reducing action of ferrous hydroxide. S. MIYAMOTO (Sci. Papers Inst. Phys. Chem. Res., 1922, **1**, 31—56).—See A., 1922, ii, 648; 1923, ii, 76. B. FULLMAN.

Ruthenium. VIII. Isomeric chlorides. J. L. HOWE and L. P. HAYNES (J. Amer. Chem. Soc., 1925, **47**, 2920—2925).—α-Potassium pentachlororuthenite crystallises from hot acid solution largely as anhydrous, dark brownish-red, tetragonal octahedra; from cold solutions reddish-buff, feather-like crystals, apparently the hydrated form, are obtained. Dechlorination of potassium hexachlororuthenate yields a pentachlororuthenite having properties similar to those of dehydrated β-salt, which is Aoyama's γ-salt, since recrystallisation of both the latter and dehydrated β-salt from acidulated water yields β-salt (cf. Aoyama, A., 1924, ii, 771; Howe, A., 1902, ii, 86). Dehydrated β-salt only hydrates in solution after some hours; when first made, the solution becomes blue with sodium hydroxide and gives a black precipitate with bromine. Briggs' salt, K_2RuCl_5,K_2RuCl_5OH, is considered to be a mixture of anhydrous and monohydrated ordinary α-salts (cf. A., 1925, ii, 703). Hexachlororuthenates are precipitated from concentrated, strongly acid solutions of β-salts by leading in chlorine; concentration of the mother-liquor after precipitation yields chiefly α-pentachlororuthenite. Evaporation of solutions of hexa-salts seems to yield α-penta-salts. α-Salts are converted into β-salts by the action of reducing agents (*e.g.*, stannous chloride) and organic compounds (*e.g.*, phenol, but not acetic acid).

S. K. TWEEDY.

Ruthenium. IX. Solubility of ruthenium in hypochlorite solutions; attempted determination of the metal. J. L. HOWE and F. N. MERCER (J. Amer. Chem. Soc., 1925, **47**, 2926—2932).—Finely divided ruthenium is readily soluble in concentrated alkaline solutions of hypochlorites, sodium hypochlorite being more effective than the potassium salt. Ruthenium may be separated from the other platinum metals, except osmium, by this means. The hypochlorite oxidises the ruthenium to tetroxide; free alkali hydroxide converts the latter into ruthenate. Even in the absence of alkali much ruthenium may be retained as ruthenate. Ruthenium may be completely distilled as tetroxide from a potassium ruthenate solution after treatment with chlorine; no evidence for the intermediate formation of perruthenate during the latter process was obtained. No satisfactory way of quantitatively precipitating ruthenium from the tetroxide in a weighable form was discovered. S. K. TWEEDY.

Rhodium chlorides and oxides. L. WÖHLER and W. MÜLLER (Z. anorg. Chem., 1925, **149**, 125—138).—Rhodium reacts with chlorine only between 300° and 968°, the product being the trichloride below 948°, and a mixture of two new reddish-brown *chlorides*, RhCl and $RhCl_2$, at 948—968°. The dissociation tensions of all three chlorides, measured at a series of temperatures, agree with a formula of the type proposed by Wöhler and Günther (A., 1923, ii, 471). Attempts to prepare a tetrachloride have been unsuccessful. By dissociation of rhodium trioxide, prepared by heating the trichloride to above 750° in oxygen, two new *oxides*, RhO and Rh_2O, have been obtained. These are insoluble in acids, but readily reduced by hydrogen. The dissociation tensions of all the oxides have been determined at various temperatures. Rhodium is not volatile in air even at 1150°. R. CUTHILL.

Compounds of metallic salts and carbon monoxide. XII. Behaviour of carbon monoxide towards salts of palladium and platinum and separation of palladium and platinum depending thereon. W. MANCHOT (Ber., 1925, **58**, [*B*], 2518—2521).—Re-examination of the action of carbon monoxide on platinum chloride has confirmed the existence of the three compounds, $PtCl_2,CO$, $PtCl_2,2CO$, and $2PtCl_2,3CO$, described by Schützenberger. The analogous compounds of palladium, described by Fink, do not, however, exist; the compounds actually isolated were the platinum salts due to the presence of platinum in the palladium employed. Dry palladous chloride does not give a sublimate when heated in carbon monoxide at any temperature below red heat, whereas at a higher temperature palladous chloride sublimes; this behaviour is also exhibited when chlorine is substituted for carbon monoxide. Moist palladous chloride is reduced by carbon monoxide at about 250° and reduction becomes complete at a higher temperature. Small quantities of platinum in palladium may be determined by heating the dry mixture of the chlorides in a dry current of carbon monoxide at 250° until increase in the amount of sublimate is not observed; platinum, ruthenium, rhodium, and osmium sublime as their compounds with carbon monoxide. The sublimate is removed from the tube by water and aqua regia; the solution is evaporated to dryness and the residue ignited, leaving the platinum present in the palladium.

Palladium appears to occupy a unique position in the platinum family, since it yields no compound with carbon monoxide; the reducibility of palladous chloride in aqueous solution by carbon monoxide points to the existence of such a compound, but the conditions necessary for the production of the primary additive compound appear to lie very close to those of its decomposition. In the absence of water, palladous chloride is not reduced by carbon monoxide and addition of carbon monoxide does not occur.

Reaction of carbon monoxide with platinous chloride commences at about 120°; at 150°, the compound, $PtCl_2,2CO$, is directly obtained; this substance was isolated by Schützenberger from the product of the action at 250°. H. Wren.

Simple preparation of fluorine. P. Lebeau and A. Damiens (Compt. rend., 1925, **181**, 917—919).—Fluorine is prepared by the electrolysis of acid fluorides of the alkali metals which are richer in hydrogen fluoride than the compounds MF,HF (*e.g.*, $KF,3HF$). These compounds are readily made and fuse below 150°. Carbon-free iron or nickel anodes are used, the nickel or copper containing-vessel acting as cathode (cf. A., 1924, ii, 847). S. K. Tweedy.

Ashing of small amounts of material. O. Dafert (Biochem. Z., 1925, **164**, 444—445).—A method of ashing small quantities of substance and a new form of fume-trap for Kjeldahl determinations are described. E. C. Smith.

Determining hydrogen and methane in gas mixtures. W. Steuer.—See B., 1926, 3.

Determination of hydrogen-ion concentration in liquids and suspensions. Application of Biilmann's quinhydrone method. C. W. G. Hetterschij and J. Hudig (Chem. Weekblad, 1926, **23**, 2—3).—A method and apparatus for carrying out large numbers of determinations, by unskilled persons, very rapidly and with great accuracy, are described. The quinhydrone electrode gives more rapid and accurate results in determinations of hydrogen-ion concentration in soils than any alternative method, and is very cheap. Compensating resistances are employed to obviate the necessity for much calculation in obtaining results. S. I. Levy.

Reaction of neutral and distilled water. I. M. Kolthoff (Chem. Weekblad, 1925, **22**, 590—594).—The employment of methyl-red may involve great errors, which may amount with neutral water to as much as 100 times the real hydrogen-ion concentration. For distilled water, the sodium salt of methyl-red is recommended; this gives a value of $p_{\rm H}$ 5·9—6·0 for distilled water in equilibrium with air. The sodium salt of chlorophenol-red is also suitable, but the most accurate indicator is 2 : 4 : 6 : 2′ : 4′ : 2″ : 4″-heptamethoxytriphenylcarbinol. After rapid boiling for 1 min. and subsequent cooling, the $p_{\rm H}$ for distilled water, using the sodium salt of methyl-red, is found to be 6·7—6·6, but falls very rapidly after shaking with air; this indicator is proposed for the determination of carbon dioxide in air. The sources of error in the determination of the reaction of a very dilute solution of a weak acid are considered theoretically. S. I. Levy.

Reliability of vacuum analysis for solid metallic hydrides. E. J. Weeks (Chem. News, 1926, **132**, 17—18).—A mathematical paper based on results obtained in the analysis of metallic hydrides by heating them in a vacuum, showing that more accurate results are obtained from weighing the residual metal than from measuring the volume of hydrogen evolved. A. R. Powell.

Determination of hydrochloric acid by means of potassium iodate, as compared with the results obtained with sodium carbonate and borax. I. M. Kolthoff (Pharm. Weekblad, 1925, **63**, 37—48).—A solution of potassium iodate, potassium iodide, and a slight excess of sodium thiosulphate can be employed for the titration of hydrochloric acid. The mixture must be shaken continuously to avoid decomposition of the thiosulphate. With dimethyl-yellow as indicator, a correction must be made for the slight excess of acid necessary to effect the colour change; with methyl-red, no correction is necessary, but the titration is slower, since time is required for the colour to become stable. The titration is extremely accurate. Anhydrous sodium carbonate is less suitable, on account of its hygroscopic nature and the necessity of boiling off carbon dioxide. Borax is very suitable; the results indicate that the accepted atomic weight of boron, 10·82, is correct. The decahydrate is easily obtained pure by recrystallisation and drying over fused sodium bromide. S. I. Levy.

Micro-titration of iodide. I. M. Kolthoff (Mikrochem., 1925, **3**, 75—79).—The method is based on the reaction $IO_3' + 2I' + 3HCN + 3H^{\cdot} \rightleftharpoons 3ICN + 3H_2O$. Ten c.c. of the iodide solution are mixed with 80 c.c. of water, 20 c.c. of 25% hydrochloric acid, and 5 c.c. of a 10% solution of potassium cyanide in a stoppered conical flask. After addition of a few c.c. of carbon tetrachloride or chloroform the solution is titrated with potassium iodate until the violet colour in the lower layer disappears. Starch is not a suitable indicator, owing to the slowness with which the blue colour disappears towards the end of the titration. For very small amounts of iodide a 5-c.c. micro-burette graduated in 0·01 c.c. is used with 0·00016M-potassium iodate solution. Even very large amounts of bromide do not interfere. In the presence of other substances which are oxidised by iodate, the solution is acidified with acetic or succinic acid and boiled with hypochlorite to convert the iodide into iodate. The converse of the above method is then used for the determination of the iodate. A. R. POWELL.

Micro-determination of the oxygen content of water. C. RISCH (Biochem. Z., 1925, **161**, 465—467). —A method is described exactly similar in principle to that of Winkler, the apparatus being adapted so that only small quantities of the water are required. H. I. COOMBS.

Determination of molecular oxygen in aqueous solution in the presence of nitrous acid. H. NOLL (Biochem. Z., 1925, **165**, 497—499).—A reply to Alsterberg's criticisms (cf. A., 1925, ii, 1198). P. W. CLUTTERBUCK.

Measurement of the amount of ozone in the earth's atmosphere. G. M. B. DOBSON and D. N. HARRISON (Proc. Physical Soc., 1925, **38**, 74—76).— The quantity of ozone present in the atmosphere was determined by measuring the intensity of a number of Fraunhofer transmission lines in the region of the ultra-violet absorption band of ozone (3000—3300 Å.). Observations made over a period of 4 months show that the amount of ozone is low during an anticyclone and high during a cyclone, with a variation of 50%. The average quantity of ozone in the atmosphere would form a layer on the earth's surface 3 mm. thick if reduced to *N.T.P.* C. J. SMITHELLS.

Apparatus for the determination of helium in natural gas mixtures and minerals. W. CHLOPIN and A. LUKAŠUK.—See B., 1926, 51.

Determination of free calcium ions by Brinkmann and van Dam's method. H. SCHULTEN (Biochem. Z., 1925, **164**, 47—52).—In this method, supersaturated solutions arise, the solubility product cannot be obtained, and the method is therefore subject to an unknown and varying error. P. W. CLUTTERBUCK.

Electrolytic determination of zinc in ores. R. E. SULLIVAN and H. S. LUKENS.—See B., 1926, 16.

Determination of copper by Feigl's method. E. AZZALIN (Annali Chim. Appl., 1925, **15**, 373—377; cf. Feigl, A., 1923, ii, 880).—With copper alone, the method is unsatisfactory, since the excess of benzoinmonoxime is difficult to eliminate and washing is tedious because of the bulk and compactness of the precipitate, and it is difficult to secure constant weight. The method is rendered more exact and expeditious by igniting the precipitate and weighing the copper as oxide. Benzoinmonoxime is not a specific reagent for copper; it does not separate the latter completely from iron, aluminium, zinc, etc., and so is incapable of affording a rapid technical means of determining copper. W. E. ELLIS.

Simple acidimetric determination of mercuric chloride. E. RUPP and P. MAISS (Apoth.-Ztg., 1925, **40**, 474; from Chem. Zentr., 1925, II, 332).— Mercuric chloride may be titrated with 0·5N-potassium cyanide solution, using phenolphthalein as indicator. Since hydrocyanic acid is without effect on dimethylaminoazobenzene, methyl-orange, or methyl-red, mercuric chloride may also be determined, using these indicators and titrating with sodium hydroxide as follows. Potassium cyanide solution (0·2 g. in 30 c.c.) is neutralised with 0·1N-hydrochloric acid, using one of the above indicators. Mercuric chloride solution is added and titration carried out with 0·1N-sodium hydroxide. When mercuric chloride is to be determined in pastilles, eosin must first be removed by animal charcoal if either methyl-orange or dimethylaminoazobenzene is to be used as indicator. G. W. ROBINSON.

Sensitive differential reaction of cerium. L. FERNANDES (Gazzetta, 1925, **55**, 616—618).—As little as 1 part of cerium per 400,000 parts of solution is detectable by the coloration given with pyrocatechol. If rare elements only are present, the solution is made neutral or but slightly acid by addition of ammonia solution, a crystal of sodium thiosulphate and about 1 g. of pyrocatechol being then dissolved in a small portion of the liquid, which may require dilution. Treatment with excess of ammonia solution then gives a more or less intense violet coloration if the solution contains cerium. A control test is desirable when very small traces of cerium are present. If the total proportion of rare-earth metals is relatively high, a white precipitate is formed on addition of the excess of ammonia solution, but the colour of the liquid is readily seen after settling. When the rare-earth elements have been separated in the form of oxalate, direct treatment of this with pyrocatechol and ammonia is permissible. Other elements yielding highly coloured complexes with pyrocatechol must be removed before the test is applied; the elements of the first two analytical groups are eliminated by precipitation with their usual reagents, and any iron by agitation of the liquid with ether in presence of ammonium thiocyanate and hydrochloric acid until the red coloration vanishes. T. H. POPE.

Detection and separation of indium. I. WADA and S. ATO (Sci. Papers Inst. Phys. Chem. Res., 1922, **1**, 57—77).—See A., 1923, ii, 657.

Electrometric determination of iron with bromate. O. COLLENBERG and K. SANDVED (Z. anorg. Chem., 1925, **149**, 191—202; cf. Kolthoff, A., 1919, ii, 352).—The ferric salt is reduced with excess of stannous chloride, and the mixture, to which are added 10—20 c.c. of concentrated hydrochloric acid for each 100 c.c., and 5 c.c. of a 6% solution of cobalt chloride, is titrated at 50° with standard potassium bromate solution. From the positions of the two turning points (stannous to stannic and

ferrous to ferric) on the titration curve the amount of bromate used in the latter oxidation can be determined. In the absence of such a catalyst as cobalt chloride, the rate of establishment of a steady potential at the end-point is too slow. Ferrous salts act similarly in the oxidation of stannous salts. In the oxidation of ferrous salts the potential set up at the end-point is independent of the experimental conditions, but in the oxidation of stannous salts it depends on the amount of hydrochloric acid present.
R. CUTHILL.

Determination of foreign elements in scheelite, tungstic acid, and metallic tungsten. K. AGTE, H. BECKER-ROSE, and G. HEYNE.—See B., 1926, 60.

Separation and determination of bismuth. A. GIRARD and E. FOURNEAU (Bull. Soc. chim., 1925, [iv], **37**, 1669—1673).—See A., 1925, ii, 1207.

Benzoylmethylglyoxime as a precipitant of palladous salts. J. HANUŠ, A. JILEK, and J. LUKAS (Chem. News, 1925, **131**, 401—402; 1926, **132**, 1—4).—Palladium may be separated from the other platinum metals and from the common base metals by addition of a 2% alcoholic solution of benzoylmethylglyoxime to the solution of the chlorides of the metals in dilute hydrochloric acid (6 c.c. of the concentrated acid per 100 c.c. of solution). After boiling for a few minutes, the solution is kept over-night and the yellow, flocculent precipitate is then collected on a Gooch crucible, washed first with dilute hydrochloric acid, then with water, dried at 100—105°, and weighed as $C_{20}H_{18}O_6N_4Pd$ (20·64% Pd). If the solution contains antimony, tartaric acid must be added before precipitation of the palladium, and if molybdenum, vanadium, or tungsten is present a soluble phosphate must be added. *Palladium benzoylmethylglyoxime* is a yellow substance, m. p. 254—256°, insoluble in dilute acids but soluble in ammonia.
A. R. POWELL.

Separation of iridium from rhodium and platinum, and the separation of platinum and rhodium. I. WADA and T. NAKAZONO (Sci. Papers Inst. Phys. Chem. Res., 1923, **1**, 139—154).—Titanous sulphate, in the cold, immediately reduces salts of bismuth, copper, gold, palladium, and platinum to metals or lower oxides; mercury as nitrate is reduced to metal, as mercuric chloride to a mixture of mercurous chloride and metal; complete reduction of rhodium salts takes some minutes; tellurites are reduced to tellurium. In hot solution, ruthenium salts are partly reduced to metal. Most of the elements of the sulphide group may be separated from the iridium, rhodium, and platinum by treatment with hydrogen sulphide in 0·3*N*-acid solution, ruthenium and molybdenum, which remain in solution, being then removed. The mixed chlorides of platinum, iridium, and rhodium are treated with titanous sulphate in the absence of nitric acid. The precipitated rhodium and platinum are heated with a mixture of 1 vol. of 6*N*-nitric acid and 3 vols. of 6*N*-hydrochloric acid, which dissolves the platinum and only a small part of the rhodium, a black residue indicating the presence of the latter. The platinum and rhodium in the aqua regia are converted into the chlorides, the metals precipitated from the latter by treatment with aluminium in hydrochloric acid, and fused with potassium hydrogen sulphate. The rhodium and only a small part of the platinum are removed, and on treatment of the fusion product with water a black residue shows the presence of platinum. If 1 c.c. of a solution containing 1 mg. of platinum and not more than 1 mg. of rhodium as chlorides be treated with 1 c.c. of 95% alcohol and then with solid ammonium chloride almost to saturation, nearly all the platinum separates out as ammonium chloroplatinate if the liquid is kept, whilst the remaining red solution contains all the rhodium.

The iridium in the filtrate from the titanous sulphate reaction may be precipitated as sulphide by treating the solution with an equal volume of glycerol or 30 g. of tartaric acid per 100 c.c., saturating with hydrogen sulphide, and heating in a closed vessel at 100°.
B. FULLMAN.

Calorimetric bomb. P. LANDRIEU.—See B., 1926, 34.

Steel bomb calorimeter. W. KOHEN.—See B., 1926, 3.

Thermoregulator. H. J. WING and T. J. THOMPSON (Ind. Eng. Chem., 1925, **17**, 1242).—The inner tube (25 mm. diameter with a wall 1·5 mm. thick) is sealed inside the expansion bulb, and the stopcock and overflow cup are sealed to the upper end of the tube, whilst another tube is sealed to the bulb (for filling) and a second to the inner tube between the stopcock and the point where it enters the bulb. This latter carries the electrodes. The bulb is filled with mercury well above the end of the inner tube, and for a 100° range of the regulator 10 c.c. of mercury are added for each 100 c.c. volume of the bulb, which is then filled with toluene, heated to drive off air, cooled, completely filled, and sealed off. Dry hydrogen is drawn through into the side tube after filling with mercury, and the tube sealed off so that the contact points are left in an atmosphere of hydrogen. The regulator is set by drawing the mercury surface below the level of the upper contact point and the temperature of the bath adjusted by use of the stopcock.
D. G. HEWER.

Establishment of the temperature scale to −193° by means of platinum-resistance thermometers. A. G. LOOMIS and J. E. WALTERS (J. Amer. Chem. Soc., 1925, **47**, 2851—2856).—It is shown that suitably constructed thermometers of the flat-coil calorimetric type enable the thermometric scale to be reproduced precisely at low temperatures by calibration at one low-temperature point only. The deviations found by Keyes, Townshend, and Young (J. Math. Phys. Massachusetts Inst. Tech., 1922, **1**, 243) are attributed to strains. The experimental results, together with those of Van Dusen (A., 1925, ii, 590), establish the reproducibility of pure platinum as a thermometric resistance wire when used under strain-free conditions at low temperatures, so that Henning's proposed method of establishing the thermodynamic temperature scale is valid and reproducible.
S. K. TWEEDY.

Small resistance thermometer. G. F. Taylor (Physical Rev., 1925, [ii], **26**, 841—850).—The method of making the thermometer is described; a lead filament 1·5 cm. by 2×10^{-3} mm. in a glass tube embedded in a type metal for contact is employed. A sensitivity of 0·005° is readily obtained. The type metal employed (lead 85%, antimony 12%, tin 3%) has a coefficient of thermal expansion $25{\cdot}23\times10^{-6}$ per 1° between 0° and 100°.
A. A. Eldridge.

Pressure-temperature charts; extended ranges. G. Calingaert and D. S. Davis (Ind. Eng. Chem., 1925, **17**, 1287—1289; cf. B., 1925, 690; 1923, 699a).—Cox's method of laying off the non-uniform temperature scale from a straight line, taken as the vapour-pressure curve for water and along which the temperature ordinates may be marked by means of a steam table, drawn at any convenient angle with the logarithmic pressure abscissæ, is extended for temperatures above the critical (370°) by making use of the equation $1/y=a+b/t$, where y is the distance from 0° to t°, the constants depending on the scale and units chosen. The non-uniform scale of temperature ordinates as given by Cox's method is shown to be the equivalent of a reciprocal temperature scale, the reciprocal being $1/(t+230)$. The graphical representations are fairly straight lines, and the lines of a given family of substances intersect at a common point, so that only a single experimental point is required once the point of convergence is known. Graphs are shown for halogen-substituted benzene and alcohol series, silicon hydrides, certain metals (silver, lead, cadmium, and mercury show a point of convergence), etc. and vapour-pressure data for a large number of compounds have been plotted.
D. G. Hewer.

Photographic spectro-polarimeter for the ultra-violet region. A. Cotton and R. Descamps (Compt. rend., 1926, **182**, 22—26).—The instrument is constructed so that rotation of the analyser, which is replaced by the prisms of the spectrograph, produces automatically and continuously a corresponding movement in the image on the photographic plate, the angle of rotation being measured from the photograph. S. K. Tweedy.

Spectrograph with a non-inclined plate. P. Sève (Compt. rend., 1926, **182**, 57—58).—A simple spectrograph for use in the ultra-violet region is described in which, by the aid of quartz lenses and a reflector of small aperture, the spectrum is obtained normal to the photographic plate. S. K. Tweedy.

Light-filter for polarimetry. N. Schoorl (Pharm. Weekblad, 1926, **63**, 21—23).—Coebergh's filter No. 5, a solution of 8·8 g. of hydrated copper sulphate and 9·4 g. of potassium dichromate in 200 c.c. of water, employed with a 50 c.p. metal-filament lamp with matte surface, may be used to replace the sodium flame with very good results. S. I. Levy.

Dark field illumination. H. Siedentopf (Kolloid-Z., 1925, **37**, 327—335).—The theory of dark field illumination is discussed and two new dark field condensers by Zeiss and some of their applications are described. N. H. Hartshorne.

Ebullition device for low-temperature and vacuum distillation. A. F. O. Germann and D. M. Birosel (J. Physical Chem., 1925, **29**, 1528—1532).—An ebullition tube is described which can be used for all types of distillation, but is particularly designed for vacuum distillation. The essential feature of the device is a tube, closed at its upper end and drawn out into a capillary at its lower, which is sealed into the neck of the distilling bulb. A series of parallel fractional distillations made with the new and the old types of bulb, using technical carbonyl chloride or a solution of sulphur dioxide in pure carbonyl chloride, showed that the vacuum ebullition tube is considerably more efficient than the ordinary type of distilling tube. The action of the tube is explained, and it is claimed that it is quite as efficient in the fractional distillation of liquefied gases as is the use of an inert gas as recommended by Ramsay and Travers (Phil. Trans., 1901, **A**, **197**, 58).
L. L. Bircumshaw.

Viscosimetry. W. Stauf (Kolloid-Z., 1925, **37**, 397—405).—An account of the theory of viscosimetry and a description of capillary, torsion, and technical viscosimeters. N. H. Hartshorne.

Micro-determination of melting and transition temperatures. D. Vorländer and U. Haberland (Ber., 1925, **58**, [*B*], 2652—2656).—The microscope hot plate consists of a nickel disc in the centre of which is a quartz plate pierced with a hole in the edges of which platinum foil is inset. The foil is heated electrically. A small watch glass is fixed below the quartz plate and, during the measurements, covered by a second watch glass in such a manner that the substance under investigation and the quartz plate are in a very small, lens-shaped, hot-air bath. The instrument is calibrated by noting the current strength and potential at the platinum foil necessary to melt standard compounds. H. Wren.

Laboratory pure culture apparatus. F. M. Hildebrandt (Ind. Eng. Chem., 1925, **17**, 1279).—In order to deal with relatively large quantities of active pure culture, an apparatus has been evolved consisting essentially of a culture tube connected by a side tube to the side tube of a Pasteur flask which holds sterile nutrient solution. Both are mounted on a wooden frame, and the culture tube is drawn down to a small diameter at the bottom, and is furnished at the top with a small bent-over tube with a cotton plug. A T-piece is interposed in the connexion of the flask, with glass beads in rubber for stopcocks, and the Pasteur flask is furnished with a guard at the top. After filling the Pasteur flask two-thirds full of nutrient solution, the whole apparatus is sterilised, and tubes of antiseptic are hung under the lower openings of the culture tube and the connecting T-piece. A suspension of organisms is blown into the culture flask through the bottom opening with due precautions, and nutrient solution run in by raising the Pasteur flask. The culture can easily be withdrawn when required. The apparatus may readily be adapted for anaërobic work, and may be used in acclimatising organisms to various types of solution. D. G. HEWER.

History of investigation of internal pressures. T. W. RICHARDS (Chem. Reviews, 1925, **2**, 315—348).

Mineralogical Chemistry.

Sources of carbon in the pre-Cambrian formations. E. S. MOORE (Trans. Roy. Soc. Canada, 1925, [iii], **19**, IV, 21—26).—Carbon occurs in pre-Cambrian rocks as carbonates, graphite, and solid bitumen (anthraxolite). These may have been derived from the primary hydrocarbons and carbon dioxide of igneous rocks; but in recent years much evidence has been forthcoming of the presence of algal plant remains in these ancient rocks, and it is therefore likely that the carbon may be of organic origin. A limestone from Belcher Islands, Hudson Bay, containing algal concretions, showed specks of graphite, and an analysis gave 0·21%.

L. J. SPENCER.

Equilibrium between carbon dioxide and carbonates in the air, water, and earth of the globe. R. LEGENDRE (La Nature, 1925, **53**, ii, 138—142).—A discussion of the causes tending to increase or decrease the carbon dioxide content of the terrestrial atmosphere. The existing content is an equilibrium quantity, the resultant of reservoirs of atmospheric carbon dioxide and of carbonates in the earth, both dissolving and reacting in an intervening stratum of water. Chlorophyll at the atmosphere–water interface acts as a biological membrane, diminishing the partial pressure of the carbon dioxide at the surface of contact.

CHEMICAL ABSTRACTS.

Origin of terrestrial helium and its association with other gases. S. C. LIND (Proc. Nat. Acad. Sci., 1925, **11**, 772—779).—The inert gases cannot have been produced or retained in the earth's crust by chemical action; in the case of helium, its origin may be either primordial or due to radioactive decomposition. The gas will have been migrating slowly to the surface, be swept along at times by other gases, and be retained where a bed of shale capped by clay forms a favourable geological structure. It is generally, but not always, found in hydrocarbon gases, but in some cases with nitrogen which may possibly have been produced by the action of α-particles on nitrogenous organic matter or nitrides; it is almost universally associated with some nitrogen. The various hypotheses are discussed and analyses are given of gases collected recently from Dakota and Belgian Congo. E. B. LUDLAM.

Colour and composition of thunderbolts. E. MATHIAS (Compt. rend., 1925, **181**, 1111—1114).—The colours most frequently observed are those of black bodies cooling, *i.e.*, yellow, orange, or red. In many cases, however, blue, or a colour produced by superposition of blue on one of the preceding, is observed; these are attributed to burning sulphur, possibly arising from sulphur-containing organic matter in the atmosphere. The blackening of gilded objects, and the nature of odours observed in some cases, support this conclusion. S. I. LEVY.

Epidote of Monte Rosso di Verra (Monte Rosa group). T. CARPANESE (Atti R. Accad. Lincei, 1925, [vi], **2**, 349—355).—The epidote has a composition agreeing with the formula $HCa_2(Al,Fe)_3Si_3O_{13}$, and *d* 3·343. A comparison of its optical properties with its chemical composition indicates that it is to be regarded as a normal member of the clinozoizite–epidote series of mixed crystals. F. G. TRYHORN.

Identity of composition of planchéite and shattuckite. A. SCHOEP (Bull. Soc. chim. Belg., 1925, **6**, 315—321).—A well-crystallised sample of planchéite from Tantara was found to have the percentage composition: SiO_2, 39·23; CuO, 44·99; CaO, 6·93; H_2O, 5·74; Co_3O_4, 0·49; CO_2, 2·75, total 100·22. After deducting Co_3O_4 and $CaCO_3$ the molecular formula indicated is $2SiO_2,2(Cu,Ca)O,H_2O$, identical with that of shattuckite, but for the partial molecular replacement of copper oxide by calcium oxide. Indices of refraction were $\alpha=1{\cdot}665$, $\gamma=1{\cdot}720$, whilst all water was eliminated at 600—620°.

A. COUSEN.

Autunite from Lurisia. C. PORLEZZA and A. DONATI (Annali Chim. Appl., 1925, **15**, 518—534).—The results are given of chemical and spectrometrical analyses of autunite from the mines of Lurisia.

T. H. POPE.

Beidellite, a new mineral name. E. S. LARSEN and E. T. WHERRY (J. Washington Acad. Sci., 1925, **15**, 465—466).—A gouge-clay from Beidell, Colorado, previously described as leverrierite (A., 1917, ii, 324), is now named beidellite. It is a metasilicate with the formula $Al_2O_3,3SiO_2,nH_2O$, where *n* is about 4, coming between kaolinite and pyrophyllite. It is optically negative with small axial angle; $n(\alpha)$ 1·494, $n(\beta)$ and $n(\gamma)$ 1·536; and is probably orthorhombic.

L. J. SPENCER.

Composition and optical properties of beidellite. C. S. ROSS and E. V. SHANNON (J. Washington Acad. Sci., 1925, **15**, 467—468).—New analyses are given of: I, the finer separation from bentonite from Nashville, Arkansas; II, the coarser separation of the same; III, iron-beidellite from Spokane, Washington. These, and earlier analyses of material previously referred to leverrierite, suggest the formula $Al_2O_3,3SiO_2,4H_2O$. In the green iron-beidellite, with rather higher refractive indices, there is a passage to $Fe_2O_3,3SiO_2,4H_2O$.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I.	45·52	—	27·52	2·80	—	0·52	3·00	19·60	98·96
II.	45·12	—	28·24	4·12	—	0·88	2·32	18·72	99·40
III.	46·06	0·84	12·22	18·54	0·28	1·66	1·62	17·26	98·48

L. J. SPENCER.

Japanese minerals containing rarer elements. I—III. Y. Shibata, K. Kimura, and T. Uemura (Japanese J. Chem., 1923, 2, 1—20).—English translations, with some rearrangement, of papers previously published in Japanese (A., 1921, ii, 269; 1922, ii, 220, 305, 516, 861). L. J. Spencer.

Japanese minerals containing rarer elements. IV. Analyses of zircon, xenotime, and allanite. K. Kimura (Japanese J. Chem., 1925, 2, 73—79).—Crystals of reddish-brown zircon (*d* 4·3—4·4) and brownish-grey xenotime (*d* 4·4) were washed from a stream in the pegmatite region of Ishikawa, prov. Iwaki. The two are intimately intermixed and sometimes show parallel intergrowths. Zircon separated as far as possible from xenotime gave analysis I (also MgO, CaO, MnO traces). The rare-earths in excess of the phosphoric acid presumably belong to the zircon rather than to the xenotime. Analysis II (also CaO 0·35) of radial aggregates of xenotime shows the material to be a mixture of xenotime and zircon.

	SiO_2.	ZrO_2.	UO_2.	$(Nb,Ta)_2O_5$.	P_2O_5.	Al_2O_3.	Fe_2O_3.	Rare earths.	Ign.	Total.
I.	32·40	58·71	1·06	trace	1·31	0·25	0·95	3·79	2·10	100·57
II.	12·49	19·84	1·92	0·44	23·87	0·48	0·23	37·37	2·35	99·34

Allanite from the pegmatite of Ishikawa is black and radioactive with *d* 3·60. Analysis gave SiO_2 32·93, ThO_2 1·64, Al_2O_3 14·51, Ce_2O_3 4·87, La_2O_3 etc. 8·19, FeO 15·23, MnO 4·32, CaO 12·61, MgO 0·74, CO_2 0·11, H_2O 4·58, UO_2, SnO_2 traces, total 99·73. Spectrum analysis of the rare-earth fraction (free from ceria) shows a predominance of lanthanum and neodymium, and presence of yttrium, gadolinium, etc. L. J. Spencer.

Japanese minerals containing rarer elements. V. Analyses of fergusonite, hagatalite, and oyamalite. K. Kimura (Japanese J. Chem., 1925, 2, 81—85).—Crystals of fergusonite, *d* 5·30, from the pegmatite of Hagata, province Iyo, gave on analysis: $(Nb,Ta)_2O_5$ 44·97, SiO_2 0·79, TiO_2 1·15, UO_2 3·18, SnO_2 0·35, Al_2O_3 1·35, Fe_2O_3 0·66, Y_2O_3 etc. 40·39, Nd_2O_3 etc. 0·89, CaO 1·40, MgO 0·58, CO_2 0·35, H_2O 3·92, total 99·98. Spectrum analysis showed the presence of predominant yttrium, together with scandium, neodymium, praseodymium, europium, dysprosium, holmium, erbium, and thulium; and, in the tin precipitate, of lead, copper, and germanium. Hagatalite is the name given to a variety of zircon, which occurs as small crystals embedded in biotite from the pegmatite of Hagata. The crystalline form is that of zircon, *d* 4·4. Analysis I [also $(Nb,Ta)_2O_5$ 2·7, UO_2 trace] shows the presence of more rare-earths (mainly yttria) and less zirconia than in naegite (A., 1921, ii, 269). Another variety of zircon, named oyamalite, occurs in the pegmatite of Oyama, province Iyo, as green to brown radial aggregates resembling naegite; analysis II (also P_2O_5 7·6) shows that in addition to rare-earths it contains a considerable amount of phosphoric acid.

	SiO_2.	ZrO_2.	ThO_2.	Al_2O_3.	Fe_2O_3.	Rare earths.	CaO.	MgO.	Ign.	Total.
I.	29·7	42·0	1·5	2·8	2·3	13·1	0·3	0·2	5·5	100·1
II.	25·7	40·9	0·6	2·0	0·6	17·7	0·6	0·8	3·5	100·0

L. J. Spencer.

Buttgenbachite, a new mineral. A. Schoep (Bull. Soc. chim. Belg., 1925, **34**, 313—314).—See A., 1925, ii, 1196.

Organic Chemistry.

Identification of primary alkyl bromides and iodides. C. S. Marvel, C. G. Gauerke, and E. L. Hill (J. Amer. Chem. Soc., 1925, **47**, 3009—3011).—The alkyl halide (1 c.c.) is treated with magnesium (0·3 g.) in dry ether (15 c.c.), the solution filtered into a test-tube containing 4·5—5·0 g. of mercuric bromide or iodide, the mixture warmed and shaken for a few min., and then evaporated to dryness. The residue is boiled with 95% alcohol (20 c.c.), the extract filtered, diluted with water (10 c.c.), and cooled, when the corresponding mercuric alkyl halide separates. These derivatives are well crystallised, have well-defined m. p., and are well adapted to the identification of alkyl halides. The following new mercuric alkyl halides are described: *mercuric ethyl*, m. p. 193·5°; n-*propyl*, m. p. 138°; iso*butyl*, m. p. 55·5°; n-*amyl*, m. p. 122°; n-*hexyl*, m. p. 118·5°; n-*heptyl*, m. p. 114·5°; and n-*octyl bromide*, m. p. 109°; *mercuric* n-*propyl*, m. p. 112·5°; n-*butyl*, m. p. 117°; and iso*butyl iodide*, m. p. 72°. F. G. Willson.

Catalytic hydrogenation of organic substances. O. Schmidt.—See this vol. 134.

Narcotic and toxic effects of halogen derivatives of hydrocarbons. J. Müller.—See B., 1926, 75.

Oxonium compounds. D. McIntosh (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 71—72; cf. J.C.S., 1905, **87**, 784; A., 1912, i, 825).—*n*-Propyl alcohol adds 1 atom of chlorine or bromine, methyl ethyl ketone 2 atoms, methyl acetate, *n*-propyl acetate, and *iso*amyl acetate (bromine only) 3 atoms. The additive compounds melt at a low temperature, are formed with slight heat evolution, and when substitution is prevented are not electrically conductive. The above substances, together with *iso*propyl alcohol, methyl propionate, ethyl butyrate, and acetic anhydride, give compounds with hydrogen bromide which in solution are electrically conducting. Ethylene glycol gives compounds containing 1 and 2 mols. of hydrogen bromide, but forms no additive compounds with hydrogen chloride or iodide or with the halogens. J. S. Carter.

Condensations of the sodium derivatives of trimethylene glycol and glycerol. A. Fairbourne and G. E. Foster (J.C.S., 1925, **127**, 2759—2764; cf. *ibid.*, 1921, **119**, 1035, 2077).—1-Chloro-2 : 4-dinitrobenzene reacts at 100° with a solution of sodium in trimethylene glycol, and treatment with acetic acid leads to the separation of *trimethylene glycol mono-*2 : 4-*dinitrophenyl ether*, m. p. 52° (*acetyl* derivative, m. p. 85°, *benzoyl* derivative, m. p. 95°), and *trimethylene glycol bis*-2 : 4-*dinitrophenyl ether*, m. p. 180°, the relative yields of which vary with the concentration of the sodium derivative. Benzoyl chloride with monosodium glyceroxide yields α-benzoylglycerol, but with disodium glyceroxide it yields tribenzoylglycerol, m. p. 71—72° (from light petroleum), 76° (from alcohol). Mono- or di-sodium glyceroxide reacts with one equivalent of *p*-toluenesulphonyl chloride in ether or benzene solution to give *glyceryl tri*-p-*toluenesulphonate*, m. p. 103°, whilst *glyceryl tribenzenesulphonate*, m. p. 80°, is similarly prepared. In spite of this, and of the fact of the formation of the bisdinitrophenyl ether, it is concluded that in the above condensation of 1-chloro-2 : 4-dinitrobenzene, direct interaction between halogen and hydroxyl groups does not occur, since no ionisable halogen is detected when 1-chloro-2 : 4-dinitrobenzene, in presence of calcium carbonate, is heated with glycerol, ethylene glycol, or trimethylene glycol, or with trimethylene glycol mono-2 : 4-dinitrophenyl ether in a solvent. Treatment of the mono-ether with a solution of sodium in trimethylene glycol does not give rise to the bis-ether.

iso*Propylideneglycerol* 3 : 5-*dinitrobenzoate*, m. p. 85° (prepared by interaction of 3 : 5-dinitrobenzoyl chloride and *iso*propylideneglycerol in presence of quinoline and chloroform), is converted by dilute hydrochloric acid at 70—80° into *glycerol* α-3 : 5-*dinitrobenzoate*, m. p. 118°; since this is also prepared by condensation of monosodium glyceroxide and 3 : 5-dinitrobenzoyl chloride in ethereal solution, and since monosodium glyceroxide and *p*-nitrobenzoyl chloride similarly yield α-*p*-nitrobenzoylglycerol, the α-structure of monosodium glyceroxide is confirmed.

F. M. Hamer.

Oxidation of ethyl ether to oxalic acid in presence of uranyl nitrate. S. W. Rowell and A. S. Russell (J.C.S., 1925, **127**, 2900—2902).—When an ethereal solution of uranyl nitrate is exposed to sunlight in presence of water, after removal of the ether and of unchanged uranyl nitrate there remains the normal hydrated uranium oxalate, $UO_2C_2O_4,2H_2O$; sometimes a basic oxalate is formed, probably $U(OH)_4,UO_2C_2O_4,2H_2O$ or $UO_2(OH)_2,UO_2C_2O_4,2H_2O$. Exposure to sunlight of a neutralised ethereal solution of uranyl nitrate yields uranous hydroxide. Even carefully purified ether with uranyl nitrate gives the oxalate, but none results when ether is replaced by alcohol, although the latter favours the formation of uranium hydroxide in neutral solution. It is suggested that sunlight reduces the uranyl to the uranous ion and oxidises ether to diglycol, of which part is oxidised to diglycollic acid and part hydrolysed to glycol, which is further oxidised to oxalic acid.

F. M. Hamer.

Formation of ethyl mercaptan by the action of phosphorus pentasulphide on alcohol. P. S. Pischtschimuka (J. Russ. Phys. Chem. Soc., 1925, **56**, 11—14).—The interaction of ethyl alcohol and phosphorus pentasulphide is expressed, according to Kekulé, by the equation $5EtOH+P_2S_5=P_2O_5+5EtSH$ and, according to Carius (Diss., Heidelberg, 1861), by the equation $5EtOH+P_2S_5=H_2O+H_2S+Et_3PO_2S_2+Et_2HPO_2S_2$. The author finds that the reaction between anhydrous alcohol and phosphorus pentasulphide under various conditions always yields diethyl dithiophosphate, $SH{\cdot}SP(OEt)_2$. At a high temperature, this acid decomposes with evolution of ethyl mercaptan in small proportions. Treatment of the lead salt of the acid with ethyl iodide yields its *ethyl* derivative, $SEt{\cdot}SP(OEt)_2$, which may be obtained also by heating in a sealed tube a mixture of sulphur with the compound $PCl_2{\cdot}SEt$ (cf. Michaelis, A., 1872, 283) and treating with dry sodium ethoxide the resulting *ethyldithiophosphoryl chloride*, $SEt{\cdot}SPCl_2$, b. p. 92°/10 mm., d_0^0 1·4453. The ethyl derivative of diethyl dithiophosphate, but not the acid itself, readily gives ethyl mercaptan when heated with water.

T. H. Pope.

Hydroxy- and ethoxy-mercaptans and their condensation products. C. A. Rojahn and G. Lemme (Arch. Pharm., 1925, **263**, 612—624).—The following compounds have been prepared in an effort to obtain alkyloxy- or hydroxy-derivatives of the sulphonal or veronal series. The effort has up to the present proved abortive because the mercaptols resist oxidation. The compounds, unless otherwise specified, are oils without unpleasant odour. Those for which no b. p. is given decompose on heating.

γ-*Ethoxypropyl mercaptan*, b. p. 52—54°/20 mm., is prepared by treating γ-bromopropyl ethyl ether with potassium hydrogen sulphide; when treated with dilute alcoholic sodium hydroxide and benzyl chloride, it yields γ-*ethoxypropyl benzyl sulphide*, b. p. 161°/18 mm., which is oxidised by hydrogen peroxide to the corresponding *sulphone*, m. p. 45—46°. When γ-ethoxypropyl mercaptan is dissolved in acetone and the solution heated with zinc chloride, *acetone di-γ-ethoxypropylmercaptol* (iso*propylidene di-γ-ethoxypropyl disulphide*), $CMe_2[S{\cdot}[CH_2]_3{\cdot}OEt]_2$, is formed. An analogous product is formed when methyl ethyl ketone is used, or is prepared also by ethylating (with ethyl sulphate) the corresponding dihydroxymercaptol (see below). By treating γ-chloropropyl alcohol with sodium hydrogen sulphide γ-*hydroxypropyl mercaptan*, b. p. 85—90°/15 mm., is obtained. It yields a *dibenzoate*, and, when heated with fuming hydrochloric acid, γ-*thiolpropyl* γ-*chloropropyl sulphide*, the *benzoate* of which is described. γγ-*Dihydroxypropyl disulphide* is obtained by oxidising the mercaptan with sodium hydroxide and iodine. Its *dibenzoate* is described. γ-*Hydroxypropyl benzyl sulphide* has b. p. 185—188°/20 mm. (slight decomp.) and also affords a *benzoate*. iso*Propylidene di-γ-hydroxypropyl disulphide* and its *dibenzoate*, and the corresponding mercaptols from methyl ethyl ketone and benzaldehyde, and their *dibenzoates*, are also described. The *diacetate* of β-hydroxyethyl mercaptan (Bennett, J.C.S., 1921, **119**, 423) has b. p. 118—120°/25 mm. β-*Ethoxyethyl mercaptan*, which is obtained in poor yield owing to side reactions, diethylene disulphide and other products being formed, has b. p. 37—40°/15 mm. The corresponding *disulphide*, which also is a by-product, has b. p. 150—152°/15 mm. β-*Ethoxyethyl benzyl sulphide* has b. p. 146°/16 mm., and is oxidised to the corresponding sulphone, m. p. 53°

(Fromm and Jörg, A., 1925, i, 352). iso*Butylidene di-β-ethoxyethyl disulphide* is described.

When dichloroacetone interacts with mercaptans, the chlorine atoms, and not the ketonic group, take part. An alternative way of obtaining the sulphones referred to above is therefore not feasible. *αγ-Diethylthiolacetone,* from dichloroacetone and ethyl mercaptan, has b. p. 117—121°/15 mm. (*semicarbazone,* m. p. 98—99°, *dimethiodide,* m. p. 182°); it is accompanied by *αββγ-tetrathioethylpropane,* b. p. 51—53°/15 mm., which is the chief product when an excess of ethyl mercaptan is used.

W. A. SILVESTER.

Methyltrichloromethylsulphur chloride. CHEM. FABR. SCHERING.—See B., 1926, 38.

γγ′-Dichlorodipropyl sulphide. G. M. BENNETT and A. L. HOCK (J.C.S., 1925, **127**, 2671—2677).—The action of sodium sulphide on γ-chloropropyl alcohol yielded *γγ′-dihydroxydipropyl sulphide* (*bisphenylurethane,* m. p. 146—148°), and this on chlorination gave *γγ′-dichlorodipropyl sulphide,* b. p. 162°/43 mm., d_4^{20} (vac.) 1·175, n_α^{20} 1·5075, which formed a *compound* with platinic chloride, m. p. 83·5—85°, and an unstable *dibromide.* The chloro-sulphide gave on oxidation *γγ′-dichlorodipropylsulphone,* m. p. 66°, and with methyl iodide and mercuric iodide yielded *dichlorodipropylmethylsulphonium mercuri-iodide,* m. p. 84—88°. When heated with phenol and sodium ethoxide, the chloro-sulphide formed *γγ′-diphenoxydipropyl sulphide,* m. p. 45°, and similarly *γγ′-di*-p-*tolyloxydipropyl sulphide,* m. p. 50—52°, was obtained. With piperidine, *γγ′-dipiperidinodipropyl sulphide* (*picrate,* m. p. 200°) was formed. The rates of reaction of ββ′-dichlorodiethyl and γγ′-dichlorodipropyl sulphides with alcoholic alkali are approximately as 60 : 1.

B. W. ANDERSON.

Isomerism in compounds containing two similar asymmetric sulphur atoms. E. WEDEKIND (Ber., 1925, **58**, [*B*], 2510—2518).—Diethyl ethylene sulphide slowly unites with methyl iodide at the atmospheric temperature to yield ethylenedimethylethylsulphonium iodide, $C_2H_4(SMeEt{\cdot}I)_2$, which is separable by crystallisation from dilute alcohol into a sparingly soluble *α-salt,* decomp. 154°, and a more freely soluble *β-salt,* m. p. 123—124°. Measurable crystals have not been obtained, but the compounds are sharply differentiated from one another by crystalline form and solubility in 75% alcohol. It remains uncertain whether the isomerism persists in a series of salts; those of the two series do not appear to differ from one another markedly in appearance or temperature of decomposition, but complete identity cannot be assumed, since measurable crystals have not been obtained, and instances are on record in which isomeric salts decompose at the same temperature. The following salts have been obtained from the α- and β-iodides: mercuric chloride *compound,* $C_8H_{20}S_2Hg_2Cl_6$, m. p. 191°; cadmium iodide *compound,* $C_8H_{20}S_2CdI_4$, decomp. 147—148°; *chloroplatinate,* decomp. 236° after softening; *chloroaurate,* $C_8H_{20}S_2Au_2Cl_8$, decomp. 225°; *picrate,* decomp. 170°; *perchlorate,* decomp. 227°. The β-perchlorate appears to dissolve in water rather more freely than the α-perchlorate. Attempts to resolve the salts by means of *d*-camphorsulphonic acid or *d*-bromocamphor-π-sulphonic acid gave negative results on account of experimental difficulties. The d-*camphorsulphonate* from the α-iodide has m. p. 183°, whereas the corresponding *salt* from the β-iodide has m. p. 189—190°. The d-*bromocamphor-π-sulphonates* of the α- and β-series have m. p. 157—159° and 160° (indef.), respectively; the α-salt crystallises in long needles which, when preserved beneath the mother-liquor, become transformed into thick, coarse prisms. An actual interconversion of the salts of the two series could not be achieved.

Diethyl trimethylene disulphide, b. p. 228—231°, is converted by methyl iodide into the corresponding *sulphonium iodide,* $C_9H_{22}I_2S_2$, m. p. (indef.) 112°, which could not be separated into two possible isomerides.

H. WREN.

Acid and salts strongly absorbing ultra-violet rays. T. SUZUKI and S. SAKURAI.—See B., 1926, 76.

Acetato- and formato-cations of cadmium, manganese, lead, and the alkaline-earth metals. R. WEINLAND and H. SCHLAICH (Z. anorg. Chem., 1925, **150**, 35—46).—The following complex *salts* of cadmium acetate are described:

$$[Cd_2(OAc)_2](OAc)(ClO_4),3H_2O;$$
$$[Cd_2(OAc)_2](NO_3)_2,3H_2O; \quad [Cd_3(OAc)_4](ClO_4)_2,2H_2O;$$
$$[Cd_2(OAc)_2][O{\cdot}C_6H_2(NO_2)_3]_2,CH_3{\cdot}CO_2H,3H_2O;$$
$$[Cd_2(OAc)_2](O{\cdot}C_6H_4{\cdot}NO_2)_2,2OH{\cdot}C_6H_4{\cdot}NO_2,CH_3{\cdot}CO_2H,6H_2O;$$
$$[Cd_2(HCO_2)_2][O{\cdot}C_6H_2(NO_2)_3]_2,6H_2O.$$

The first three are obtained by mixing cadmium acetate and the appropriate acid in aqueous solution, but the picrates and *p*-nitrophenoxides are obtained fron concentrated acetic or formic acid. A *picrate* of manganese acetate, $[Mn_2(OAc)_2][O{\cdot}C_6H_2(NO_2)_3]_2$, and the following p-*nitrophenoxides* are similarly obtained:

$$[Mn_3(OAc)_4](O{\cdot}C_6H_4{\cdot}NO_2)_2,CH_3{\cdot}CO_2H,9H_2O;$$
$$[Pb_2(OAc)_2](O{\cdot}C_6H_4{\cdot}NO_2)_2,2CH_3{\cdot}CO_2H,$$
$$[Ba_2(OAc)_2](O{\cdot}C_6H_4{\cdot}NO_2)_2,2CH_3{\cdot}CO_2H,6H_2O;$$
$$[Sr_2(OAc)_2](O{\cdot}C_6H_4{\cdot}NO_2)_2,2CH_3{\cdot}CO_2H,6H_2O;$$
$$[Ca_2(OAc)_2](O{\cdot}C_6H_4{\cdot}NO_2)_2,2CH_3{\cdot}CO_2H,4H_2O.$$

A. GEAKE.

α-Ethyloctoic acid and its esters. A. W. DOX (J. Amer. Chem. Soc., 1925, **47**, 3008—3009).—dl-*α-Ethyloctoic acid,* b. p. 252—255°, d^{25} 0·8905, is obtained in practically quantitative yield by distilling ethylhexylmalonic acid (cf. A., 1924, i, 1037). The following esters were prepared: *methyl,* b. p. 213—215°; *ethyl,* b. p. 221—223°, d^{25} 0·8580; *propyl,* b. p. 238—240°, d^{25} 0·8578; and n-*butyl,* b. p. 255—257°, d^{25} 0·8571. The first two esters do not react with cold, saturated, alcoholic ammonia.

F. G. WILLSON.

Evolution of hydrogen peroxide from oils on exposure to light. G. F. A. STUTZ, H. A. NELSON, and F. S. SCHMUTZ.—See B., 1926, 20.

Decomposition of oxalic acid by acetic anhydride. E. L. WHITFORD (J. Amer. Chem. Soc., 1925, **47**, 2934—2938).—The decomposition of oxalic acid in acetic anhydride solution is a reaction of the first order, $k^{25}=0{\cdot}0128$, $k^{35}=0{\cdot}0375$, and $k^{45}=0{\cdot}1105$. The decomposition is not catalysed by carbamide,

pyrrole, aniline, phenylhydrazine, or aceto-, propio-, or butyro-nitriles. Impure picoline, lutidine, and collidine increase the rate of decomposition. The addition of pyridine also increases the rate of decomposition, but causes the temporary separation of pyridine hydrogen oxalate, which disappears as the reaction proceeds. The insolubility of this oxalate of pyridine in acetone, in comparison with those of pyridine derivatives, renders it suitable for the isolation of small quantities of pure pyridine from the commercial material. In pyridine solution, 1 mol. of acetic anhydride brings about the decomposition of 1 mol. of oxalic acid, indicating the probable formation of an intermediate compound between the two, the decomposition then being formulated $H_2C_2O_4 + Ac_2O \rightleftharpoons H_2C_2O_4,Ac_2O \longrightarrow CO + CO_2 + 2HO{\cdot}Ac$. The reaction-velocity constants, in pyridine solution, are independent of the amount of acetic anhydride added.
F. G. WILLSON.

Uranyl oxalate. A. RAYNAUD (Bull. Soc. chim., 1925, [iv], **37**, 1375—1376).—The original work of the author (A., 1912, i, 535) was corrected by a later paper (Soc. Sci. Phys. Nat. Bordeaux, Meeting on March 26, 1914), which anticipates and confirms the results of Colani (A., 1925, i, 1235) on the hydration and dehydration of uranyl oxalate. W. HUME-ROTHERY.

Formation and growth of silver nuclei in the decomposition of silver oxalate. J. T. MACDONALD and C. N. HINSHELWOOD.—See this vol., 134.

Aluminioxalates of some optically active bases. T. B. CHILD, E. ROBERTS, and E. E. TURNER (J.C.S., 1925, **127**, 2971—2972).—By the action of barium aluminioxalate on the sulphate of the base, *strychnine aluminioxalate*, $[\alpha]_D^{20}$ −24·0° to −21·0°, was prepared, and similarly 1-*menthylamine aluminioxalate*, $[\alpha]_D^{20}$ −28·5°, and 1-*phenylethylamine aluminioxalate*, $[\alpha]_D^{20}$ −3·00°, were obtained. Recrystallisation of these compounds gave no evidence of resolution. *Potassium distrychnine aluminioxalate* and *dipotassium* d-*phenylethylamine aluminioxalate* gave no better results. *Cinchonidine aluminioxalate* was obtained as a gummy solid. B. W. ANDERSON.

Ethyl γγ-diethoxyacetoacetate as a reagent for the synthesis of glyoxalines. E. W. RUGELEY and T. B. JOHNSON (J. Amer. Chem. Soc., 1925, **47**, 2995—3002).—For the preparation of ethyl γγ-diethoxyacetoacetate, moist silver diethoxyacetoacetate may be agitated for 12 hrs. with ethyl iodide in moist ether at the ordinary temperature (cf. Johnson and Cretcher, A., 1915, i, 1002; 1916, i, 756). Synthesis of this ester could not be accomplished by the method of Hamel (A., 1921, i, 537). When treated with nitrous acid (cf. Jovitschitsch, A., 1895, i, 447), the ester yields an iso*nitroso*-derivative, decomposing when heated, which could not be reduced to the corresponding amine. *Ethyl α-bromo-γγ-diethoxyacetoacetate*, decomposing when heated, appears to be formed by the action of bromine in carbon disulphide on the above ester. It does not react with carbamide, and the products of reaction with ammonia could not be purified. Treatment with hydrogen bromide affords *ethyl α-bromoglyoxalacetate*, m. p. 119°. Condensation of ethyl γγ-diethoxyacetate or ethyl formate with ethyl hydantoate, or of the first-named with ethylurethane acetate, in presence of sodium ethoxide, could not be accomplished. When treated with chlorodimethyl ether, ethyl sodio-γγ-diethoxyacetoacetate affords *ethyl α-methoxymethyl-γγ-diethoxyacetoacetate*, b. p. 130°/4 mm., n^{23} 1·4387. *Diethyl γγ-diethoxyacetosuccinate*, b. p. 156°/3 mm., n^{21} 1·4370, is obtained by alkylation of ethyl γγ-diethoxyacetoacetate with ethyl chloroacetate, or by application of the Claisen reaction to the former with diethyl succinate. It yields, on hydrolysis with barium hydroxide, succinic acid [identified as its *benzyl-ψ-thiocarbamide* salt ($+2H_2O$), m. p. 153°], and glyoxalpropionic acid, a small proportion of the latter being also obtained on hydrolysis with sulphuric acid or sodium hydroxide. The bearing of these results on the production of therapeutically valuable glyoxaline derivatives is discussed. F. G. WILLSON.

Formation of citric acid from gluconic acid by moulds. C. WEHMER (Ber., 1925, **58**, [*B*], 2616—2619).—Calcium gluconate is converted by a species of *Aspergillus niger* (strain 8 of A., 1924, i, 1282) into citric acid and smaller amounts of oxalic acid, whereas oxalic acid is almost exclusively produced by *A. niger cinnamomeus*. Additional confirmation is thus given to the hypothesis that the oxidative degradation of sugar follows the course dextrose ⟶ gluconic acid ⟶ citric acid ⟶ oxalic acid ⟶ carbon dioxide, but the mechanism of the formation of citric acid remains unexplained. H. WREN.

Formation of citric acid from gluconic acid by *Aspergillus*. R. SCHREYER (Ber., 1925, **58**, [*B*], 2647; cf. Falck and Kapur, A., 1924, i, 917).—Citric acid is formed by the action of *A. fumaricus* on 15%, but not on 10% solutions of calcium gluconate.
H. WREN.

Constitution of α-ketogluconic acid. M. HÖNIG (Ber., 1925, **58**, [*B*], 2644—2646; cf. Hönig and Tempus, A., 1924, i, 712).—In reply to van Niel and Hooft (A., 1925, i, 1237), the author accepts the possibility of the non-homogeneity of the yeast used in the fermentation of α-ketogluconic acid, but maintains the identity of the *d*-arabinose produced thereby, which does not rest solely on the isolation of the osazone, but also on the oxidation of the carbohydrate to carbon dioxide and *d*-arabonic acid, isolated as the calcium and phenylhydrazine salts. The relationship of the α-ketogluconic acid to the product obtained by Bertrand (A., 1904, ii, 760) and by Kiliani (A., 1922, i, 1111) remains undecided.

The substance, $C_{18}H_{24}O_6N_4$, described (*loc. cit.*) as the osazone of α-ketoglutaric acid is identified as the *phenylhydrazone* of the *phenylhydrazide* of the *ketonic acid*. H. WREN.

Electrolytic reduction of aldehydes. I. Formaldehyde and acetaldehyde. G. SHIMA (Mem. Coll. Sci. Kyōtō, 1925, **9**, 183—196).—The electrolytic reduction of formaldehyde and acetaldehyde yields in each case 80—90% of the corresponding alcohol, but the current efficiency in the former case is 52% as against 80% in the latter. The concentration of the aldehyde must not be high, on account of possible polymerisation. Reduction of acetaldehyde to ethyl alcohol is best carried out at 20°, using 10—15% sulphuric acid solution, a lead cathode, and a current density of 3·5—4 amp./cm.^{2} The aldehyde concentration should be kept at about 5%.

B. W. Anderson.

Assimilation hypothesis. D. Vorländer (Ber., 1925, **58**, [*B*], 2656—2658).—Previous results on the production of formaldehyde and oxygen from carbon dioxide and water under the influence of light in the absence of protoplasm or organised matter are contradictory, possibly on account of reversibility of the reaction. Attempts are described to remove the formaldehyde as produced by precipitating it with 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione. Negative results are obtained when water saturated with 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione is treated with a current of carbon dioxide for months in sunlight or daylight or for weeks in the light from a mercury–quartz arc. Reaction is not induced by the presence of salts, alkalis, acids, uranyl sulphate, cerium carbonate or chloride, titanous sulphate, ferrous sulphate, or pyridine.

H. Wren.

Aldehyde acetal of methylglyoxal. C. Neuberg and O. Dalmer (Biochem. Z., 1925, **162**, 488—489).—Commercial dichloroacetic acid can be used in the preparation of ethyl diethoxyacetate, since the mono- and di-ethoxy-esters are readily separable by fractionation.

P. W. Clutterbuck.

Reduction of ketones in presence of platinum-black. M. Faillebin (Compt. rend., 1926, **182**, 138—140).—See this vol., 50.

Claisen reaction. G. T. Morgan and E. Holmes (J.C.S., 1925, **127**, 2891—2896).—The higher methyl monoketones, $C_nH_{2n+1}\cdot CO\cdot CH_3$, from $n=7$ to $n=19$, condense normally with ethyl acetate, giving a satisfactory yield of $\alpha\gamma$-diketone,

$$C_nH_{2n+1}\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

The acids $C_nH_{2n+1}\cdot CO_2H$, where $n=10$, 12, 14, and 18, are obtained by oxidising the methyl ketone of the next higher acid and are isolated as barium salts. The method consists in condensing the ketone, prepared by distillation of the barium salt of the corresponding fatty acid with barium acetate, with sodium and ethyl acetate, acidifying with acetic acid, and isolating the co-ordinated copper derivative of the diketone, from which treatment with sulphuric acid in presence of ether liberates the diketone itself. The following are described: n-*octoylacetone*, b. p. 248°/755 mm., 118°/5 mm., *copper* salt, m. p. 118°; n-*nonoylacetone*, b. p. 150°/15 mm., *copper* salt, m. p. 115·5°; *n*-decoylacetone; n-*undecoylacetone*, m. p. 28°, *copper* salt, m. p. 112°; n-*dodecoylacetone*, m. p. 31—32°, *copper* salt, m. p. 112·5°; n-*tridecoylacetone*, m. p. 35°, *copper* salt, m. p. 111°; n-*tetradecoylacetone*, m. p. 39°, *copper* salt, m. p. 112°; n-*pentadecoylacetone*, m. p. 42°, *copper* salt, m. p. 111°; n-*hexadecoylacetone*, m. p. 49°, *copper* salt, m. p. 112°; n-*heptadecoylacetone*, m. p. 51°, *copper* salt, m. p. 112°; n-*octadecoylacetone*, m. p. 52·5°, *copper* salt, m. p. 113°; n-*nonadecoylacetone*, m. p. 55°, *copper* salt, m. p. 112·5°; n-*eicosanoylacetone*, m. p. 57°, *copper* salt, m. p. 114°. The influence of lengthening the carbon chain on the b. p. of the lower diketones, m. p. of the higher members, and fusibility of their copper salts, is shown in the form of graphs. The blue colour of the copper salts becomes less pronounced as the series is ascended. Probably the whole series of diketones would condense with tellurium tetrachloride (cf. this vol., 188).

F. M. Hamer.

Dynamic isomerism. XX. Amphoteric solvents as catalysts for the mutarotation of the sugars. T. M. Lowry and I. J. Faulkner (J.C.S., 1925, **127**, 2883—2887; cf. A., 1925, i, 886).—A mixture of pyridine with twice its weight of water gives a maximum velocity of mutarotation for dextrose, or for tetramethylglucose, which is twenty times as great as the velocity for a solution of the sugar in pure water. Neither pyridine nor cresol has appreciable catalytic properties when water is not present, but a mixture of two parts of cresol to one part of pyridine is twenty times more active than is water in promoting the mutarotation of tetramethylglucose. The great activity of the mixed solvent is attributed to its amphoteric character. It is concluded that, for a proton within the sugar molecule to change its position, it is necessary to supply a medium into which a proton can escape and from which a proton can be provided. This theory is supported by the fact that the only substances known to act as catalysts for the mutarotation of the sugars possess either acidic or basic properties or both. Acetone and ethyl acetate, even in presence of water, do not accelerate mutarotation.

F. M. Hamer.

Mechanism of carbohydrate oxidation. I. Dextrose, *d*-mannose, lævulose, *d*- and *l*-arabinose, and *dl*-glyceraldehyde. W. L. Evans, C. A. Buehler, C. D. Looker, R. A. Crawford, and C. W. Holl (J. Amer. Chem. Soc., 1925, **47**, 3085—3098).—When the above compounds are oxidised by dilute aqueous potassium permanganate, the product, in neutral solution, is carbon dioxide in practically quantitative yield. In alkaline solution, oxalic acid and a volatile acid (probably acetic) are also formed. Elevation of temperature of oxidation results generally in increase of carbon dioxide, and decrease of oxalic acid, in the product. Results at 50° are identical for dextrose, lævulose, and *d*-mannose, and at 75° for dextrose and lævulose, which affords a verification of the results of de Bruyn with regard to the action of alkalis on these carbohydrates; it is concluded that these identities must be due to equilibria in aqueous solution leading, from either carbohydrate, to the same active component, in accordance with the views of Nef. At 50—100°, with increasing concentrations of alkali, the yield of oxalic acid from lævulose reaches a maximum, a minimum, and a second maximum, the yield of carbon dioxide varying conversely. It is concluded that this is due to the intermediate formation, in amount varying with the alkali concentration, of formaldehyde, glycollaldehyde, and glyceraldehyde, the first being oxidised to carbon dioxide, and the last two to oxalic acid and carbon dioxide. The second maximum of oxalic acid is ascribed to the intermediate formation of lactic acid.

F. G. Willson.

Mechanism of carbohydrate oxidation. II. Oxidation of *d*-galactose. W. L. Evans and C. A. Buehler (J. Amer. Chem. Soc., 1925, **47**, 3098—3101; cf. preceding abstract).—The oxalic acid–carbon dioxide ratio in the product of oxidation of *d*-galactose varies with the alkalinity, owing to the shifting of the equilibria between the above carbohydrate and its isomerides with varying alkalinity. With increase in alkalinity, the above ratio tends to become identical for dextrose and *d*-galactose, a result ascribed to the increasing predominance of glyceraldehyde in the equilibria derived from both carbohydrates. As elevation of temperature shifts the equilibria also in the direction of glyceraldehyde, it also tends to identity in the oxalic acid–carbon dioxide ratio in the oxidation products from the two carbohydrates. F. G. Willson.

Mechanism of carbohydrate oxidation. III. Oxidation of the hexitols *d*-mannitol, *d*-sorbitol, and dulcitol. W. L. Evans and C. W. Holl (J. Amer. Chem. Soc., 1925, **47**, 3102—3105; cf. preceding abstracts).—The oxidation of the above hexitols by aqueous potassium permanganate yields results qualitatively similar to those reported for dextrose and galactose; it is concluded that the oxidation proceeds through the intermediate formation of aldohexoses. F. G. Willson.

Oxidation of dextrose by means of copper in sodium carbonate solution (Soldaïni's reagent). F. W. Jensen and F. W. Upson (J. Amer. Chem. Soc., 1925, **47**, 3019—3024).—Copper chloride (275 g.) was added, in aqueous solution, to an aqueous solution of sodium carbonate (275 g., anhydrous). Dextrose (25 g.) was then added, the mixture diluted to 2500 c.c., and vigorously agitated at 100° until precipitation of cuprous oxide was complete, the reaction requiring about 8 hrs. After removal of the cuprous oxide, the filtrate was acidified with hydrochloric acid and excess of copper removed as sulphide, the filtrate from this being then evaporated at 50—70°/20—30 mm., and the residue freed from volatile acids by several distillations to dryness with 100-c.c. portions of distilled water. The following products, in amounts quoted, were in this way obtained from 200 g. of dextrose. Formic acid, 30·86 g.; glycollic acid, 15·3 g.; gluconic acid, 1—2 g.; mannonic acid, small amount; arabonic acid, 6 g., isolated as the brucine salt; erythronic acid, 3·6 g., isolated as the brucine salt and identified as the lactone; *dl*-glyceric acid, 6·2 g., isolated as the brucine salt; and *d*-threonic acid, trace. These products differ from those obtained by oxidation with Fehling's solution only in the relatively smaller amount of hexonic acids present in the oxidation product. F. G. Willson.

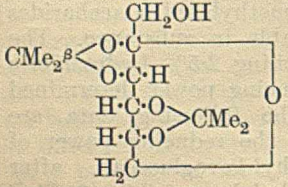
Behaviour of dextrose and certain other carbohydrates towards dyes and towards potassium ferricyanide in an alkaline medium. E. Knecht and E. Hibbert (J.C.S., 1925, **127**, 2854—2860).—In the presence of potassium or sodium hydroxide, under specified conditions, certain carbohydrates are oxidised to a definite degree by methylene-blue or by potassium indigotintetrasulphonate, the excess of which is titrated with titanous chloride. The amount of indigotin reduced corresponds with 3 atoms of oxygen per mol. of dextrose, galactose, or glucosamine hydrochloride, 4 atoms per mol. of lævulose, 3½ per mol. of invert-sugar, and 6 per mol. of maltose, whence it appears that maltose has undergone hydrolysis. 2 : 2′-Bisoxythionaphthendisulphonic acid behaves similarly with dextrose and lævulose, whilst with dextrose, lævulose, and glucosamine, potassium ferricyanide gives the same results as does indigotin. It is concluded that dextrose and galactose are converted into tetrahydroxyhexanedicarboxylic acids, and that lævulose gives equimolecular proportions of a mono- and a di-carboxylic acid. On using potassium ferricyanide to oxidise dextrose, titration with alkali yields results which confirm the hypothesis that a dicarboxylic acid is formed. Use of an alkali carbonate and hydrogen carbonate in the titration of dextrose with indigotin does not give rise to a higher degree of oxidation. If dextrose or lævulose is boiled for 2 min. with excess of sodium hydroxide, the amount of alkali neutralised corresponds with 2 mols. of lactic acid. Glycuronic acid can be determined volumetrically by means of potassium indigotintetrasulphonate, or by the osazone titration method. In presence of alkali hydroxide, kitone-blue A supplies two atomic proportions of oxygen to both dextrose and lævulose, corresponding with production of glycuronic acid and hydroxygluconic acid, respectively; by superimposing an indigotin titration on the kitone-blue titration, one more atom of oxygen is taken up in each case. Rosinduline 2B (or G) supplies one atomic proportion of oxygen to dextrose, and on superimposing a methylene-blue titration no further oxidation occurs; it is suggested that gluconic acid is the oxidation product. F. M. Hamer.

Reducing power of methylated sugars. G. Zemplén and G. Braun (Ber., 1925, **58**, [*B*], 2566—2570).—A method is described for the identification of partly methylated sugars if obtained in small amount by the hydrolysis of methylated disaccharides and thus not actually isolable in substance. The sugar is hydrolysed with boiling 2·5% hydrochloric acid for 3 hrs. and the reducing power determined by Bertrand's method. The following data are obtained on the basis that the reducing power of dextrose=100 : βγε-trimethyl-lævoglucosan, after hydrolysis, 10·6; βγε-trimethylglucose, 9·8; βγε-trimethylmethylglucoside, after hydrolysis, 9·4; βγζ-trimethylglucose, 27·1; βγεζ-tetramethylglucose, 13·6; βγεζ-tetramethylmethylglucoside, after hydrolysis, 12·5; heptamethylmethylgentiobioside, after hydrolysis, 12·1; heptamethylmethylcellobioside, after hydrolysis, 20·2. H. Wren.

Synthesis of βγε(or βγδ)-trimethylglucose. J.C. Irvine and J. W. H. Oldham (J.C.S., 1925, **127**, 2729—2735).—The constitution of βγε-trimethylglucose has been confirmed by the following synthesis : triacetylglucosan was converted into triacetyldibromoglucose; from this was formed triacetylmethylglucoside bromohydrin, which with alcoholic ammonia yielded methylglucoside bromohydrin. The bromohydrin when methylated gave a mixture from which pure trimethylmethylglucoside bromohydrin was isolated. This, when heated at 150° with alcoholic potassium acetate, gave a 72% yield of a pure crystalline trimethyl-β-methylglucoside identical with that obtainable from the trimethylglucose under investigation. In the glucoside finally obtained, the hydroxy-group occupies the position of the bromine atom in triacetylmethylglucoside bromohydrin, and as Fischer reduced the latter to triacetylmethyl*iso*rhamnoside, the group must be in the ζ-position and the methyl groups in the corresponding sugar must be in the positions β, γ, and ε. Dibromotriacetyl-glucose, -maltose, and -glucosan are all convertible into the same form of trimethylglucose.

B. W. Anderson.

Acetone [*iso*propylidene] compounds of sugars and their derivatives. III. Constitution of β-di*iso*propylidenefructose. H. Ohle [with I. Koller and G. Berend] (Ber., 1925, **58**, [*B*], 2577—2584; cf. A., 1924, i, 1168).—To elucidate the structure of β-di*iso*propylidenefructose (*loc. cit.*), the compound has been converted by the methods of Purdie, Freudenberg, and Hixon, and, most advantageously, by methyl sulphate and sodium hydroxide, into β-*diisopropylidenemethylfructose*, m. p. 48—49°, $[\alpha]_D^{20}$ −38·26° in alcohol, −29·53° in chloroform, and the latter substance has been hydrolysed with alcoholic sulphuric acid at 38—40°. The specific rotation of the solution during the hydrolysis varies in the manner characteristic of β-di*iso*propylidenefructose, thus showing that structural alteration has not occurred during methylation, and that during removal of the acetone residues the derivative of an unstable fructose passes into the derivative of a stable form. The failure of the resulting methylfructose to solidify in contact with γ-methylfructose (cf. Irvine and Hynd, J.C.S., 1909, **95**, 1220) and its inability to yield an osazone preclude the possibility of the presence of the methyl group in the γ- or ζ-position, and hence the annexed formula is the only possible expression of the constitution of β-di*iso*propylidenefructose. To obtain evidence of a positive nature, β-di*iso*propylidenefructose has been oxidised by potassium permanganate in aqueous alkaline solution, whereby an acid, $C_{12}H_{18}O_7$, is obtained which retains all the carbon atoms of the parent sugar. The acid has not been obtained crystalline, but is characterised as the *potassium* salt, $C_{12}H_{17}O_7K,H_2O$, $[\alpha]_D^{21}$ −31·75° in water, and the *aniline* salt, m. p. 120°, $[\alpha]_D^{20}$ −31·3° in chloroform. Removal of the acetone residues results in the production of a ketohexonic acid, of which the *potassium* salt, $C_6H_9O_7K,H_2O$, $[\alpha]_D^{20}$ −70° in water, *brucine* salt, $C_{29}H_{36}O_{11}N_2,3H_2O$, $[\alpha]_D^{20}$ −56·9° in water, and *phenylhydrazine* salt of the corresponding phenylosazone, $C_{24}H_{28}O_5N_4$, m. p. 102—103°, are described. The acid is not identical with the expected α-ketogluconic acid, but is possibly an isomeride thereof.

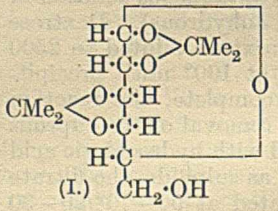


H. Wren.

Acetone [*iso*propylidene] compounds of sugars and their derivatives. IV. Constitution of diacetonegalactose [galactose di*iso*propylidene ether]. H. Ohle and G. Berend (Ber., 1925, **58**, [*B*], 2585—2589).—Even under the mildest experimental conditions, the oxidation of galactose di*iso*propylidene ether by potassium permanganate proceeds less definitely than that of β-di*iso*propylidenefructose (preceding abstract), yielding oxalic acid in addition to *diisopropylidenegalacturonic acid*, m. p. 157° (*potassium* salt, $C_{12}H_{17}O_7K,0\cdot5H_2O$, $[\alpha]_D^{20}$ −61·09° in water). The acid is hydrolysed to *d*-galacturonic acid, which could not be caused to crystallise; the specific rotation, as judged from the behaviour of the barium salt dissolved in dilute hydrochloric acid, is $[\alpha]_D^{20}$ +46·7°, whereas Ehrlich gives +53·4° for the pure acid. The solution does not exhibit mutarotation. The acid gives a sparingly soluble basic lead salt and a characteristic *brucine* salt,

$$C_{29}H_{36}O_{11}N_2,H_2O,$$

m. p. 189° (decomp.), $[\alpha]_D^{20}$ −7·5° in water, but the characteristic cinchonine salt could not be obtained. With phenylhydrazine it gives the *phenylhydrazine* salt of the phenylosazone of *d*-galacturonic acid, $C_{24}H_{28}O_5N_6$, m. p. 140° (decomp.). The behaviour of the acid leaves no doubt as to its identity with *d*-galacturonic acid (cf. Svanberg and Bergman, A., 1924, i, 1285), and thereby establishes the presence of the terminal $\cdot CH_2\cdot OH$ group in galactose di*iso*propylidene ether. Contrary to Svanberg, however, the authors do not accept the presence of an αγ-bridge in the sugar, since galactose di*iso*propylidene ether is obtained by treatment of galactose with acetone in the presence of anhydrous copper sulphate (the *acetate* of galactose *di*isopropylidene ether has m. p. 108°, $[\alpha]_D^{20}$ −48·08° in chloroform), and in these conditions it is scarcely possible to assume a displacement of the oxygen bridge which Haworth, Ruell, and Westgarth (J.C.S., 1924, **125**, 2468) have shown to be in the αε-position. The constitution (I) is most probable for galactose di*iso*propylidene ether.

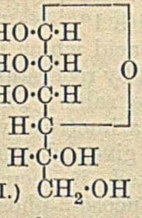


(I.)

H. Wren.

Acetone [di*iso*propylidene] compounds of sugars and their derivatives. V. Constitution of diacetonemannose [mannose di*iso*propylidene ether]. H. Ohle and G. Berend (Ber., 1925, **58**, [*B*], 2590—2592).—Mannose di*iso*propylidene ether is very readily oxidised by potassium permanganate in dilute aqueous-alkaline solution, but the action practically ceases when one atomic proportion of oxygen has been utilised and *potassium* d-*diisopropylidenemannonate*, $C_{12}H_{18}O_7K,H_2O$, m. p. above 210° (decomp.), $[\alpha]_D^{20}$ −31·8° in water, is obtained in more than 80% yield. The corresponding free acid could not be isolated on account of the readiness with which it becomes converted into d-*diisopropylidenemannonolactone*, $C_{12}H_{18}O_8$, m. p. 126°, $[\alpha]_D^{20}$ +51° in chloroform, which is also obtained when the potassium salt is treated with benzoyl chloride in the presence of pyridine. The acetone residues are very easily removed from the potassium salt by means of *N*-sulphuric acid, yielding *d*-mannonolactone, m. p. 149—151°, $[\alpha]_D^{20}$ +54° in water. The constitution of mannose di*iso*propylidene ether is thereby established, and, since it can be prepared from acetone and mannose in the presence of anhydrous copper sulphate, the similar structure (I) may be assigned to mannose; this is contrary to the conception of Haworth (A., 1925, i, 1133), who has assigned the amylene oxide structure to all aldoses.

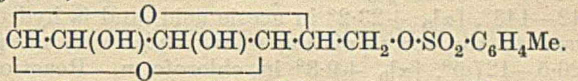
H. WREN.



I.)

Acetone (di*iso*propylidene) compounds of sugars and their derivatives. VI. Acyl derivatives of monoacetoneglucose [glucose *iso*propylidene ether]. H. OHLE and E. DICKHÄUSER (Ber., 1925, 58, [*B*], 2593—2606).—In continuation of the authors' work on the sulphates and benzoates of glucose *iso*propylidene ether (A., 1923, i, 539; 1924, i, 498), it is found that the *p*-toluenesulphonyl derivatives resemble the sulphates and that the differences observed between the latter compounds and the benzoates are therefore to be ascribed to the presence of the sulphur atom.

γ-p-*Toluenesulphonylglucose* iso*propylidene ether* is prepared as an amorphous substance, $[\alpha]_D^{20}$ −11·65° in chloroform, by the partial hydrolysis of γ-*p*-toluenesulphonylglucose di*iso*propylidene ether (Freudenberg and Ivers, A., 1922, i, 523) with aqueous acetic acid; it is readily reconverted by acetone in the presence of anhydrous copper sulphate into 3-*p*-toluenesulphonylglucose di*iso*propylidene ether, and does not exhibit any tendency to pass into the ζ-isomeride in the presence of sodium hydroxide solution. It is transformed by benzoyl chloride in the presence of pyridine at 40° into the amorphous γ-p-*toluenesulphonyl-ζ-benzoylglucose di*iso*propylidene ether*, $[\alpha]_D^{21}$ −11·21° in chloroform, or by a larger proportion of the acid chloride into the crystalline γ-p-*toluenesulphonyl-εζ-dibenzoylglucose di*iso*propylidene ether*, m. p. 156°, $[\alpha]_D^{22}$ −68·38° in chloroform. With *p*-toluenesulphonyl chloride in the presence of chloroform at 40°, it affords γζ-*di*-p-*toluenesulphonylglucose* iso*propylidene ether*, an amorphous substance, $[\alpha]_D^{20}$ −4·92° in chloroform, which, with benzoyl chloride and pyridine, gives an amorphous compound not identical with γε-di-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether. ζ-p-*Toluenesulphonylglucose* iso*propylidene ether*, m. p. 108°, $[\alpha]_D^{20}$ −9·29° in chloroform, is prepared by the action of the acid chloride on glucose *iso*propylidene ether in the presence of pyridine and chloroform; with benzoyl chloride and pyridine, it affords amorphous ζ-p-*toluenesulphonyl-γε-dibenzoylglucose di*iso*propylidene ether*, $[\alpha]_D^{21}$ −51·38° in chloroform. The action of a considerable excess of *p*-toluenesulphonyl chloride on glucose *iso*propylidene ether or ζ-*p*-toluenesulphonylglucose *iso*propylidene ether in the presence of pyridine and chloroform leads to the production of εζ-*di*-p-*toluenesulphonylglucose* iso*propylidene ether*, m. p. 160°, $[\alpha]_D^{20}$ −6·37° in chloroform; the amorphous εζ-*di*-p-*toluenesulphonyl-γ-acetylglucose* iso*propylidene ether* has $[\alpha]_D^{22}$ −28·02° in chloroform. When εζ-di-*p*-toluenesulphonylglucose *iso*propylidene ether is treated with an excess of benzoyl chloride in the presence of pyridine, one of the *p*-toluenesulphonyl groups is replaced by benzoyl, and since the product is not identical with the crystalline ε-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether, it is regarded as ζ-p-*toluenesulphonyl-ε-benzoylglucose* iso*propylidene ether*, $[\alpha]_D^{20}$ −29·6° in chloroform. Confirmation of this view is found in the comparative difficulty in forming the di-*p*-toluenesulphonyl compound, for which a large excess of the reagent is necessary, and in the very ready loss of a *p*-toluenesulphonyl group by the hydrolysis of γ-di-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether by alkali hydroxide. The same ease of replacement is observed in the hydrolysis by acid of εζ-di-*p*-toluenesulphonylglucose *iso*propylidene ether, which, somewhat unexpectedly, yields a compound, $[\alpha]_D$ about +38·6°, regarded as ζ-p-*toluenesulphonylglucose anhydride*,



$$\mathrm{CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot CH\cdot CH_2\cdot O\cdot SO_2\cdot C_6H_4Me.}$$

A third p-*toluenesulphonylglucose* iso*propylidene ether*, m. p. 132°, $[\alpha]_D^{21}$ +34·3° in chloroform, is prepared by the action of a large excess of *p*-toluenesulphonyl chloride on glucose *iso*propylidene ether dissolved in a boiling mixture of pyridine and chloroform.

γ-Benzoylglucose *iso*propylidene ether is obtained from the corresponding di*iso*propylidene ether by a modification of the method of Fischer and Noth (A., 1918, i, 225). Attempts to transform glucose *iso*propylidene ether into a dibenzoyl derivative were only partly successful, and the product was not transformed by *p*-toluenesulphonyl chloride into the crystalline γ-*p*-toluenesulphonyl-εζ-dibenzoylglucose *iso*propylidene ether. ζ-Benzoylglucose *iso*propylidene ether is transformed by benzoyl chloride in the presence of pyridine and chloroform into ε-p-*toluenesulphonyl-ζ-benzoylglucose* iso*propylidene ether*, m. p. 142°, $[\alpha]_D^{22}$ +9·34° in chloroform, or γε-*di*-p-*toluenesulphonyl-ζ-benzoylglucose* iso*propylidene ether*, m. p. 113°, $[\alpha]_D^{22}$ +1·61° in chloroform, according to the relative proportion of the reactants. In general, it appears that the primary alcoholic group, if free, reacts most readily in the substitution of glucose *iso*propylidene ether. If the ζ-position is already substituted, the acyl group enters mainly in the ε-position. The preparation of γ-monosubstituted derivatives does not appear directly possible.

H. WREN.

Reaction of lævulose with alanine. C. NEUBERG and M. KOBEL (Biochem. Z., 1925, **162**, 496—501).—When a lævulose solution is mixed at the ordinary temperature with a solution of *dl*-alanine, a momentary increase in rotation occurs. Dextrose does not show this phenomenon.

P. W. CLUTTERBUCK.

Transformations of the sugar nitrates. J. W. H. OLDHAM (J.C.S., 1925, **127**, 2840—2845).—Although αζ-diacetyl-βγε-trimethylglucose yields a non-crystallising syrup when treated with fuming nitric acid, interaction of βγε-trimethylglucosan and

fuming nitric acid, in presence of chloroform and phosphorus pentoxide, yields *βγε-trimethylglucose αζ-dinitrate*, m. p. 86°, [α]$_D$ +149·3° in chloroform; this dinitrate has no action on Fehling's solution. By boiling with methyl alcohol in presence of barium carbonate, it gives *trimethylmethylglucoside ζ-mononitrate*, m. p. 53—54°, n_D 1·4565, which is hydrolysed, by boiling with iron dust in acetic acid, to the same trimethylmethylglucoside as is obtained from trimethylglucosan; the mononitrate is unchanged by heating with alcoholic ammonia, but treatment with sodium iodide gives the same trimethylmethylglucoside iodohydrin as was obtained from Fischer's acetodibromoglucose (Irvine and Oldham, this vol., 149). Triacetylglucosan on treatment with fuming nitric acid in presence of chloroform, phosphoric oxide, and nitrogen pentoxide yields a syrup, together with *triacetylglucose αζ-dinitrate*, m. p. 132—133°, [α]$_D$ +144·2° (in fuming nitric acid and chloroform); *tetra-acetylglucose ζ-mononitrate* has m. p. 142—143°, [α]$_D$ +23·2° in acetic acid, and is hydrolysed to the corresponding *tetra-acetylglucose*, m. p. 126·5—127·5°, [α]$_D$ +9·8° in chloroform. Reaction of triacetylglucose αζ-dinitrate with methyl alcohol yields *triacetylmethylglucoside ζ-mononitrate*, m. p. 133·5—134·5°, [α]$_D$ −14·3° in chloroform, and this is hydrolysed to *triacetylmethylglucoside*, m. p. 134—134·5°, [α]$_D$ −19·1° in chloroform, and converted by sodium iodide into *triacetylmethylglucoside ζ-iodohydrin*, m. p. 111—112·5°, [α]$_D$ +0·9° in chloroform. Treatment of triacetylmethylglucoside ζ-mononitrate with methyl-alcoholic dimethylamine yields methylglucoside ζ-mononitrate in the form of a syrup, which on methylation by the silver oxide reaction gives trimethylmethylglucoside ζ-mononitrate, whilst triacetylmethylglucoside ζ-iodohydrin is converted by dimethylamine into *methylglucoside ζ-iodohydrin*, m. p. 157—158°, [α]$_D$ −16·1° in chloroform. Mother-liquors from the recrystallisation of triacetylmethylglucoside ζ-mononitrate contain an *acetonitropentose*, m. p. 168—169°, [α]$_D$ +92·0° in chloroform. The specific rotations of the compounds in various solvents are recorded.
F. M. Hamer.

Soluble and insoluble salts of hexosediphosphoric acid. C. Neuberg and S. Sabetay (Biochem. Z., 1925, **161**, 240—243).—A pure calcium salt can be obtained from the commercial product "candiolin." It is sparingly soluble in cold or hot water, but a soluble form is obtained by adding ammonia to its solution in lactic acid and precipitating the filtered solution by alcohol. On heating a solution of this substance the less soluble modification is precipitated.

The barium salt has similarly been obtained in a soluble and an insoluble form. Magnesium yields a normal salt which is remarkably soluble in cold water, but separates on boiling. It is also more resistant to alkalis than hexosediphosphoric acid. The presence of ammonium chloride prevents the precipitation of the magnesium and also of the calcium salts by heat.

Hexosediphosphoric acid can be acetylated by the action of acetic anhydride on the calcium salt.
C. Rimington.

Glucosephosphoric acid. S. Sabetay and L. Rosenfeld (Biochem. Z., 1925, **162**, 469—478).—Sucrosephosphoric acid on hydrolysis with 1% oxalic acid solution gives a glucosephosphoric acid which is separated as the barium salt and purified by recrystallisation of the cinchonidine or brucine salts. The presence of dextrose is confirmed polarimetrically. Since treatment with phenylhydrazine gives glucosazone, phosphoric acid being eliminated, it seems probable that the substance is glucose-β-phosphoric acid. It is not identical with glucose-α-, -γ-, or -ζ-phosphoric acid, and from the structure of sucrose it appears unlikely that the phosphoric acid is attacked in the δ-position. The acid is not identical with Robison's glucosephosphoric acid.
P. W. Clutterbuck.

Nomenclature of polysaccharides. M. Bergmann (Ber., 1925, **58**, [*B*], 2647—2650).—The method of indicating the position of the oxygen bridge in saccharides by figures placed after the name of the compound, *e.g.*, methylglucoside (1 : 4), becomes involved when saccharide residues are linked through an oxygen atom and the points of union must also be indicated. It is proposed to indicate oxygen bridges which unite saccharide residues by a two-headed arrow placed over or, if necessary, under the name of the polysaccharide and extending at either end to the name of the component indicated; a figure at either end of the arrow shows the position of the bridge. Thus raffinose (cf. Haworth, Hirst, and Ruell, J.C.S., 1923, **123**, 3127) may be expressed,

1←——————————→6 1←——————→2
galactosido (1 : 5)-glucosido (1 : 4)-fructoside (2 : 6)

and trihexosan may be written

1←——————————————————→4
glucosido (1 : 6)-glucosido (1 : 4)-glucosan (1 : 6).
4←——————————→1 6←——————————→1

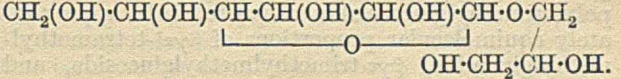
It is proposed to use the suffix "osan" in naming the anhydride, $C_{12}H_{20}O_{10}$, of a disaccharide, $C_{12}H_{22}O_{11}$, only in those cases in which a carbonyl or lactol group is involved in the loss of water. The term anhydro-sugar, *e.g.*, anhydroglucose, is used for sugar derivatives which contain the intact lactol or carbonyl group.
H. Wren.

Syntheses of *iso*maltose and gentiobiose. A. Pictet and A. Georg (Compt. rend., 1925, **181**, 1035—1037).—That di-*l*-glucosan (A., 1921, i, 766) is the anhydride of *iso*maltose (Fischer, A., 1896, i, 119) is confirmed by the conversion of the former into the latter by two methods. Di-*β*-glucosan is allowed to remain in solution in concentrated hydrochloric acid, the acid is removed in a vacuum, and by means of silver carbonate, dextrose is removed by fermentation, and *iso*maltose is obtained. To obviate the possibility that the *iso*maltose is formed by hydrolysis of the di-*β*-glucosan to dextrose and conversion of the dextrose into *iso*maltose by the agency of the hydrochloric acid, a second synthesis has been effected. On treatment with acetyl bromide and pouring on ice, di-*β*-glucosan yields *octa-acetyliso-maltose bromohydrin*, which on treatment with barium hydroxide gives *iso*maltose. Acetylation of Fischer's *iso*maltose (*loc. cit.*) gives, in addition to an iso*maltose* *acetate*, 3% of gentiobiose octa-acetate (Zemplen, A., 1915, i, 119). L. F. Hewitt.

Digitoxin. A. Windaus and C. Freese (Ber., 1925, **58**, [*B*], 2503—2510).—Pure digitoxin is prepared by extracting the crude glucoside with chloroform, whereby gitoxin remains undissolved. Ether is added to the chloroform extracts and the precipitated digitoxin is crystallised from ethyl acetate, dilute alcohol, or a mixture of chloroform and ether until the m. p. 255—257° is attained. Analyses of the air-dried substance agree with the formula $C_{42}H_{66}O_{13},H_2O$, whereas for the material dried in a vacuum they are in harmony with Cloetta's formula, $C_{44}H_{70}O_{14}$ (cf. A., 1921, i, 39). Determinations of *M* give low values for a compound $C_{44}H_{70}O_{14}$, and the composition $C_{42}H_{66}O_{13},0{\cdot}5H_2O$ is therefore suggested. Hydrolysis of digitoxin by acids leads, according to Cloetta (*loc. cit.*), to digitoxigenin (1 mol.), digitoxose (2 mols.), and an oily compound, $C_8H_{14}O_4$, obtained in the crystalline state by distillation of digitoxin in a high vacuum; analyses and determinations of mol. wt. agree with the formula $C_6H_{10}O_3$ better than with $C_8H_{14}O_4$ and it is therefore concluded that it is an anhydrodigitoxose analogous to *β*-glucosan. Hence, digitoxigenin and digitoxose may be regarded as the sole products of the hydrolysis of digitoxin, which probably proceeds thus: $C_{42}H_{66}O_{13}+3H_2O=C_{24}H_{36}O_4+3C_6H_{12}O_4$. The yield of digitoxigenin actually obtained is in good agreement with this conception. Digitoxin, $C_{42}H_{66}O_{13}$, and gitoxin, $C_{42}H_{66}O_{14}$, must therefore be closely related compounds. Both compounds yield digitoxose (3 mols.) when hydrolysed, together with digitoxigenin, $C_{24}H_{36}O_4$, and gitoxigenin, $C_{24}H_{36}O_5$, respectively, and the possibility therefore exists that the latter substance is oxydigitoxigenin. To test the presence of the same carbon skeleton in the compounds, digitoxigenin has been converted by the methods employed previously for gitoxigenin (cf. Windaus and Bandte, A., 1923, i, 1107; Windaus and Schwarte, A., 1925, i, 1295) into its anhydro-derivative, $C_{24}H_{34}O_3$, and subsequently hydrogenated in aqueous methyl alcohol in the presence of colloidal palladium to *tetrahydroanhydrodigitoxigenin*, $C_{24}H_{38}O_3$, m. p. 146—147°; in glacial acetic acid solution, hydrogenation proceeds less satisfactorily, the most sparingly soluble *product*, m. p. 163—164°, having also the composition $C_{24}H_{38}O_3$, so that probably a mixture of stereoisomerides is formed. Tetrahydroanhydrodigitoxigenin is isomeric with hexahydrodigitaligenin. *Tetrahydroanhydrodigitoxigenone*, m. p. 240—241° [*oxime*, m. p. 217° (decomp.)], prepared by oxidation of tetrahydroanhydrodigitoxigenin, is isomeric with the ketone, $C_{24}H_{36}O_3$, derived from gitoxigenin; this is also true of the *lactone*, $C_{24}H_{38}O_2$, m. p. 180—181°, obtained from it by reduction with zinc amalgam and concentrated hydrochloric acid.

In confirmation of Cloetta's observations (*loc. cit.*), it is found that digitoxigenin is converted by dehydrating agents into anhydrodigitoxigenin, $C_{24}H_{34}O_3$, m. p. 183—184°; the compound, m. p. 223°, described by Kiliani (A., 1899, i, 71) under this name appears to be a transformation product of the anhydro-compound which it is proposed to designate "β-anhydrodigitoxigenin." Toxigenone, obtained by oxidation of anhydrodigitoxigenin, for which Kiliani has proposed the formula $C_{19}H_{24}O_3$, certainly contains 24 carbon atoms in its molecule, since it can be converted into tetrahydroanhydrodigitoxigenin; the low analytical figures are probably due to obstinately retained solvent of crystallisation. Digitoxigenone, to which Kiliani has ascribed the formula $C_{19}H_{26}O_4$, is probably $C_{24}H_{34}O_4$. H. Wren.

Glycerol glucoside. H. S. Gilchrist and C. B. Purves (J.C.S., 1925, **127**, 2735—2745).—Glycerol glucoside is best obtained by heating a solution of dextrose in glycerol at 100° with 0·25% of dry hydrogen chloride. The product on methylation yields a *hexamethyl* derivative, b. p. 190—192°/12 mm., n_D 1·4497, and this on hydrolysis forms βγεζ-tetramethylglucose together with a dimethylglycerol. Thus the constitution of the parent glucoside is



$$CH_2(OH){\cdot}CH(OH){\cdot}\underbrace{CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH}_{O}{\cdot}O{\cdot}CH_2 / OH{\cdot}CH_2{\cdot}CH{\cdot}OH.$$

The compound, as prepared, is a mixture of α- and β-forms containing only up to 1·95% of glycerol γ-glucosides. The course of the condensation with varying amounts of acid has been followed polarimetrically. The dimethylglycerol mentioned above was shown to be *αβ-dimethoxy-γ-hydroxypropane*, b. p. 69·5—70·5°/15 mm., n_D 1·4219, d_4^{15} 1·016 (*benzoate*, b. p. 162°/12 mm.; *malate*, b. p. 200°/0·5 mm.). Methylation of αγ-dichlorohydrin yielded the same αβ-dimethylglycerol, but under other conditions β-monomethylchlorohydrin, b. p. 58°/14 mm., n_D 1·4560, was obtained, which on hydrolysis gave the α- and not the β-monomethylglycerol, b. p. 110—112°/11 mm., n_D 1·4462. Pure *trimethylglycerol*, b. p. 148°/765·4 mm., n_D^{15} 1·4069, d_4^{15} 0·9401, was prepared. B. W. Anderson.

Polymerisation of β-glucosan. Constitution of synthetic dextrins. J. C. Irvine and J. W. H. Oldham (J.C.S., 1925, **127**, 2903—2922).—The investigation is an extension of Pictet's work (A., 1918, i, 527; 1921, i, 766; cf. also Pringsheim, A., 1922, i, 1118). Polymerisation of β-glucosan is effected by heating it with zinc dust at 250°/15 mm., in an atmosphere of hydrogen. Fractional precipitation by addition of alcohol to the aqueous solution effects separation into three main fractions (I—III), which in order of increasing solubility show the specific rotations +83·9°, +60·7°, +29·9°. All three dextrins yield the same *triacetate*, m. p. 142°, $[\alpha]_D$ +85·1° (converted on hydrolysis into dextrin I), and all, on heating with methyl alcohol and hydrogen chloride, yield, initially, β-methylglucoside, but, finally, its equilibrium mixture with α-methylglucoside. Each dextrin, on treatment by the methyl sulphate method, is converted into its *trimethyl* derivative and, from cryoscopic determinations of the mol. wts. of these, dextrins I—III are characterised as *heptaglucosan* (*trimethyl* derivative, $[\alpha]_D$ +89·4°); *tetraglucosan* (*trimethyl* derivative, $[\alpha]_D$ +68·7°), which is different from that previously described (*loc. cit.*), and *triglucosan*. By heating the trimethyl-dextrins with alcohol and hydrogen chloride, and subsequently hydrolysing, there is formed in each case a mixture of di-, tri-, and tetra-methylglucose; βγεζ-tetramethylglucose and βγε-trimethylglucose have been characterised. The tetramethylglucose is shown to be a genuine scission product of the methylated dextrins.

On a large scale, methylation of the total polymerised glucosan, followed by distillation, yields *trimethylglucosan*, b. p. 135°/0·2 mm., *di*(*trimethylglucosan*), b. p. 205—210°/0·2 mm., n_D 1·4720, $[\alpha]_D^{20}$ +46·5° in chloroform, and *poly*(*trimethylglucosan*). Treatment of di(trimethylglucosan) with methyl alcohol and hydrogen chloride yields approximately equimolecular proportions of dimethylmethylglucoside, $[\alpha]_D$ +108·4° in methyl alcohol, n_D 1·4743, and tetramethylmethylglucoside, together with a little trimethylmethylglucoside, and the proportions are confirmed by hydrolysis, which gives dimethylglucose and βγεζ-tetramethylglucose. Similarly, the poly(trimethylglucosan) is converted into approximately equimolecular proportions of βγεζ-tetramethylmethylglucoside, βγε-trimethylmethylglucoside, and dimethylmethylglucoside, together with a little monomethylmethylglucoside; hydrolysis yields equimolecular proportions of the tetra-, tri-, and di-methylglucoses. A series of polymerides from mono- to octa-glucosan is now complete with the exception of the penta-form; the specific rotations of the parent glucosides and their trimethyl derivatives are tabulated, as also are those of the methylated sugars to which the glucosans give rise.

From all the polyglucosans, invariable products are βγεζ-tetramethylglucose and dimethylglucose, which must be either the βγ- or, more probably, the βε-derivative. As regards the mechanism of the polymerisation, it is supposed that glucosan is first converted into glucose, one molecule of which condenses with a second molecule of glucosan, and the process continues catalytically. Provisional formulæ are assigned to the di- and tri-glucosans; triglucosan may be regarded as glucosan maltoside. Besides the condensation type of reaction which occurs in polymerisation, a type involving association may take place. Evidence is adduced to show that the methylation process does not alter the configuration of a sugar, and does not disturb the positions in which sugar residues are attached, and that, during methylation and hydrolysis, non-glucosidic methoxy-groups do not migrate, whence it is concluded that the process is valid for determining the structure of carbohydrates. F. M. HAMER.

Distillation of cellulose etc. in presence of hydrogen under pressure and catalysts. H. E. FIERZ-DAVID and M. HANNIG.—See B., 1926, 35.

Action of diazomethane on cellulose. M. NIERENSTEIN (Ber., 1925, **58**, [*B*], 2625).—Contrary to the observations of Schmid (A., 1925, i, 1386), diazomethane causes slight methylation of cotton cellulose (cf. Geake and Nierenstein, A., 1914, i, 1146). H. WREN.

Stability of nitrocelluloses. J. DUCLAUX.—See B., 1926, 46.

Cellulose esters of higher fatty acids. G. KITA, T. MAZUME, I. SAKURADA, and S. NAKAJIMA.—See B., 1926, 45.

Solubility of lignins in phenols. A. HILLMER.—See B., 1926, 46.

Ionisation of ethoxytrimethylammonium hydroxide, trimethylamine oxide, and their derivatives. W. A. NOYES (J. Amer. Chem. Soc., 1925, **47**, 3025—3030; cf. A., 1923, i, 444).—The conductivities of phenyltrimethylammonium hydroxide, ethoxytrimethylammonium hydroxide, and trimethylamine oxide have been redetermined, in solutions of concentration 0·509, 0·159, and 0·5*M*, respectively. In the cases of the first two bases, addition of hydrobromic acid, in amount not quite sufficient for complete neutralisation, increased the resistance of the solutions, indicating that the association of the hydroxide is similar to that of the bromide. The conductance of the amine oxide solution was considerably increased by the addition of a similar proportion of hydrobromic acid. These results confirm the observation of Stewart and Maeser (A., 1925, i, 12) that ethoxytrimethylammonium hydroxide is completely ionised in dilute aqueous solution, the discordant results of previous experiments being probably due to the ease with which this compound decomposes into trimethylamine and acetaldehyde. The structure of trimethylamine oxide is discussed, and it is concluded that this base is correctly represented by the formula $[NMe_3{\cdot}OH]OH$. It is pointed out that the polar valency of nitrogen in ammonium salts is none the less a real valency because it is polar, and as this valency has been shown to be capable of holding a nitrogen atom in a stable ring formation in solution, it is to be regarded as attached to the nitrogen atom, and not belonging to the group as a whole (cf. Noyes and Potter, A., 1915, i, 79). The differences between "polar" and "non-polar" valencies are therefore of degree rather than of kind. F. G. WILLSON.

Action of Grignard reagent on amino-acids. VI. Decomposition of amino-alcohols by heat. F. BETTZIECHE and A. EHRLICH (Z. physiol. Chem., 1925, **150**, 191—196).—β-Amino-ααβ-triphenylethanol when heated in a sealed tube with 10% sodium hydroxide gives a good yield of a mixture of benzophenone and benzylamine, together with small amounts of benzoic acid. On heating this alcohol in a sealed tube with 5% ammonia or even with water to 130°, the same end-products are obtained. Heating alone in a sealed tube to 150° brings about the same decomposition. β-Amino-β-phenyl-αα-dibenzylethanol may be similarly decomposed by heating with water to 160°, yielding dibenzyl ketone and benzylamine. β-Amino-αα-diphenylethanol is decomposed by heating with water to 200° to give methylamine and benzophenone. β-Amino-αα-dibenzylethanol requires to be heated with water to 210° before decomposition ensues, when methylamine and dibenzyl ketone are produced. If this alcohol is heated alone in a sealed tube to 220°, the same decomposition takes place. The yields throughout are from 50 to 80% of the theoretical. H. D. KAY.

Action of Grignard reagent on amino-acids. VII. Deamination of β-amino-αα-dibenzylethanol. F. Bettzieche and A. Ehrlich (Z. physiol. Chem., 1925, **150**, 197—201).—By the action of nitrous acid on substituted β-amino-αα-diphenylethanols, a migration of a phenyl group between two neighbouring carbon atoms ensues, and a ketone is produced thus: $\mathrm{R\cdot CH(NH_2)\cdot CPh_2\cdot OH} \longrightarrow \mathrm{R\cdot CHPh\cdot CO\cdot Ph}$. The same type of reaction occurs with β-amino-αα-dibenzylethanol, with β-amino-αα-dibenzylpropanol, with β-amino-β-phenyl-αα-dibenzylethanol, and with β-amino-ααβ-tribenzylethanol, one of the benzyl groups migrating.

H. D. Kay.

Basis for the physiological activity of certain -onium compounds. III. Choline derivatives. R. R. Renshaw and J. C. Ware (J. Amer. Chem. Soc., 1925, **47**, 2989—2995).—*Chloroacetylcholine chloroacetate*, m. p. 303° (indef.), obtained by heating choline chloride in a sealed tube with excess of chloroacetyl chloride at 100°, has about one-thousandth of the activity of acetylcholine (cf. Hunt and Renshaw, A., 1925, i, 861). *Iodomethyl acetate*, b. p. 65°/14 mm., α^{22} 1·902, obtained by the action of paraformaldehyde on acetyl iodide, condenses with trimethylamine in absolute alcohol with formation of *acetylformocholine iodide*, $\mathrm{NMe_3I\cdot CH_2\cdot OAc}$, m. p. 152°, which is 12—24 times as active as formocholine (cf. Hunt and Renshaw, *loc. cit.*). *Acetylformocholine chloride* (*chloroplatinate*), obtained similarly, affords a 90% yield of formocholine chloride (cf. Hunt and Taveau, Hygienic Lab. Bull., 1911, **73**, 28; Dale, J. Pharmacol., 1914, **6**, 147) when warmed for 24 hrs. with 95% alcohol to which a few drops of concentrated hydrochloric acid have been added. Condensation of β-chloroethyldichloroarsine with trimethylamine in cold toluene yields *dichloroarsinylethyltrimethylammonium chloride*, $\mathrm{NMe_3Cl\cdot CH_2\cdot CH_2\cdot AsCl_2}$, m. p. 181·1°, which, when treated with alcoholic sodium hydroxide, yields *arsinylethyltrimethylammonium chloride*, $\mathrm{NMe_3Cl\cdot CH_2\cdot CH_2\cdot AsO}$, m. p. 194°, the toxicity of which is greater to animals infected with trypanosomes than to normal animals.

Neurine bromide is obtained in 90% yield by treating powdered bromocholine bromide, in suspension in an equal weight of absolute alcohol, with 1 mol. of potassium hydroxide in absolute alcoholic solution (0·094 g. per c.c.). When bromine is added to an alcoholic solution of neurine bromide, it is rapidly absorbed at first, but the reaction velocity diminishes considerably before 1 mol. of the halogen is absorbed, and considerable decomposition takes place when the solution is evaporated. An unstable *perbromide*, which decomposes in a few days when kept in a stoppered bottle, was isolated, and it is suggested that the retardation of the addition of bromine to neurine is due to the formation of this substance, the bromine in which is more active in substitution than in addition reactions. Bromoethenyltrimethylammonium bromide (cf. Bode, A., 1892, 806) melts sharply at 145° when heated 4° per min., and sharply at 155·5—156° when heated 7° per min.

When choline chloride is heated with phosphoryl chloride, the *compound* $\mathrm{NMe_3(O\cdot POCl_2)\cdot CH_2\cdot CH_2Cl}$ is obtained.

F. G. Willson.

Hydroxyamino-acids. I. F. Bettzieche (Z. physiol. Chem., 1925, **150**, 177—190).—Pyruvic acid is produced in small quantities when serine is boiled with 15% sulphuric acid. It is identified as the phenylhydrazone. From the same amino-acid, by warming with nitrous acid, a yield of 7·2% of the theoretical quantity of acetaldehyde is obtained. When phenylserine is boiled with 10% sulphuric acid, phenylacetaldehyde is produced in small yield, and also a very small quantity of β-phenylnaphthalene. Phenylpyruvic acid is present in the ethereal extract of the reaction mixture. The yield of β-phenylnaphthalene may be increased to 65% by conducting the reaction in a sealed tube at 160—170°. Concentrated sulphuric acid at the ordinary temperature produces traces of phenylpyruvic acid from phenylserine, and at a later stage phenylacetaldehyde, also in minute quantity. If the mixture is kept for 1—2 days, a poor yield of β-phenylnaphthalene is obtained. By boiling phenylserine with 10% sodium hydroxide, the benzylidene compound of β-amino-αα-diphenylethanol is obtained. The first action of the alkali is to decompose the phenylserine into benzaldehyde and glycine, which then react together to give the substituted ethanol.

H. D. Kay.

Trihydroxytriethylamine oxide and substituted hydroxylamines with hydroxyethyl radicals. L. W. Jones and G. R. Burns (J. Amer. Chem. Soc., 1925, **47**, 2966—2973).—When treated with excess of ethylene oxide, first at 0° for 2 days, then at the ordinary temperature in a closed vessel for 2 weeks, hydroxylamine yields *trihydroxytriethylamine oxide*, $\mathrm{[CH_2(OH)\cdot CH_2]_3N{:}O}$, m. p. 104—105·5° (*benzoyl* derivative and *hydrochloride*, oils; *picrate*, m. p. 73—74°; *chloroplatinate*, two forms, m. p. 99° and 158·0—158·5°). Reduction of trihydroxytriethylamine oxide with zinc dust and water affords trihydroxytriethylamine. When the latter is refluxed with acetyl chloride in excess, it yields the oily *hydrochloride* of *triacetoxytriethylamine*, b. p. 206—207°/27 mm. (*chloroplatinate*, m. p. 123·5°), which is oxidised to the above amine oxide when treated with ethereal benzoyl peroxide or aqueous hydrogen peroxide and the resulting ester hydrolysed with hydrochloric acid. When heated with aqueous sodium hydroxide, trihydroxytriethylamine oxide yields mainly dihydroxydiethylamine, whilst the action of concentrated hydrochloric acid at 100° affords trihydroxytriethylamine and probably an *oxidation product* of this base. The action of ethylene oxide on 1 mol. of hydroxylamine affords *dihydroxydiethylhydroxylamine* (*hydrochloride*; *picrate*, m. p. 104—106°; *chloroplatinate*, m. p. 117·5—118°; *tribenzoate*), which is converted into morpholine on reduction with zinc dust and hydrochloric acid, followed by treatment with 70% sulphuric acid, the primary reduction product being dihydroxydiethylamine. *O*-Ethylhydroxylamine reacts similarly with ethylene oxide, with formation of O-*ethyldihydroxydiethylhydroxylamine*, $\mathrm{[CH_2(OH)\cdot CH_2]_2N\cdot OEt}$ (*chloroplatinate*, m. p. 166—167°), together with the *ether*, $\mathrm{[CH_2(OH)\cdot CH_2\cdot O\cdot CH_2\cdot CH_2]_2N\cdot OEt}$ (*chloroplatinate*, mobile liquid), whilst *O* : *N*-diethylhydroxylamine yields analogously O-*ethyl*-N-*ethyl*-N-*hydroxyethylhydroxylamine*, b. p. 63°/10 mm., b. p. 170°/760 mm. (*hydrochloride*; *chloroplatinate*, m. p. 143—143·5°). When heated with ethylene oxide at 100° *O* : *N*-diethylhydroxylamine yields, in addition to the last-named base, a *base*, b. p. 150—165°/15 mm., probably $CH_2(OH)\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot NEt\cdot OEt$ (*chloroplatinate*, oily). Ethylene oxide has no action on hydroxyurethane at temperatures up to 100°. Addition of alcoholic potassium hydroxide to an alcoholic solution of hydroxyurethane causes precipitation of the *salt* $CO_2Et\cdot NH(OH)\cdot CO_2Et\cdot NH\cdot OK$, which puffs when heated. Ethylene oxide is without action on *m*-nitrobenzhydroxamic acid at the ordinary temperature. The sodium and potassium salts of hydroxyurethane are not alkylated by ethylene chloro- or iodo-hydrins. β-*Chloroethyl* 3 : 5-*dinitrobenzoate*, m. p. 92°, is described. When heated with ethylene glycol, naphthylcarbimide is converted into the *urethane*, $CH_2(OH)\cdot CH_2\cdot O\cdot CO\cdot NH\cdot C_{10}H_7$, m. p. 102—103°.

F. G. Willson.

Action of nitrous acid on amides and other "amino"-compounds. R. H. A. Plimmer (J.C.S., 1925, **127**, 2651—2659).—Amides and urethane do not react with nitrous acid in presence of acetic acid but react quantitatively in presence of 2*N*-hydrochloric acid. Similar results are given by guanine and creatine, but carbamide reacts quantitatively in presence of acetic acid. Biuret reacts with one nitrogen atom in presence of acetic acid, two nitrogen atoms in presence of small amounts of hydrochloric acid, and three nitrogen atoms in presence of 2*N*-hydrochloric acid (molecule disrupted). These results are best interpreted by giving to amides and similar compounds alternative formulæ, such as $R\cdot C(OH):NH$, which changes into the form $R\cdot CO\cdot NH_2$ in the presence of mineral acid. B. W. Anderson.

Behaviour of cyanamide in acid and alkaline solution. G. Grube and G. Motz.—See this vol., 131.

Preparation of *s*-trimethylguanidine. M. Schenck (Z. physiol. Chem., 1925, **150**, 121—132).—The hydriodide of *s*.-trimethylguanidine may be prepared as follows: (*a*) in 55% yield by heating cyanogen iodide with an alcoholic solution of methylamine in a sealed tube to 130°; (*b*) in 45% yield by similar treatment of symmetrical dimethylguanidine hydriodide; (*c*) in 27% yield by treating methylguanidine hydriodide in the same way; (*d*) in 23% yield from guanidine hydriodide in the same way. The same end-product is obtained if the hydrochloride of guanidine and methylamine are the reagents, and the reaction mixture after heating for 4 hrs. at 125—130° is treated with sodium iodide in absolute alcohol, giving a yield of 36%. *s*-Trimethylguanidine may be characterised by the insolubility of its hydriodide in absolute alcohol, and by the preparation and analysis of its chloroaurate and chloroplatinate.

H. D. Kay.

Acetyl derivatives of thiocarbamide and carbamide. Constitution of thiocarbamide. A. Hugershoff (Ber., 1925, 58, [*B*], 2477—2487).—The action of acetic anhydride (1·5 mols.) on thiocarbamide at the lowest possible temperature gives a *triacetyl* derivative, $C_8H_{14}O_3N_4S_2$, m. p. 154°, which is also produced with 3 mols. of the anhydride or when mono- or di-acetylthiocarbamide is dissolved in hot alcohol and the solution is cooled. The compound dissolves unchanged in cold *N*-sodium hydroxide solution, but yields thiocarbamide and unchanged triacetyl compound when the solution is warmed. Warm 94% sulphuric acid hydrolyses it to monoacetylthiocarbamide, whereas an excess of hydrochloric acid (25%) converts it into thiocarbamide. It reacts with aromatic bases at 100°, giving monoacetylthiocarbamide and the corresponding acetylated amine. Its constitution is most readily explained by the hypothesis that it is a salt-like compound of the mono- and di-acetyl derivative in which the former functions as base and the latter as acid; attempts to prepare a similar substance from the more strongly basic thiocarbamide and diacetylthiocarbamide were, however, unsuccessful. The direct production of the triacetyl compound, non-formation of the mono- and di-acetylated product (cf. Kohmann, A., 1915, i, 944; Werner, J.C.S., 1916, **109**, 1120), and failure to obtain a compound from thiocarbamide and diacetylthiocarbamide are only explicable if the *M* usually assigned to thiocarbamide is doubled and the compound is regarded as a salt, $NH_2\cdot C(:NH)\cdot SH,H_2N\cdot C(:NH)\cdot SH$, in which only three hydrogen atoms can be acetylated. A diacetyl derivative can only be obtained from thiocarbamide when the salt-like union is dissolved by the addition of a stronger acid or a base (cf. Werner, *loc. cit.*). This conception of the constitution of thiocarbamide has not yet been confirmed by determinations of *M* in neutral solvents.

Thiocarbamide has m. p. 176° and, after resolidification, m. p. 147—148°. Acetylation of the resolidified product yields monoacetylthiocarbamide. It appears, therefore, that the basic half of the molecule undergoes transformation, but remains united to the acidic portion of the thiocarbamide molecule, thus preventing the salt-like union of the simple thiocarbamide molecules. It is probable that the thiocarbamide molecule suffers preliminary fission in all cases in which it appears to function in the unimolecular form.

Werner has assumed diacetylthiocarbamide to be a *NS*-derivative, thereby accounting for its formation from the potassium compound, $CH_3N_2\cdot SK$. Since, however, the author's work on the acetylation of arylated thiocarbamides (cf. Gibson, Diss., Göttingen, 1901) has led him to the conclusion that the first phase of the reaction consists in the addition of acetic anhydride to the thiocarbamide, this conception does not appear well founded and the behaviour of the diacetyl derivative toward sodium hydroxide is more readily harmonised with the structure

$$NAc:C(SH)\cdot NHAc.$$

The strongest argument in favour of the addition theory is found in the contrasted behaviour of *s*- and *as*-disubstituted thiocarbamides, the former of which alone yield acetyl derivatives, whereas according to the customary formulation the latter contain a free amino-group. If the *iso*-structure of the thiocarbamide derivatives be accepted, the constitutions

AcO·C(SH)(NHR)·NRAc and AcO·C(NR_2)(SH)·NHAc may be assigned to the additive compounds from which acetic acid can be eliminated only if a hydrogen atom is attached to the other nitrogen atom, as is the case with thiocarbamide, its monosubstituted and symmetrically disubstituted derivatives. The constitution NAc:C(SH)·NHAc,NH_2·C(SH):NAc, is therefore assigned to the triacetyl compound.

In contrast to thiocarbamide, carbamide yields directly a monoacetyl compound and cannot give a triacetyl derivative, since it does not form a salt with itself. Carbamide reacts vigorously with acetic anhydride at 120—130°, giving monoacetylcarbamide in about 32% yield. With the object of causing isomerisation of $CO(NH_2)_2$ to NH:C(OH)·NH_2, Werner has added sulphuric acid, thereby increasing the yield to 78%, but this yield is also attained in the absence of acid if the reactants are heated cautiously on the water-bath. The production of acetylcarbamide is attributed to the initial addition of the anhydride to the *iso*-form of carbamide, and the constitution NAc:C(OH)·NHAc is ascribed to the diacetyl derivative. In this case, also, the acetyl group attached to the amido-nitrogen is more readily removed than that present in the imido-group. Werner's conception that the readily removed acetyl group is attached to oxygen is regarded as improbable.

H. Wren.

Catalytic hydrogenation of azines. III. Hydrogenation of di*iso*butylideneazine. K. A. Taipale (J. Russ. Phys. Chem. Soc., 1925, **56**, 81—107).—Much of this paper has been already published (A., 1923, i, 547). The hydrogenation of *iso*butaldazine proceeds in two stages. One molecule of hydrogen first combines in the α : β (γ : δ)- and α : δ-positions, with formation of *iso*butyl*iso*butylidenehydrazine and azo*iso*butane. Union of a second hydrogen molecule with these compounds then yields *s*-di*iso*butylhydrazine, which on further hydrogenation gives *iso*butylamine and di*iso*butylamine. In certain of its properties, hydrazo*iso*butane resembles hydrazo-methane and -ethane, but in others it differs from these and from hydrazo*iso*propane.

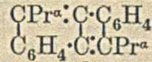
*Hydrazo*iso*butane* (*di*iso*butylhydrazine*), $CHMe_2·CH_2·NH·NH·CH_2·CHMe_2$, b. p. 169·5—170°/735 mm., 63·5°/10 mm., d_0^0 0·8166, n_D^{20} 1·42757, oxidises readily in the air; it reduces ammoniacal silver solution and Fehling's solution, and gives unstable violet-blue colorations with nitrous acid and with ferric chloride. Its acid *oxalate*, $C_8H_{20}N_2,H_2C_2O_4$, has m. p. 170° (decomp.). αβ-*Di*iso*butyl-δ-phenylsemicarbazide*, $NHPh·CO·N(C_4H_9)·NH·C_4H_9$, has m. p. 68·5—69°. *Dicarbanilyldi*iso*butylhydrazine*, $NHPh·CO·N(C_4H_9)·N(C_4H_9)·CO·NHPh$, prepared by the action of phenylcarbimide on di*iso*butylhydrazine, has m. p. 219·5°. αβ-*Di*iso*butyl-δ-phenylthiosemicarbazide*, $NHPh·CS·N(C_4H_9)·NH·C_4H_9$, m. p. 118·5—119°.

*Azo*iso*butane*, $CHMe_2·CH_2·N:N·CH_2·CHMe_2$, prepared by oxidation of hydrazo*iso*butane, by decomposition of the nitroso-compound of di*iso*butylhydrazine, or by partial reduction of the corresponding aldazine, has b. p. 145—145·5°/752 mm., d_0^0 0·7933—0·7947, n_D^{20} 1·41271—1·41291, remains unchanged at 150—160°, undergoes isomerisation into the hydrazone when heated with aqueous alkali hydroxide, and is readily reduced to hydrazo*iso*butane by hydrogen in presence of platinum-black. iso*Butylhydrazine* forms a hygroscopic *dihydrochloride*, a *monohydrochloride*, m. p. 92—93°, a *hydrogen oxalate*, m. p. 168—169°, and a *dibenzoyl* derivative, m. p. 169·5—170°. iso*Butylsemicarbazide*, $NH_2·CO·N(NH_2)·C_4H_9$, has m. p. 91·5—92°. iso*Butyl*iso*butylidenehydrazine*, $CHMe_2·CH:N·NH·CH_2·CHMe_2$, b. p. 175—176°/740 mm., 64·5°/12 mm., d_0^0 0·8389, n_D^{20} 1·44482—1·44502, reduces ammoniacal silver solution slowly and Fehling's solution when heated.

T. H. Pope.

Proposed international rules for numbering organic ring systems. A. M. Patterson (Rec. trav. chim., 1926, **55**, 1—18).—See A., 1925, i, 824.

Diphensuccindene series. XII. Colourless and coloured isomeric hydrocarbons of the diphensuccindene series. K. Brand and T. Sasaki (Ber., 1925, **58**, [*B*], 2546—2550).—An extension of previous work (Brand and Schläger, A., 1924, i, 157) to compounds containing the propyl and *iso*propyl groups.

Diphensuccindane-9 : 12-dione is converted by magnesium propyl bromide in the presence of ether into 9 : 12-*di*-n-*propyldiphensuccindane*-9 : 12-*diol*, m. p. 121—122°, which is transformed by boiling formic acid or by boiling alcohol and hydrochloric acid into a mixture of colourless 9 : 12-*di*-n-*propylidenediphensuccindane*, m. p. 157—158°, and red 9 : 12-*di*-n-*propyl*-$\Delta^{9:11}$-*diphensuccindadiene*,  $\begin{matrix} CPr^{\alpha}:C·C_6H_4 \\ | \quad\quad | \quad | \\ C_6H_4·C:CPr^{\alpha} \end{matrix}$, m. p. 135—136°. The propylidene compound is oxidised by chromic acid in the presence of sulphuric acid to propaldehyde and diphensuccindanedione. Either hydrocarbon is hydrogenated in the presence of palladised charcoal and aqueous alcohol to 9 : 12-*di*-n-*propyldiphensuccindane*, m. p. 98—99°. Similarly, diphensuccindanedione and magnesium *iso*propyl bromide afford 9 : 12-*di*iso*propyldiphensuccindane*-9 : 12-*diol*, m. p. 132—133° (*compounds* +3MeOH and +3EtOH are also described), which, when boiled with a mixture of formic and glacial acetic acids, or with alcoholic hydrogen chloride, passes into red 9 : 12-*di*iso*propyl*-$\Delta^{9:11}$-*diphensuccindadiene*, m. p. 178—179°, and colourless 9 : 12-*di*iso*propylidenediphensuccindane*, m. p. 189°. The latter hydrocarbon is oxidised by chromic acid to acetone and diphensuccindanedione. Either hydrocarbon is hydrogenated to 9 : 12-*di*iso*propyldiphensuccindane*, m. p. 80—81°.

H. Wren.

Parachor and chemical constitution. III. Orientation isomerism in aromatic compounds. S. Sugden and H. Wilkins (J.C.S., 1925, **127**, 2517—2522; cf. A., 1924, ii, 662; 1925, ii, 936, 937).—In order to show that the values of the parachor for benzene derivatives are not dependent on the orientation of the substituents and are in agreement with the values arrived at by summation of the atomic parachors, several *o*-, *m*-, and *p*-disubstituted benzenes have been investigated. The parachors, together with the calculated values, are: xylenes, *o*-, 283·3, *m*-, 283·8, *p*-, 283·8, calc., 285·1; nitrotoluenes, *o*-, *301·1*, *m*-, *300·6*, *p*-, 302·8, calc., 303·1; chloronitrobenzenes, *o*-, *299·9*, *m*-, *298·9*, *p*-, 300·0, calc., 301·2; bromonitrobenzenes, *o*-, *312·9*, *m*- *313·5*, *p*-, *313·5*, calc., 315·0; toluonitriles, *o*-, *290·6*, *m*-, *295·6*, *p*-, *294·4*, calc., 292·9. Ten of these values (printed in italics) are based on new surface tension measurements carried out by the method of maximum bubble pressure (A., 1924, ii, 154). The values for *m*-toluonitrile given by Turner and Merry (J.C.S., 1910, **97**, 2075) are shown to be inaccurate.

E. E. Walker.

Condensation of phenylacetylene under the influence of primary amines. K. Krasyski and A. Kiprianov (J. Russ. Phys. Chem. Soc., 1925, **56**, 1—10).—When heated in a sealed tube with an aqueous solution of methylamine or ethylamine, phenylacetylene is converted into *s*-triphenylbenzene, the yield with the former amine being quantitative. Under similar conditions, dimethylamine, diethylamine, trimethylamine, or piperidine converts phenylacetylene into an oily substance, whilst aqueous ammonia, potassium hydroxide solution, or water yields tarry products. *s*-Triphenylbenzene is formed by the condensation of phenylacetaldehyde with methylamine but not by that of acetophenone with methylamine. It seems probable that, when phenylacetylene and a primary amine are heated together, the former is converted by the action of the water into phenylacetaldehyde, which reacts with the amine to give either $CH_2Ph{\cdot}CH{:}NMe$ or $CHPh{:}CH{\cdot}NHMe$; polymerisation of the latter, with regeneration of the amine, would then yield triphenylbenzene.

T. H. Pope.

Derivatives of β-methylnaphthalene. K. Dziewoński, (Mlle.) J. Schoenówna, and E. Waldmann (Bull. Intern. Acad. Polonaise, 1925, **A**, 55—68).—See A., 1925, i, 1056.

Dissociation into free radicals of substituted dixanthyls. II. Dissociating influence of the *cyclo*hexyl group. J. B. Conant and L. F. Small (J. Amer. Chem. Soc., 1925, **47**, 3068—3077; cf. A., 1925, i, 955).—Condensation of magnesium *p*-chlorobenzyl chloride and xanthone in ethereal suspension, followed by hydrolysis with ice and ammonium chloride, affords p-*chlorobenzylidenexanthen*, yellow, m. p. 131—131·5°, as a precipitate, whilst treatment of the dried ethereal layer with a cold acetic anhydride solution of perchloric acid yields p-*chlorobenzylxanthyl perchlorate*, m. p. 209° to a black liquid, after darkening at 200°. Reduction of the latter with vanadous sulphate affords *di*-p-*chlorobenzyldixanthylethane*, m. p. 147—149° in air, with brown coloration, 152° in carbon dioxide. In bromobenzene solution, this absorbs oxygen in amount corresponding with that required for complete formation of a *peroxide*. The power of absorbing oxygen is destroyed by heating the bromobenzene solution at 100° for 1 hr. Condensation of magnesium *iso*amyl bromide with xanthone affords similarly iso*amylxanthydrol*, m. p. 95—97°, decomposing into xanthone and *iso*amyl alcohol when kept. iso*Amylxanthyl perchlorate*, yellow, m. p. 165°, yields, when reduced with vanadous sulphate, *di*iso*amyldixanthylethane*, m. p. 137—145° in air, 158—160° in carbon dioxide. This absorbs oxygen in bromobenzene solution, the end-product of the oxidation being xanthone. It gives a colourless solution in naphthalene at 80° under carbon dioxide, which deepens to red at the b. p. of the solvent, and then rapidly fades if boiling is continued. n-*Hexylxanthyl perchlorate*, yellow, m. p. 126—127°, obtained similarly, is reduced by vanadous sulphate to *di*-n-*hexyldixanthylethane*, m. p. 119—133° in air, 138° in carbon dioxide. This absorbs oxygen in solution, and shows colour changes, in solution, typical of dissociable ethanes. cyclo*Hexylxanthydrol*, m. p. 152°, and cyclo*hexylxanthyl perchlorate*, m. p. 163° with blackening, after darkening at 160°, are obtained analogously. Reduction of the latter with vanadous sulphate affords *di*cyclo*hexyldixanthyl*, light yellow, which absorbs oxygen instantaneously and exhibits the usual colour changes in solution, increased dissociation on dilution being indicated by deviation from Beer's law. cyclo*Hexylxanthyl peroxide*, m. p. 147—148° (decomp.), decomposes violently when heated in hydrogen at 145—150°, with formation of xanthone and a yellow *liquid*.

F. G. Willson.

Replacement of halogens from aromatic compounds. R. H. Clark and R. N. Crozier (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 153—156).—Various aromatic halogen compounds were heated with an alcoholic solution of potassium hydroxide, sodium methoxide, or sodium ethoxide in sealed tubes. The following numbers represent the percentage replacement of halogen after 42 hrs. at 151°, the numbers in parentheses representing the replacement calculated from a consideration of the electronic theory as elaborated by Fry ("Electronic Conception of Valency and the Constitution of Benzene"): *o*-dichlorobenzene 6·8 (50); *m*-dichlorobenzene 9·3 (100); 1 : 2 : 4-trichlorobenzene 29·4 (33·3); 1 : 2 : 4 : 5-tetrachlorobenzene 35 (50); hexachlorobenzene 38·7 (50); pentabromophenol 39·1 (40); 2 : 4-dichloroaniline 0 (0); 2 : 4 : 6-trichlorophenol 0 (0); 2 : 6 : 4-dichloronitroaniline 0 (0); *p*-chloroaniline 0 (0); *m*-chloroaniline 1·5 (100); *o*-bromotoluene 2·4 (100); *m*-bromotoluene 2·1 (100).

J. S. Carter.

Sulphuryl chloride. IV. New chlorinating agent. Preparation of polychloro-derivatives of toluene. O. Silberrad (J.C.S., 1925, **127**, 2677—2684).—When sulphuryl chloride containing about 1% of sulphur chloride is run into a mixture of toluene and anhydrous aluminium chloride at 70°, aluminium sulphur chloride is instantaneously formed, and by adjusting the relative proportions of hydrocarbon and reagent an almost theoretical yield of mono- (1 : 2 and 1 : 4), di- (1 : 2 : 4), tri- (1 : 2 : 3 : 4 and 1 : 2 : 4 : 5), and penta-chlorotoluene may be obtained. The new reagent does not attack the side chain.

B. W. Anderson.

Reactions of aromatic compounds containing multivalent iodine. C. Willgerodt (J. pr. Chem., 1925, [ii], **111**, 353—367).—A systematic review of the known facts regarding the formation and reactions of this type of compound.

R. W. West.

Halogen derivatives of diphenylmethane. A. E. Tschitschibabin and A. A. Schesler (J. Russ. Phys. Chem. Soc., 1925, **56**, 149—152).—The method previously used for the reduction of alcohols of the diphenyl- and triphenyl-methane series (A., 1911, i, 277) serves for the preparation of various halogenated diphenylmethane derivatives (cf. also A., 1911, i, 278).

Phenyl-p-*chlorophenylcarbinol*, $C_6H_4Cl{\cdot}CHPh{\cdot}OH$, m. p. 61°, prepared from *p*-chlorobenzaldehyde and magnesium phenyl bromide, is reduced by means of hydriodic acid in glacial acetic acid to phenyl-*p*-chlorophenylmethane. *Phenyl*-o-*chlorophenylcarbinol*, m. p. 65—65·5°, similarly obtained, yields *phenyl*-o-*chlorophenylmethane*, m. p. 13·2°, b. p. 164·5°/19 mm., d_0^0 1·1530. *Phenyl*-m-*chlorophenylcarbinol*, similarly obtained, has m. p. 38°. T. H. Pope.

Derivatives of toluene. R. Poggi (Atti R. Accad. Lincei, 1925, [vi], **2**, 423—427).—m-*Nitrobenzyl iodide*, m. p. 84·5—86°, and 2 : 4-*dinitrobenzyl iodide*, m. p. 75·5—76°, are obtained by boiling the alcoholic solutions of the corresponding chlorides with a slight excess of potassium iodide. By boiling *p*-nitrobenzyl thiocyanate with concentrated sulphuric acid, p-*nitrobenzyl thiocarbamate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}NH_2,$$

m. p. 140—141°, is obtained. By prolonged boiling of this compound with 20% hydrochloric acid, hydrogen sulphide, carbon dioxide, and ammonia are eliminated, giving p-*nitrobenzyl mercaptan*. m-*Cyanobenzyl bromide*, m. p. 94—95·5°, is prepared by the Sandmeyer reaction from *m*-toluonitrile. m-*Cyanobenzyl iodide*, m. p. 113—114°, and o-*cyanobenzyl iodide*, m. p. 77—78°, were prepared by boiling the corresponding chloro-derivatives in alcoholic solution with potassium iodide. By boiling an alcoholic solution of *p*-cyanobenzyl chloride with sodium thiosulphate for an hour, *sodium* p-*cyanobenzyl thiosulphate*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}S_2O_3Na$, was obtained, which on prolonged heating at 70° with concentrated sulphuric acid gave p-*cyanobenzyl mercaptan*, m. p. 43°. Oxidation of this compound in the cold by alcoholic iodine solution gave pp′-*dicyanobenzyl disulphide*, m. p. 147·5°. F. G. Tryhorn.

Two forms of *o*-nitrotoluene. R. H. Clark and R. N. Crozier (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 157—158).—The α- and β-forms of *o*-nitrotoluene (Knoevenagel, A., 1907, i, 202) have practically the same refractive index and density and the same *M* as determined by the f. p. method. It is, however, claimed that the assumption of the existence of two electronic forms, $C_6H_4\overset{-}{M}e{\cdot}\overset{+}{N}O_2$ and $C_6H_4\overset{+}{M}e{\cdot}\overset{-}{N}O_2$, as an explanation for the existence of the two modifications is supported by the results of chemical tests.

J. S. Carter.

2-Nitro-3 : 4-dimethoxy-1-methylbenzene (**2-nitrohomoveratrole**). E. Merck Chem. Fabr.—See B., 1926, 30.

Reactions of organic thiosulphates. H. B. Footner and S. Smiles (J.C.S., 1925, **127**, 2887—2891).—The organic sodium thiosulphates,

$$RS{\cdot}SO_2{\cdot}ONa$$

(cf. Price and Twiss, *ibid.*, 1907, **91**, 2021) share with the disulphoxides (A., 1925, i, 391) certain characteristic reactions of the thiol-sulphone group, due to instability of the dithio-system in substances of the type $RS{\cdot}SO_2X$; this group is readily split by alkali mercaptides and with varying ease by other reagents, the activity depending on the character of the group X. The organic thiosulphates are readily decomposed in aqueous solution by sodium mercaptides: $R{\cdot}S{\cdot}SO_3Na+NaSR' \longrightarrow RS{\cdot}SR'+Na_2SO_3$. When R and R′ are the same, a single symmetrical disulphide is produced; when they are dissimilar, a mixture of the two possible symmetrical disulphides is usually obtained, probably because of secondary reaction of the mercaptide with the disulphide (Lecher, A., 1920, i, 433), $RS{\cdot}SR'+NaSR \rightleftharpoons RS{\cdot}SR+R'SNa$. The organic thiosulphates are quickly and almost quantitatively decomposed by aqueous alkali cyanide, giving the corresponding thiocyanates in excellent yield, $RS{\cdot}SO_3Na+NaCN \longrightarrow R{\cdot}SCN+Na_2SO_3$. The disulphoxides behave similarly but are much less reactive, $RS{\cdot}SO_2R+NaCN \longrightarrow R{\cdot}SO_2Na+R{\cdot}SCN$.

Di-*p*-toluenesulphonyl sulphide (Tröger, A., 1899, i, 905) behaves similarly towards the mercaptans, the sulphur chain being ruptured with formation of sulphinate and thiosulphonate together with the disulphide corresponding with the mercaptan used, $(C_7H_7{\cdot}SO_2)_2S+2RSNa \rightarrow C_7H_7{\cdot}SO_2{\cdot}SNa+C_7H_7{\cdot}SO_2Na+(RS)_2$. Whilst sodium dithionate is not attacked by alkali mercaptides, the tri- and tetra-thionates are rapidly decomposed, giving the disulphide $Na_2S_3O_6+2R{\cdot}SNa \longrightarrow (RS)_2+Na_2SO_3+Na_2S_2O_3$; $Na_2S_4O_6+2R{\cdot}SNa \longrightarrow (RS)_2+2Na_2S_2O_3$. This result is, in the authors' opinion, adequately explained by the structures proposed by Mendeléev for the polythionates. o-*Nitrophenyl benzyl disulphide* has m. p. 54°; *benzyl 9-anthryl disulphide*, m. p. 128°; p-*nitrobenzyl thiocyanate*, m. p. 79°, and 9-*anthryl thiocyanate*, m. p. 181°. M. Johnson.

Dependence of rotatory power on chemical constitution. XXVII. Optical properties of *n*-alkyl *p*-toluenesulphinates. H. Phillips (J.C.S., 1925, **127**, 2552—2587).—When an optically inactive *n*-alkyl ester of *p*-toluenesulphinic acid is heated gently with *l*-β-octanol a mixture of a lævorotatory *n*-alkyl *p*-toluenesulphinate and a lævorotatory β-octyl *p*-toluenesulphinate is produced which can be separated by fractional distillation under very low pressures. Alcoholysis of the *l*-β-octyl *p*-toluenesulphinate thus produced yields an optically active *n*-alkyl ester of opposite sign. By these methods, using *l*-β-octanol, *n*-alkyl *p*-toluenesulphinates have been prepared with α^{25}_{5461} −6·72° and +0·92° and *n*-butyl esters with α^{25}_{5461} −3·46° and +16·52° (l=1 dm. in each case). The asymmetry must be attributed to the sulphur, and since only three groups are attached to this atom, the reason for this asymmetry is sought in the electronic structure. According to Lowry's theory, the oxygen should be attached to the sulphur atom through a semipolar linking, the oxygen atom being negatively and the sulphur atom positively charged. The parachor (A., 1924, ii, 662) of ethyl *p*-toluenesulphinate has been determined by S. Sugden, and this confirms the presence of a semipolar linking (A., 1925, ii, 936). The observed asymmetry might have been attributed to the tetrahedral arrangement of three different groups and one lone pair of electrons, but the view that the asymmetry is due to the three groups not being coplanar with the positively charged sulphur atom is shown to be more in accordance with cognate facts. The existence of a positive charge is regarded as the essential factor making optical activity possible for a ter-covalent atom containing three different groups. The corresponding sulphonic acid and its *n*-alkyl esters do not give any indication that they can exist in optically active forms.

It is suggested that carboxylic esters contain a small proportion of an isodynamic form possessing a semipolar linking, the constitution of which is analogous to that of the sulphinic esters. The additional centre of asymmetry thus introduced would explain the complex dispersion of these esters.

Optically active *p*-toluenesulphinic esters undergo changes analogous to the Walden inversion. Thus if *l*-β-octanol is heated with ethyl *p*-toluenesulphinate, a lævorotatory ethyl ester remains. If this in turn is heated with *n*-butyl alcohol, a dextrorotatory *n*-butyl *p*-toluenesulphinate is obtained. On the other hand, if the inactive butyl ester is heated with *l*-β-octanol, a lævorotatory *n*-butyl *p*-toluenesulphinate is produced.

By means of a cycle of changes involving the oxidation of *p*-toluenesulphinic esters to the corresponding sulphonic esters, *l*-β-octanol has been converted into *d*-β-octanol and *l*-menthol into *d*-*neo*menthol. It is shown that when the *p*-toluenesulphinate of an optically active carbinol (such as *l*-β-octanol) is treated with potassium acetate and ethyl alcohol the optically active alcohol is regenerated without inversion, but when the sulphinate is oxidised to the sulphonate and this then treated with potassium acetate and ethyl alcohol the acetate of *d*-β-octanol is produced, showing that inversion has taken place. The slow mutarotation of *p*-toluenesulphinic esters of *l*-β-octanol and of *l*-menthol caused by the labile nature of the rotation due to the sulphinic acid group has been studied. An equilibrium value of α^{25}_{5893} −35·1° is obtained after about 1000 hrs.

Ethyl dl-p-*toluenesulphinate* has b. p. 99—104°/0·1 mm., n^{25}_{D} 1·5309, d^{25}_{4} 1·114; *butyl* dl-p-*toluenesulphinate*, b. p. 90—95°/0·1 mm., n^{25}_{D} 1·5195, d^{25}_{4} 1·066; l-*menthyl* dl-p-*toluenesulphinate*, m. p. 108—109°, in acetone solution (c=2·609) gave $[\alpha]^{17}_{5461}$ −239·9° and $[\alpha]^{17}_{4359}$ −433·8°. E. E. WALKER.

Constitution of the so-called diphenyl*cyclo*butane. R. STOERMER and C. THIER [and, in part, E. LAAGE] (Ber., 1925, 58, [*B*], 2607—2615).—The "diphenyl*cyclo*butane" obtained by Stoermer and Biesenbach (A., 1905, i, 524) by the action of alcoholic potassium hydroxide on phenylacetaldehyde at high temperature and pressure is identified as αγ-diphenylpropene. The reaction appears to consist in the primary formation of the aldol,

$$CH_2Ph{\cdot}CH(OH){\cdot}CHPh{\cdot}CHO,$$

which passes into the corresponding, unsaturated aldehyde by loss of water and subsequently loses the aldehydic group as formic acid, thus giving αγ-diphenylpropene. The hydrocarbon, b. p. 178—179° (corr.)/14 mm., m. p. 15—16°, may be conveniently prepared in 67% yield by heating phenylacetaldehyde with alcoholic potassium hydroxide under reflux. It is identical with the compound obtained from α-benzylcinnamic acid by Dieckmann and Kämmerer (A., 1906, i, 820) and yields the same dibromide, m. p. 109°, and *pseudo*nitrosite, m. p. between 142° and 150°, according to the manner of heating; the latter compound is converted by diethylamine in boiling alcoholic solution into the *substance*, $C_{19}H_{24}O_2N_2$, m. p. 93°. The *nitrosochloride* has m. p. 166° (decomp.). αγ-Diphenylpropene is readily converted into αγ-diphenylpropane, b. p. 301—303° (corr.), 166—168°/16 mm., by sodium and boiling alcohol or hydrogen in the presence of palladised calcium carbonate. Oxidation of αγ-diphenylpropene by permanganate in alkaline solution yields only benzaldehyde, benzoic and phenylacetic acids; in acetone solution, particularly in the presence of sulphuric acid, benzaldehyde and βγ-*diphenylpropaldehyde hydrate*, $CH_2Ph{\cdot}CHPh{\cdot}CHO,H_2O$, m. p. 116—117° (*semicarbazone*, m. p. 189°), are produced. Ozonisation of αγ-diphenylpropene and subsequent decomposition of the ozonide yields only benzaldehyde, and benzoic and phenylacetic acids.

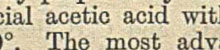
Under the modified conditions of preparation of αγ-diphenylpropene, three isomeric β-*benzyl*-αγ-*diphenyl*-δ-*valerolactones*, m. p. 109°, 133°, and 165°, respectively, are obtained as by-products. A fourth *isomeride*, m. p. 135°, was prepared during attempts to obtain the methyl ester from the dry sodium salt from the lactone, m. p. 109°, and methyl sulphate. Further, the lactone, m. p. 109°, exists in a dimorphous *form*, m. p. 122°. Apparently, the primary aldol passes into the corresponding unsaturated aldehyde which unites with a further molecule of phenylacetaldehyde, yielding the dialdehyde,

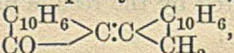
$$CH_2Ph{\cdot}CH(CHPh{\cdot}CHO)_2,$$

this is transformed by Cannizzaro's reaction into the compound,

$$CH_2Ph{\cdot}CH(CHPh{\cdot}CH_2{\cdot}OH){\cdot}CHPh{\cdot}CO_2H,$$

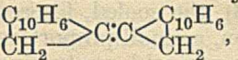
from which four isomeric β-benzyl-αγ-diphenyl-δ-valerolactones are derived by loss of water. H. WREN.

Diacene [diacenaphthylidene] and its ketonic derivatives. K. DZIEVOŃSKI and T. LITYŃSKI (Ber., 1925, 58, [*B*], 2539—2544).—Diacenaphthylidenedione,  $\left.\begin{array}{l}C_{10}H_6\\|\\CO\end{array}\right>C{:}C<\left\{\begin{array}{l}C_{10}H_6\\|\\CO\end{array}\right.$, m. p. 287—288°, is conveniently prepared by the oxidation of acenaphthene in glacial acetic acid with potassium dichromate at 40—50°. The most advantageous method for the preparation of diacenaphthylidenone,



$$\left.\begin{array}{l}C_{10}H_6\\|\\CO\end{array}\right>C{:}C<\left\{\begin{array}{l}C_{10}H_6\\|\\CH_2\end{array}\right.,$$

m. p. 258°, consists in boiling acenaphthylene dibromide in concentrated alcoholic solution with concentrated hydrochloric acid, whereby acenaphthenone is formed as by-product. Diacenaphthylidene,



$\underset{CH_2-}{\overset{C_{10}H_6}{|}}\!>C\!:\!C<\!\underset{CH_2}{\overset{C_{10}H_6}{|}}$, m. p. 271—273° [*picrate*, m. p. 214° (decomp.)] (cf. Doliński and Dzievoński, A., 1916, i, 138), is prepared by the reduction of diacenaphthylidenedione or diacenaphthylidenone by zinc dust in the presence of acetic anhydride and anhydrous sodium acetate. H. WREN.

Composition of rubicene. K. DZIEVOŃSKI and J. SUSZKO (Ber., 1925, **58**, [*B*], 2544—2546).—New analyses of rubicene confirm the composition, $C_{26}H_{12}$, assigned to it by Dzievoński and Suszko (A., 1922, i, 730) in place of the formula, $C_{26}H_{14}$, suggested by Pummerer and Ulrich (A., 1925, i, 1259; cf. also Pummerer, A., 1912, i, 182). H. WREN.

Action of amines on di- and tri-chloroacetic acids. A. S. WHEELER and E. DE W. JENNINGS (J. Elisha Mitchell Sci. Soc., 1924, **40**, 112).—When substituted amines are used, the di- and tri-chloroacetates are formed, respectively. However, with such amines as aniline and *o*-toluidine the dichloroacid produces trichloroacetates.

CHEMICAL ABSTRACTS.

Action of aromatic amines on semicarbazide hydrochloride. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **56**, 55—60).—When semicarbazide hydrochloride is boiled with a primary aromatic amine, such as aniline, *o*- or *p*-toluidine, 2 : 3-xylidine, or benzylamine, the corresponding substituted carbamides are obtained: $NH_2R+NH_2\cdot NH\cdot CO\cdot NH_2=NH_2\cdot NH\cdot CO\cdot NHR+NH_3$ and $NH_2\cdot NH\cdot CO\cdot NHR+NH_2R=NHR\cdot CO\cdot NHR+N_2H_4$ (cf. A., 1925, i, 984). T. H. POPE.

Action of magnesium butyl bromide on aromatic thiocarbimides. D. E. WORRALL (J. Amer. Chem. Soc., 1925, **47**, 2974—2976).—The following substituted amides of thiovaleric acid were obtained by the action of magnesium butyl bromide on the appropriate thiocarbimides (cf. Sachs and Loevy, A., 1903, i, 334; 1904, i, 307; Gilman, A., 1924, i, 382); *thiovaleryl-anilide*, m. p. 38—39°; -p-*toluidide*, m. p. 69—70°; -p-*anisidide*, m. p. 62—63°; -p-*chloroanilide*, m. p. 101·5—102°; -p-*bromoanilide*, m. p. 112°; -*diphenylamide*, m. p. 147—148°; -β-*naphthylamide*, m. p. 79—80°; and *bisthiovaleryl*-p-*phenylenediamide*, m. p. 198—199°. The action of hydroxylamine on these derivatives affords *oximes*, hydrogen sulphide and some ammonia being liberated. F. G. WILLSON.

Isomeric change in aromatic compounds. I. Conversion of diacylanilides into acylamino-ketones. A. W. CHAPMAN (J.C.S., 1925, **127**, 2818—2820).—When a current of dry hydrogen chloride is passed through fused diacetanilide or dibenzanilide, the acyl chloride and monoacylanilide result. Diacylanilides, when heated in presence of either hydrogen chloride or zinc chloride, are converted into the corresponding acylamino-ketones. The catalytic activity of the zinc chloride, which is ineffective when absolutely dry, is ascribed to the presence of a little free hydrogen chloride, without which rearrangement does not occur. Since the necessary conditions are exactly those under which hydrogen chloride decomposes the diacylanilides, it is suggested that this change, previously regarded as intramolecular (Chattaway, J.C.S., 1904, **85**, 386), is, in reality, a decomposition followed by recondensation, thus: $NPhAc_2+HCl \rightarrow NHPhAc+AcCl \rightarrow Ac\cdot C_6H_4\cdot NHAc+HCl$. M. JOHNSON.

Preparation of *p*-bromophenylhydroxylamine by the emulsification process. R. D. HAWORTH and A. LAPWORTH (J.C.S., 1925, **127**, 2970).—Reduction of *p*-bromonitrobenzene by the method previously described (*ibid.*, 1921, **119**, 770) is frequently unsuccessful. Good results are obtained by the use of more solvent benzene and more reducing solution. *p*-Bromonitrobenzene (5 g.), benzene (40 c.c.), hydrosulphide solution (120 g., *loc. cit.*, p. 769), and calcium chloride (5 g., in a little water) are emulsified. After 1½ hrs., solid ammonium chloride (5 g.) is added. After shaking, the precipitated *p*-bromophenylhydroxylamine (about 2·9 g.) is collected. A further yield (0·5 g.) can be obtained from the benzene layer by precipitation with petroleum (b. p. 40—60°). The sodium sulphide crystals used in making the reducing solution must be of good quality.

M. JOHNSON.

Dibromination of aceto-*m*-toluidide. S. C. J. OLIVIER (Rec. trav. chim., 1925, **44**, 1109—1112).—By the action of 2 mols. of bromine on an acetic acid solution of aceto-*m*-toluidide, a mixture is obtained which after hydrolysis consists of 73% of 4 : 6-dibromo-*m*-toluidine and 27% of 2 : 6-*dibromo*-m-*toluidine*, m. p. 66·5—67°. It is shown that the 2 : 6-dibromo-compound, m. p. 33—35°, previously described (Neville and Winther, J.C.S., 1880, **37**, 440) is a eutectic mixture of the two isomerides.

R. W. WEST.

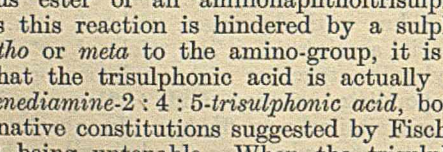
Trinitrophenylnitroaminoethyl nitrate. R. C. MORAN.—See B., 1926, 78.

Preparation of some primary amines by the catalytic reduction of nitriles. W. H. CAROTHERS and G. A. JONES (J. Amer. Chem. Soc., 1925, **47**, 3051—3057).—*p*-Toluonitrile is reduced smoothly in acetic anhydride solution by hydrogen in presence of platinum oxide, with formation of *p*-methylbenzylacetamide, m. p. 110—111° (cf. Lustig, A., 1895, i, 162), in 88% yield. The reduction requires over 5 hrs. with hydrogen under 3 atm. pressure. In glacial acetic acid, a 71% yield of *pp*′-dimethyldibenzylamine, together with small proportions of the corresponding primary and tertiary amines, was obtained similarly in 6½ hrs. In absolute alcohol, reduction proceeds more slowly, and both primary and secondary amines are produced. In *n*-butyric anhydride, a 74% yield of p-*methylbenzyl*-n-*butyramide*, m. p. 71—72°, was obtained. Benzonitrile affords similarly, in acetic anhydride solution, benzylacetamide; in glacial acetic acid, benzylamine and dibenzylamine, the former predominating; and in absolute alcohol, ammonia and the primary and secondary amines. *o*-Toluonitrile is reduced similarly in acetic anhydride solution to *o*-methylbenzylacetamide, m. p. 76—76·5° (cf. Strassmann, A., 1888, 474), whilst phenylacetonitrile affords β-phenylethylacetamide, in 63% yield. The above acetyl derivatives of primary amines are soluble in cold dilute hydrochloric acid, from which they are precipitated unchanged on addition of alkali; the corresponding aromatic sulphonyl derivatives are only slightly soluble in dilute alkali. The following acyl-derivatives of the above amines are described: p-*methylbenzyl-phenylcarbamide*, m. p. 188—188·2°, -p-*toluenesulphonamide*, m. p. 94·7—95·5°, and p-*bromobenzenesulphonamide*, m. p. 126·5—127·5°; o-*methylbenzylphenylcarbamide*, m. p. 167·5—168°, -*benzenesulphonamide*, m. p. 128·3—129·1°, -p-*toluenesulphonamide*, m. p. 118·7—119·2°, and -p-*bromobenzenesulphonamide*, m. p. 106·5—107°; β-*phenylethyl*-p-*bromobenzenesulphonamide*, m. p. 88·5—89·5°, and -phenylcarbamide, m. p. 153·5—154·5° (cf. Forster and Stötter, J.C.S., 1911, **99**, 1338). The success of the preparation of primary amines by reduction of nitriles in acid anhydride solution is ascribed to prevention of hydrolysis of the imine usually assumed to be formed intermediately, and to prevention of its condensation with the primary amine by the prior acylation of the latter. F. G. WILLSON.

Benzidine derivatives of thiocarbamide and azo dyes therefrom. L. PINTO.—See B., 1926, 43.

Action of sulphites on aromatic amino- and hydroxy-compounds. XII. Products of the action of sulphites on 1 : 8-dinitronaphthalene. H. T. BUCHERER and H. BARSCH (J. pr. Chem., 1925, [ii], **111**, 313—339; cf. A., 1925, i, 1338).—When 1 : 8-dinitronaphthalene is boiled with aqueous sodium hydrogen sulphite solution (8·3 mols. per mol. of dinitro-compound), and the cooled, filtered solution acidified, a naphthylenediaminetrisulphonic acid separates (cf. Fischesser, D.R.-P. 79577) in a yield of 8·8% of the theoretical, calculated on the dinitronaphthalene used, whilst the mother-liquor contains a further 15·4% yield of the acid, together with the sulphurous ester of an aminonaphtholtrisulphonic acid. The latter is hydrolysed by boiling with alkali, after which the above mother-liquor contains active material (evaluated by titration with diazo-solution) corresponding with 31·9% of the applied dinitronaphthalene. When the naphthylenediaminetrisulphonic acid is boiled with aqueous sodium hydrogen sulphite, it is converted into the sulphurous ester of an aminonaphtholtrisulphonic acid. As this reaction is hindered by a sulphonic group *ortho* or *meta* to the amino-group, it is concluded that the trisulphonic acid is actually 1 : 8-*naphthylenediamine*-2 : 4 : 5-*trisulphonic acid*, both of the alternative constitutions suggested by Fischesser (*loc. cit.*) being untenable. When the trisulphonic acid is boiled with *cyclo*hexanone in presence of concentrated hydrochloric acid, a condensation *product*, probably (I), is formed, which is not attacked by boiling sodium hydrogen sulphite solution.

(I.)



When 1 : 8-dinitronaphthalene is treated at 90° with sodium hydrogen sulphite solution in presence of ammonia (cf. D.R.-P. 215338), the cooled, filtered solution deposits, on acidification, a small proportion of α-naphthylamine-4 : 7-disulphonic acid, containing traces of the corresponding aminonaphtholdisulphonic acid and naphthylenediaminedisulphonic acid. The total yield of disulphonic acids corresponds with 6·9% of the dinitronaphthalene used, whilst the mother-liquor contains further an approximately equal proportion of the sulphurous ester of the aminonaphtholdisulphonic acid. When boiled with aqueous sodium hydrogen sulphite, α-naphthylamine-4 : 7-disulphonic acid is converted into the sulphurous ester of the corresponding naphtholdisulphonic acid.

Treatment of 1 : 8-naphthylenediamine with 11 pts. of 2% fuming sulphuric acid at 95—100° for several hrs. affords 1 : 8-naphthylenediamine-4-sulphonic acid, which, when warmed with 5 pts. of 20% fuming sulphuric acid, yields a disulphonic acid, probably 1 : 8-naphthylenediamine-4 : 5-disulphonic acid (cf. D.R.-P. 72584). F. G. WILLSON.

Reactions of azoxy-compounds. I. Action of light. W. M. CUMMING and G. S. FERRIER (J.C.S., 1925, **127**, 2374—2379).—*o*-Hydroxyazo-compounds result when solutions of certain azoxy-compounds are exposed to the light of a mercury-vapour lamp. The yields are highest in alcohol and lowest in benzene. Azobenzene in 85% alcohol gives a 63·3% yield of *o*-hydroxyazobenzene, m. p. 82—83°, in 200 hrs. (44% in 100 hrs.). The same transformation occurs under the influence of sunlight or electric light (filament lamp). 2 : 2′-, 3 : 3′-, and 4 : 4′-Azoxytoluene, 4 : 4′-dichloroazoxybenzene, 2 : 2′-diamino-4 : 4′-azoxytoluene, and 4 : 4′-azoxyanisole react similarly. 2-*Hydroxy*-3 : 3′-*azotoluene* has m. p. 61·5—62·5°. 4 : 4′-Azoxyphenetole and 4 : 4′-dinitroazoxybenzene are unchanged.

The existence of an isomeric 4 : 4′-azoxytoluene, m. p. 75° (Janovsky and Reimann, A., 1889, 392), is unconfirmed, and a setting-point curve shows that it cannot be a solid solution of *p*-azo- in *p*-azoxytoluene. C. HOLLINS.

Azo dyes. BRITISH DYESTUFFS CORP., LTD., K. H. SAUNDERS, and H. GOODWIN.—See B., 1926, 7.

***o*-Hydroxyazo dyes.** A.-G. F. ANILIN-FABR.—See B., 1926, 7.

Azo dyes. SOC. OF CHEM. IND. IN BASLE.—See B., 1926, 43.

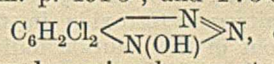
Azo dyes. G. KALISCHER, K. KELLER, and L. CASSELLA U. CO.—See B., 1926, 44.

Phenylhydrazine and factors affecting hydrazone formation. E. G. R. ARDAGH and J. G. WILLIAMS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 75, and J. Amer. Chem. Soc., 1925, **47**, 2976—2983).—The iodometric method (Ardagh and Williams, this vol., 189) for the determination of phenylhydrazine gives low results when a buffer solution is present. Correct results are obtained when the solution is just acid to methyl-orange. Aqueous solutions of phenylhydrazine and its salts oxidise fairly rapidly on exposure to air, the solutions being stable when prepared with water free from oxygen and preserved in an atmosphere of nitrogen.

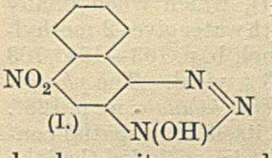
Hydrazone formation is a reversible process, the equilibrium being greatly influenced by the acidity of the medium. Acetonephenylhydrazone formation is almost complete over the p_H range 5—7, provided the hydrazone is at the same time salted out. If the hydrazone be extracted with some suitable solvent, immiscible with water, the reaction is quantitative. The rôle of sodium acetate in hydrazone formation is solely that of a buffer. J. S. Carter.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. I. E. Müller (J. pr. Chem., 1925, [ii], **111**, 273—276).—A summary of previous researches in this field, introductory to the following three papers. F. G. Willson.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. II. Action of hydrazine hydrate on some nitro- and chloronitro-compounds. E. Müller and G. Zimmermann (J. pr. Chem., 1925, [ii], **111**, 277—292).—Whilst the action of hydrazine hydrate on *m*-nitrobenzoic acid in alcoholic solution affords only the corresponding *hydrazine* m-*nitrobenzoate*, m. p. 182°, in absence of solvent the nitrobenzoic acid is reduced at water-bath temperature in 30 min. with formation of *m*-aminobenzoic acid. *p*-Nitrobenzoic acid behaves similarly (cf. Curtius and Bollenbach, A., 1907, i, 1078). *p*-Nitrotoluene is reduced to *p*-toluidine when heated with hydrazine hydrate for 4 hrs. at 130° in a sealed tube, *o*- and *m*-toluidines being also analogously produced. At 150°, hydrazine hydrate reduces *o*-, *m*-, and *p*-nitroanilines to the corresponding phenylenediamines. 2 : 4-Dinitrotoluene is reduced by alcoholic hydrazine hydrate at water-bath temperature to *o*-nitro-*p*-toluidine, and this is further reduced to 2 : 4-tolylenediamine when heated with hydrazine hydrate at 140°. Reduction of *m*-chloronitrobenzene to *m*-chloroaniline by the action of hydrazine hydrate proceeds at water-bath temperature, but *o*-chloronitrobenzene, when boiled with hydrazine hydrate, yields hydroxybenzotriazole as the *hydrazine* salt, m. p. 110—120° with loss of hydrazine; *o*-nitrophenylhydrazine is probably the primary product. 2 : 4-Dichloronitrobenzene reacts with hydrazine hydrate in hot alcoholic solution with formation of the *hydrazine* salt, m. p. 182—183° (decomp.), of the corresponding 4-*chlorohydroxybenzotriazole*, exploding at 204—205° (*potassium* salt, explodes above 300°; *ethyl ether*, m. p. 59—60°; *benzoyl* derivative, m. p. 126°). The 5-*chloro*-2 : 4-*dinitrophenylhydrazones* of *benzaldehyde*, orange, m. p. 242°, *acetone*, yellow, m. p. 123°, *ethyl acetoacetate*, m. p. 115°, and *formaldehyde*, yellow, m. p. 124°, are described. *Benzoyl*-5-*chloro*-2 : 4-*dinitrophenylhydrazine*, reddish-yellow, has m. p. 219°. When treated with sodium nitrite in suspension in cold aqueous-alcoholic hydrochloric acid, 5-chloro-2 : 4-dinitrophenylhydrazine affords an unstable *nitrosoamine*, yellow, decomp. at 85°, which, when heated, loses water and nitrogen with formation of 5 : 5′-*dichloro*-2 : 4 : 2′ : 4′-*tetranitroazobenzene*, yellow, m. p. 93°, exploding at higher temperatures with evolution of a yellow, irritant vapour. 5-Chloro-2 : 4-dinitrophenylhydrazine dissolves in alkali with darkening and evolution of gas. Acidification of the solution affords brown flocks which could not be purified, but which did not appear to represent a hydroxytriazole derivative. The *dihydrochloride*, pale yellow, readily hydrolysed, the *sulphate*, pale yellow, decomp. at 213°, and the *dibenzoyl* derivative, pale orange-yellow, m. p. above 300°, of 2 : 4-*dinitro*-1 : 5 *dihydrazinobenzene*, are described. F. G. Willson.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. III. Action of hydrazine hydrate on 2 : 4 : 5-trichloronitrobenzene. E. Müller and W. Hoffmann (J. pr. Chem., 1925, [ii], **111**, 293—306).—Hydrazine hydrate reacts with 2 : 4 : 5-trichloronitrobenzene in boiling alcoholic solution with formation of 3 : 4-*dichloro*-6-*nitrophenylhydrazine*, orange-yellow, m. p. 194·5°, and 4 : 5-*dichlorohydroxybenzotriazole*,  $C_6H_2Cl_2{<}\begin{smallmatrix}\text{——N}\\ \text{N(OH)}\end{smallmatrix}{\gg}N$, exploding at 194—196° after becoming brown at 190° [*hydrazine* salt, m. p. 205° (decomp.); *potassium* salt, explodes at 230—250°; *barium*, *magnesium*, *copper*, and *silver* salts; *aniline* salt, m. p. 168° (decomp.); *methyl ether*, m. p. 129°; *ethyl ether*, m. p. 90°; *benzoyl* derivative, m. p. 152°; *acetyl* derivative, m. p. 150°; *carbethoxymethyl* derivative, m. p. 109°; *carbethoxy*-derivative, m. p. 123°]. Formation of the triazole is favoured by the application of excess of hydrazine hydrate, and by the action of hydrazine or of alkalis on the dichloronitrophenylhydrazine. The following 3 : 5-*dichloro*-6-*nitrophenylhydrazones* are described: *benzaldehyde*-, yellowish-red, m. p. 184°; *salicylaldehyde*-, yellowish-green, m. p. 207°; *resorcylaldehyde*-, orange-red, m. p. 251°; *acetone*-, lemon-yellow, m. p. 157°; and *benzophenone*-3 : 5-*dichloro*-6-*nitrophenylhydrazone*, pale yellow, m. p. 162°. Treatment with nitrous acid converts the dichloronitrophenylhydrazine into 3 : 4-*dichloro*-6-*nitrophenylazoimide*, yellowish-brown, m. p. 56°, which is decomposed by alkalis into azoimide and a *compound*, m. p. 34°, possessing phenolic properties. The action of anhydrous hydrazine on 2 : 4 : 5-trichloronitrobenzene affords, together with the above triazole, 2 : 3-*dichloro*-6-*nitrophenylhydrazine*, red, m. p. 172° [*hydrochloride*, m. p. 195° (decomp.); *benzylidene* derivative, red, m. p. 225°]. F. G. Willson.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. IV. Action of hydrazine on 1-chloro-2 : 4-dinitronaphthalene. E. Müller and K. Weisbrod (J. pr. Chem., 1925, [ii], **111**, 307—312).—When treated with hydrazine hydrate in hot alcoholic solution, 1-chloro-2 : 4-dinitronaphthalene affords 2 : 4-dinitronaphthalene, the *hydrazine* salt of 2 : 4-*dinitro*-α-*naphthol*, m. p. 203—205°, 5-*nitro*-3-*hydroxynaphthotriazole*, (I), yellow, m. p. 215° (decomp.), and 4 : 4′-*dinitro*-2 : 2′-*azonaphthalene*. The primary product is probably 2 : 4-dinitronaphthylhydrazine, from which the triazole derivative is derived by reduction and condensation with the adjacent nitro-group, but which also loses nitrogen and hydrogen with formation of


(I.)

dinitronaphthalene, the latter being then further reduced to the azo-derivative, whilst the naphthol is formed by hydrolysis of the chlorodinitronaphthalene. The same products are obtained when the reaction is carried out at the ordinary temperature, but when anhydrous hydrazine is used, neither the dinitronaphthol nor the triazole derivative is formed.

F. G. Willson.

Nitrogen tetroxide as a reagent for diazotisation. B. Houston and T. B. Johnson (J. Amer. Chem. Soc., 1925, 47, 3011—3018).—Nitrogen tetroxide forms a convenient reagent for diazotising primary aromatic amines in anhydrous solvents. The reaction proceeds according to the equation $R{\cdot}NH_2+N_2O_4=R{\cdot}N{:}N{\cdot}O{\cdot}NO_2$, and is in accordance with the structure $ON{\cdot}O{\cdot}NO_2$ for nitrogen tetroxide. When *m*-nitroaniline, dissolved in dry benzene, is treated with pure nitrogen tetroxide in the cold until the reddish colour of the solution indicates an excess of the gas, 3 : 3′-*dinitrodiazoaminobenzene*, yellow, m. p. 195—196° (violent decomp.), is precipitated in practically quantitative yield. By using 3 mols. of nitrogen tetroxide to 1 mol. of *m*-nitroaniline, a yield of 69% of *m*-nitrobenzenediazonium nitrate can be obtained, together with 24% of the diazoamino-compound. In the case of *p*-nitroaniline, a molar ratio of nitrogen tetroxide to base of 1 : 2 affords 84% of diazoamino-derivative with 12% of diazonium nitrate, whilst a corresponding ratio of 2·25 : 1 yields 91% of diazonium nitrate, the diazoamino-compound not being formed under these conditions. *o*-Nitroaniline yields, with corresponding ratios of nitrogen tetroxide, 12% of diazoamino-compound and 8% of diazonium nitrate, and 64% of diazonium nitrate free from diazoamino-compound, respectively.

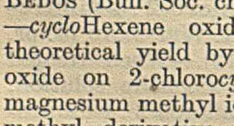
F. G. Willson.

Decomposition of diazo-compounds under the influence of copper. J. S. P. Blumberger (Chem. Weekblad, 1925, 22, 599—604).—A consideration of the various methods of reaction of diazo- and diazonium-compounds in presence of copper and copper compounds in relation to the theory of induced alternate polarity. Many of the configurations assumed are found to be contradictory.

S. I. Levy.

Stereoisomerism in the *cyclo*hexane series. I. 2-Methyl*cyclo*hexanols. M. Godchot and P. Bedos (Bull. Soc. chim., 1925, [iv], 37, 1451—1466).—*cyclo*Hexene oxide, obtained in 55% of the theoretical yield by the action of potassium hydroxide on 2-chloro*cyclo*hexanol, reacts readily with magnesium methyl iodide, yielding first a magnesium methyl derivative which gives 2-iodo*cyclo*hexanol with water. Further reaction on distilling off the ether in place of decomposing with water yields a product (I), which when finally treated with water gives 2-methyl*cyclo*hexanol, b. p. 163—164°/763 mm., in 63% yield. The *phenylurethane* has m. p. 71° and the *acid phthalate*, m. p. 128°. Since *cyclo*hexene oxide should itself from spatial considerations be a *cis*-compound, it is concluded that the 2-methyl*cyclo*hexanol is itself the *cis*-isomeride, the alternative possibility of its being 1-methyl*cyclo*hexan-1-ol being excluded by the fact that on oxidation with chromic and acetic acids it yields 2-methyl*cyclo*hexanone. The 2-chloro*cyclo*hexanol, m. p. 29°, previously described (A., 1923, i, 327; cf. Detœuf, A., 1922, i, 327) similarly reacts with magnesium methyl iodide in two stages (cf. Grignard, A., 1905, i, 593), giving finally 50% of the theoretical yield of a mixture of two stereoisomeric 2-methyl*cyclo*hexanols, b. p. 163—164°/763 mm. Since the phenylurethane of the *cis*-isomeride has m. p. 71°, the isomeride yielding a phenylurethane, m. p. 105° (cf. Sabatier and Mailhe, A., 1905, i, 275), and an *acid phthalate*, m. p. 122°, is regarded as the *trans*-compound. Accordingly the original chloro*cyclo*hexanol is either a mixture of *cis*- and *trans*-forms or some interconversion has taken place in the reaction. It is possible that the product obtained by Detœuf (b. p. 84—85°/16 mm., m. p. 8°) is the other isomeride. *cis*-2-Methyl*cyclo*hexanol obtained by hydrolysis of the acid phthalate, m. p. 128°, has b. p. 166·5°/760 mm., d_{26}^{26} 0·9187, n_D^{26} 1·45437; the *trans*-isomeride, similarly obtained from the phthalate m. p. 122°, has b. p. 167—167·5°/760 mm., d_{26}^{26} 0·9236, n_D^{26} 1·4581. Commercial 2-methyl*cyclo*hexanol, obtained by catalytic reduction of *o*-cresol in the presence of nickel, consists of a mixture of about 80% of the *trans*- with 20% of the *cis*-form. Hydrogenation of the 2-methyl*cyclo*hexanone in acetic acid in the presence of platinum-black similarly yields a mixture of the *cis*- and *trans*-isomerides, but reduction with sodium and alcohol yields almost entirely the *trans*-form of 2-methyl*cyclo*hexanol (cf. Skita, A., 1922, i, 534; 1923, i, 460).

R. Brightman.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Sulphonation of *p*-chlorophenol. J. M. Gauntlett and S. Smiles (J.C.S., 1925, 127, 2745—2746).—Sulphonation of *p*-chlorophenol yields an acid which on methylation forms 4-chloroanisole-2-sulphonic acid (*sodium* salt, loses $2H_2O$ at 120°; *chloride*, m. p. 104°). Reduction of the acid chloride yields 4-*chloroanisole*-2-*sulphinic acid*, m. p. 116°, and from this 4-*chloroanisole*-2-*methylsulphone*, m. p. 94°, and 4-*chloroanisole*-2-*disulphoxide*, m. p. 125°, are obtained. 4-*Chloroanisole*-2-*mercaptan*, m. p. 42°, and 4-*chloroanisole*-2-*disulphide*, m. p. 105°, were also prepared.

B. W. Anderson.

Complete synthesis of thymol from *iso*propyl alcohol. L. Bert and P. C. Dorier (Compt. rend., 1926, 182, 63—65).—*p*-Chloromethyl*iso*propylbenzene is obtained from *iso*propyl alcohol (Blanc, A., 1923, i, 549) and yields a magnesium derivative which when treated with water gives *p*-cymene; this may be transformed into 5-bromo-2-amino-*p*-cymene (Wheeler and Smithey, A., 1922, i, 332; Wheeler and Taylor, J. Amer. Chem. Soc., 1925, 47, 178), which when diazotised and heated with ethyl alcohol gives 5-bromo-*p*-cymene. The last-named yields a magnesium derivative which when treated with oxygen and water gives thymol.

L. F. Hewitt.

Derivatives of azoimide—a correction. A. Korczynski and St. Namyslovski (Bull. Soc. chim., 1925, [iv], 37, 1397).—Picryl azide (2 : 4 : 6-trinitro-1-azidobenzene) described by the authors

(A., 1924, i, 1354) had previously been described by Schrader (A., 1917, i, 595). W. HUME-ROTHERY.

Pyrocatechol compounds of bi-, ter-, and quadri-valent metals. R. WEINLAND and H. SPERL (Z. anorg. Chem., 1925, **150**, 69—83).—When a solution of manganous acetate is treated with pyrocatechol and an alkaline hydroxide, the manganese is rapidly oxidised by the air, and complex *salts* of tervalent manganese are obtained of the formulæ: $[Mn(C_6H_4O_2)_3]Na_3,0{\cdot}5NaOH,6H_2O$; $[Mn(C_6H_4O_2)_3]K_3,3H_2O$;

$$[Mn(C_6H_4O_2)_3]H(NH_4)_2,5H_2O;$$

these are decomposed by acids. If dilute ammonia is used, an unstable *base*, $Mn_6(C_6H_4O_2)_5(OH)_2,10H_2O$, is precipitated. Pyridine yields a crystalline *compound*, $4[Mn(C_6H_4O_2)_2]H_2,2C_5H_5N,C_6H_4(OH)_2$; nickel forms a similar *compound*, but the zinc *compound* has the normal formula $[Zn(C_6H_4O_2)_2]H_2,2C_5H_5N$. Unlike most complex pyrocatechol compounds, these pyridine salts are stable in air. From stannous chloride a *compound*, $[ClSnC_6H_4O_2]H,C_5H_5N$, is obtained, and thorium nitrate yields a *substance*, $Th(O{\cdot}C_6H_4{\cdot}OH)_4,2C_5H_5N$. The yellow colour of this latter compound is surprising because an ammonium salt, containing 3 mols. of pyrocatechol, is colourless; it may be a pseudo-ammonium salt. The *zirconium* compound,

$$[Zr(C_6H_4O_2)_3]H_2,C_5H_5N,0{\cdot}5[C_6H_4(OH)_2,C_5H_5N],$$

is also yellow, whilst aluminium forms a yellow, tarry compound which rapidly changes to a colourless, powdery *substance*, $[Al(C_6H_4O_2)_2]H,C_5H_5N,H_2O$. From bismuth nitrate a *compound*, $Bi(C_6H_4O_2)(O{\cdot}C_6H_4{\cdot}OH)$, is obtained, the constitution of which is uncertain, and also an *acid*, $Bi(NO_3)(O{\cdot}C_6H_4{\cdot}OH)_2$.

A. GEAKE.

2-Nitro-3:4-dimethoxytoluene [2-nitrohomoveratrole]. E. MERCK.—See B., 1926, 28.

Reduction of cinnamaldehyde to cinnamyl alcohol in presence of platinum oxide–platinum-black and promoters. XI. W. F. TULEY with R. ADAMS (J. Amer. Chem. Soc., 1925, **47**, 3061—3068).—Reduction of cinnamaldehyde with hydrogen in presence of platinum oxide–platinum-black ceases when 0·15 mol. of hydrogen has been absorbed per mol. of aldehyde. The catalyst can be reactivated by shaking with air, but many reactivations are necessary before reduction is complete, and the product, when 1 mol. of hydrogen has been absorbed, contains unchanged aldehyde, phenylpropaldehyde, cinnamyl alcohol, and phenylpropyl alcohol. A quantitative yield of cinnamyl alcohol is obtained when the aldehyde (0·2 mol. in 100 c.c. of 95% alcohol) is treated with an equivalent of hydrogen in presence of 0·2 g. of catalyst and 0·00002 mol. of ferrous chloride. Increase in the proportion of ferrous chloride to 0·0005 mol. results in a less pure product. Phenylpropyl alcohol is obtained by allowing a second mol. of hydrogen to be absorbed, but this takes place much more slowly. If 0·00002 mol. of zinc acetate is substituted for the ferrous chloride, reduction proceeds similarly, but much more slowly, to phenylpropyl alcohol, whilst 0·0006 mol. of zinc acetate completely inhibits the reduction. In presence of 0·0002 mol. of ferrous chloride and 0·00003 mol. of zinc acetate, reduction proceeds rapidly until 1 mol. of hydrogen is absorbed, when it ceases abruptly, and the product is very pure cinnamyl alcohol. The optimum proportions of the two salts are specific for each set of reaction quantities. Best results are obtained when the platinum oxide is reduced before the aldehyde is added to the solvent, and by keeping the temperature of reaction below 40°.

F. G. WILLSON.

***cyclo*Hexylglycerol.** R. DELABY and M. M. JANOT (Compt. rend., 1925, **181**, 1146—1147; cf. Klages and Klenk, A., 1906, i, 638; Moureu and Gallagher, A., 1922, i, 34; Delaby, A., 1923, i, 85).—cyclo*Hexylvinylcarbinol*, b. p. 93—94°, d_0^0 0·9352, $n_D^{17\cdot5}$ 1·4811, *allophanate*, m. p. 169—170°, when treated with bromine in acetic acid yields the *dibromide*, m. p. 73·5° (cf. Valeur and Luce, Bull. Soc. chim., 1920, [iv], **27**, 611). The dibromide when treated with potassium acetate gives cyclo*hexylglyceryl triacetate*, which is hydrolysed by hydrochloric acid and methyl alcohol, yielding cyclo*hexylglycerol*, b. p. 188—190°/20 mm., m. p. 73·5°. L. F. HEWITT.

[Syntheses by means of organic peroxides.] E. O. VON LIPPMANN (Ber., 1925, **58**, [*B*], 2706).—The observations attributed to the author by Gelissen and Hermans (this vol., 63) were made by E. Lippmann. H. WREN.

Chlorination of *o*- and *p*-aminobenzoic acids. L. ELION (Rec. trav. chim., 1925, **44**, 1106—1108).—By passing the calculated amount of chlorine into an acetic acid solution of anthranilic acid, a 75% yield of 3:5-dichloroanthranilic acid, m. p. 231°, is conveniently obtained. On boiling with acetic anhydride, this acid yields 3:5-*dichloroacetylanthranil*, m. p. 151°, which is converted by alkali hydroxides into 3:5-*dichloro-2-acetamidobenzoic acid*, m. p. 203°. By this method, *p*-aminobenzoic acid yields trichloroaniline and 35% of 3:5-dichloro-4-aminobenzoic acid. R. W. WEST.

Action of formaldehyde and secondary amines on acids with mobile hydrogen atoms. C. MANNICH and L. STEIN (Ber., 1925, **58**, [*B*], 2659—2662).—The synthesis of β-amino-acids from malonic and acetoacetic esters by means of formaldehyde and secondary amines has already been reported (A., 1922, i, 351; 1924, i, 946, 947). Attempts to extend the synthesis to other similar acids are irregularly successful. Phenylacetic acid does not condense, but its hydrogen atoms become sufficiently mobile if the negative character of the phenyl group is strengthened by the introduction of one or more nitro-groups. *o*-Nitromandelic acid may also be used, but *o*-nitrophenylacetic, *m*- and *p*-nitromandelic, *o*-nitrophenylpyruvic, sulphoacetic, βββ-trichloro-α-hydroxypropionic, and *o*- and *p*-hydroxydiphenylacetic acids are unsuitable. *p*-Nitrophenylacetic acid, piperidine, and formaldehyde afford β-*piperidino*-α-p-*nitrophenylpropionic acid*,

$$C_5H_{10}N{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NO_2){\cdot}CO_2H,$$

m. p. 138—139° (decomp.), which is readily converted by boiling water into piperidine and α-p-*nitrophenylacrylic acid*, m. p. 176—177°. Reduction of the nitro-acid by tin and hydrochloric acid yields β-piperidino-α-*p*-aminophenylpropionic acid, isolated as the *dihydrochloride*, m. p. 213° (decomp.). β-*Dimethylamino*-α-p-*nitrophenylpropionic acid* has m. p. 167—168°. β-*Methylamino*-α-p-*nitrophenylpropionic acid*, decomp. about 177°, its *hydrochloride*, decomp. 170°, and *phenylacetyl* derivative, m. p. 175°, are described. The action of formaldehyde and secondary amines on 2 : 4-dinitrophenylacetic acid leads to diamines in place of amino-acids, since carbon dioxide is lost during the reaction. Thus with piperidine, αγ-*dipiperidino*-β-2 : 4-*dinitrophenylpropane*, m. p. 133—134° [dihydrochloride, m. p. about 144° (decomp.)], is obtained. αγ-*Bisdimethylamino*-β-2 : 4-*dinitrophenylpropane*, m. p. 85—86°, and αγ-*bisdiethylamino*-β-2 : 4-*dinitrophenylpropane* (*picrate*, decomp. 165—166°) are described. *o*-Nitromandelic acid, formaldehyde, and piperidine afford β-*piperidino*-α-*hydroxy*-α-o-*nitrophenylpropionic acid*, $C_{14}H_{18}O_5N_2,H_2O$, decomp. 109°.

H. Wren.

Chemical isomerism of the three *cis*-cinnamic acids. H. Stobbe (Ber., 1925, **58**, [*B*], 2620—2626).—A reply to De Jong (A., 1920, i, 162), a critical review of whose experiments shows that the *cis*-cinnamic acids, m. p. 68° and 58°, respectively, can be recrystallised unchanged from concentrated solutions if the operation is effected rapidly so that there is little chance of infection. If these conditions are not fulfilled and the solutions are dilute, are preserved for 8—14 days or longer, and are decanted from one vessel to another in the laboratory so that the risk of infection is increased, the acid of m. p. 42° separates from solutions of the other two acids. The acid of m. p. 68° is never obtained from solutions of that of m. p. 58°, and the reverse transformation is never observed; it follows, therefore, that the solutions of the two acids are not identical. De Jong's arguments against the chemical isomerism of the three *cis*-cinnamic acids are regarded as refuted from his own observations. The supposed identity of the three double acids obtained from *trans*-cinnamic acid and the three *cis*-acids rests on the identity of the very indefinite m. p. of the compound, and cannot be regarded as established until the crystals have been measured and further constants established.

H. Wren.

Qualitative resemblance between the velocity of hydration of acid anhydrides and the velocity of hydrolysis of diacyl peroxides. J. Böeseken and H. Gelissen (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 624—629).—By an examination of the existing data on the hydrolysis of diacyl peroxides and acid anhydrides, the authors show that in both cases (1) it is the C:O linking that is ruptured by the water; (2) the reaction products are two acids; (3) the velocity is accelerated by alkali hydroxides, carbonates, and hydrogen carbonates (cf. Orton and Jones, J.C.S., 1912, **101**, 1708; Baeyer and Villiger, A., 1900, i, 437); and (4) the reaction is catalytically affected by acids (cf. Clover and Richmond, A., 1903, i, 396; Orton and Jones, *loc. cit.*). They conclude, therefore, that the diacyl peroxides are anhydrides of peracids and acids, and that those derived from acid anhydrides which have a small hydration constant do not hydrolyse, or do so exceedingly slowly, the velocity of hydrolysis of the peroxide being always smaller than that of the corresponding anhydride. This conclusion is supported by existing data and by the preparation of the following new peroxides, derived from acids the anhydrides of which are not attacked by water, and which are themselves stable towards that reagent: *cinnamoyl peroxide*, m. p. 144°; *phenylpropionyl peroxide*, m. p. 38·5°; *trichloroacrylyl peroxide*, m. p. 49°. The agreement also holds for the corresponding derivatives of benzenesulphonic acid.

J. W. Baker.

Derivatives of *p*-hydroxymethylbenzoic acid. II. Ether esters. F. H. Case (J. Amer. Chem. Soc., 1925, **47**, 3003—3005; cf. A., 1925, i, 815).—*p*-Chloromethylbenzoic acid is obtained in 78% yield by hydrolysis of *p*-chloromethylbenzonitrile with concentrated hydrochloric acid. When boiled with water until solution is complete, this is converted into *p*-hydroxymethylbenzoic acid. Hydrolysis of *p*-bromomethylbenzonitrile with hydrobromic acid yields similarly *p*-bromomethylbenzoic acid (cf. Swiss Pat. 93500). p-*Ethoxymethylbenzoyl chloride*, b. p. 136—138°/8 mm., obtained by the action of thionyl chloride on the corresponding acid, was used for preparing the following esters: *benzyl*, b. p. 198—201°/5 mm.; p-*carbethoxybenzyl*, m. p. 36—37°, b. p. 243—244°/3 mm.; and β-*diethylaminoethyl* p-*ethoxymethylbenzoate*, b. p. 183—185°/5 mm. (*hydrochloride*, m. p. 122—123°). The last-named salt appears to possess local anæsthetic properties.

F. G. Willson.

Derivatives of *p*-hydroxymethylbenzoic acid. III. Amino-esters. F. H. Case (J. Amer. Chem. Soc., 1925, **47**, 3005—3008; cf. preceding abstract).—*Ethyl* m-*nitro*-p-*chloromethylbenzoate*, yellow, b. p. 170—174°/4 mm., is obtained by heating *m*-nitro-*p*-chloromethylbenzonitrile (cf. Banse, A., 1894, i, 574) with absolute alcohol and sulphuric acid. When boiled with 1 mol. of anhydrous sodium acetate in alcohol, it affords *ethyl* m-*nitro*-p-*acetoxymethylbenzoate*, yellow, m. p. 57—58°, which, on hydrolysis with alcoholic hydrogen chloride, yields *ethyl* m-*nitro*-p-*hydroxymethylbenzoate*, yellow, m. p. 115—116° (*benzoate*, pale yellow, m. p. 129—130°; *phenylurethane*, m. p. 125—126°). Reduction of ethyl *m*-nitro-*p*-hydroxymethylbenzoate with tin and hydrochloric acid, or with hydrogen in presence of colloidal palladium or platinum oxide, affords *ethyl* m-*amino*-p-*hydroxymethylbenzoate*, m. p. 85—86° [*hydrochloride*, m. p. 129—130° (decomp.)]. n-*Butyl* m-*nitro*-p-*hydroxymethylbenzoate*, yellow, b. p. 198—203°/3 mm., and n-*butyl* m-*amino*-p-*hydroxymethylbenzoate*, m. p. 76—77°, obtained analogously, are described.

F. G. Willson.

6-Thiol-*m*-toluic acid. F. Krollpfeiffer [with H. Schultze and E. Sommermeyer] (Ber., 1925, **58**, [*B*], 2698—2701).—6-Thiol-*m*-toluic acid has been obtained by Krollpfeiffer (A., 1925, i, 1306) by the action of alkali on 3-bromo-2 : 6-dimethylthiochromanone and also by Arndt (*ibid.*, 1309) from 2 : 2-dichloro-6-methylthiochromonol, but the properties of the compounds are not in agreement.

Re-examination of Arndt's product shows that it cannot possibly be a homologue of *o*-thiolbenzoic acid, since it evolves carbon dioxide and does not yield a disulphide when oxidised by potassium ferricyanide. Further, when treated with molten potassium hydroxide it affords 4-methylthionaphthenquinone. Analysis of Arndt's compound suggests that it is 2 : 3 : 4-triketothiochroman.

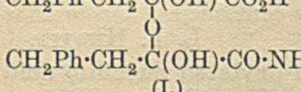
6-Thiol-*m*-toluic acid is prepared synthetically as follows: 6-amino-*m*-toluic acid is diazotised and the solution is treated successively with sulphur dioxide and copper powder; the sulphinic acid thus produced is reduced by zinc dust in the presence of alcohol to 6-thiol-*m*-toluic acid, m. p. 155°, identical with the product derived from 3-bromo-2 : 6-dimethylthiochromanone. Either acid reacts with chloroacetic acid to form o-*carboxy*-p-*tolylthiolacetic acid*, decomp. 220°, which is transformed by fusion with sodium hydroxide into 3-hydroxy-5-methylthionaphthen.

The conversion of 3-bromochromanone into chromone by boiling pyridine or dimethylaniline is incidentally recorded. H. Wren.

Some peculiarities of inactive mandelic acid. N. Kishner (J. Russ. Phys. Chem. Soc., 1925, **56**, 15—17).—When inactive mandelic acid is heated to 130° either in the anhydrous state or in a sealed tube with water, its m. p. at first has the normal value, 118°, but if the resulting acid is allowed to solidify and is then re-melted in the same capillary tube, it melts at 105—106°; if this acid is then recrystallised from benzene, its m. p. is 118° at the first, and 103° at the second, fusion. Further, if the molten acid with the abnormal m. p. is seeded with a crystal of the ordinary acid, the crystals separating melt at 118° at the first time and at 101—103° at the second time.

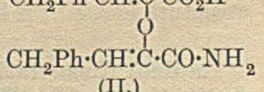
Crystallisation of the abnormal acid from hot benzene solution gives long, hexagonal plates which, in the mother-liquor, gradually change into rhombohedral crystals, $C_8H_8O_3,C_6H_6$, which lose their benzene and their form when kept. T. H. Pope.

α-Hydroxy-γ-phenylcrotonamide. An example of an ether of a ketone hydrate. J. Bougault (Bull. Soc. chim., 1925, [iv], **37**, 1420—1436).—A general account of work which has in part been published previously (A., 1912, i, 770; 1913, i, 269, 366; 1925, i, 921). The structure (I), representing the ether of a ketone hydrate assigned to the acid amide obtained by the action of dilute sodium hydroxide on an alcoholic solution of α-hydroxy-γ-phenylcrotonamide, has now been confirmed. The sodium salt of the amide is first precipitated and converted into the acid amide by treatment with hydrochloric acid.



$$\begin{array}{c}CH_2Ph{\cdot}CH_2{\cdot}C(OH){\cdot}CO_2H\\ |\\ O\\ |\\ CH_2Ph{\cdot}CH_2{\cdot}C(OH){\cdot}CO{\cdot}NH_2\end{array}$$

(I.)

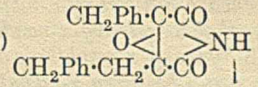


$$\begin{array}{c}CH_2Ph{\cdot}CH{:}C{\cdot}CO_2H\\ |\\ O\\ |\\ CH_2Ph{\cdot}CH{:}C{\cdot}CO{\cdot}NH_2\end{array}$$

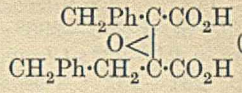
(II.)

On account of the ease with which the amide undergoes dehydration, its m. p. could not be determined. Alkalis, even sodium carbonate, produce hydrolysis to benzylpyruvic acid, but with ammonia phenylpropionylbenzylalanineamide is produced, as a result of secondary reaction with the benzylpyruvic acid (cf. A., 1921, i, 177). Dehydration at 100° yields the acid amide (II), which is only slightly soluble in acetone and is precipitated from its solutions in alkali by acetic acid. Boiling alkalis hydrolyse it to benzylpyruvic acid. Besides the acid amide (I), a small amount of the corresponding *diamide*, m. p. 198°, is formed in the action of sodium hydroxide on α-hydroxy-γ-phenylcrotonamide, and this similarly yields benzylpyruvic acid on hydrolysis. Potassium permanganate in acetic acid oxidises (I) to an imide, m. p. 120°, which is now regarded as possessing the structure (III) for the following reasons: (1) it is only feebly acid and can be alkylated by means of its potassium salt; (2) the *methylimide*, m. p. 86°, on treatment with sodium carbonate, yields a mixture of two acids, m. p. 175° and 150°, which probably possess the structures (V) and (VI), and are decomposed by boiling potassium or sodium hydroxide into methylamine and a dibasic acid, m. p. 204°, regarded as *benzyl-β-phenylethyloxidomaleic acid* (IV) (*dimethyl* ester, m. p. 74°); (3) hydrolysis with dilute sodium hydroxide yields ammonia and a mixture of benzylpyruvic and phenylpropionic acids.

(III.)



$$\begin{array}{c}CH_2Ph{\cdot}C{\cdot}CO\\ O{<}|\ \ {>}NH\\ CH_2Ph{\cdot}CH_2{\cdot}C{\cdot}CO\ \ |\end{array}$$

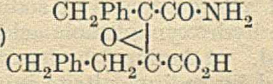


$$\begin{array}{c}CH_2Ph{\cdot}C{\cdot}CO_2H\\ O{<}|\\ CH_2Ph{\cdot}CH_2{\cdot}C{\cdot}CO_2H\end{array}$$

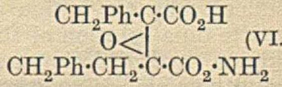
(IV.)

Partial hydrolysis of the imide (III) yields a new *acid amide*, m. p. 170° (decomp.), possessing the structure (V) or (VI) (*methyl* derivative, m. p. 154°); boiling dilute sodium hydroxide or a mixture of acetic and hydrochloric acids converts it into (IV) and the *anhydride*, m. p. 104°.

(V.)



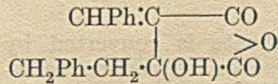
$$\begin{array}{c}CH_2Ph{\cdot}C{\cdot}CO{\cdot}NH_2\\ O{<}|\\ CH_2Ph{\cdot}CH_2{\cdot}C{\cdot}CO_2H\end{array}$$



$$\begin{array}{c}CH_2Ph{\cdot}C{\cdot}CO_2H\\ O{<}|\\ CH_2Ph{\cdot}CH_2{\cdot}C{\cdot}CO_2{\cdot}NH_2\end{array}$$

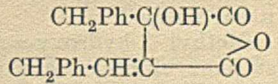
(VI.)

Prolonged boiling with excess of acetic anhydride yields a second *anhydride*, m. p. 75°, which is considered to have formula (VII) or (VIII). It forms a *methyl ether*, m. p. 53°, and an *imide* with ammonia, m. p. 122°, whilst sodium amalgam converts it into α-benzyl-α′β-phenylethylsuccinic acid, m. p. 170°.



$$\begin{array}{l}CHPh{:}C\text{——}CO\\ \qquad\ |\qquad\quad {>}O\\ CH_2Ph{\cdot}CH_2{\cdot}C(OH){\cdot}CO\end{array}$$

(VII.)

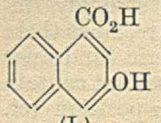


$$\begin{array}{l}CH_2Ph{\cdot}C(OH){\cdot}CO\\ \qquad\ |\qquad\quad {>}O\\ CH_2Ph{\cdot}CH{:}C\text{——}CO\end{array}$$

(VIII.)

Warm ammonia yields in addition a *substance*, m. p. 154°. R. Brightman.

3-Hydroxy-α-naphthoic acid and attempts to prepare an unsymmetrical naphthoxthin. R. Lesser and S. Sad (Ber., 1925, **58**, [*B*], 2551—2559).—Examination of a series of derivatives of 3-hydroxy-α-naphthoic acid leads the authors to assign to the acid the normal constitution (I) (cf. Lesser, Kranlpuhl, and Sad, A., 1925, i, 1424). This conception depends largely on the difference of the behaviour of the anilide and 2-hydroxy-3-naphthanilide towards vegetable fibres and of 4-amino-3-hydroxynaphthoic acid and 1-amino-2-hydroxy-3-

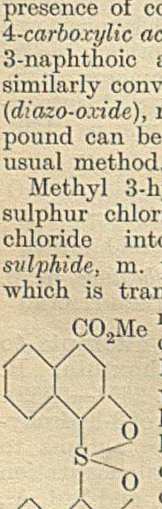


(I.)

naphthoic acid towards sodium nitrite. Since the presence of the double linking between the carbon atoms 2 and 3 in 2-hydroxy-3-naphthoic acid is regarded as established (*loc. cit.*), the alternative position of the double linking must be assumed in the acid under consideration.

The following compounds are described: 3-hydroxy-α-naphthoic acid, m. p. 248—249° (corr.); 3-acetoxy-α-naphthoic acid, m. p. 173—174° [Royle and Schedler (J.C.S., 1923, **123**, 1641) record m. p. 169—170°]; 3-*benzoyloxy-α-naphthoic acid*, m. p. 222—223°; 3-*methoxy-α-naphthoic acid*, m. p. 159°; 3-*acetoxy-α-naphthoyl chloride*, m. p. 96—97°; 3-*acetoxy-α-naphthamide*, m. p. 180—181°, from which 3-*hydroxy-α-naphthamide*, m. p. 209—211°, is obtained by cautious hydrolysis; 3-*acetoxy-α-naphthanilide*, m. p. 178—179°, and thence 3-*hydroxy-α-naphthanilide*, m. p. 112—113°; 4-p-*nitrobenzeneazo*-3-*hydroxy-α-naphthanilide*, m. p. 295—296°; *methyl* 3-*hydroxy-α-naphthoate*, m. p. 91—92°; 4-*bromo*-3-*hydroxy-α-naphthoic acid*, m. p. 231—232°; 4-*benzeneazo*-3-*hydroxy-α-naphthoic acid*, m. p. 273° (decomp.). 3-Hydroxy-α-naphthoic acid couples with *p*-diazobenzenesulphonic acid, and the product (*disodium* salt) is reduced by sodium hyposulphite in faintly alkaline solution to 4-*amino*-3-*hydroxy-α-naphthoic acid*, m. p. 204° (decomp.), of which the *sodium* salt and *hydrochloride* are described. The acid readily loses carbon dioxide in boiling dilute hydrochloric acid solution, forming 1-amino-β-naphthol. 4-*Acetamido*-3-*acetoxy-α-naphthoic acid* has m. p. 225° (decomp.). 4-Amino-3-hydroxy-α-naphthoic acid is readily oxidised by nitric acid to 3 : 4-naphthaquinonecarboxylic acid, m. p. 173° (decomp.); the corresponding *oxime* has m. p. 181—182° (decomp.). 4-*Nitroso*-3-*hydroxy-α-naphthoic acid*, m. p. above 300°, is prepared with difficulty by the action of a large excess of sodium nitrite on a solution of the hydroxynaphthoic acid in dilute hydrochloric acid. 4-Amino-3-hydroxy-α-naphthoic acid is converted by sodium nitrite in the presence of copper sulphate into β-*naphthoxadiazole*-4-*carboxylic acid*, decomp. 151°. 1-Amino-2-hydroxy-3-naphthoic acid, m. p. 241° (decomp.), can be similarly converted into the corresponding *oxadiazole* (*diazo-oxide*), m. p. 182—183° (decomp.), but the compound can be obtained with equal readiness by the usual method.

Methyl 3-hydroxy-α-naphthoate is converted by sulphur chloride in the presence of carbon tetrachloride into *di*-4-*carbomethoxy*-2-*hydroxynaphthyl sulphide*, m. p. 210—211° (*dibenzoate*, m. p. 225°), which is transformed by bromine and alkali, but not by potassium ferricyanide, into the corresponding *dehydrosulphide* (II), m. p. 188—189°; this substance does not react with phenylhydrazine, *p*-nitrophenylhydrazine, phenylcarbamhydrazide, or hippurylhydrazine, thus strongly indicating the spiran structure, since there can be no question of steric hindrance with a compound which does not contain a substituent in the *ortho*-position (cf. von Auwers and Kehrmann, Ber., 1923, **56**, 1802). The dehydrosulphide is reduced by excess of zinc dust and fuming hydrochloric acid in boiling benzene to the corresponding iso*sulphide*, $C_{24}H_{18}O_6S$, m. p. 146° (*dibenzoate*, m. p. 147—148°). Di-4-carbomethoxy-2-hydroxynaphthyl sulphide gives a *dipotassium* salt, whereas β-naphthol sulphide, di-6-bromo-β-naphthol 1-sulphide, di-3-carbomethyl-2-hydroxynaphthyl sulphide, and di-5-chloro-2-hydroxy-4 : 6-dimethylphenyl sulphide yield only *monopotassium* salts.



(II.)

Unsuccessful attempts to prepare unsymmetrical naphthoxthins are described. Thus α-naphthol-2-sulphonic acid is converted by ethyl chloroformate into 1-ethylcarbonatonaphthalene-2-sulphonic acid, which is transformed into the corresponding *sulphonyl chloride*, m. p. 127—128°, and subsequently reduced to 2-thiol-α-naphthol, which could not be obtained in the pure condition; the compound could not be condensed with 1-iodo-β-naphthol. 4-*Chloro*-1-*hydroxynaphthyl* 2′-*hydroxynaphthyl* 2 : 1′-*sulphide*, m. p. 167—168° (decomp.), is obtained by the action of sulphur chloride on 4-chloro-α-naphthol and β-naphthol dissolved in chloroform. H. Wren.

Lactonic esters derived from phenacyl bromide by condensation with ethyl sodiomalonate and analogous substances. R. M. Rây and J. N. Rây (J.C.S., 1925, **127**, 2721—2723).—Phenacyl bromide condenses with ethyl sodiomalonate in presence of alkali to form the *lactone* of α-carbethoxy-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid, m. p. 105°; similarly, with ethyl acetylsodiomalonate, the *lactone* of α-acetyl-α-carbethoxy-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid, m. p. 136°, is formed. Another *lactone*, m. p. 135°, is formed with ethyl sodioethylmalonate, and the condensation with ethyl sodiobenzylmalonate and with ethyl sodioisopropylmalonate yields *lactones*, m. p. 125° and 151°, respectively. On oxidation, the lactones yield benzoic acid. Phenacyl bromide and ethyl sodiocyanoacetate heated in alcoholic solution yield *ethyl diphenacylcyanoacetate*, m. p. 141°, together with a *substance*, m. p. 125—127°. B. W. Anderson.

Constitution of chlorine derivatives of the phthalonic acid series. A. Cornillot (Compt. rend., 1925, **181**, 1071—1073).—Ethyl α-chlorophthalide-α-carboxylate (cf. A., 1924, i, 515, 1071) in benzene solution on treatment with aluminium chloride yields *ethyl α-phenylphthalide-α-carboxylate*,  $CO\left<{}^{C_6H_4}_{-O-}\right>CPh\cdot CO_2Et$, m. p. 70°, and a small amount of benzhydrol-*o*-carboxylic acid. Ethyl α-phenylphthalide-α-carboxylate does not react with semicarbazide, but reacts readily with alkalis and rather less so with acids, giving α-phenylphthalide, ethyl alcohol, and carbon dioxide. The mobility of the terminal carboxyl group is thus increased by the introduction of the phenyl group into ethyl α-chlorophthalide-α-carboxylate, of which the suggested structure (*loc. cit.*) is hereby confirmed. L. F. Hewitt.

Radical dissociation of arylated succinic acid derivatives. II. Radical dissociation of tetraarylsuccinodinitriles. A. Löwenbein and R. F. Gagarin (Ber., 1925, **58**, [*B*], 2643—2644; cf. Löwenbein, A., 1925, i, 552; Blicke, *ibid.*, 811).—Since tetraphenylsuccinodinitrile undergoes radical dissociation at a somewhat inconveniently high temperature, *tetra*-p-*anisylsuccinodinitrile*, m. p. (indef.) 220—240°, has been prepared by the action of potassium ferricyanide on di-*p*-anisylacetonitrile in boiling sodium hydroxide solution. The colourless solutions of the compound in cold chloroform, alcohol, benzene, or glacial acetic acid become vivid pink when warmed, and exhibit an intense yellow fluorescence which slowly disappears when they are cooled. The presence of free di-*p*-anisylcyanomethyl radicals is established by the conversion of the product with phenylhydrazine in boiling solution into di-*p*-anisylacetonitrile. H. WREN.

Dichlorodiphenylmethanedicarboxylic acids. H. WEIL.—See B., 1926, 8.

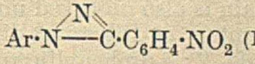
Chenodeoxycholic acid. II. A. WINDAUS and A. VAN SCHOOR (Z. physiol. Chem., 1925, **148**, 225—231).—Oxidation of sodium chenodeoxycholate with sodium hypobromite solution gives deoxybiliobanic acid, m. p. 253°, yield 20% of the pure acid (from ethyl acetate), together with 10% of the crude acid; the dimethyl ester has m. p. 107°. Chenodehydrodeoxycholic acid on oxidation with nitric acid gives a *dinitroketotricarboxylic acid*, m. p. 222° (decomp.), yield 10%; *trimethyl* ester, m. p. 156° (cf. A., 1925, i, 405). P. W. CLUTTERBUCK.

Naphthalene-1 : 4 : 5 : 8-tetracarboxylic acid and its derivatives. FARBW. VORM. MEISTER, LUCIUS, U. BRÜNING.—See B., 1926, 7.

Vat dyes [from perylenetetracarboxymonoimide]. KALLE U. Co. A.-G.—See B., 1926, 7.

Substituted *iso*diazomethanes. F. D. CHATTAWAY and A. J. WALKER (J.C.S., 1925, **127**, 2407—2414; cf. A., 1925, i, 1193).—The chlorination and bromination of *o*-nitrobenzaldehydephenylhydrazone proceeds exactly as for the *m*- and *p*-nitro-compounds (*loc. cit.*). The ω-halogen derivatives (I), however, when treated with sodium acetate and acetic acid, or with pyridine or ammonia, or even by recrystallisation from alcohol, readily lose a molecule of hydrogen halide and form 1-aryl-3-*o*-nitrophenyl*iso*diazomethanes (II). These compounds explode when

(I.) $\mathrm{Ar{\cdot}NH{\cdot}N{:}CX{\cdot}C_6H_4\,NO_2}$



(II.) $\mathrm{Ar{\cdot}N\!\!<\!\!\overset{N}{\vphantom{x}}\!\!>\!\!C{\cdot}C_6H_4{\cdot}NO_2}$

heated to a definite temperature in each case, which is lower for mixtures than for pure substances and may be used as a means of identification, in the same way as the mixed m. p.

Addition of bromine to a suspension of *o*-nitrobenzaldehydephenylhydrazone in acetic acid gives, with 1 mol. of halogen, *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone, m. p. 183°, and with 2 mols. of halogen, the 2 : 4-dibromophenylhydrazone, m. p. 204°, and ω-*bromo*-o-*nitrobenzaldehyde*-p-*bromophenylhydrazone*. This, shaken in benzene solution with a little aqueous ammonia, is converted readily into 1-p-*bromophenyl*-3-o-*nitrophenyl*iso*diazomethane*, which explodes at 144°, and is conveniently prepared by adding bromine (2 mols.) in acetic acid to *o*-nitrobenzaldehydephenylhydrazone or -*p*-bromophenylhydrazone and sodium acetate suspended in acetic acid. With 3 mols. of bromine, the product is ω-*bromo*-o-*nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 110°, from which 1-(2′ : 4′-*dibromophenyl*)-3-o-*nitrophenyl*iso*diazomethane*, exploding at 145—146°, is prepared (cf. Ciusa and Vecchiotti, A., 1916, i, 437, who give an erroneous constitution).

The following ω-bromo-*o*-nitrobenzaldehydearylhydrazones are also described, together with the related *iso*diazomethanes : 2 : 4-*dichlorophenyl*-, m. p. 122° (iso*diazomethane* explodes at 140°); 2 : 4 : 6-*trichlorophenyl*-, m. p. 115—116° (iso*diazomethane* explodes at 163°); 3 : 4 : 5-*trichlorophenyl*-, m. p. 170° (decomp.; iso*diazomethane* explodes at 151°). 1-p-*Chlorophenyl*-3-o-*nitrophenyl*iso*diazomethane* (explodes at 147°) is prepared directly.

Chlorination is more vigorous than bromination and proceeds best in chloroform. The first isolable product is *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, m. p. 192°. ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, m. p. 132°, and the 2 : 4 : 6-*trichloro*-compound, m. p. 107°, yield the same *iso*diazomethanes as the corresponding ω-bromo-derivatives. C. HOLLINS.

Chloro-1-methyl*cyclo*hexan-2-one. M. GODCHOT and P. BEDOS (Compt. rend., 1925, **181**, 919—921).—On direct chlorination in presence of chalk, or on treatment with chlorocarbamide, 1-methyl*cyclo*hexan-2-one yields 1-*chloro*-1-*methyl*cyclo*hexan*-2-*one*, b. p. 78—79°/14 mm., d^{14} 1·099, n_D^{14} 1·4696; these physical constants and the constitution assigned to the reaction product differ from those given by Kötz and Steinhorst (A., 1911, i, 210). This chlorinated ketone gives a red coloration with ferric chloride, but no tautomeride has been obtained. On distillation with pyridine, it yields 1-methyl-Δ^6-*cyclo*hexen-2-one, which on treatment with magnesium methyl iodide gives cantharenol (Haworth, J.C.S., 1913, **103**, 1246), phenylurethane, m. p. 105°. 1-Chloro-1-methyl*cyclo*hexan-2-one when treated with magnesium methyl iodide gives 1 : 1 : 2-*trimethyl*-Δ^2-cyclo*hexene*, b. p. 144—146°, d^{14} 0·862, n_D^{14} 1·459, together with a small amount of a *dimethyl*cyclo*hexadiene*.

L. F. HEWITT.

Preparation of thiosemicarbazones and semicarbazidesemicarbazones of *cyclo*hexenones and investigation of the properties of the latter compounds. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **56**, 19—44; cf. A., 1914, i, 292; 1924, i, 969).—The introduction of aromatic or heterocyclic radicals into the nuclei of *cyclo*hexenones does not influence the union of semicarbazide with the double linking, the reaction proceeding normally. If the hydroaromatic ketone contains conjugated linkings, that is, if a double linking occurs outside the nucleus, as with pulegone, or if, as in carvone, there is a second double linking within the nucleus, the double linking becomes inactive towards semicarbazide. The inactivity of the double linking of aliphatic–aromatic ketones towards semicarbazide is confirmed. Replacement of the oxygen atom of semicarbazide by a sulphur atom prevents the formation of compounds analogous to semicarbazidesemicarbazones; unsaturated αβ-hydroaromatic ketones give only thiosemicarbazones, which crystallise well and may be used for characterising *cyclo*hexenones.

The action of cold, dilute mineral or organic acid solution on semicarbazidesemicarbazones results in the detachment of the semicarbazide molecule united with the αβ-double linking of the nucleus, with formation of the semicarbazones of the *cyclo*hexenones. Semicarbazidesemicarbazones of *cyclo*hexenones are decomposed by nitrous acid, with formation of the original ketones; with those of the aliphatic series, this decomposition to ketone may be effected by change in the conditions of the reaction. Attempts to prepare nitroso-compounds of semicarbazidesemicarbazones of *cyclo*hexenones proved unsuccessful. When boiled with water, semicarbazidesemicarbazones of *cyclo*hexenones first yield semicarbazide and the corresponding semicarbazones, which then decompose into semicarbazide and the ketones and, in some cases, partly into azine and hydrazine. Boiling alkali hydroxide solutions rapidly decompose semicarbazidesemicarbazones into the ketones and tarry products. Cold hydrocyanic acid combines with neither the semicarbazones nor the semicarbazidesemicarbazones of *cyclo*hexenones. The latter are decomposed at a high temperature into ammonia, tarry matters, and probably hydrazodicarbonamide. Di- and in some instances tri-hydrochlorides of semicarbazidesemicarbazones are obtainable; the third hydrogen chloride molecule probably combines at the double linking, with the carbonyl oxygen atom united with the semicarbazide residue.

3-*Methyl*-5-*furyl*-Δ^2-cyclo*hexenonesemicarbazone*, $C_{12}H_{15}O_2N_3$, decomp. 177—178·5°, is accompanied by another *compound*, $C_{13}H_{20}O_3N_6$, when 2 mols. of the semicarbazide act on 1 mol. of the ketone. The *semicarbazidesemicarbazone*, $C_{15}H_{22}O_2N_6$, decomposes at about 201—202°.

Thiosemicarbazones of the following are described: 3-*methyl*-Δ^2-cyclo*hexenone*, $C_8H_{13}N_3S$, m. p. 136—138°; 3 : 5-*dimethyl*-Δ^2-cyclo*hexenone*, m. p. about 187°, decomp. at 194·5—195·5°; 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone*, m. p. 150—151°; 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone*, m. p. 160—161°; 3-*methyl*-5-iso*butyl*-Δ^2-cyclo*hexenone*, m. p. 128—129° (decomp.); 5-*furyl*-3-*methyl*-Δ^2-cyclo*hexenone*, decomp. at 186—187·5°; 5-*phenyl*-3-*methyl*-Δ^2-cyclo*hexenone*, m. p. 201—203° (decomp.). T. H. Pope.

Preparation of phenylcarbamic acid hydrazones of *cyclo*hexenones. I. Macurevitsch (J. Russ. Phys. Chem. Soc., 1925, 56, 45—53; cf. preceding abstract).—Borsche and Merkwitz (A., 1902, i, 186; 1904, i, 945; 1905, i, 305) have shown that the action of the semicarbazones of aliphatic, aromatic, and hydroaromatic aldehydes and ketones on primary aromatic amines results in liberation of ammonia and formation of phenylcarbamic acid hydrazones of the aldehydes or ketones, these ultimately undergoing transformation into azines. The author has investigated the reactions taking place when aniline is boiled with the semicarbazones and semicarbazidesemicarbazones of 3-methyl-, 3 : 5-dimethyl-, 3-methyl-5-ethyl-, and 3-methyl-5-*iso*propyl-Δ^2-*cyclo*hexenones, and with mesityl oxide semicarbazidesemicarbazone.

The last of these compounds, when boiled with aniline, yields hydrazocarbonamide and a *compound* containing 13·6—13·8% of nitrogen and decomposing at 234—236°. The latter is also formed, under similar conditions, from 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone-semicarbazone and -semicarbazidesemicarbazone. In every case, the reaction with aniline gives as final product the *cyclo*hexenonephenylsemicarbazone (phenylcarbamic acid hydrazone), which does not react further with aniline to form an azine (see above). These results are in agreement with Borsche's statement (A., 1902, i, 186) that, with the semicarbazones of ketones, the reaction usually stops at the first phase.

The phenylsemicarbazones obtained, which may be used for characterising the *cyclo*hexenones, are as follows: 3-*methyl*-Δ^2-cyclo*hexenone*, m. p. 173—174°; 3 : 5-*dimethyl*-Δ^2-cyclo*hexenone*, decomp. at 191—192°; 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone*, m. p. (decomp.) about 210—211°; 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone*, m. p. (decomp.) 152—153°.

T. H. Pope.

Superheating of uniform organic compounds. II. Mono- and di-ketones. S. Skraup and S. Guggenheimer (Ber., 1925, 58, [*B*], 2488—2500).—*p*-Anisyl methyl, ethyl, propyl, and *iso*propyl ketones are considerably more stable to heat than the corresponding hydrocarbons (cf. Skraup and Nieten, A., 1924, i, 1185), but at a relatively high temperature they lose water and undergo autocondensations which rapidly lead to resinification and carbonisation without apparently yielding simple organic fission products. In this respect they differ strikingly from acetophenone, which at 330° gives dypnone, diphenylfuran, and triphenylbenzene in 70% yield.

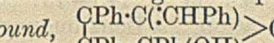
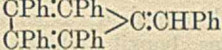
Well-defined products are obtained by superheating diketones of the type $Ar\cdot CO\cdot[CH_2]_n\cdot CO\cdot Ar$ (n=2—5), the compounds with an even number of carbon atoms being more reactive than those with an odd number. Loss of water from αδ-, αζ-, and αη-diketones occurs in much the same manner as under the influence of condensing agents, and the abnormal behaviour of αε-diketones which results in scission of the carbon chain is also observed under the influence of chemical agents. αδ-Diketo-αδ-diphenylbutane at 300—310° yield 2 : 5-diphenylfuran in 80% yield. αε-Diketo-αε-diphenylpentane at 330° affords acetophenone and, presumably, phenyl vinyl ketone, which undergoes further condensation; *αε-diketo-αε-di*-p-*chlorophenylpentane*, m. p. 117°, prepared in unsatisfactory yield from glutaryl chloride and chlorobenzene, appears to yield *p*-chloroacetophenone. αζ-Diketo-αζ-diphenylhexane appears to be converted at 300—310° into a mixture of 2-benzoyl-1-phenyl-Δ^5-*cyclo*pentene and 2-benzoyl-1-phenyl-Δ^1-*cyclo*pentene. Adipyl chloride and chlorobenzene in the presence of aluminium chloride yield *αζ-diketo-αζ-di*-p-*chlorophenylhexane*, m. p. 166—167°, and *δ*-p-*chlorobenzoylvaleric acid*, m. p. 130°; if excess of aluminium chloride is employed and the temperature is allowed to rise during the reaction, a partial condensation of the diketone to 2-p-*chloro*-

benzoyl-1-p-*chlorophenyl*-Δ^5-cyclo*pentene*, m. p. 130°, occurs, although this substance could not be obtained by the action of aluminium chloride on pre-formed diketone. When concentrated sulphuric acid is used as condensing agent the diketone affords 2-p-*chlorobenzoyl*-1-p-*chlorophenyl*-Δ^1-cyclo*pentene*, m. p. 108°. A mixture of the *cyclo*pentene derivatives is obtained from the diketone at 255—265°, whereas at a higher temperature secondary changes occur, causing polymerisation and carbonisation with production of *p*-chlorobenzoic acid. αη-Diketo-αη-diphenyl-*n*-heptane at 325—330° affords a mixture of 2-benzoyl-1-phenyl-Δ^6-*cyclo*hexene and 2-benzoyl-1-phenyl-Δ^1-*cyclo*hexene. Pimelyl chloride and chlorobenzene in the presence of aluminium chloride yield *αη-diketo-αη-di*-p-*chlorophenylheptane*, m. p. 112°, and ε-p-*chlorobenzoylhexoic acid*, m. p. 139—140°. The diketone is not affected by concentrated sulphuric acid at 100°, but when heated at 285—295°, gives *p*-chlorobenzoic acid and a *substance*, $C_{19}H_{15}OCl_2$, m. p. 156°, thus indicating the probable production of a mixture of 2-*p*-chlorobenzoyl-1-*p*-chlorophenyl-Δ^6- and -Δ^1-*cyclo*hexenes. H. WREN.

Mechanism of reduction. VI. H. J. PRINS (Rec. trav. chim., 1925, **44**, 1093—1100; cf. A., 1925, ii, 1169).—The difference between reducing agents is discussed in terms of the degree of activation of the hydrogen atom. Experiments on the reduction in acid media of benzophenone with formation of benzopinacone and benzhydrol show that the theory of alkalinity of the metallic surface (Böeseken and Cohen, A., 1913, i, 1062) is incorrect. The formation of hydrol depends on the ratio between the velocity of condensation and of reduction of the half-pinacone, $CPh_3{\cdot}OH$, both of these reactions taking place on the metallic surface. Increase in the active surface and decrease in the reduction velocity both tend towards pinacone formation, so that with aluminium amalgam in alcoholic hydrochloric acid solution only pinacone is obtained. R. W. WEST.

Transformation of trisubstituted aldehydes into disubstituted ketones. A. ORÉKHOV and M. TIFFENEAU (Compt. rend., 1926, **182**, 67—69).—The transformation of aldehydes of the type $CR'_2R''{\cdot}CHO$ into the ketones $CHR'R''{\cdot}CO{\cdot}R'$ and $CHR'_2{\cdot}CO{\cdot}R''$ by the agency of cold sulphuric acid has been studied (cf. Danilov, A., 1923, i, 680, 787, 788). αα-Diphenylpropaldehyde yields exclusively phenyl α-phenylethyl ketone; αα-diphenylbutaldehyde gives a mixture of about 66% of phenyl α-phenylpropyl ketone and about 33% of diphenylmethyl ethyl ketone; α-phenyl-α-methylpropaldehyde gives solely α-phenylethyl methyl ketone and α-phenyl-α-ethylbutaldehyde yields exclusively α-phenylpropyl ethyl ketone. These products are the same as those obtained by the action of sulphuric acid on the corresponding glycols from which the aldehydes are obtained (cf. A., 1921, i, 565, 788; 1922, i, 458; 1923, i, 333, 788, 789; 1924, i, 729). It would thus seem that the transformation of the glycols and hydrobenzoins into ketones is not a semipinacolinic transformation, but takes place *via* the trisubstituted aldehyde. L. F. HEWITT.

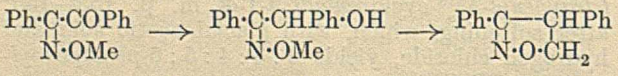
Phenyl α-acenaphthyl ketone and phenyl-α-acenaphthylmethane. K. DZIEVOŃSKI and M. RYCHLIK (Bull. Intern. Acad. Polonaise, 1925, A., 179—195).—See this vol., 70.

Synthesis of substituted indones and *cyclo*pentadienones. A. LÖWENBEIN and G. ULICH (Ber., 1925, **58**, [*B*], 2662—2667).—Benzylidenediphenylmaleide, dissolved in benzene, is converted by an ethereal solution of magnesium phenyl bromide into the *compound*,  $\left.\begin{matrix}CPh{\cdot}C(:CHPh)\\ |\\ CPh{-}CPh(OH)\end{matrix}\right>O$, m. p. 210° (decomp.), the constitution of which rests on analyses, indifference towards ketonic reagents, insolubility in aqueous sodium hydroxide, and indifference towards Grignard's reagents. It is converted by treatment with alcoholic sodium hydroxide, or, preferably, with sulphuric acid or hydrogen chloride in glacial acetic acid, into 2 : 3 : 4 : 5-*tetraphenyl*-$\Delta^{2:4}$-cyclo*pentadien*-1-*one*, having an intense violet-black colour, m. p. 218°. The ketone is transformed by magnesium benzyl chloride into 1-*benzyl*-2 : 3 : 4 : 5-*tetraphenyl*-$\Delta^{2:4}$-cyclo*pentadien*-1-*ol*, m. p. 155—156° after softening, which, with glacial acetic acid and hydrogen chloride, yields 2 : 3 : 4 : 5 : 6-*pentaphenylfulvene*,  $\left.\begin{matrix}CPh{:}CPh\\ |\\ CPh{:}CPh\end{matrix}\right>C{:}CHPh$, m. p. 204°; the latter compound is also obtained by condensing 2 : 3 : 4 : 5-tetraphenyl-$\Delta^{2:4}$-*cyclo*pentadiene with benzaldehyde.

Benzylidenephthalide is converted by magnesium phenyl bromide into 2 : 3-diphenylindone, m. p. 150—151°; the compound does not appear to be the primary product of the change, since the yield is increased by increasing the relative proportion of the Grignard reagent and the solution is only pale yellow in colour, passing into the intensely red colour of the indone after hydrolytic decomposition of the solution. H. WREN.

Methylation of the oximes of benzil. O. L. BRADY and H. M. PERRY (J.C.S., 1925, **127**, 2874—2882).—A reinvestigation of the methyl ethers of the oximes of benzil, using methyl sulphate as the methylating agent, abolishes confusion in the literature of these compounds (cf. Auwers and Meyer, A., 1889, 403; Dittrich, A., 1891, 317). The constitutions of the ethers are established by heating with hydriodic acid and determining the methyl iodide obtained from the *O*-ethers and by detecting the methylamine from the *N*-ethers by Valton's method (A., 1925, ii, 446). The usual configurations are adopted for the oximes, and not those suggested by Meisenheimer. α-Benzildioxime yields α-*benzildioxime* NN-*dimethyl ether*, $C_{16}H_{16}O_2N_2,\frac{1}{2}C_6H_6$, m. p. 185° [anhyd., m. p. 192° (decomp.)], and α-benzildioxime *NO*-dimethyl ether, m. p. 109° (Auwers and Meyer, m. p. 109—110°). Methylation with methyl iodide yields the latter compound together with α-benzildioxime *OO*-dimethyl ether, m. p. 163—164° (Auwers, m. p. 165°), which could not be obtained by use of methyl sulphate. β-Benzildioxime, obtained by an improved method by solution of α-benzildioxime in boiling aniline and removal of aniline of crystallisation from the crystalline deposit, gives β-benzildioxime *NO*-dimethyl ether, m. p. 102—103°

(identical with Auwers' compound, m. p. 88—89°), and β-benzildioxime *OO*-dimethyl ether, m. p. 72—73° (Auwers, m. p. 72°). Attempts to prepare the *NN*-dimethyl ether were unsuccessful. γ-Benzildioxime gives γ-benzilmonoxime *O*-methyl ether and benzil, probably formed respectively by hydrolysis of an *ON*-dimethyl ether and of an *NN*-dimethyl ether, since the *N*-methyl compounds are unusually easily hydrolysed. Methylation with methyl iodide gave crystals of a *compound*, m. p. 145—157°, insufficient for further purification. α-Benzilmonoxime gives α-benzilmonoxime *O*-methyl ether, m. p. 58—59° (Dittrich, m. p. 62—63°). The *N*-methyl ether could not be obtained. γ-Benzilmonoxime gives *γ-benzilmonoxime* N-*methyl ether*, m. p. 109—110°, and γ-benzilmonoxime *O*-methyl ether, m. p. 63° (Dittrich, m. p. 64—65°). The latter gives curiously low analytical results for methoxyl. A possible explanation, based on Meisenheimer's configuration, and involving reduction of the carbonyl group and ring formation by elimination of water, is being investigated :

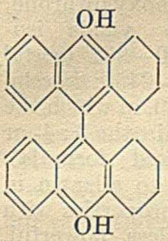


$$\mathrm{Ph{\cdot}\underset{N{\cdot}OMe}{\overset{}{C}}{\cdot}COPh} \longrightarrow \mathrm{Ph{\cdot}\underset{N{\cdot}OMe}{C}{\cdot}CHPh{\cdot}OH} \longrightarrow \mathrm{Ph{\cdot}\underset{N{\cdot}O{\cdot}CH_2}{C{-}{-}CHPh}}$$

On boiling with hydrochloric acid, α-benzildioxime *NN*-dimethyl ether gives benzil, whilst the *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether, probably through α-benzilmonoxime *O*-methyl ether, which is converted into the γ-compound under these conditions. β-Benzildioxime *ON*-dimethyl ether also gives γ-benzilmonoxime *O*-methyl ether. α-Benzildioxime *OO*-dimethyl ether, when heated with concentrated hydrochloric acid in a sealed tube at 110°, gives β-benzildioxime *OO*-dimethyl ether. The *O*-ethers are exceptionally stable to hydrolysing agents, whereas the *N*-ethers are readily hydrolysed; the latter form hydrochlorides, the former do not; and the β-forms of the dioximes and the γ-forms of the monoximes are the most stable at high temperatures.
M. JOHNSON.

Hydrobenzoin transformation. II. *s*-Phenylanisyl glycol (*p*-methoxyhydrobenzoin). A. OREKHOV and M. TIFFENEAU (Bull. Soc. chim., 1925, [iv], **37**, 1410—1420; cf. A., 1923, i, 333).—*s*-Phenylanisyl glycol, $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHPh{\cdot}OH$, on dehydration with 20% sulphuric acid, partly undergoes the usual "pinacoline dehydration," yielding phenyl-*p*-anisylacetaldehyde, $OMe{\cdot}C_6H_4{\cdot}CHPh{\cdot}CHO$, but is also partly converted into *p*-methoxydeoxybenzoin, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}COPh$, by "vinyl dehydration," thus $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHPh{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}COPh$. Since the alternative "vinyl dehydration" $\longrightarrow OMe{\cdot}C_6H_4{\cdot}C(OH){:}CHPh \longrightarrow OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$, does not take place, it is concluded that the hydroxyl group in the neighbourhood of the anisyl group is less stable than that attached to the carbon atom carrying the phenyl group, a result which indicates that the affinity of the anisyl group is greater than that of the phenyl group. Since hydrobenzoin under similar conditions gives exclusively diphenylacetaldehyde, it is evident that the introduction of a *p*-methoxy-group diminishes the tendency of the eliminated hydroxyl group to take with it hydrogen from the adjacent hydroxyl group rather than from the carbon in the dehydration process. p-*Anisylbenzyl carbinol*, $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH_2Ph$, m. p. 57—58°, obtained in 88% yield from magnesium benzyl chloride and anisaldehyde (cf. C. Hell, A., 1904, i, 242), is readily converted (yield 84%) by 50% sulphuric acid into s-*phenyl*-p-*anisylethylene* (p-*methoxystilbene*), m. p. 135—136°. This gives a *dibromide*, m. p. 175—176° (decomp.), reconverted by aqueous acetone into *p*-methoxystilbene; potassium carbonate converts it into p-*methoxytolane*, m. p. 89—90° [*dibromide*, m. p. 166—167° (decomp.)], whilst sodium acetate and acetic acid yield a mixture of a crystalline, m. p. 65—75°, and an oily *diacetate*, probably stereoisomerides. On hydrolysis with alcoholic potassium hydroxide the former yields *phenyl*-p-*anisyl glycol*, m. p. 111—112°, whilst from the oily diacetate the stereoisomeric glycol, m. p. 134—135°, is obtained similarly. Both isomerides on dehydration yield a mixture of *p*-methoxydeoxybenzoin and *phenyl*-p-*anisylacetaldehyde*, a viscous oil (*semicarbazone*, m. p. 127—128°), oxidised to phenyl-*p*-anisyl ketone by chromic and acetic acids. Phenyl-*p*-anisylacetaldehyde is obtained more readily by the action of dry potassium hydroxide on the iodohydrin of *as*-phenyl-*p*-anisylethylene in ethereal solution. The oily product, probably the ethylene oxide, on treatment with sodium hydrogen sulphite yields the hydrogen sulphite compound of phenyl-*p*-anisylacetaldehyde, from which the aldehyde is obtained on hydrolysis with 10% sodium carbonate.
R. BRIGHTMAN.

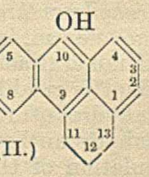
Catalytic hydrogenations under pressure in the presence of nickel salts. IX. Anthraquinone, phenanthraquinone, and benzanthrone. J. VON BRAUN and O. BAYER (Ber., 1925, **58**, [*B*], 2667—2685).—Confirmation of the view of von Braun (A., 1924, i, 545) and Schroeter (A., 1925, i, 127) that 9 : 10-dihydroanthracene is the primary product of the catalytic hydrogenation of anthracene and that this compound passes subsequently into 1 : 2 : 3 : 4-tetrahydroanthracene is found in the behaviour of dihydroanthranol, which is reduced in decahydronaphthalene solution to 1 : 2 : 3 : 4-tetrahydroanthranol (yield 15%), 9 : 10-dihydroanthracene, and 1 : 2 : 3 : 4-tetrahydroanthracene. Whether catalytic hydrogenation of anthracene occurs exclusively through the 9 : 10-dihydro-compound or whether the primary attack takes place also at the side nucleus cannot be decided for the hydrocarbon, but a decision can be reached for its oxygenated derivatives using anthranol as starting point; if hydrogenation occurs initially in the 9 : 10-position, the yield of tetrahydroanthranol from this substance cannot, under identical conditions, exceed that from dihydroanthranol. Actually the yield is far greater, so that for anthranol the primary attack occurs mainly or possibly exclusively at the side nucleus. The possibility that tetrahydroanthranol is readily attacked by hydrogen with elimination of the hydroxy-group and formation of tetrahydroanthracene is invalidated by the observation that it absorbs hydrogen less readily than anthranol or dihydroanthranol and yields successively 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthranol and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene, m. p. 39° (Schroeter, *loc. cit.*, records m. p. 35°). Anthraquinone is hydrogenated with great ease under pressure, the first isolable product being anthranol, which, if the supply of hydrogen is suitably controlled, is obtained in quantitative yield; further addition of hydrogen leads to the production of tetra- and octa-hydroanthranols. 1 : 2 : 3 : 4-*Tetrahydroanthranol*, m. p. 108°, its *acetate*, m. p. 109°, *benzoate*, m. p. 142°, and *methyl ether*, b. p. 197° /14 mm. (slight decomp.), are described. It does not give a coloration with ferric chloride. With bromine in glacial acetic acid, it affords a *monobromo*-derivative, m. p. 123°. Chromic acid in glacial acetic acid oxidises it to a mixture of little anthraquinone and much 1 : 2 : 3 : 4-tetrahydroanthraquinone, m. p. 154° (cf. Schroeter, *loc. cit.*). It is converted by nitric acid into black, smeary products. Nitrous acid acts on a 10% solution of it in alcohol, precipitating *di-tetrahydrodianthranol*, (I), m. p. 167°, and giving also tetrahydroanthraquinone and the *nitroso*-derivative, $C_{14}H_{13}O_2N$, m. p. 210°; in more concentrated solution, the nitroso-compound is obtained in better yield, accompanied by tetrahydroanthraquinone substances, difficult to characterise, but ditetrahydrodianthranol is not formed. It couples very readily with diazonium salts, but the products crystallise with difficulty; reduction of the benzeneazo-derivative by sodium hyposulphite gives *aminotetrahydroanthranol*, which could not be caused to crystallise; the *hydrochloride* is described. 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 - *Octahydroanthranol*, m. p. 125°, is very sparingly soluble in alkali hydroxide solutions; the *acetyl* derivative, m. p. 52°, *benzoyl* compound, m. p. 128°, and p-*bromo*-derivative, m. p. 123°, are described. It is oxidised by chromic acid in acetic acid solution to *octahydroanthraquinone*, m. p. 182°, which is quantitatively reduced by sodium hyposulphite to *octahydroanthraquinol*, m. p. 234—236°. Nitric acid transforms it into an amorphous compound, m. p. above 300°. Nitrous acid yields the corresponding *nitroso*-derivative, m. p. 190°, together with octahydroanthraquinone and *dioctahydrodianthranol*, which could not be obtained in the homogeneous state. *Benzeneazooctahydroanthranol*, m. p. 163°, is smoothly reduced by sodium hyposulphite in alcoholic solution to 9-*amino-octahydroanthranol*, which is insoluble in alkali hydroxide solutions and very sparingly soluble in acids; its constitution is, however, established by its oxidation to octahydroanthraquinone.



(I.)

Hydrogenation of phenanthraquinone proceeds similarly to that of anthraquinone, affecting first the quinone complex and subsequently one side nucleus after the other. Differences are found in the possibility of so moderating the reduction of phenanthraquinone that phenanthraquinol in addition to 9-phenanthrol can be isolated, thus clearly establishing the first step in the action. Also, owing to the lower stability of the hydrogenated derivatives of phenanthrene in comparison with those of anthracene, the individual products are obtained in lower yield, and it is not possible to trace the several phases of the change in so quantitative a manner. Phenanthraquinone dissolved in decahydronaphthalene readily absorbs two atomic proportions of hydrogen at 160°, yielding 9-phenanthrol, m. p. 149—150° (acetate, m. p. 76°), and phenanthraquinol, m. p. 148°. Further hydrogenation occurs only at a much higher temperature and, after eight atomic proportions of hydrogen have been absorbed, gives a mixture of di- and *tetra-hydrophenanthrol*, m. p. 114—115°; the acetyl, benzoyl, *p*-nitrobenzoyl, bromo-, and benzeneazo-derivatives are oily or badly crystallised, pointing to the possibility that the tetrahydro-compound is a mixture of two isomeric forms, although this view is not supported by its definite m. p. and non-separability by solvents. It is oxidised by chromic acid in glacial acetic acid solution to *tetrahydrophenanthraquinone*, decomp. 90—100°, according to the rate of heating. More complete hydrogenation of phenanthraquinone or 9-phenanthrol affords a mixture of octahydrophenanthrene (cf. Schroeter, *loc. cit.*) and *octahydrophenanthrol*, m. p. 133° (*acetyl* derivative, m. p. 133°; *monobromo*-derivative, m. p. 110°). The phenol is oxidised by chromic acid to *octahydrophenanthraquinone*, decomp. 150°. It couples with diazobenzene, yielding *benzeneazo-octahydrophenanthrol*, m. p. 140°, which is reduced by sodium hyposulphite to *aminohydroxyoctahydrophenanthrene*, m. p. 184°.

Technical benzanthrone is readily purified by recrystallisation from decahydronaphthalene and in this solvent absorbs four atomic proportions of hydrogen at 160°, a further four somewhat more slowly at 200°, and the final two at 250°. 1 : 9-*Trimethyleneanthranol*, (II), m. p. 148°, readily yields a *benzoyl* derivative, m. p. 135°. [In naming these derivatives, it does not appear possible to express the genetic relationship to benzanthrone in any simple manner, and the authors propose to regard them as substituted anthracene derivatives in which the fourth ring is 1 : 9-trimethylene.] 1 : 9-*Trimethylene*-5 : 6 : 7 : 8-*tetrahydroanthranol*, m. p. 137° (*acetate*, m. p. 123°), is obtained together with 1 : 9-*trimethylene*-5 : 6 : 7 : 8-*tetrahydroanthracene*, b. p. 228—230°/16 mm. (*picrate*, m. p. 125°), at 180—200°; at 250°, the hydrocarbon is practically the sole product of the change, even when the reaction is very prolonged. It is not smoothly dehydrogenated by sulphur or oxidised by nitric acid. Treatment of 1 : 9 - trimethylene - 5 : 6 : 7 : 8 - tetrahydroanthracene with sodium and alcohol yields a hydrocarbon, b. p. 212—214°/13 mm., which by analogy with the mode of reduction of naphthalene, is regarded as 1 : 9-*trimethylene*-1 : 4 : 5 : 6 : 7 : 8-*hexahydroanthracene*; it immediately decolorises permanganate and gives an oily dibromide. H. WREN.



(II.)

Preparation of hydrogenated, polynuclear quinones. A. SKITA [with K. WARNAT, C. WULFF, H. SIEGEL, and B. SCHREYER] (Ber., 1925, 58, [*B*], 2685—2697).—The methods adopted previously for the reduction of anthraquinone and similar substances lead to products poorer in oxygen. It is therefore remarkable that catalytic hydrogenation of *para*- and *ortho*-quinones in the presence of platinum affords nuclear-hydrogenated quinols or glycols which are readily oxidised to hydrogenated quinones.

Phenanthraquinone in the presence of glacial acetic acid, concentrated hydrochloric acid, chloroplatinic acid, colloidal platinum, and water readily absorbs twelve atomic proportions of hydrogen at 50—60°, yielding 9 : 10-*dihydroxydecahydrophenanthrene*, b. p. 352—355°, m. p. 136° (*diacetate*, m. p. 160°), which is oxidised by boiling, dilute mercuric acetate solution to *octahydrophenanthraquinone*, m. p. 142° (cf. p. 173). If the mineral acid is omitted, the reaction terminates with the production of 9 : 10-*dihydroxy*-9 : 10-*dihydrophenanthrene* (*diacetate*, m. p. 183°).

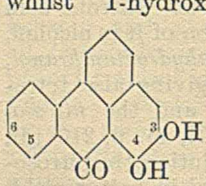
Anthraquinone in acid solution in the presence of colloidal platinum affords octahydroanthraquinol, m.p. 242° (*acetate*, m. p. 224°), which is converted by the action of air on its solution in benzene or acetone into octahydroanthraquinone, m. p. 183°. The quinol or quinone is transformed by bromine into *octahydroanthraquinone dibromide*, m. p. 128°. The mother-liquors from the preparation of octahydroanthraquinol contain octahydroanthranol, m. p. 125° (benzoate, m.p. 129°); bromo-octahydroanthranol, m.p. 123°, and the *acetate*, m. p. 143°, are described (see p. 173). It is remarkable that the hydrogenation of anthraquinone under these conditions does not invariably proceed to the production of the octahydroanthraquinol, but sometimes ceases when tetra- or hexahydroanthraquinol has been produced; the phenomenon appears to depend on the size of the colloidal platinum particles. The isolation of *tetrahydroanthraquinol*, decomp. (indef.) 206—216° (*acetate*, m. p. 204—206°), is effected with certainty if mineral acid is omitted from the mixture; the quinol is readily oxidised by air to 1 : 2 : 3 : 4-tetrahydroanthraquinone. Certain reduction to the hexahydroanthraquinol stage is effected by careful regulation of the quantities of hydrochloric acid and platinum. 1 : 2 : 3 : 4 : 5 : 8-*Hexahydroanthraquinone*, m. p. 170°, and its *dibromide*, m. p. 118°, are described; the position of the hydrogen atoms is deduced from the conversion of the quinone by sodium acetate and acetic anhydride into 1 : 2 : 3 : 4-tetrahydroanthraquinol diacetate, m. p. 204—206° (see above). 1 : 2 : 3 : 4 : 5 : 8-*Hexahydroanthraquinol* has m. p. 229—230° (*diacetate*, m. p. 209°); an isomeric *diacetate* of hexahydroanthraquinol, m. p. 212°, is obtained by the reduction of tetrahydroanthraquinone with acetic acid and excess of zinc dust.

Reduction of 2-methylanthraquinone in the presence of mineral acid affords 2-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinol*, m. p. 193° (*diacetate*, m. p. 143°), which is very readily oxidised to 2-*methyl-octahydroanthraquinone*, m. p. 158—159°. Similarly, 2-aminoanthraquinone yields 2-amino-octahydroanthraquinol (*hydrochloride*, m. p. above 300°), which is converted by air into 2-*amino-octahydroanthraquinone*, m. p. 140—145°.

Hydrogenation of acenaphthenequinone under the conditions described for anthraquinone proceeds with unusual ease, and if reaction is stopped after the absorption of ten atomic proportions of hydrogen, gives a mixture of products from which the following compounds are isolated: a *dihydroxytetrahydroacenaphthene*, b. p. 185°/9 mm., which gives a *diacetate*, m. p. 115—116°; *hexahydroacenaphthene*, $C_{12}H_{16}$, b. p. 114—115°/10 mm.; more highly hydrogenated acenaphthenequinones from which individual substances could not be isolated; and a *substance*, $C_{24}H_{30}O_4$, m. p. 206°. H. WREN.

Reduction products of the hydroxyanthraquinones. VII. W. B. MILLER and A. G. PERKIN (J.C.S., 1925, **127**, 2684—2685).—Alizarin 2-methyl ether yields on reduction chiefly 1-*hydroxy*-2-*methoxyanthrone*, m. p. 135—137° (*diacetyl* derivative, m. p. 202°), with 4-*hydroxy*-3-*methoxyanthrone*, m. p. 202° (*acetyl* derivative, m. p. 186°), in smaller amounts. By the benzanthrone reaction *benzalizarin monomethyl ether*, m. p. 247—249° (*acetyl* derivative, m. p. 205—207°), is obtained from 4-hydroxy-3-methoxyanthrone, whilst 1-hydroxy-2-methoxyanthrone yields *isobenzalizarin*, m. p. 260—262° (*acetyl* derivative, m. p. 243—245°; *diacetyl* derivative, m. p. 214°), in which the hydroxyl groups are in the 3 : 4- or 5 : 6-positions (annexed formula). Benzalizarin is akin to alizarin in its powerful dyeing properties with mordants; *iso*benzalizarin is much less powerful. This suggests that the dyeing properties of alizarin are due to the presence of a *para*-quinonoid rather than an *ortho*-quinonoid grouping. *Anthrapurpurin dimethyl ether*, m. p. 235° (*acetyl* derivative, m. p. 205°), has been prepared, and from it *diacetylanthrapurpurinanthranol dimethyl ether*, m. p. 178°, was obtained by reduction followed by acetylation.

B. W. ANDERSON.



Action of hydrazine hydrate on phenanthraquinone. Correction. S. DUTT (J.C.S., 1925, **127**, 2971; cf. *ibid.*, 1923, **123**, 3420).—Anhydrous hydrazine reacts with phenanthraquinone in absolute alcohol, giving a good yield of phenanthrone. In presence of small quantities of moisture or with ordinary commercial hydrazine hydrate, 9 : 10-dihydroxyphenanthrene is obtained almost exclusively. M. JOHNSON.

1-Benzoylbenzanthrone. FARBW. VORM. MEISTER, LUCIUS, U. BRÜNING.—See B., 1926, 44.

Menthone series. I. J. READ and A. M. R. COOK (J.C.S., 1925, **127**, 2782—2788).—The alkaline reduction of *dl*-piperitone yields some *dl*-α-phellandrene and a mixture of *dl*-*iso*menthols, from which *dl*-*iso*menthone is obtained by oxidation with chromic acid, and this on reduction yields crystalline *dl*-menthol with some *dl*-*iso*menthols. Reduction of *dl*-piperitone with hydrogen in presence of colloidal palladium yields *dl*-*iso*menthone direct. There exists a definite dynamic equilibrium between *iso*menthone and menthone in the presence of alkali. From pure *dl*-*iso*menthone have been obtained the *oxime*, m. p. 99—100°, *benzoyloxime*, m. p. 55·5°, and *iso*oxime, m. p. 94—95°. *dl*-Menthone yields an oxime, m. p. 81—82°, *benzoyloxime*, m. p. 72—73°, iso*oxime*, m. p.

114—115°, *α-semicarbazone*, m. p. 185—186°, and *β-semicarbazone*, m. p. 161—162°. B. W. ANDERSON.

Determination of menthol in alcoholic solution. DONATH and SEBOR.—See B., 1926, 75.

Carbylamines. XIII. Reaction of phenylcarbylamine with pernitrosomenthone. M. PASSERINI (Gazzetta, 1925, **55**, 721—726).—Pernitrosomenthone dissolved in the smallest possible quantity of ether is treated with phenylcarbylamine. The crystals collected after 8 to 10 days consist of *α-mentholcarboxy-δ-anilide* (I), m. p. 166—168°, $[\alpha]_D^{10}+62{\cdot}62°$; a small yield of an *isomeride*, m. p. 134—136°, is also obtained. When compound (I) is heated for 80 hrs. with alcoholic potassium hydroxide in a closed tube at 120—130°, *α-mentholcarboxylic acid*, m. p. 112—113°, is formed. Compound (I) is oxidised by potassium dichromate and sulphuric acid to *l*-menthone, which is characterised by its oxime and its semicarbazide. W. E. ELLIS.

Action of phosphoric acid on terpenes etc. P. G. CARTER, H. G. SMITH, and J. READ.—See B., 1926, 75.

Rhodesian eucalyptus oils. P. G. CARTER and J. READ.—See B., 1926, 76.

Chemico-physical investigations on certain acid phthalates of terpenic alcohols. V. PAOLINI (Annali Chim. Appl., 1925, **15**, 411—413).—The solution of a weak acid containing the salt of a strong base with the same acid obeys approximately the relationship: $\log(1/[H^+]) = \log(1/K_a) + \log([S]/[A])$, where $[H^+]$ is the hydrogen-ion concentration of the solution, K_a the dissociation constant of the weak acid, [S] the concentration of the salt, and [A] the concentration of the free acid in the same solution. Measurements made with acid phthalates at 25° in accordance with this equation give the following mean values for the dissociation constants: β-thujyl hydrogen phthalate, $7{\cdot}5\,.\,10^{-6}$; *l*-β-carvomenthyl hydrogen phthalate, $3{\cdot}02\,.\,10^{-6}$; *l*-α-terpinyl phthalate, $1{\cdot}42\,.\,10^{-5}$. T. H. POPE.

Isomeric thujones (tanacetones). *d*-α-Thujones. V. PAOLINI (Annali Chim. Appl., 1925, **15**, 414—416).—If α-thujonesemicarbazone is hydrolysed by phthalic anhydride (cf. A., 1912, i, 635), the resulting α-thujone has $[\alpha]_D+10{\cdot}23°$, whereas that obtained by Wallach by mineral acid hydrolysis has $[\alpha]_D-10{\cdot}23°$ (A., 1905, i, 147). When, however, the thujone given by the semicarbazone and phthalic anhydride is displaced, as it is formed, by a current of steam, the lævorotatory modification is obtained. Conversion into the dextrorotatory isomeride is evidently due to prolonged action of the hydrogen ions. T. H. POPE.

Camphor series. X. Synthesis of camphor. I. Catalytic action of reduced copper on borneols. B. MASUMOTO (Mem. Coll. Sci. Kyōtō, 1925, **9**, 219—224).—The oxidation of *d*- and *l*-borneols to camphor takes place without any side reactions when reduced copper at 200—220° is employed as a catalyst. Copper oxide, prepared from copper nitrate and sodium hydroxide and reduced with hydrogen at 200°, furnishes the best copper catalyst. No borneol is formed when camphor vapour and hydrogen are together passed over reduced copper. B. W. ANDERSON.

Camphor from turpentine oil. Y. MURAYAMA.—See B., 1926, 75.

Making *iso*bornyl esters. J. EBERT.—See B., 1926, 28.

Constituents of rosins and rosin oil, and polymerisation of turpentine oil. E. KNECHT and N. B. MAURICE.—See B., 1926, 21.

Nepetella, pennyroyal, and origanum oils. G. ROMEO and U. GIUFFRÈ.—See B., 1926, 107.

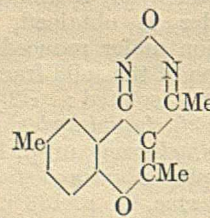
Vinylene-homologous furfuraldehydes. W. KÖNIG [with K. HEY] (Ber., 1925, **58**, [*B*], 2559—2566].—Aldehydes of the type, $C_4H_3O\cdot[CH{:}CH]_n\cdot CHO$, are obtained by the condensation of furfuraldehyde with acetaldehyde in cold, aqueous alkaline solution. The depth of colour of the compounds increases with increasing number of vinylene groups, but the increment per group, as measured by the displacement of the maximum of absorption, diminishes somewhat as the series is ascended. The depth of colour of the adducts of the aldehydes and stannic chloride or hydrogen chloride increases with increasing number of vinylene groups. 2-Furylacraldehyde (*streptomonovinylenefurfuraldehyde*; for nomenclature see A., 1924, i, 669), m. p. 54° (*oxime*, m. p. 123°), is prepared in 60% yield by the interaction of furfuraldehyde and acetaldehyde at 0° in the presence of dilute aqueous sodium hydroxide. With more concentrated alkali hydroxide at 20° and with an increased proportion of acetaldehyde, a mixture of vinylene-homologous aldehydes is obtained, from which, by fractional distillation under reduced pressure followed by crystallisation of the solid fractions, the following individuals are isolated: ε-2-*furylpentadienal* (2-strepto*divinylenefurfuraldehyde*), m. p. 66° (*oxime*, m. p. 127°; *phenylhydrazone*, m. p. 153°); *η-2-furylheptatrienal* [2-strepto*trivinylenefurfuraldehyde*), m. p. 111° (*phenylhydrazone*, m. p. 183°). H. WREN.

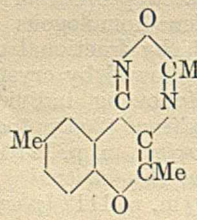
Stereochemistry of the oximes of 1 : 3-diketones. I. Action of hydroxylamine on 3-acetyl-2 : 6-dimethylchromone. G. WITTIG and F. BAUGERT (Ber., 1925, **58**, [*B*], 2627—2636).—The possibilities of ring opening to compounds of the *cis*- or *trans*-configuration are critically discussed from a theoretical point of view (cf. Meisenheimer, A., 1922, i, 152; Kuhn and Ebel, A., 1925, i, 780, 1237; Böeseken, *ibid.*, 1237) and, for present purposes, the views of Meisenheimer are adopted.

3-Acetyl-2 : 6-dimethylchromone is converted by hydroxylamine in acetic acid solution into a mixture of 3-*acetyl*-2 : 6-*dimethylchromone-γ-monoxime*, m. p. 100—100·5°, which is very stable towards hydrochloric acid and does not undergo the Beckmann change when treated with concentrated sulphuric and glacial acetic acids or with acetyl chloride, and 3-*acetyl*-2 : 6-*dimethylchromone-α-dioxime*, m. p. 222—224° (decomp.). Oximation of the yellow monoxime, m. p. 100—100·5°, in the presence of cold sodium hydroxide solution, affords 3-*acetyl*-2 : 6-*dimethyl-*

chromone-γ-dioxime, m. p. 159—159·5°, or, if slowly heated, m. p. 165—167° after softening at 159—159·5°, which is unaffected by sodium alkoxide solution, boiling water, or sodium carbonate solution, or by cold sulphuric acid; it is hydrolysed to the γ-monoxime by boiling hydrochloric acid. With acetyl chloride it yields the corresponding *diacetate*, m. p. 131—132°. When the γ-dioxime is boiled with 2*N*-sodium hydroxide solution or distilled under diminished pressure it is converted into 3 : 4-2′ : 6′-*dimethylchromo*-5-*methyl*-2 : 6-*oxdiazine* (I), m. p. 88—88·5°, whereas, when treated with concentrated sulphuric acid, phosphorus pentachloride, or acetyl chloride, it yields the isomeric 3 : 4-2′ : 6′-*dimethylchromo*-6-*methyl*-2 : 5-*oxdiazine*, (II), m. p. 144—144·5°. During the second change, the Beckmann isomerisation occurs in the oximated side-chain, leading to the production of a pyrazolone or oxdiazine ring; since the product is not basic and does not react with hydroxylamine, the former possibility is excluded. If Meisenheimer's views are adopted, the configuration (III) or (IV) follows for the dioxime, and its ability to lose water and form compound (I) decides in favour of (IV). Since the γ-monoxime is formed from the dioxime by concentrated hydrochloric acid and itself does not undergo the Beckmann change, and therefore has the oximino-group attached to the nucleus (which is also shown by the stability of the pyrone ring towards alkalis), it must have the configuration (V). Protracted treatment of the γ-monoxime with boiling 2*N*-sodium carbonate solution leads to the production of 3-*acetyl*-2 : 6-*dimethylchromone*-α-*monoxime*, m. p. 157°, which is not reconverted into the γ-oxime by hot, concentrated acids. Since further oximation transforms it into 3-acetyl-2 : 6-dimethylchromone-α-dioxime, it follows that the pyrone ring does not suffer fusion followed by re-closure to a structurally isomeric oxime during the action of the alkali. The monoxime must therefore have the constitution (VI). During the oximation of 3-acetyl-2 : 6-dimethylchromone in acetic acid solution, therefore, the γ- and α-monoximes are simultaneously produced and the latter is further converted into the α-dioxime. Since the α-dioxime is hydrolysed by acids to the α-monoxime and does not form the compound (I) (see above) by loss of water, it cannot be the δ-compound, and the α-configuration [formula (III) above] is regarded as established, which is in harmony with its stability towards alkali. With concentrated sulphuric acid, transformation does not occur in the side-chain, but the oximino-group is removed with production of the α-monoxime and, under definite conditions, of an intermediate *compound*, $C_{26}H_{24}O_5N_2$, m. p. 184—184·5°, the constitution of which has not been elucidated.

(I.)





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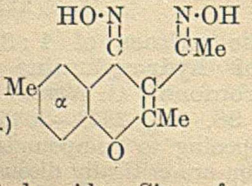
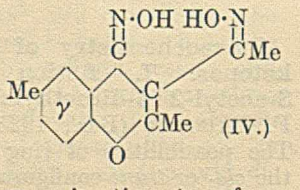


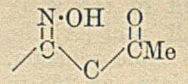
(III.)



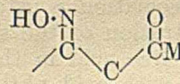
(IV.)

If the γ-monoxime reacts with hydroxylamine in boiling sodium carbonate solution, a mixture of the γ-dioxime and of a new *dioxime*, m. p. 156°, is formed, which, since it is hydrolysed by acids to the γ-monoxime, must have the β-configuration (VII), since the γ-form is already assigned. When distilled in a vacuum it yields the anhydride (I), together with the γ-dioxime, thus proving that the β- is first transformed into the γ-variety, which subsequently loses water. A similar transformation is observed when the β-form is digested with concentrated sulphuric acid. A fourth stereoisomeric *dioxime*, m. p. 195°, is obtained together with the anhydride (I) by prolonged treatment of the γ-form with boiling sodium hydroxide solution; for this only the δ-configuration (VIII) is available. Hydrolysis of the δ-dioxime leads to the formation of a new *monoxime*, m. p. 126°, in place of the expected α-oxime; since it is reconverted by hydroxylamine under mild conditions into the δ-dioxime it must have the δ-configuration (IX).

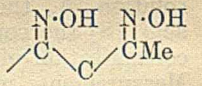
It is remarkable that the β-dioxime is converted by alkali into the anhydride (I): preliminary isomerisation to the γ-dioxime appears scarcely likely and probably the δ-dioxime is first formed, although this could not be established experimentally.



(V.)

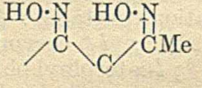


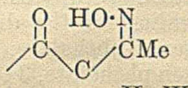
(VI.)



(VII.)

(VIII.)





(IX.)

H. Wren.

Action of hydroxylamine on chromones. G. Wittig and F. Baugert (Ber., 1925, **58**, [*B*], 2636—2642).—Chromones generally react extremely slowly with ketonic reagents, but, in this respect, hydroxylamine is exceptional, so that it appears probable that intermediate additive compounds are formed which subsequently become oximated. 2 : 8-Dimethylchromone and 2 : 8-dimethylthiochromone are converted by hydroxylamine in neutral solution into 2 : 8-*dimethylchromoneoxime*, m. p. 145°; by-products are also formed which indicate addition of hydroxylamine to the pyrone ring, but these have not been investigated completely. In alkaline solution, oximation of 2 : 8-dimethylchromone occurs differently; if the warm solution of the reaction product is immediately acidified with dilute mineral acid, 2 : 8-dimethylchromoneoxime is obtained, whereas cautious addition of acetic acid precipitates the *dioxime* of 3-*acetoacetyl*-o-*cresol*,

$OH{\cdot}C_6H_3Me{\cdot}C(:N{\cdot}OH){\cdot}CH_2{\cdot}CMe:N{\cdot}OH$,

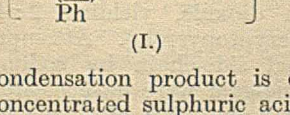
m. p. 148—149° (slight decomp.), identical with the product obtained from hydroxylamine and 6-acetoacetyl-*o*-cresol. If the dioxime is warmed with dilute mineral acids, the oximino-group remote from the phenyl radical is hydrolysed, and ring closure follows with production of 2 : 8-dimethylchromoneoxime. Treatment of the dioxime with cold acids yields the monoxime and an isomeric *substance*, $C_{11}H_{16}O_2N$, m. p. 90·5—91°, which is also obtained by the action of alcoholic ammonia on the dioxime or by heating the latter at 160°, and is therefore regarded as 5 : 2′-*hydroxy*-m-*tolyl*-3-*methyl*iso*oxazole*.

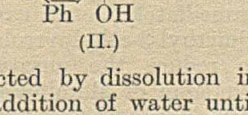
Fission of the ring also occurs during the oximation of 2 : 6-dimethylchromone in alkaline solution, whereby an extremely unstable substance, $C_{11}H_{16}O_4N_2$, m. p. 70—73°, is isolated, which passes above its m. p. into the *dioxime* of 3-*acetoacetyl*-p-*cresol*, m. p. 122—122·5° (slight decomp.); according to analyses and properties, the compound is regarded as the hydroxylamino-oxime,

$OH{\cdot}C_6H_3Me{\cdot}C(\colon N{\cdot}OH){\cdot}CH_2{\cdot}CMe(OH){\cdot}NH{\cdot}OH$.

It is transformed by cold mineral acids into 2 : 6-*dimethylchromoneoxime*, m. p. 184—185°, which is also obtained from the dioxime and hot acids. On the other hand, the dioxime is not converted by cold mineral acid into the expected iso*oxazole* derivative, $C_{11}H_{11}O_2N$, m. p. 53—54°, which is obtained, together with 2 : 6-dimethylchromoneoxime, by heating the dioxime above its m. p. Somewhat unexpectedly, the dioxime is converted by alcoholic ammonia into the hydroxylamino-oxime described above. Prolonged treatment of the dioxime with boiling sodium hydroxide solution leads to the formation of (?) 5 : 6′-*hydroxy*-m-*tolyl*-3-*methyl*iso*oxdiazine*, m. p. 168—169° (slight decomp.) (*dibenzoate*, m. p. 123·5—124°), and (?) 3 : 6′-*hydroxy*-m-*tolyl*-5-*methyl*iso*oxdiazine*, m. p. 185—187° (slight decomp.) (*diacetate*, m. p. 155·5—156°). H. WREN.

Pyrylium compounds. XVI. Triphenylpyrylium salts containing amino-groups. W. DILTHEY and C. BERRES (J. pr. Chem., 1925, [ii], **111**, 340—352; cf. A., 1925, i, 1441).—Condensation of *p*-acetamidobenzylideneacetophenone with acetophenone in acetic anhydride in presence of zinc chloride affords the *zinc chloride* double salt of 4-p-*acetamidophenyl*-2 : 6-*diphenylpyrylium chloride* (I), straw-yellow, m. p. 158°, which, when treated with aqueous pyridine, yields 4-p-*acetamidophenyl*-2 : 6-*diphenylpyranol*, (II), pale yellow, m. p. 188—189° [*perchlorate*, orange-yellow, m. p. 220—225° (decomp.)]. De-acetylation of the above first-named condensation product is effected by dissolution in concentrated sulphuric acid, addition of water until turbidity is produced, and subsequent boiling. From the resulting solution, the *monopicrate*, violet-black, decomp. above 250°, the *dipicrate*, brick-red, converted into the monopicrate on recrystallisation, and the *perchlorate*, steel-blue, decomp. 295°, of 4-p-*aminophenyl*-2 : 6-*diphenylpyrylium*, can be precipitated by addition of the appropriate acids. p-*Acetamidostyryl* p-*methoxyphenyl ketone*, pale yellow, m. p. 186—187°, yields *p*-aminostyryl *p*-methoxyphenyl ketone (cf. Pfeiffer, A., 1925, i, 408) when boiled with concentrated alcoholic hydrochloric acid, whilst condensation with *p*-methoxyacetophenone in acetic anhydride, in presence of zinc chloride, affords a *zinc chloride* double salt, which, when treated with alcoholic perchloric acid, yields 4-p-*acetamidophenyl*-2 : 6-*di*-p-*anisylpyrylium perchlorate*, orange-red, decomp. above 250°, or, rapidly heated, m. p. 294°. The corresponding *picrate*, brick-red, m. p. 267° (decomp.), *bromide*, violet, m. p. 196°, and *dihydrochloride*, dark brown, m. p. 205° (decomp.), are described. When heated with concentrated hydrochloric acid at 160°, the last-named salt affords 4-p-*aminophenyl*-2 : 6-*di*-p-*hydroxyphenylpyrylium dihydrochloride*, violet-red, decomp. 240°, from which the corresponding *perchlorate*, reddish-yellow, was prepared. 6-*Phenyl*-4-p-*acetamidophenyl*-2-p-*anisylpyrylium perchlorate*, orange-red, m. p. 143°, is obtained by condensing *p*-acetamidostyryl phenyl ketone with *p*-methoxyacetophenone, or *p*-acetamidostyryl *p*-anisyl ketone with acetophenone, in acetic anhydride in presence of zinc chloride. Boiling with concentrated hydrochloric acid affords 6-*phenyl*-4-p-*aminophenyl*-2-p-*anisylpyrylium dihydrochloride*, violet-red, decomp. when heated, and this, when heated with concentrated hydrochloric acid at 160—170°, yields 6-*phenyl*-4-p-*aminophenyl*-2-p-*hydroxyphenylpyrylium dihydrochloride*, violet-red, decomp. 240°. Crystallisation of the last-named salt from *N*-hydrochloric acid converts it into the corresponding *chloride*, violet with green reflex, decomp. 230°. 6-*Phenyl*-2 : 4-*di*-p-*aminophenylpyrylium picrate*, violet-black, solutions of which in aqueous alcohol have considerable dyeing properties, was prepared analogously.


(I.)

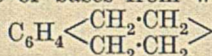

(II.)

Whilst *p*-hydroxyphenylpyrylium salts are readily hydrolysed with formation of the corresponding anhydro-bases, the amino-derivatives are considerably more stable, and whilst the action of alkalis appears to lead to the production of violonimines, these could not be isolated in a pure condition, as they appear to possess a facility for polymerisation similar to that exhibited by the fuchsonimines (cf. Baeyer and Villiger, A., 1904, i, 786). F. G. WILLSON.

Degradation of 2 : 2-dichlorothiochromonol. F. ARNDT (Ber., 1925, **58**, [*B*], 2702).—The product obtained by the action of alkali on 2 : 2-dichlorothiochromonol is not 6-thiol-*m*-toluic acid, as recorded previously (A., 1925, i, 1309), but probably 2 : 3-dihydroxythiochromone (cf. Krollpfeiffer, this vol., 166). H. WREN.

1-Methylpyrrolidine from 1-methylpyrrole by catalytic reduction. J. P. WIBAUT (Rec. trav. chim., 1925, **44**, 1101—1105).—By shaking 1-methylpyrrole in acetic acid solution with hydrogen for 41 hrs. under a pressure of 20 cm. of water, successive small quantities of platinic oxide being added as a catalyst, a 74% yield of 1-methylpyrrolidine is obtained. Increasing the temperature of the reaction mixture to 50° has no effect on the reaction velocity. R. W. WEST.

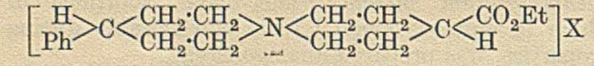
Existence of the simplest, monomeric dihydroquinolines. W. König and R. Buchheim (Ber., 1925, **58**, [*B*], 2868—2870; cf. Meisenheimer and Stotz, this vol., 76).—The compound obtained by the action of chloro- or bromo-acetal on *o*-toluidine (cf. Räth, A., 1924, i, 555, 667) is identified as 4-ethyl-*o*-toluidine. Simple monomeric 1 : 2- or 1 : 4-dihydroquinolines should therefore be deleted from the literature at present. H. Wren.

Synthesis of *s*-homotetrahydro*iso*quinoline. J. von Braun and H. Reich (Ber., 1925, **58**, [*B*], 2765—2767).—Reduction of the lactam of *o*-β-aminoethylphenylacetic acid (von Braun and Reich, A., 1925, i, 1407) by sodium and ethyl alcohol affords a mixture of bases from which s-*homotetrahydro*iso-*quinoline*,  $C_6H_4<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>NH$, b. p. 115°/12 mm., d_4^{19} 1·034, is readily isolated by distillation with steam. The corresponding *hydrochloride*, m. p. 250°, *chloroplatinate*, m. p. 253° (decomp.) after darkening at 230°, *picrate*, m. p. 220°, *methiodide*, m. p. 227°, and *nitroso*-derivative, m. p. 71—72°, are described. o-β′-*Aminoethyl*-β-*phenylethyl alcohol*,

$$NH_2\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH,$$

b. p. about 180°/12 mm., is obtained as by-product; the *di*-p-*nitrobenzoyl* derivative has m. p. 153°. H. Wren.

Configuration of the ammonium ion. W. H. Mills and E. H. Warren (J.C.S., 1925, **127**, 2507—2514). The facts hitherto known indicate that the ammonium ion must have either a pyramidal or a tetrahedral configuration. In order to test which of these is correct, 4-phenyl-4′-carbethoxybispiperidinium-1 : 1′-spiran salts



$$\left[\genfrac{}{}{0pt}{}{H}{Ph}>C<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>N<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>C<\genfrac{}{}{0pt}{}{CO_2Et}{H}\right]X$$

have been prepared. These are molecularly asymmetric on the tetrahedral, but not on the pyramidal, configuration. They have now been resolved, and the tetrahedral arrangement is therefore judged to be correct. The *bromide*, m. p. 276—277°, of the *dl*-base was prepared by condensing ethyl di-β-bromoethylacetate with 4-phenylpiperidine. The *iodide* had m. p. 209—210°. The d-*iodide*, m. p. 222—223°, obtained from the d-α-*bromocamphor*-π-*sulphonate* (m. p. 210—212°) had $[\alpha]^{20}_{5780}+8{\cdot}9°$ and $[\alpha]^{20}_{5461}+9{\cdot}7°$ in ethyl alcohol. The d-*bromide*, m. p. 274—275°, had $[\alpha]^{20}_{5780}+11{\cdot}76°$ and $[\alpha]^{20}_{5461}+13{\cdot}23°$, and the l-*bromide*, −11·75° and −13·3°. E. E. Walker.

Constitution of Fischer and Hepp's phenylpyrrole. G. Plancher and E. Ghigi (Gazzetta, 1925, **55**, 757—759).—Direct confirmation is now obtained of the view formerly expressed (A., 1925, i, 597) that the compound prepared by Fischer and Hepp (A., 1886, 1042) by the action of bromobenzene on the potassium derivative of pyrrole is 2- and not 1-phenylpyrrole. T. H. Pope.

Synthesis of carboxylated cryptopyrrolecarboxylic acids etc. H. Fischer and C. Nenitzescu (Z. physiol. Chem., 1925, **145**, 295—307).—An attempt has been made to investigate the mechanism of Ehrlich's dimethylaminobenzaldehyde reaction (a red coloration which this substance gives with certain pathological constituents of urine) by preparing some of the cryptopyrrole derivatives and synthesising methenes from them. Thus, *bis*-(2 : 4-*dimethyl*-3-*methylmalonic*-*pyrrole*)-5-*methene*, m. p. 218°, is prepared by condensing the trisodium salt of β-5-carboxy-β-2 : 4-dimethyl-3-pyrrylmethylmalonic acid with formic acid in the presence of perchloric acid. If Ehrlich's reagent is used instead of formic acid, the deep violet (p-*dimethylaminophenyl*)(2 : 4-*dimethylpyrrolene*-3-β-*methylmalonic*)-*methene*, m. p. 190°, is obtained. Ethyl β : 3-carbethoxy-2 : 5-dimethyl-4-pyrrylmethylmalonate is obtained from ethyl 2 : 5-dimethylpyrrole-3-carboxylate and ethyl methoxymethylmalonate. The ester has m. p. 81°, and the acid, 195°. By rapid heating of the acid above its m. p., the corresponding propionic acid is formed, m. p. 178°.

Hæmatic acid has been synthesised by heating together ethyl methoxymethylmalonate, ethyl acetoacetate, acetic anhydride, and zinc chloride, and treatment of the distilled product with hydrocyanic acid, followed by hydrolysis of the resulting nitrile. H. P. Marks.

Synthesis of ethyl 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate and its conversion into cryptopyrrole. H. Fischer and B. Walach (Ber., 1925, **58**, [*B*], 2818—2822).—The preparation of ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate (cf. A., 1922, i, 758) is considerably simplified by the observation that ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is hydrolysed by concentrated sulphuric acid at 40° to 5-*carbethoxy*-2 : 4-*dimethylpyrrole*-3-*carboxylic acid*, m. p. 273° (yield 70—95%), which loses carbon dioxide when heated and forms ethyl 2 : 4-dimethylpyrrole-5-carboxylate. Application of the Gattermann synthesis to the latter compound affords ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate, which condenses with malonic acid in the presence of piperidine, yielding 5-*carbethoxy*-2 : 4-*dimethylpyrrole*-3-*acrylic acid*, m. p. 240° (2 : 4 : 5-*trimethylpyrrole*-3-*acrylic acid*, m. p. 203°, and 2 : 4-*dimethyl*-5-*ethylpyrrole*-3-*acrylic acid*, m. p. 205°, are obtained similarly). *Ethyl* 2 : 4-*dimethyl*-3-*vinylpyrrole*-5-*carboxylate*, m. p. 112°, is obtained in 70% yield when the corresponding acrylic acid is heated at 200°/12—15 mm. It is hydrolysed to 2 : 4-*dimethyl*-3-*vinylpyrrole*-5-*carboxylic acid*, m. p. 101—102°, and hydrogenated in the presence of spongy platinum and methyl alcohol to *ethyl* 2 : 4-*dimethyl*-3-*ethylpyrrole*-5-*carboxylate*, m. p. 94°. Catalytic reduction of 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylic acid affords the very unstable 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylic acid, which immediately loses carbon dioxide, yielding 2 : 4-dimethyl-3-ethylpyrrole (cryptopyrrole). Attempts to reduce the unsaturated side-chain by sodium amalgam or aluminium amalgam were unsuccessful. Hydriodic acid does not cause reduction, but displaces the vinyl group with production of 2 : 4-dimethylpyrrole. H. Wren.

Derivatives of 4-aminopyridine. E. Koenigs, H. Friedrich, and H. Jurany (Ber., 1925, **58**, [*B*], 2571—2576).—The action of methyl iodide on

4-aminopyridine yields 4-aminopyridine methiodide, m. p. 184—185°, which is converted through the methochloride into the chloroplatinate, m. p. 230—232° (decomp.). The substances, m. p. 187—188° and 226—227° (decomp.), have been described previously (A., 1925, i, 1328) by Tschitschibabin and Ossetrova, who consider them to be derived from the tautomeric 1-methyl-4-pyridoneimine; this view is not shared by the authors, mainly on account of the close analogy in behaviour of 4-aminopyridine and 4-dimethylaminopyridine, with which such tautomerism is impossible. 4-Chloropyridine-2 : 6-dicarboxylic acid is converted by methylamine solution at 150° into 4-methylaminopyridine-2 : 6-dicarboxylic acid, m. p. 245—255° (decomp.), and *4-methylaminopyridine-2 : 6-dicarboxylmethylamide*, m. p. 269°. The acid is transformed by distillation in a vacuum into 4-methylaminopyridine, m. p. 108—110°, the picrate, m. p. 172°, and chloroplatinate, m. p. 232°, of which are described; Tschitschibabin and Ossetrova (*loc. cit.*) record the respective m. p. 115—118°, 168·5—169°, and 214—215°. *4-Dimethylaminopyridine*, m. p. 114°, obtained by heating 4-dimethylaminopyridine-2 : 6-dicarboxylic acid, functions as a mono-acid base, thus resembling 2- and 4-aminopyridine and differing from the 3-amino-compound; the *chloroplatinate*, m. p. 265° (decomp.) after softening, *chloroaurate*, m. p. 176—178°, *picrate*, m. p. 204°, and somewhat impure *hydrochloride*, m. p. 73°, are described. 4-Chloropyridine-2 : 6-dicarboxylic acid is converted by 4-aminopyridine at 150° into *4 : 4'-dipyridylamine-2 : 6-dicarboxylic acid*,

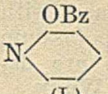
$$C_5H_4N{\cdot}NH{\cdot}C_5H_2N(CO_2H)_2,$$

m. p. 255° (decomp.), which is transformed by loss of carbon dioxide into *4 : 4'-dipyridylamine*, m. p. 138° after softening at 110°; the indefinite m. p. indicates the possibility of the presence of the isomeric pyridoneimine. To limit this possibility, 4-chloropyridine-2 : 6-dicarboxylic acid is converted by 4-aminopyridine-2 : 6-dicarboxylic acid into *4 : 4'-dipyridylamine-2 : 6 : 2' : 6'-tetracarboxylic acid*, m. p. 272° (decomp.), and the latter is decarboxylated, yielding, however, a base with almost identical properties. The *chloroplatinate* (+H_2O) and *picrate* of the base from the di- and tetra-carboxylic acids have m. p. 260° and (decomp.) above 280°, 168—170°, and 170—174°, respectively. H. WREN.

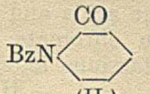
Acylation of 2-hydroxypyridine. A. E. TSCHITSCHIBABIN and P. G. SZOKOW (Ber., 1925, **58**, [*B*], 2650—2652).—The great instability of the acylated derivatives of 2- and 4-hydroxypyridones has led Meyer (A., 1907, i, 179) to doubt the existence of more than a very limited number of members of this class. *2-Pyridyl* p-*nitrobenzoate*, m. p. 115—116°, is, however, readily prepared by the action of *p*-nitrobenzoyl chloride on 2-pyridone in the presence of concentrated alkali hydroxide. In the complete absence of moisture, *2-pyridyl acetate*, b. p. 110—112°/10 mm., is obtained from acetyl chloride and anhydrous sodium 2-pyridone; it is so rapidly decomposed by water or alcohol that treatment of its solutions in these media with chloroplatinic acid affords 2-pyridone chloroplatinate.

Sodium-2-pyridone, obtained by precipitating 2-pyridone from a solution in sodium hydroxide and crystallisation of the precipitate from alcohol, has the composition $C_5H_4ONNa,2H_2O$ (cf. Tschitschibabin and Riazancev, A., 1916, i, 224). H. WREN.

Benzoylation of 2-pyridone. A. E. TSCHITSCHIBABIN and O. P. OPARINA (J. Russ. Phys. Chem. Soc., 1925, **56**, 153—156).—Benzoylation of 2-pyridone under various conditions yields always one and the same benzoylpyridone, which exhibits distinct basic properties and has hence structure (I); the tautomeric form (II) could not be obtained. Meyer's statement that 2-pyridone is incapable of undergoing acylation (A., 1906, i, 107) is thus inaccurate.



(I.)



(II.)

Benzoyl-2-pyridone (*2-benzoxypyridine*), obtained by the action of benzoyl chloride in presence of sodium hydroxide, or of benzoic anhydride, on 2-pyridone, by the action of sodium benzoate on 2-iodopyridine, or by the action of benzoic anhydride on pyridine-2-diazotate, has m. p. 42°, b. p. 183—186°/30 mm., and forms a *chloroplatinate*, m. p. 186° (decomp.) T. H. POPE.

Preparation of indole from *o*-ω-dinitrostyrene. J. VAN DER LEE (Rec. trav. chim., 1925, **44**, 1089—1092).—It is suggested that *o*-ω-diaminostyrene and *o*-aminophenylacetaldehyde are formed as intermediate products during the reduction of *o*-ω-dinitrostyrene (cf. Nenitzescu, A., 1925, i, 973). R. W. WEST.

Quinoline derivatives. II. Syntheses of β-2-phenyl-4-quinolylethylamine and β-6-methoxy-2-phenyl-4-quinolylethylamine. H. JOHN [with V. GROSSMANN] (Ber., 1925, **58**, [*B*], 2799—2805; cf. A., 1925, i, 1317).—*γγγ-Trichloro-α-2-phenyl-4-quinolylpropan-β-ol*, $C_9H_5NPh{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3$, m. p. 195°, prepared by heating 2-phenyl-4-methylquinoline with chloral at 118—120°, is converted by potassium hydroxide dissolved in absolute alcohol into β-*2-phenyl-4-quinolylacrylic acid*, m. p. 201° (*hydrochloride*, m. p. 210°; *picrate*; *methyl* ester, m. p. 123°). The unsaturated acid is reduced by hydriodic acid and red phosphorus in glacial acetic acid solution to β-*2-phenyl-4-quinolylpropionic acid*, m. p. 215° (*hydrochloride*, m. p. 189°; *hydriodide*, m. p. 208°; *sulphate*; *picrate*; *methyl* ester, m. p. 63°). The methyl ester and hydrazine hydrate afford β-*2-phenyl-4-quinolylpropionhydrazide*, m. p. 158° (*hydrochloride*), which is converted by nitrous acid into the *azide* and thence by ethyl alcohol into β-*2-phenyl-4-quinolylethylurethane*, m. p. 72°, and by water into *di*-β-*2-phenyl-4-quinolylethylcarbamide*, m. p. 175°. The urethane is hydrolysed by boiling hydrochloric acid to β-*2-phenyl-4-quinolylethylamine*, m. p. 4° (*dihydrochloride*, m. p. 158°; *chloroplatinate*, $C_{17}H_{18}N_2Cl_6Pt$, which does not melt below 270°; *picrate*).

Starting from 6-methoxy-2-phenyl-4-methylquinoline, a precisely similar series of derivatives is prepared, the following being described: *γγγ-trichloro-α-6-methoxy-2-phenyl-4-quinolylpropan-β-ol*, m. p. 222°; β-*6-methoxy-2-phenyl-4-quinolylacrylic acid*,

m. p. 239° (*hydrochloride*; *sulphate*; *picrate*; *methyl ester*, m. p. 140°); β-6-*hydroxy-2-phenyl-4-quinolylpropionic acid*, m. p. 245° (*hydrochloride*, m. p. 160°; *picrate*); *methyl* β-6-*methoxy-2-phenyl-4-quinolylpropionate*, m. p. 100°; β-6-*methoxy-2-phenyl-4-quinolylpropionhydrazide*, m. p. 116°; β-6-*methoxy-2-phenyl-4-quinolylpropionazide*; β-6-*methoxy-2-phenyl-4-quinolylethylurethane*, m. p. 125°; β-6-*methoxy-2-phenyl-4-quinolylethylamine*, m. p. 54° (*dihydrochloride*, m. p. 209°; *chloroplatinate*; *sulphate*; *picrate*). The reactions of the acids and bases with mercuric chloride, potassium chromate, potassium ferrocyanide, and iodine–potassium iodide are described. H. Wren.

Barbituric acids and the picric acid reaction. A. W. Dox (Z. physiol. Chem., 1925, **150**, 118—120).—The picric acid reaction, used by Abderhalden for the detection of diketopiperazines in the breakdown products of protein, is not given by every compound containing a carbonyl group. Barbituric acid, containing three ·CO· groups, gives a characteristic picric acid reaction, but four monoalkyl- and sixteen dialkyl-barbituric acids tested do not react with it, although they contain carbonyl groups. Parabanic acid does not give this reaction. H. D. Kay.

Synthesis of 5-β-hydroxyethylbarbituric acid and its alkyl derivatives. L. H. Cretcher, J. A. Koch, and W. H. Pittenger (J. Amer. Chem. Soc., 1925, 47, 3083—3085).—β-Chloroethyl vinyl ether (cf. A., 1925, i, 627) condenses with sodium diethyl malonate and sodium diethyl monoalkylmalonates with formation of the corresponding vinyloxyethylmalonates. The latter condense with carbamide and thiocarbamide, with production of 5-β-vinyloxyethylbarbituric acids, which, on hydrolysis with dilute mineral acid, afford acetaldehyde and the corresponding 5-β-hydroxyethylbarbituric acids. The following are described: *diethyl ethyl*-β-*vinyloxyethyl*-, b. p. 151°/18 mm., d_{15}^{15} 1·0264; *diethyl propyl*-β-*vinyloxyethyl*-, b. p. 157°/17 mm., d_{15}^{15} 1·0145; *diethyl butyl*-β-*vinyloxyethyl*-, b. p. 165°/17 mm., d_{15}^{15} 0·9992; and *diethyl bis*-(β-*vinyloxyethyl*)-*malonate*, b. p. 133°/3 mm., d_{15}^{15} 1·0566; 2-*thio*-5-*ethyl*-5-β-*vinyloxyethyl*-, m. p. 136°; 5-*ethyl*-5-β-*vinyloxyethyl*-, m. p. 158°; 5-*butyl*-5-β-*vinyloxyethyl*-, m. p. 141°; 2-*thio*-5-β-*hydroxyethyl*-, m. p. 181° (decomp.); 5-β-*hydroxyethyl*-, m. p. above 300°; 5-*ethyl*-5-β-*hydroxyethyl*-, m. p. 176°; 2-*thio*-5-*ethyl*-5-β-*hydroxyethyl*-, m. p. 143—145°; 5-*propyl*-5-β-*hydroxyethyl*-, m. p. 168°; and 5-*butyl*-5-β-*hydroxyethyl-barbituric acid*, m. p. 147°. F. G. Willson.

Synthesis of the polypeptide hydantoin: tyrosylalaninehydantoin. II. D. A. Hahn and E. Gilman (J. Amer. Chem. Soc., 1925, 47, 2941—2953; cf. A., 1923, i, 487).—The substance previously described as a stereoisomeric form of ethyl 4-*p*-anisylidenehydantoin-3-α-propionate, m. p. 176°, has now been found to be actually *ethyl* 4-p-*anisylidenehydantoin*-1-*acetate*, whilst that described as another isomeride, m. p. 143°, is a mixture (mixed crystals) of the above two compounds, the m. p. of the mixture being now reported as 140—142°. The individual components can be separated from the mixed crystals only by employing very dilute solutions, and on hydrolysis with dilute hydrochloric acid the mixture yields an acid, m. p. 245°, previously reported as 4-*p*-anisylidenehydantoin-3-α-propionic acid, but which actually is probably also a eutectic. The assumption that the ester group entered the hydantoin nucleus in position 3 was based on the observation that ammonia is evolved during the hydrolysis of the polypeptide hydantoin, but it has since been noted that 1-derivatives also yield ammonia when subjected to intense hydrolysis. It is now concluded that the ester groups enter in position 1. When ethyl α-bromopropionate containing the corresponding bromoacetate is condensed with the sodium derivative of anisylidenehydantoin, the ethyl anisylidenehydantoinacetate, m. p. 176°, separates first. The corresponding propionate is formed later, and unites with the acetate immediately to form the mixture of m. p. 140—142°. Condensation of pure ethyl α-bromopropionate with sodium anisylidenehydantoin yields *ethyl* 4-p-*anisylidenehydantoin*-1-α-*propionate*, m. p. 158—158·5°. On hydrolysis, this affords 4-p-*anisylidenehydantoin*-1-α-*propionic acid*, m. p. 255—256° [*potassium* salt, m. p. 280° (decomp.)]. On reduction with hydrogen in alcohol in presence of colloidal palladium, the ester yields two isomeric *ethyl* 4-p-*anisylhydantoin*-1-α-*propionates*, m. p. 117·5—118·5° and 97·5—98·5°, respectively. On hydrolysis with hydrochloric acid, the above isomeride, m. p. 117·5—118·5°, yields 4-p-*anisylhydantoin*-1-α-*propionic acid*, m. p. 160—161°, whilst the ester of lower m. p. affords similarly an isomeric *acid*, m. p. 182—183°. A mixture of the isomeric acids is also obtained by condensing ethyl α-bromopropionate with 4-*p*-anisylhydantoin and hydrolysing the reaction product. Treatment of ethyl 4-*p*-anisylidenehydantoin-1-α-propionate with hydriodic acid affords a mixture, m. p. 168—190°, of two isomeric 4-p-*hydroxybenzylhydantoin*-1-α-*propionic acids*, m. p. 193·5—195° and 187—188·5°, respectively, from which the *ethyl* esters, m. p. 133—138° and 152—155°, were prepared. Hydrolysis of the last-named acids or esters with barium hydroxide yields alanine and tyrosine, whilst similar hydrolysis of the polypeptide hydantoin obtained analogously from ethyl 4-*p*-anisylidenehydantoin-1-acetate affords glycine and tyrosine. F. G. Willson.

Absorption spectra of some derivatives of anisylidenehydantoin. E. P. Carr and M. A. Dobbrow (J. Amer. Chem. Soc., 1925, 47, 2961—2965).—Comparison of the absorption spectra of the substances obtained by condensing different samples of ethyl α-bromopropionate with sodium 4-*p*-anisylidenehydantoin with those of ethyl 4-*p*-anisylidenehydantoin-1-acetate (cf. Johnson and Hahn, A., 1917, i, 475) and ethyl 1-methyl-4-*p*-anisylidenehydantoin-3-acetate (cf. Hahn and Renfrew, A., 1925, i, 581) indicates that the ester group is in all cases attached to the hydantoin nucleus in the 1-position, a result since confirmed by Hahn and Gilman (preceding abstract). The m. p. of mixtures of ethyl 4-anisylidenehydantoin-1-acetate, m. p.

176°, and the corresponding -1-α-propionate, m. p. 158°, form, when plotted, a curve characteristic of substances which form mixed crystals, with a minimum at 140° for the mixture containing 60% of the former ester, in close proximity to the m. p. first quoted (A., 1923, i, 487) for ethyl 4-*p*-anisylidenehydantoin-3-α-propionate (cf. Hahn and Gilman, *loc. cit.*). This mixture melts completely in a range of 2°, whilst the remaining mixtures require ranges of 6—16° for complete liquefaction.

F. G. Willson.

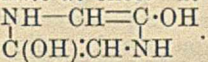
Isomerisation in the hydantoin series induced by the action of hydrogen chloride. D. A. Hahn and E. Gilman (J. Amer. Chem. Soc., 1925, **47**, 2953—2961).—Whilst the existence of isomerides of benzylidene- and anisylidene-hydantoins and their 1-substitution products could not be demonstrated, the corresponding 1 : 3-disubstitution products can be obtained in two isomeric forms. This is explained on the assumption that the former compounds can undergo keto-enol tautomerisation, by which the double linking responsible for stereoisomerism may be saturated. In the following cases examined, the isomeride of higher m. p. is obtained from that of lower m. p. by treatment with alcoholic hydrogen chloride. The reverse change could be effected only by the action of aqueous-alcoholic alkali in one case, probably owing to the instability of the compounds examined in presence of alkali.

When treated with hot alcoholic hydrogen chloride, ethyl 1-methyl-4-anisylidene-3-acetate, m. p. 107—108° (cf. A., 1925, i, 581), is converted into an *isomeride*, m. p. 127—128°. 1 : 3-Dimethyl-4-anisylidenehydantoin, m. p. 91—92·5° (cf. Johnson and Nicolet, A., 1912, i, 585), affords similarly an *isomeride*, m. p. 127·5—128·5°, which crystallises either in long, colourless needles or in large, yellow prisms, the latter being converted into the colourless form by recrystallisation from alcoholic hydrochloric acid. Treatment of the isomeride of higher m. p. with 0·2 mol. of alkali in aqueous-alcoholic solution gave a small yield of the other isomeride. Partial isomerisation appears to be effected by heating either isomeride at 135—150°. Both isomerides yield 1 : 3-*dimethyl-4-anisylhydantoin*, m. p. 78·5°, on reduction. *Methyl* 3-*methyl*-4-*benzylidenehydantoin*-1-*acetate* exists in two isomeric forms, m. p. 66·5—68° and 101—102·5°, respectively. *Methyl* 4-*anisylidenehydantoin*-1-*acetate*, long needles, m. p. 183—184°, which change in contact with the mother-liquor into compact prisms of the same m. p., was prepared from the corresponding ethyl ester (cf. Johnson and Hahn, A., 1917, i, 475) by hydrolysis and re-esterification. When treated with methyl iodide and potassium hydroxide in alcoholic solution, it yields *methyl* 3-*methyl*-4-*anisylidenehydantoin*-1-*acetate*, m. p. 84—85°, which is converted into an *isomeride*, m. p. 129·5—131°, when treated with alcoholic hydrogen chloride. *Methyl* 4-*anisylidenehydantoin*-1-*propionate*, m. p. 163—164°, obtained from the corresponding ethyl ester (cf. preceding abstract), affords, on methylation, *methyl* 3-*methyl*-4-*anisylidene*-1-*propionate*, m. p. 103—104°, converted similarly into the *isomeride*, m. p. 142—143°.

F. G. Willson.

Methylated piperazines. E. Abderhalden and R. Haas (Z. physiol. Chem., 1925, **149**, 94—99).—From 2 : 5-dimethylpiperazine ("lycetol") the dihydriodide of 1 : 2 : 4 : 5-tetramethylpiperazine has been prepared by direct methylation with methyl iodide in methyl alcohol. From this substance by treatment with cold 4*N*-alkali the monohydriodide is obtained. The removal of a further molecule of hydriodic acid is accomplished by shaking with silver sulphate. The tetramethylated piperazine is a syrup, which becomes partly crystalline on long keeping. The dihydriodide of 1 : 1 : 2 : 4 : 4 : 5-hexamethylpiperazine may be prepared in good yield by long boiling of the dimethyl compound with methyl iodide. The corresponding hexamethylpiperazinium hydroxide, m. p. 224°, is obtained by treatment with silver sulphate and the calculated quantity of barium hydroxide. 2 : 5-Dimethylpiperazine may also be methylated by methyl sulphate in presence of alkali. The dichloride of the hexamethyl compound is prepared by acidifying the reaction mixture with hydrochloric acid, precipitating the mercury salt with mercuric chloride, decomposing the crystalline precipitate with hydrogen sulphide, and evaporating the mercury-free filtrate almost to dryness. The dichloride is then crystallised from its alcoholic solution.

H. D. Kay.

Desmotropic forms of diketopiperazines. E. Abderhalden and E. Schwab (Z. physiol. Chem., 1925, **149**, 100—103).—A new *form* of glycine anhydride has been isolated from a reaction mixture of ordinary glycine anhydride and tyrosine which had been heated with glycerol at 180°. It gives a strong xanthoproteic reaction and reduces cold permanganate at once. It is considered to have the formula  $\begin{array}{l}\mathrm{NH{-}CH{=}C{\cdot}OH}\\ \mathrm{C(OH){:}CH{\cdot}NH}\end{array}$. By treating it with diazomethane, the dimethyl ether may be obtained. Glycine anhydride heated alone with glycerol appears to give the same unsaturated desmotropic modification.

H. D. Kay.

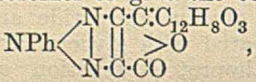
***o*-Hydroxyazo [pyrazolone] dye.** O. Kaltwasser, H. Kirchhoff, and H. Oehrn.—See B., 1926, 7.

Pyrazolone azo dyes. British Dyestuffs Corp., Ltd., K. H. Saunders, and H. Goodwin.—See B., 1926, 7.

Velocity of decomposition of heterocyclic diazonium salts. I. Diazonium salts of the pyrazole and pyrazolone series. J. Reilly and D. Madden (J.C.S., 1925, **127**, 2936—2940).—Solutions of the diazonium chlorides derived from *m*- and *o*-nitroaniline, 4-aminopyrazole, 4-aminoantipyrine, and 4-amino-3 : 5-dimethylpyrazole, maintained at 100° in a special apparatus, showed a stability increasing in the order given, the time for half decomposition varying from 10 to 1020 min. The diazonium sulphates of both 4-aminoantipyrine and 4-amino-3 : 5-dimethylpyrazole decompose much more rapidly than the corresponding chlorides.

B. W. Anderson.

Microchemical reactions for the identification of *p*-hydroxyphenylethylamine (tyramine) and 4-β-aminoethylglyoxaline (histamine). L. van Itallie and A. J. Steenhauer (Mikrochem., 1925, 3, 65—67).—A 1% solution of tyramine hydrochloride gives pale yellow needles and prisms with picric acid, pale yellow prisms and hexagonal tablets with chloroplatinic acid, large brownish-violet dichroic prisms in stellate aggregates with sodium iodide and chloroplatinic acid, large orange-red prisms in stellate aggregates with potassium bismuth iodide and hydrochloric acid, and oily drops which soon crystallise in warty or stellate aggregates with phosphotungstic acid. A 1% solution of histamine phosphate gives a crop of pale yellow, feathery needles with picric acid, large yellow prisms with chloroplatinic acid, brownish-black prisms in diamond-shaped aggregates with sodium iodide and chloroplatinic acid, small orange-red prisms with potassium bismuth iodide, and a finely-divided white precipitate, which slowly changes into prisms and diamond-shaped crystals, with silicotungstic acid. A. R. Powell.

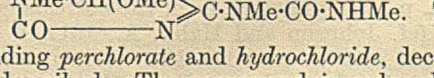
Triazole-*o*-dicarboxylic acids analogous to phthalic acid. A. Beretta (Gazzetta, 1925, 55, 788—792).—2-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid may be obtained in good yield by oxidising either 5-amino-2-phenyl-1 : 3-benztriazole or 5-amino-2-phenyl-6-methyl-1:3-benztriazole in alkaline solution by means of potassium permanganate. In presence of zinc chloride, the anhydride of this acid condenses with resorcinol to give the corresponding *triazolefluorescein*,  $\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{N\cdot C\cdot C{:}C_{12}H_8O_3}\\ \;|\;\;\;\Vert\;\;>\mathrm{O}\\ \mathrm{N\cdot C\cdot CO}\end{array}$, a reddish-yellow, amorphous compound giving, in presence of alkali, solutions which are deep red when concentrated and exhibit pronounced yellowish-green fluorescence even when highly dilute. Triazolefluorescein combines with bromine (4 atoms) to give the bright red *triazole-eosin*, $C_{22}H_9O_5N_3Br_4$, the sodium derivative of which dyes wool and silk brilliant red. 2-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic anhydride condenses also with diethyl-*m*-aminophenol to give the deep red rhodamine similar to ordinary rhodamine.

For the preparation of 5-amino-1-phenylaziminobenzene, better results are obtained if the corresponding nitro-compound, suspended in aqueous alcohol, is heated with zinc dust in presence of calcium chloride, than if Zincke and Petermann's method of reduction (A., 1901, i, 104) is employed. Oxidation of this amino-compound by means of potassium permanganate in alkaline solution furnishes a new method for preparing 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid. T. H. Pope.

Hydroxy-derivatives of 1 : 2 : 4-triazole. H. J. Backer and C. H. K. Mulder (Rec. trav. chim., 1925, 44, 1113—1117).—By ferric chloride oxidation of the appropriate semicarbazones the following compounds were obtained: 3-*hydroxy*-5-p-*methoxyphenyl*-2-*methyl*-1 : 2 : 4-*triazole*, m. p. 223·5°; 3-*hydroxy*-5-*methylenedioxyphenyl*-2-*methyl*-1 : 2 : 4-*triazole*, m. p. 273°, from *piperonal-2-methylsemicarbazone*, m. p. 226°; 3-*hydroxy*-2 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 234·5°; 3-*hydroxy*-4 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 260—261°, from *benzylidene-3-phenylsemicarbazone*, m. p. 177°. On nitration, 3-hydroxy-5-phenyl-2-methyl-1 : 2 : 4-triazole gave 3-*hydroxy*-5-p-*nitrophenyl*-2-*methyl*-1 : 2 : 4-*triazole*. R. W. West.

Degradation of uric acid–glycol ethers by alkali hydroxide. H. Biltz and H. Klein (Ber., 1925, 58, [*B*], 2740—2747; cf. Biltz and Max, A., 1921, i, 893, 895).—The smooth conversion of uric acid–glycol dimethyl ether (4 : 5-dimethoxy-4 : 5-dihydrouric acid) into allantoin by potassium hydroxide appears to be exceptional. Tetramethyluric acid–glycol dimethyl ether is transformed by barium hydroxide solution into tetramethylallantoin, but the yield is very poor, whereas 1- and 7-methyluric acid–glycol dimethyl ethers are unexpectedly resistant towards alkali hydroxide and after protracted action yield ill-defined products from which a homogeneous material could not be isolated.

The action of more concentrated alkali hydroxide on the glycol ethers of 3 : 7- and 3 : 9-dimethyluric acids followed by acidification assumes an unexpected course, since cyanic acid is lost and a substituted hydantoin is produced. It appears essential for the "cyanic acid degradation" that the pyrimidine ring of the uric acid should contain an alkyl group in position 3. The effect of the alkali hydroxide appears to consist essentially in opening the ring between positions 1 and 6; loss of methylamine, cyanic acid, and carbon dioxide takes place after acidification. 3 : 7-Dimethyluric acid–glycol diethyl ether is converted by 40% potassium hydroxide solution into 5-*ethoxy*-1-*methylhydantoin*, m. p. 99·5—100·5°. 3 : 7-Dimethyluric acid–glycol dimethyl ether affords 5-*methoxy*-1-*methylhydantoin*, m. p. 118°, but 5-methoxy-3-methylhydantoin could not be obtained from 3 : 9-dimethyluric acid–glycol dimethyl ether.

1 : 3 : 7-Trimethyluric acid–glycol dimethyl ether loses methylamine when boiled with 1—1·5% potassium hydroxide solution and, after acidification, yields a non-crystalline product which is reduced by hydriodic acid to 1-methylhydantoin, showing thus that fission of the pyrimidine ring has occurred. Treatment of the glycol with 30% potassium hydroxide at the atmospheric temperature affords a crystalline *compound*, m. p. 123—124°, regarded as 4-s-*dimethylcarbamido*-5-*methoxy*-1-*methyl*-Δ³-*glyoxal*-2-*one*,  $\begin{array}{l}\mathrm{NMe\cdot CH(OMe)}\\ \;|\\ \mathrm{CO}\!-\!\!-\!\!-\!\!-\!\!-\!\mathrm{N}\end{array}\!\!\geqslant\!\mathrm{C\cdot NMe\cdot CO\cdot NHMe}$. The corresponding *perchlorate* and *hydrochloride*, decomp. 190°, are described. The compound is reduced by hydriodic acid to a *polyiodide*, which is converted by the successive action of sulphur dioxide, lead carbonate, and hydrogen sulphide into the *compound*, $C_5H_6ON_2S$, subliming at 350°. 1 : 3 : 7-Trimethyluric acid–glycol dimethyl ether is not affected by solutions of ammonia or methylamine at the atmospheric temperature, but, at 100°, is transformed into 4-methylimino-5-methoxy-1-methylhydantoylamide, m. p. 254° (cf. Biltz and Damm, A., 1914, i, 1096), and 4-*methylimino*-5-*methoxy*-1-*methylhydantoylmethylamide*, m. p. 270°

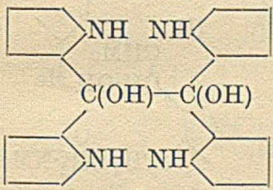
(decomp.), respectively. With ethylamine a similar change occurs, but the products could not be caused to crystallise. H. WREN.

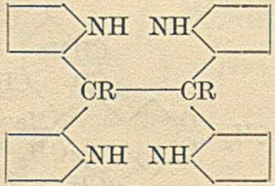
Dye formed by the action of ethyl oxalate on magnesium pyrryl bromide. T. N. GODNEV and N. A. NARYSCHKIN (Ber., 1925, **58**, [*B*], 2703—2705).—Ethyl oxalate is converted by magnesium 2-pyrryl bromide into tetra-2-pyrrylethylene glycol, which becomes dehydrated to the *dye*

$C_4H_4N\cdot C(:NC_4H_3)\cdot C(:NC_4H_3)\cdot NC_4H_4$;

the corresponding *dihydrochloride* is described. H. WREN.

Structural formula of chlorophyll and hæmin in relation to the synthesis of complex pyrrole derivatives. T. GODNEV (Astrachan Mediz. J., 1922, [2—3], pp. 14; from Chem. Zentr., 1925, II, 401).—The correctness of the Willstätter formula for chlorophyll may be tested by comparing compounds of similar but simpler structure with the degradation products of chlorophyll. The synthesis of the nucleus of the Willstätter formula, tetrapyrrylethane (Fischer and Eismayer, A., 1914, i, 993), may be investigated in the following ways. (1) Tetra-2-pyrrylethylene glycol (I) is prepared from magnesium pyrryl bromide and ethyl oxalate.


(I.)


(II.)

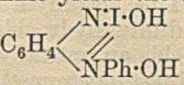
From it, tetrapyrrylethane is formed, analogously to the behaviour of diphenyl-2-pyrrylcarbinol (Tschelincev, Tronov, and Terentiev, A., 1915, i, 990). (2) In the last reaction, ethyl oxalate may be replaced by hexabromoethane. (3) Tetra-2-pyrrylethylene glycol may be obtained by reduction of di-2-pyrryl ketone. (4) Compound (II) may be prepared from magnesium pyrryl bromide and glyoxal or 1 : 2-diketones, similarly to the formation of diphenyldipyrrylmethane from benzophenone and magnesium pyrryl bromide. (5) In the last reaction, glyoxal may be replaced by *s*-tetrabromoethane and the 1 : 2-diketone by the corresponding tetrahalogen derivative (see preceding abstract). G. W. ROBINSON.

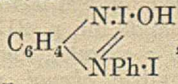
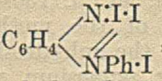
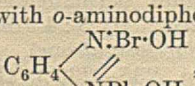
Nitro-derivative of di-iminazolyl, $C_6H_5O_{10}N_7$. K. LEHMSTEDT.—See B., 1926, 7.

2-*m*-Xylidino-5-ethoxy-4 : 5-dihydrothiazole. V. K. NIMKAR and F. L. PYMAN (J.C.S., 1925, **127**, 2746).—The base obtained by Marckwald (A., 1892, 1330) by the action of strong sulphuric acid on acetalyl-*m*-xylylthiocarbamide has now been prepared in a pure state and shown to be 2-*m*-xylidino-5-ethoxy-4 : 5-dihydrothiazole, m. p. 102—103°; picrate, m. p. 152—154°. B. W. ANDERSON.

Thiazoles. VII. Behaviour of *o*-aminophenylmercaptan with aldehydes, ketones, and *gem*-dihalides. Synthesis of benzthiazoles. M. T. BOGERT and A. STULL (J. Amer. Chem. Soc., 1925, **47**, 3078—3083).—Condensation of *o*-aminothiophenol hydrochloride with formaldehyde affords benzthiazole, b. p. 230—231° (cf. Claasz, A., 1912, i, 513; 1916, i, 669). Condensation of the aminothiophenol, or its zinc salt, with benzaldehyde yields similarly 2-phenylbenzthiazole, formation of 2-phenylbenzthiazoline not being observed. The thiazole is also obtained when benzylidene chloride is substituted for benzaldehyde in the above condensation, whilst vanillin, piperonal, and furfuraldehyde afford similarly 2-p-*hydroxy*-m-*methoxyphenylbenzthiazole*, pale yellow, m. p. 175·5°, 2-m : p-*methylenedioxyphenylbenzthiazole*, m. p. 125°, and 2-α-*furfurylbenzthiazole*, m. p. 105°, respectively. Attempts to condense the aminothiophenol with acetone, Michler's ketone, and benzophenone chloride were unsuccessful. These results confirm the original observations of Hofmann (A., 1880, 386) and are at variance with those of Claasz (*loc. cit.*). F. G. WILLSON.

Heterocyclic compounds containing quinquevalent iodine or bromine. G. HUGEL (Compt. rend., 1925, **182**, 65—67).—Aqueous solutions of equimolecular amounts of iodic acid and *o*-phenylenediamine when mixed give *piaziodonium hydroxide*, $C_6H_4{<}^{N}_{N}{\gg}I\cdot OH$, black, which with hydriodic acid gives the *hydriodide*, black amorphous, and this when warmed changes to *piaziodonium iodide*, green crystals, which on boiling is transformed into 2 : 3-diaminophenazine derivatives. 2 : 3-Diaminophenazine reacts with iodic acid, yielding the corresponding *iodonium hydroxide*, $C_6H_4{<}^{N}_{N}{\gg}C_6H_2{<}^{N}_{N}{\gg}I\cdot OH$. *o*-Aminodiphenylamine yields the *compound*,

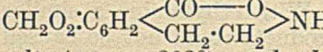

$$C_6H_4{<}\begin{array}{l}N{:}I\cdot OH\\ \quad/\!/\\ NPh\cdot OH\end{array}$$

which gives the *monoiodide*,  $C_6H_4{<}\begin{array}{l}N{:}I\cdot OH\\ \quad/\!/\\ NPh\cdot I\end{array}$, green, and the *di-iodide*,  $C_6H_4{<}\begin{array}{l}N{:}I\cdot I\\ \quad/\!/\\ NPh\cdot I\end{array}$, blue. Bromic acid reacts with *o*-aminodiphenylamine, yielding the *compound*,  $C_6H_4{<}\begin{array}{l}N{:}Br\cdot OH\\ \quad/\!/\\ NPh\cdot OH\end{array}$, green, but chloric acid does not react in this manner. L. F. HEWITT.

Sterilisation of tropacocaine hydrochloride. S. MATSUNAMI.—See B., 1926, 75.

Instability of atropine sulphate. J. BODNAR and J. FERENCZY (Arch. Pharm., 1925, **263**, 566—570).—From certain commercial preparations of atropine sulphate, chloroaurates were obtained having m. p. 127° or lower, instead of the usual 135—137°. The impure chloroaurate was produced only after the aqueous solution of the atropine sulphate had been heated. In these conditions, it is found, atropine is hydrolysed to tropine and tropic acid. Only the sulphate behaves in this way; the chloride, nitrate, and phosphate are stable. W. A. SILVESTER.

Constitutions of corycavidine and corycavamine. F. VON BRUCHHAUSEN (Arch. Pharm., 1925, **263**, 570—602).—Corycavidine, separated from corycavine as its more soluble hydrochloride, has the empirical formula $C_{22}H_{25}O_5N$ (m. p. 211—212°, $[\alpha]_D^{20}$ +210·8°); its nitrogen atom forms part of a monocyclic methylimino-group, whilst of its oxygen atoms four are combined as one methylenedioxy-group and two methoxy-groups (cf. Gadamer, A., 1902, i, 306). The function of the fifth oxygen atom, hitherto undetermined, is apparently not alcoholic, because the alkaloid is unaffected by hot acetyl chloride. Boiling acetic anhydride converts the base chiefly into an optically inactive form, m. p. 193—194° (cf. Gadamer, *loc. cit.*), but in part also into an N(?)-*acetyl* derivative, m. p. 212°, together with a little quaternary nitrogen compound, coloured red. These results are ambiguous, offering no direct evidence of the presence of either a tetrahydroquinoline or a 10-membered ring. Moreover, phosphorus oxychloride, which quantitatively isomerises corycavine (Gadamer and von Bruchhausen, Arch. Pharm., 1922, **260**, 97), has here no action at 130°, and at 160° destructive decomposition takes place. No interaction takes place with hydroxylamine or semicarbazide.

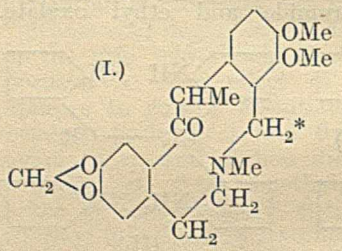
When the alkaloid is treated with methyl sulphate, the *methosulphate* (m. p. 220—222°, weakly dextrorotatory) is formed. The *methiodide* is weakly lævorotatory. The methosulphate is reduced by treatment in boiling dilute acid solution with sodium amalgam to *tetrahydromethylcorycavidine*, $C_{23}H_{31}O_5N$, an oil ($[\alpha]_D^{20}$ +39·9°; *hydrochloride*, m. p. 190°; *chloroplatinate*, m. p. 164—165°; *picrate*, m. p. 174—176°). As for a ring scission only two hydrogen atoms are needed, this result suggests reduction also of a carbonyl group. This tetrahydro-compound, when treated with hot dilute hydrochloric acid (or with acetyl chloride), yields an optically inactive, unsaturated base, *anhydrotetrahydromethylcorycavidine*, an oil (*dibromide*, m. p. 213—214°; *hydrochloride*, m. p. 233—235°; *nitrate*), together with a small proportion of a dihydric *phenol*, m. p. 130—133°, apparently formed by scission of the methylenedioxy-group. When the acetate of the anhydro-base is oxidised in ice-cold solution by potassium permanganate the following products are isolated: (i) 3 : 4-*dimethoxy-2-methylacetophenone* (*methylacetoveratrone*), m. p. 70—71° (*semicarbazone*, m. p. 235—236°), the constitution of which was determined by synthesis (see below); (ii) 5 : 6-dimethoxy-*o*-toluic acid (methylveratric acid), m. p. 183°, sublimes (Kempf) at 75°. This acid was also obtained, together with iodoform, when (i) was oxidised with sodium hydroxide and iodine, and has been described by Perkin (J.C.S., 1918, **113**, 762, and earlier reference given there, where the m. p. is given as 177°); (iii) a second *acid*, sparingly soluble in ether, m. p. 248°, containing no nitrogen, and probably produced by oxidation of the methylamino-chain; (iv) *N*-methylhydrastinine, which was not isolated as such, but was treated with methyl iodide and trimethylhydrastylammonium iodide, m. p. 264°, so obtained; (v) an amino-*acid*,  $CH_2O_2{:}C_6H_2{<}^{CO—O}_{CH_2\cdot CH_2}{>}NHMe_2$, the *mercuric* double salt (m. p. 202°), and *chloroaurate* of which are described.

In attempting the reproduction of the methylacetoveratrone, it was found that the hydroxymethylene group in ψ-meconine cannot be reduced. The synthesis was eventually carried out with 2 : 3-dimethoxytoluene as a starting point. This, treated by the Friedel–Crafts process with acetyl chloride, directly affords the required compound, substitution taking place exclusively in the 6-position. On oxidation with alkaline permanganate, the acid (ii, above) is obtained from both the synthetic and natural products, together with much of what appears to be the α-ketonic *acid*,

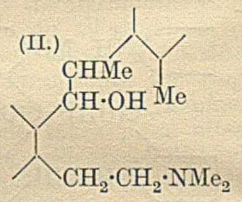
$$C_6H_2Me(OMe)_2\cdot CO\cdot CO_2H,$$

m. p. 130—133°. The above results, in spite of some discrepancies, considered in the light of earlier work in this field (Gadamer and von Bruchhausen, A., 1922, i, 675 etc.), suggest that corycavidine has the structure (I), the tetrahydromethyl and anhydrotetrahydromethyl derivatives having the constitutions indicated by (II) and (III), respectively. The conversion of (II) into (III) is considered to be analogous to that of toluylene hydrate into stilbene.

(I.)



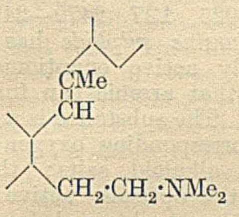
(II.)

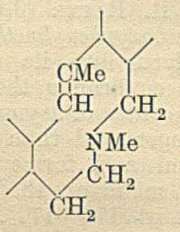


It is difficult to bring all the evidence into line with the above formula. For example, when the alkaloid is treated with ethyl chloroformate (Gadamer and Knoch, A., 1921, i, 579) it affords a *urethane*, m. p. 91° (the analogous *derivative* of inactive corycavidine has m. p. 129°), which contains chlorine. This chlorine is reactive and the compound resembles in this respect benzyl chloride, so that this urethane is presumably produced by scission between the nitrogen atom and the carbon denoted by a * in the formula above (I). On the other hand, the formation of the methine (Gadamer, 1902, *loc. cit.*) is readily explained and the following affords a further demonstration of the validity of the formula.

The proposed ketonic 10-membered ring structure, whilst suggesting how it is that corycavidine is not readily isomerised, suggests that its reduction product, a secondary alcohol, should readily change in this way. *Dihydrocorycavidine* (m. p. 147—148°, $[\alpha]_D^{20}$ −44·3°), obtained by treating the alkaloid, in dilute sulphuric acid solution, with sodium amalgam, is, in fact, converted by hot acetyl chloride into the *iso*-compound (an oil, the *hydrochloride* and *hydriodide*, m. p. 153°, are described). This yields an optically inactive anhydro-base, namely, *anhydrodihydroisocorycavidine* (m. p. 160—161°), which is found to be identical with *des-N-methyl-4-methyltetrahydroberberine*, the latter compound being prepared for comparison by boiling 4-methyltetrahydroberberine methochloride (Freund and Fleischer, A., 1915, i, 982) with methyl-alcoholic potassium hydroxide. Both compounds have therefore the constitution (IV).

(III.)

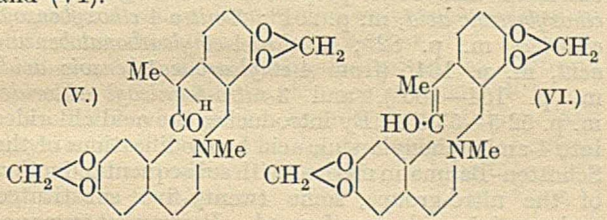




(IV.)

In the isolation of corycavidine, Gadamer separated a small quantity of another alkaloid, m. p. 191°. This, after purification *via* the hydrochloride, has m. p. 193—194°, and proves to be optically inactive corycavidine (methine, m. p. 141·5°, urethane, m. p. 129°, cf. above). It may have been formed in the extraction process.

When corycavamine (m. p. 149°; Gadamer, 1902, *loc. cit.*), which is isomeric with corycavine ($C_{21}H_{21}O_5N$, Gadamer and von Bruchhausen, A., 1922, i, 675), is heated at 155° in hydrogen, it is converted into the latter base (m. p. 153°). It is therefore considered to be the ketone of which corycavine is the enol, (V) and (VI).

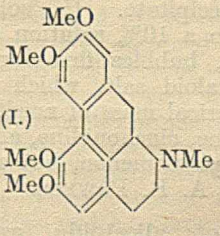

(V.) (VI.)

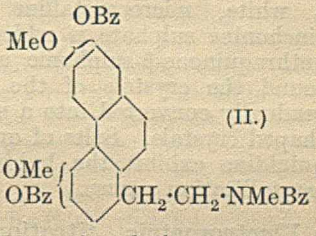
W. A. SILVESTER.

Alkaloids of *Corydalis cava*: corybulbine and *iso*corybulbine. [Synthesis of the methyl ethyl ether of nor-*m*-hemipinic acid.] F. VON BRUCHHAUSEN and K. SAWAY (Arch. Pharm., 1925, **263**, 602—605).—Späth and Dobrowsky (A., 1925, i, 1085) have anticipated the authors in their work in this field; they therefore publish the following notes on their independent synthesis of the ethylimide of the methyl ethyl ether of nor-*m*-hemipinic acid. 3-Methoxy-4-ethoxytoluene, when condensed with acetyl chloride by the Friedel–Crafts method, yields 4-*methoxy-5-ethoxy-2-methylacetophenone* (b. p. 156—160°/11 mm.; *oxime*, m. p. 99—100°; *semicarbazone*, m. p. 185—186°). This is oxidised by potassium permanganate in alkaline solution to a mixture of 4-*methoxy-5-ethoxy-2-methylbenzoylformic acid* (m. p. 75—77°; *methyl* ester, m. p. 108—109°) and 4-*methoxy-5-ethoxy-2-methylbenzoic acid* (5-*methoxy-4-ethoxy*-o-*toluic acid*; m. p. 180—183°; *methyl* ester, m. p. 64—65°). The acids are separated by fractional extraction of their ethereal solution with sodium hydroxide, the first acid being first extracted. The second acid is obtained from the first by further oxidation with hydrogen peroxide, and when again oxidised with alkaline permanganate it yields the *methyl ethyl ether* of *nor*-m-*hemipinic acid* (4-*methoxy-5-ethoxyphthalic acid*) (m. p. 184—185°), which is separated as its sparingly soluble *barium* salt. The ethylimide of this acid has the m. p. given by Späth and Dobrowsky (*loc. cit.*), viz., 205°.

W. A. SILVESTER.

Constitution of boldine. K. WARNAT (Ber., 1925, **58**, [*B*], 2768—2773).—Boldine was isolated from the South American tree, *Pneumus Boldus*, by Bourgoin and Verne in 1872, but, apart from an investigation by Merck (Jahresber., 1922, p. 110), who assigned to it the composition $C_{19}H_{24}O_4N$, it does not appear to have been examined further. Boldine contains two methoxyl groups and is converted by hydriodic acid into *norboldine*, a very unstable base which gives a characteristic *hydriodide*, m. p. 249—250°. It is converted by diazomethane into *boldine dimethyl ether*, m. p. 117—118° (*hydriodide*, m. p. 243°), which is transformed by hydriodic acid into norboldine. Analysis of these derivatives establishes the composition $C_{19}H_{21}O_4N$ for boldine. The alkaloid is converted by benzoyl chloride in alkaline solution into *tribenzoylboldine* (II), m. p. 173°, in which the third benzoyl group must be attached to nitrogen, since the product is optically inactive and does not react with methyl iodide as does the dimethyl ether. It is therefore probable that the nitrogen atom in boldine is tertiary and that benzoylation is rendered possible by fission of the ring, whereby the asymmetric carbon atom loses its asymmetry. In addition, *dibenzoylboldine*, m. p. (indef.) 124—127°, is formed in small amount. The assumption just made is confirmed by the Hofmann degradation of boldine dimethyl ether, to which the constitution (I) is therefore assigned (for position of methoxyl groups, see later).


(I.)


(II.)

Dimethylboldine and methyl iodide readily yield a *methiodide*, $C_{22}H_{28}O_4NI$, m. p. 221°, which is converted by potassium hydroxide into the oily, optically inactive, *boldinedimethylmethine*; the *methiodide*, $C_{23}H_{30}O_4NI$, m. p. 276—280° after darkening, of the latter substance is converted by successive treatment with silver oxide and potassium hydroxide into (?)2 : 3 : 5 : 6-*tetramethoxy-8-vinylphenanthrene* and trimethylamine. The hydrocarbon is oxidised by potassium permanganate in the presence of aqueous acetone to (?)2 : 3 : 5 : 6-*tetramethoxyphenanthrene-8-carboxylic acid*, m. p. 213—214°, and when distilled with zinc dust gives in very small yield a hydrocarbon which is probably ethylphenanthrene (cf. Pschorr, A., 1906, i, 820). Further confirmation of the presence of the phenanthrene nucleus in boldine is found in the production of benzene-1 : 2 : 3 : 4-tetracarboxylic acid when boldinedimethylmethine, its methiodide, or tetramethoxyvinylphenanthrene is oxidised by concentrated nitric acid.

The exclusive production of oxalic acid when boldine is oxidised by permanganate in alkaline solution appears to indicate that the two hydroxyl groups are attached to different nuclei. Oxidation of the dimethyl ether does not throw any further light on this question. Nevertheless, it appears probable from the recorded constants of glaucine (cf. Pschorr, Stählin, and Silberbach, A., 1904, i, 611; Gadamer, A., 1911, i, 483) that this substance is identical with boldine dimethyl ether (whence the position of the methoxyl group, *v.s.*). The experimental comparison of the two compounds has not yet been made. H. WREN.

Morphine in opium. E. MACHIGUCHI and S. SHIRONO.—See B., 1926, 27.

Microchemical analysis. IV. Anthraquinone-β-sulphonic acid as a reagent for alkaloids. L. ROSENTHALER (Mikrochem., 1925, 3, 80—83).—Anthraquinone-β-sulphonic acid is a general reagent for alkaloids, with which it forms more or less insoluble salts, generally amorphous. Among the crystalline precipitates produced by the addition of a solid alkaloid or alkaloidal salt to a 10% solution of the acid are the following: aniline, oily drops slowly changing to bundles of needles; antipyrine, oily drops becoming stellate aggregates of needles; atropine, amorphous precipitate changing to bundles of needles; hydrastinine, first drops, then a microcrystalline precipitate, and finally four-sided, strongly polarising leaflets; nicotine, first amorphous, then warty masses; novocaine, first orange-red droplets, then needles, and the alkaloids of the quinine group a white, microcrystalline precipitate. If solid cinchonine sulphate is added to a 10% solution of anthraquinone-β-sulphonic acid, bubbles first form round the crystals of the alkaloid salt, which is gradually converted into a spherical mass of needle-shaped crystals. Salts of quinine, cinchonidine, and quinidine exhibit the bubble phenomenon, but no crystallisation ensues. A. R. POWELL.

Electrometric titration of alkaloids and reaction of alkaloid salts. I. M. KOLTHOFF.—See B., 1926, 74.

Preparation of tertiary arsines by the Friedel–Crafts reaction. A. F. HUNT and E. E. TURNER (J.C.S., 1925, 127, 2667—2671).—Phenylmethylchloroarsine condenses with mesitylene to give *phenylmesitylmethylarsine*, b. p. 164°/17 mm., from which *phenylmesityldimethylarsonium iodide*, m. p. 187°, and *phenylmesitylbenzylmethylarsonium bromide*, m. p. 180°, were obtained. A similar condensation with toluene yielded *phenyl*-p-*tolylmethylarsine*, b. p. 165°/12 mm., which with methyl iodide formed *phenyl*-p-*tolyldimethylarsonium iodide*, m. p. 93°. With bromobenzene, the condensation yielded p-*bromodiphenylmethylarsine*, from which the *benzobromide* and p-*bromodiphenyldimethylarsonium iodide*, m. p. 87°, were prepared. The constitution of these compounds was confirmed by independent syntheses. p-*Bromophenylarsenious oxide*, m. p. 259—261°; p-*bromophenyldichloroarsine*; p-*bromophenylmethyliodoarsine*, m. p. 36·5°; p-*chlorophenyldichloroarsine*, b. p. 277°; p-*chlorophenylarsenious oxide*, m. p. 198°; and *di*-p-*chlorophenylchloroarsine*, m. p. 51°, were also prepared. B. W. ANDERSON.

Resolution of an asymmetric arsenic compound into its optically active form. W. H. MILLS and R. RAPER (J.C.S., 1925, 127, 2479—2483).—p-*Carboxyphenylmethylethylarsine sulphide* has been resolved into its optically active enantiomorphs, thus confirming the fact that arsenic can function as a centre of asymmetry. The substance is a much stronger acid than the corresponding oxygen compound and forms stable alkaloid salts; the *dl*-acid melts at 183° and the optically active acids melt at 175—177°. The *l*-acid obtained from the brucine salt has in ethyl alcohol $[\alpha]_{5780}^{20}$ $-19{\cdot}1°$ and $[\alpha]_{5461}^{20}$ $-21{\cdot}6°$, and the *d*-acid obtained from the morphine salt has in the same solvent $[\alpha]_{5780}^{20}$ $+18{\cdot}7°$, $[\alpha]_{5461}^{20}$ $+22{\cdot}2°$, and $[\alpha]_{4359}^{20}$ $+39{\cdot}4°$. The following substances are also described: p-*tolylmethyliodoarsine*, b. p. 163—165°/12 mm., m. p. 29°; p-*tolylmethylethylarsine*, b. p. 117°/15 mm. E. E. WALKER.

Trypanocidal action and chemical constitution. II. Arylamides of 4-aminophenylarsinic acid. H. KING and W. O. MURCH (J.C.S., 1925, 127, 2632—2651).—A series of *p*-substituted *m*-nitrobenzoic acids and their corresponding acid chlorides has been prepared, including 3-*nitro*-4-*ethoxybenzoic acid*, m. p. 201°; 3-*nitro*-4-*ethoxybenzoyl chloride*, m. p. 82°; 3-*nitro*-4-*ethylcarbonatobenzoic acid*, m. p. 164° (from 4-*ethylcarbonatobenzoic acid*, m. p. 154—156°), and 3-*nitro*-4-*anisoyl chloride*, m. p. 52·5—53·5°. By introducing the acid chlorides into 4-aminophenylarsinic acid by modifications of the Schotten–Baumann method with subsequent reduction of the nitro-groups, some twenty-five substituted aminoarsinic acids were formed. Permanent trypanocidal properties were shown by the *aminoanisoyl-*, *aminochlorobenzoyl-*, *diaminobenzoyl-*, *diaminotoluoyl-*, and *diaminochlorobenzoyl-aminophenylarsinic acids*. When the amino-group of aminoanisoyl-4-aminophenylarsinic acid was substituted with acetyl and other radicals, the trypanocidal action was lost. The following were prepared: 3 : 3′-*dinitrobenzoyl-*, 3′ : 5′-*dinitrobenzoyl-*, 3′-*nitro*-4′-*toluoyl-*, 3′-*amino*-4′-*toluoyl-*, 3 : 3′-*dinitro*-4′-*toluoyl-*, 3′-*nitro*-4′-*anisoyl-*, 3′-*acetamido*-4′-*anisoyl-*, 3′-*carbethoxyamino*-4′-*anisoyl-*, 3″-*nitro*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*amino*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*nitrobenzoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*aminobenzoyl*-3′-*amino*-4′-*anisoyl-*, 3′-*nitro*-4′-*ethoxybenzoyl-*, 3′-*amino*-4′-*ethoxybenzoyl-*, 4′-*chloro*-3′-*nitrobenzoyl-*, 4′-*chloro*-3 : 3′-*dinitrobenzoyl-*, 3′-*nitro*-4′-*ethylcarbonatobenzoyl-*, 3′-*nitro*-4′-*hydroxybenzoyl-*, 3′-*amino*-4′-*hydroxybenzoyl-*, 3′-*acetamido*-4′-*acetoxybenzoyl-*, and 3′-*acetamido*-4′-*hydroxybenzoyl*-4-*aminophenylarsinic acids*. 3′-*Amino*-4′-*hydroxybenzoyl*-4-*aminoarsenobenzene* and 3-*acetamido*-4-*acetoxyphenylarsinic acid* were also obtained. In the nitration of *para*-substituted benzoic acids, it was found that the relative directive powers for *ortho*-substitution of a nitro-group may be written OH, $NMe_2 > Me$, OMe, $OEt > F$, Cl, Br, $O{\cdot}CO_2Et$. B. W. ANDERSON.

Arsenical derivatives of thiophen. III. C. FINZI (Gazzetta, 1925, 55, 824—834).—The methods of synthesis previously employed (A., 1916, i, 94, 95) serve also for the preparation of halogenated thiophen-2-arsinic acids. Thus, the action of arsenic trichloride on 2-bromo- and 2-iodo-thiophen 5-mercurichloride (cf. Steinkopf and Bauermeister, A., 1914, i, 427) yields 2-bromo- and 2-iodo-5-thienyldichloroarsine, and these, when oxidised by means of hydrogen peroxide in presence of sodium hydroxide, give, respectively, crystalline *5-bromothiophen-2-arsinic acid*, $C_4H_2BrS\cdot AsO(OH)_2$, and *5-iodothiophen-2-arsinic acid*, which remain unfused at 300°, and when heated with magnesia mixture give the reaction of the primary arsinic acids. The bromo-acid is not attacked by concentrated nitric acid, but is partly decomposed, although not nitrated, by a mixture of sulphuric and nitric acids. This mixture, however, converts the iodo-acid into 3(or 4)-*nitro-5-iodothiophen-2-arsinic acid*, $NO_2\cdot C_4HIS\cdot AsO(OH)_2$, m. p. 302°.

Reduction of the above compounds by means of hypophosphorous acid (cf. Bart, A., 1922, i, 1202) yields the following derivatives. 2 : 2'-*Arsenothiophen*, $C_4H_3S\cdot As{:}As\cdot C_4H_3S$, a canary-yellow, amorphous compound, begins to soften below 100° and gradually decomposes. 5 : 5'-*Dinitro*-2 : 2'-*arsenothiophen*, greenish-yellow and amorphous, turns brown at 150° and explodes violently at 170—178°. 5 : 5'-*Dibromo*-2 : 2'-*arsenothiophen* softens at 130° and melts with frothing at about 170°. 5 : 5'-*Di-iodo*-2 : 2'-*arsenothiophen*, a yellow, amorphous substance, softens at 135° and is almost completely fused at 175°. *Dinitro*-5 : 5'-*di-iodo*-2 : 2'-*arsenothiophen* softens at 120° and decomposes with intense charring at about 140°.

Tri-2-thienylarsine (cf. Steinkopf, A., 1917, i, 303) may be readily obtained by the action of metallic sodium on an ethereal solution of 2-bromothiophen and arsenic trichloride. T. H. Pope.

Trypanocidal action and chemical constitution. III. Arsinic acids containing the glyoxaline nucleus. I. E. Balaban and H. King J.C.S., 1925, **127**, 2701—2714).—The preparation of *glyoxaline*-4(or 5)-*carboxy*-o-*nitroanilide*, m. p. 229° (*nitrate*, m. p. 196°, decomp.; *hydrochloride*), and *glyoxaline*-4(or 5)-*carboxy*-p-*nitroanilide* (with 2 mols. of acetic acid, m. p. 307°; *hydrochloride*, m. p. 265°, decomp.) was carried out and by reduction of these compounds *glyoxaline*-4(or 5)-*carboxy*-o-*aminoanilide*, m. p. 270° (*chlorostannate*; *dihydrochloride*, decomp. 310°; *dipicrate*, m. p. 242°, decomp.), and *glyoxaline* 4(or 5)-*carboxy*-p-*aminoanilide*, m. p. 228° (*dihydrochloride*, blackens at 290°; *picrate*, decomp. 266°), were obtained. Treatment of glyoxalinecarboxy-*o*-aminoanilide dihydrochloride with nitrous acid yields a sparingly soluble *diazoimide*, m. p. 196°, which will detect nitrous acid at a dilution of 1 in 6400. From the *p*-aminoanilide was prepared *glyoxaline*-4'(or 5')-*carboxy*-p-*aminophenylarsinic acid* (*hydrochloride*; *magnesium*, *calcium*, and *sodium* salts), and both this and *glyoxaline*-4'(or 5')-*carboxy*-p-*amino*-3-*aminophenylarsinic acid* (*diazoimide*; *magnesium* and *calcium* salts) showed permanent trypanocidal activity; the latter acid was prepared by reduction of *glyoxaline*-4'(or 5')-*carboxy*-p-*amino*-3-*nitrophenylarsinic acid* (*magnesium*, *calcium*, *barium*, and *lithium* salts). Unsuccessful attempts were made to introduce the arsinic acid group into 2-m-*aminophenylglyoxaline* (*monohydrate*, m. p. 203°; *dihydrochloride monohydrate*, decomp. 282°; *monopicrate*, decomp. 218°) and into 2-p-*aminophenylglyoxaline* (*dihydrochloride*; *monopicrate*, decomp. 238°). 2-p-*Nitrophenyl*-1-*methylglyoxaline*, m. p. 116·5° (*chloroaurate*, m. p. 226°; *hydrochloride*; *nitrate*, decomp. 180°; *picrate*, decomp. 212°), was obtained in poor yields, and the following were also prepared in the course of the investigation: 2-o-*aminophenylglyoxaline*, m. p. 137° (*dihydrochloride*, m. p. 234—236°; *monopicrate*, m. p. 212°); 4-p-*aminophenylglyoxaline*, m. p. 98° (*chlorostannate*; *dihydrochloride*; *dipicrate*, m. p. 240°, decomp.); *glyoxaline*-4(or 5)-*phenyl*-p-*arsinic acid*, m. p. >310° (*magnesium* and *calcium* salts); 4-o-*aminophenylglyoxaline*, m. p. 131° (*dihydrochloride monohydrate*, decomp. 256°; *dipicrate*, decomp. about 200°; normal *tartrate*, m. p. 95—97°; *di*-d-*camphor*-10-*sulphonate*, m. p. 198—200°); 2-*phenyl*-1-*methylglyoxaline*, b. p. 175°/15 mm. (*methochloride*, m. p. 272°; *picrate*, m. p. 133°; *chloroaurate*, m. p. 189°; *nitrate*, m. p. about 100°; *hydrochloride*; *hydrogen oxalate*, m. p. 135°). B. W. Anderson.

Thiazoles. X. Synthesis of some 1-phenylbenzthiazolearsinic acids. M. T. Bogert and H. B. Corbitt (Proc. Nat. Acad. Sci., 1925, **11**, 768—772).—1-*Phenylbenzthiazole-5-arsinic acid*, unmelted at 310°, is obtained in 5·4% yield by Bart's reaction from 5-amino-1-phenylbenzthiazole, copper-bronze being the best catalyst. The isomeric 4'-*arsinic acid*, unmelted at 302°, prepared similarly from 1-*p*-aminophenylbenzthiazole (yield 26%), gives 5(?)-*nitro*-1-*phenylbenzthiazole*-4'-*arsinic acid* when treated with mixed acid at 40—45°. The corresponding *amino*-derivative, obtained by reduction of the nitro-compound with ferrous sulphate and alkali, couples with β-naphthol to give a cherry-red *dye*. The amine has trypanocidal properties and is free from the powerful action on the nervous system associated with other quinquevalent arsenic compounds. 1-*p*-Hydroxyphenylbenzthiazole, nitrated and reduced, gives an *amine*, which is converted by Bart's reaction into a 1-p-*hydroxyphenylbenzthiazolearsinic acid*. C. Hollins.

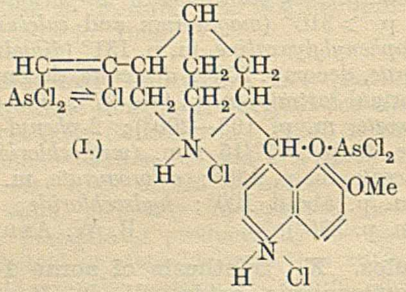
Neosalvarsan and sulpharsphenamine. E. Elvove.—See B., 1926, 27.

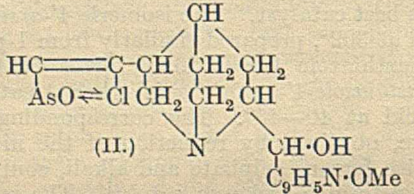
Diphenylaminechloroarsine [chlorophenarsazine]. W. L. Tanner.—See B., 1926, 76.

Arsinophenylcinchoninic acid (arsinocinchophen) and derivatives. II. H. O. Calvery, C. R. Noller, and R. Adams (J. Amer. Chem. Soc., 1925, **47**, 3058—3060; cf. A., 1925, i, 706).—5-Nitroisatin, m. p. 254—255° (cf. Baeyer, A., 1879, 937; D.R.-P. 221259), condenses with acetophenone in boiling aqueous alcoholic potassium hydroxide solution, with formation of 6-*nitro-2-phenylquinoline-4-carboxylic acid* (*nitrocinchophen*), yellow, m. p. 350—355° after darkening, as the *potassium* salt. This is reduced by stannous chloride and hydrochloric acid to 6-amino-2-phenylquinoline-4-carboxylic acid, orange, m. p. 259—260° (decomp.) after sintering at 240° (cf. D.R.-P. 287804), and this, when diazotised and treated with arsenious oxide, is converted into 6-*arsino-2-phenylquinoline-4-carboxylic acid* (*arsino-*

cinchophen), m. p. not below 360°. On reduction with sodium hyposulphite, the latter yields 2 : 2′-*diphenyl*-6 : 6′-*arsenoquinoline*-4 : 4′-*dicarboxylic acid*, red, m. p. not below 300°. Both the arsino- and the arseno-derivatives are trypanocides, but too toxic for ordinary use. F. G. Willson.

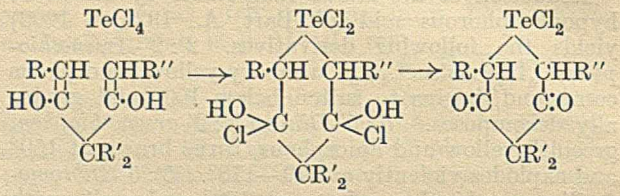
Action of arsenic trichloride on dehydroquinine, quinine, and dihydroquinine. F. X. Erben, E. Philippi, and N. Schniderschitz [with F. Sporer and E. Diamont] (Ber., 1925, 58, [*B*], 2854—2859).—The action of arsenic trichloride on dehydroquinine in the presence of chloroform at 150° yields a *substance* (I.) which is very sensitive towards moisture and is transformed by ammonium carbonate solution into *chloroarsinosoquinine* (II). The constitution assigned to substance (I) depends on the observation that six of the seven chlorine atoms are removed by the action of cold silver nitrate solution, whereas the seventh remains attached to the molecule. Further, quinine and dihydroquinine are transformed by arsenic trichloride into *compounds*, $C_{20}H_{25}O_2N_2Cl_4As$ and $C_{20}H_{27}O_2N_2Cl_4As$, which are converted by ammonium carbonate solution into the arsenious *esters*, $C_{20}H_{23}O_3N_2As$ and $C_{20}H_{25}O_3N_2As$, which contain the arsenic atom united to the secondary hydroxy-group, –CH·O·As:O. The presence of a free hydroxy-group in substance (II) and, consequently, the attachment of arsenic to the vinyl group, is established by the production of a *benzoyl* derivative, $C_{27}H_{26}O_4N_2ClAs$. H. Wren.


(I.)


(II.)

Interactions of tellurium tetrachloride and monoketones. G. T. Morgan and O. C. Elvins (J.C.S., 1925, 127, 2625—2632).—Tellurium tetrachloride undergoes condensation with many monoketones which are capable of enolisation, forming either a tellurium bisketone dichloride or a tellurium ketone trichloride. Thus *tellurium bisacetone dichloride*, m. p. 126—128°; *tellurium methyl ethyl ketone trichloride*, m. p. 101·5°; *tellurium bismethyl* n-*propyl ketone dichloride*, m. p. 92—93°; *tellurium bismethyl* iso*propyl ketone dichloride*, m. p. 90° after softening at 85°; *tellurium bismethyl* n-*butyl ketone dichloride*, m. p. 62°; *tellurium bismethyl* iso*butyl ketone dichloride*, m. p. 95°; *tellurium diethyl ketone trichloride*, m. p. 78°; and *tellurium di*-n-*propyl ketone trichloride*, m. p. 70°, have been prepared. The condensation with pinacolin yielded both *tellurium pinacolin trichloride*, m. p. 115°, and *tellurium bispinacolin dichloride*, m. p. 192°; with di*iso*propyl ketone, no condensation took place. By using mixed ketones containing aromatic radicals, *tellurium phenyl ethyl ketone trichloride*, m. p. 115°; *tellurium phenyl* n-*propyl ketone trichloride*, m. p. 129°; and *tellurium phenyl benzyl ketone trichloride*, m. p. 143°, were also obtained. B. W. Anderson.

Production of *cyclo*telluripentanedione dichlorides. G. T. Morgan [with F. J. Corby, O. C. Elvins, E. Jones, R. E. Kellett, and C. J. A. Taylor] (J.C.S., 1925, 127, 2611—2625).—The condensation occurring between tellurium tetrachloride and β-diketones yields cyclic products due to twofold terminal enolisation :



and also noncyclic products due to simple median enolisation of the diketone, the course of the reaction depending on the nature of R, R′, and R″ in the above formulæ. From n-*propylpropionylacetone*, b. p. 210° (*copper* derivative, m. p. 178°, decomp.), was obtained 2-*methyl*-4-n-*propyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, blackens at 150°, readily reduced to 2-*methyl*-4-n-*propyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 102°. Similarly, 3-iso*propylpropionylacetone*, b. p. 195°, gave 2-*methyl*-4-iso*propyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, blackens at 173°, which on reduction yielded 2-*methyl*-4-iso*propyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 127°. 4-*Benzyl*-2-*methyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 168°, was obtained from 3-*benzylpropionylacetone*, b. p. 185°/20 mm. (*copper* derivative, m. p. 182°), and the dichloride yielded the corresponding 4-*benzyl*-2-*methyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 124° (decomp.). 3-iso*Butylacetylacetone*, b. p. 94°/10 mm. (*copper* derivative, m. p. 158°), was prepared, and from it 4-iso*butyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 142°, which gave 4-iso*butyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 150°. In a similar manner, 2-*benzyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, 2-*benzyl*cyclo*telluropentane*-3 : 5-*dione* (decomp. 159°), 2-n-*decyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 89°, and 2-n-*decyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 99° (decomp.), were obtained. 3-Phenylpropionylacetone yielded no *cyclo*telluriderivatives. From 3-sec.-*butylacetylacetone*, b. p. 109—111°/13 mm., were formed 4-sec.-*butyl*cyclo*telluri-pentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 169°, and 4-sec.-*butyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 145°; and from dl-sec.-*amylacetylacetone*, b. p. 116°/15 mm. (*copper* derivative, m. p. 120°), 4-sec.-*amyl*cyclo*telluripentane*-3 : 5-*dione-dichloride*, m. p. 162°, and 4-sec.-*amyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 139°, were obtained. The condensation of tellurium tetrachloride with 3-sec.-*amyldipropionylmethane*, b. p. 137°/15 mm. (*copper* derivative, m. p. 105°), yielded only oily products. B. W. ANDERSON.

Naturally occurring porphyrins. XVII. Transformation of uroporphyrin into coproporphyrin, and certain derivatives of these porphyrins. H. FISCHER and J. HILGER (Z. physiol. Chem., 1925, **149**, 65—70).—By heating dry uroporphyrin at 180° in an atmosphere of nitrogen, decarboxylation occurs, and coproporphyrin is formed in 60% yield. Uroporphyrin is probably an ætioporphyrin, of the formula $C_{40}H_{38}O_{16}N_4$, containing thirty-two carbon atoms in the nucleus with, in addition, eight carboxyl groups. A new *porphyrin* giving a crystalline *copper* salt is obtained by the action of fuming nitric acid on the methyl ester of uroporphyrin. In similar conditions, coproporphyrin methyl ester yields a dinitro-derivative. Crystalline *cadmium* and *manganese* salts of coproporphyrin methyl ester have been prepared. H. D. KAY.

Formation of protein complexes with hydroxides of tervalent metals. De-proteinisation by means of alums. L. C. MAILLARD and H. WUNSCHENDORFF (Compt. rend., 1925, **181**, 941—942; cf. A., 1925, i, 1346).—Potassium alums of aluminium, chromium, and iron precipitate proteins quantitatively from biological fluids on addition of alkali. Thus, to a solution containing serum 2 c.c., water 5 c.c., and 5% solution of potassium aluminium alum 25 c.c., 0·5*N*-sodium hydroxide is added until the hydrogen-ion concentration reaches p_H 7, and the volume is made up to 50 c.c. The filtrate is protein-free, but contains the original amount of ammonia, carbamide, and uric acid. L. F. HEWITT.

General properties of proteins. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1925, **9**, 169—179).—Theoretical, with no new experimental evidence. It is concluded that: (1) hæmoglobin, when denatured, is probably depolymerised to hæmochromogen, and that in other proteins denaturation probably consists in depolymerisation, native proteins, therefore, being considered as aggregates of denatured proteins; (2) the globins and histones are to be regarded as denatured proteins rather than as a distinct class; (3) a non-polar group is uncovered when a protein is denatured; and (4) proteins are highly specific only in the native form. The factors affecting the equilibrium between native and denatured protein are discussed. C. P. STEWART.

Crystallisation and specific rotation of ovalbumin and an attempt to crystallise lactalbumin. C. W. CHAPMAN (Canadian Chem. Met., 1925, **9**, 268—270).—Crystallisation of ovalbumin by the method of Hopkins occurs only between p_H 4·7 and 5·4. It is uncertain at p_H above 5·1, the best yield being obtained between p_H 4·7 and 5·1, *i.e.*, near the isoelectric point of the protein. Within this p_H range, recrystallisation yields a product almost wholly crystalline and with a constant specific rotation, $[\alpha]_D+30{\cdot}68°$. Lactalbumin prepared by various methods did not crystallise when submitted to the process used for ovalbumin. C. P. STEWART.

Tryptophan-content of proteins; determination of tryptophan. J. TILLMANS and A. ALT (Biochem. Z., 1925, **164**, 135—162).—The colorimetric method of Fürth and Nobel (A., 1921, i, 74) for the determination of tryptophan in proteins gives very high results. The colour obtained with pure tryptophan solutions is bluish-violet and with proteins reddish-violet. Comparison is therefore difficult and the use of blue glass filters gives incorrect results. The methods of May and Rose (A., 1923, i, 160) and of Folin and Looney (A., 1922, ii, 539) give more trustworthy results, but are tedious. A new method based on the protein reaction with formaldehyde and sulphuric acid is elaborated which is much simpler, allows of ready comparison of colours, and is carried out directly without hydrolysis of the proteins. The tryptophan contents of a large number of proteins are tabulated. The tryptophan content of the protein of cow's and goat's milk is about the same, but is smaller than that of human milk. The tryptophan content of three types of cheese did not change during the ripening process. By means of this method, it is shown that the Fritzmann reaction (A., 1899, ii, 54) for the detection of nitrate in milk is a specific tryptophan reaction. The myosin from horse-flesh has almost the same tryptophan content as that from beef. Wheat protein contains more tryptophan than rye protein. Zein is devoid of tryptophan. Adulteration of wheat flour by rye flour can therefore be detected by determination of the tryptophan content of the alcohol-soluble proteins, which for wheat should not be below 0·8%.
P. W. CLUTTERBUCK.

Determination of halogens and sulphur in organic substances. O. WAGNER.—See B., 1926, 75.

Separation of ethyl alcohol from acetaldehyde or acetone. G. GORR and J. WAGNER (Biochem. Z., 1925, **161**, 488—491).—The liquid is boiled under a reflux condenser for 5 hrs. with freshly prepared mercuric oxide. The alcohol can now be distilled off and determined. H. I. COOMBS.

Gasometric method for the determination of acetic anhydride. E. L. WHITFORD (J. Amer. Chem. Soc., 1925, **47**, 2939—2940; cf. this vol., 146).—Anhydrous oxalic acid is added in excess to pyridine which has been dried by treatment with fused sodium hydroxide, barium oxide, and calcium carbide, and the mixture then saturated with dry carbon monoxide and dioxide. The weighed sample of acetic anhydride is added, and the gases evolved are collected over water saturated previously with carbon monoxide and dioxide. The amount of acetic anhydride present in the sample is deduced from the volume of gas generated: $C_2H_2O_4+Ac_2O=CO+CO_2+2HO{\cdot}Ac$.
F. G. WILLSON.

Accurate general iodometric method for the determination of the carbonyl group in organic compounds. E. G. R. ARDAGH and J. G. WILLIAMS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 73—74, and J. Amer. Chem. Soc., 1925, **47**, 2983—2988).—The method described consists in converting the aldehyde or ketone into a phenylhydrazone and determining the excess of phenylhydrazine iodo-

metrically. In a 100-c.c. glass-stoppered flask are placed 20 c.c. of 0·5*M*-phenylhydrazine hydrochloride, 20 c.c. of a solution of disodium phosphate slightly weaker than 0·5*M*, and sufficient carbonyl compound to react with about half of the phenylhydrazine. The volume is made up to 100 c.c. with saturated sodium chloride solution, the air removed with nitrogen, and the whole kept at the ordinary temperature (or if necessary on the water-bath) for 30 min. until the reaction is completed. If a solid hydrazone separates it is quickly filtered off. Twenty-five c.c. of this solution are shaken with 4—5 c.c. of light petroleum in a 100-c.c. separating funnel (air removed with nitrogen) for 2 min. and 2 min. allowed for separation. Ten c.c. of the aqueous layer are run into a stoppered Erlenmeyer flask, air being replaced by nitrogen, and the solution is made just acid to methyl-orange. Sufficient 0·1*N*-iodine is run in to give a 5 c.c. excess and the mixture kept for 5 min. Starch solution is added and 3—4 c.c. excess of 0·1*N*-sodium thiosulphate run in. The contents are now shaken with 5 c.c. of ether to extract iodine from the drops of iodobenzene and a final titration is made with 0·1*N*-iodine. The volumes of the remainder of the aqueous and ethereal solutions are then determined. A control is made under similar conditions on the phenylhydrazine alone. The correction to be applied is usually quite small. Distilled water boiled and cooled in an atmosphere of nitrogen is used throughout. The method described is superior to that of Benedikt and Strache (A., 1893, i, 560) using Fehling's solution for the determination of the excess of phenylhydrazine.
J. S. CARTER.

Determination of cystine and cysteine. Y. OKUDA (J. Dept. Agric. Kyusha Univ., 1925, **1**, 163—196).—Cysteine, in the absence of cystine and certain other amino-acids, may be accurately determined in acid solution containing bromide by titration with a standard solution of bromate, 1 mol. of cysteine being oxidised to cysteic acid by six atoms of the liberated bromine. Another method, not vitiated by the presence of cystine etc., is to titrate the acid cysteine solution in presence of iodide with standard iodate solution. Definite conditions, however, must be employed and corrections made from a temperature curve. This method may be applied to the determination of cystine by first reducing this compound to cysteine under regulated conditions. There is no appreciable decomposition of cystine during acid hydrolysis of proteins, but the amount precipitable as phosphotungstate decreases rapidly, as part of the cystine is transformed into an isomeride the phosphotungstate of which is soluble. A series of determinations of the cystine content of proteins using the above iodine method and Folin and Looney's method (A., 1922, ii, 539) showed that the latter is untrustworthy. The cystine present in urine may be determined by the iodine method after removing coagulable protein and thiocyanate.
B. W. ANDERSON.

Biochemistry.

Thiocyanates and cellular respiration. N. TARUGI (Annali Chim. Appl., 1925, **15**, 416—426).—A discussion of this question, the influence of the thiocyanic group on cellular respiration being regarded as analogous to that of the thiol group (cf. A., 1903, ii, 460; 1904, ii, 220; 1905, i, 176). T. H. POPE.

Carbon dioxide excreted in one minute by one cm. of nerve fibre. G. H. PARKER (J. Gen. Physiol., 1925, **9**, 191—195).—One cm. of nerve-fibre from the lateral-line nerve of the dogfish was estimated to excrete an average of $4{\cdot}2\times10^{-8}$ mg. of carbon dioxide per min. C. P. STEWART.

Tissue respiration. O. WARBURG (Biochem. Z., 1925, **163**, 252).—A comment on publications by Dixon and Thurlow (A., 1920, i, 1213) and Ahlgren ("Zur Kenntnis der tierischen Gewebsoxydation," 1925). E. C. SMITH.

Spirometer method of studying continuously the gaseous metabolism of man during and after exercise. K. FURUSAWA (Proc. Roy. Soc., 1926, **B**, **99**, 148—154).—A new method, including a specially designed apparatus, is described for studying continuously the rapidly altering gaseous metabolism of man, during and after muscular exercise.
W. O. KERMACK.

Muscular exercise, lactic acid, and supply and utilisation of oxygen. XIII. Gaseous exchanges of restricted muscular exercise in man. K. FURUSAWA (Proc. Roy. Soc., 1926, **B**, **99**, 155—166).—The gaseous metabolism occurring during exercise, involving only a comparatively small portion of the total musculature of the human body, shows certain differences as compared with exercise involving practically the whole musculature. The lactic acid formed in the exercised muscle may pass into the blood-stream and hence to the other muscles of the body. In this way, the large magnitude of the "oxygen debt" observed is rendered possible.
W. O. KERMACK.

Muscular exercise, lactic acid, and supply and utilisation of oxygen. XIV. Relation in man between oxygen intake during exercise and lactic acid content of the muscles. C. N. H. LONG (Proc. Roy. Soc., 1926, **B**, **99**, 167—172).—During moderate muscular exercise in man, the concentration of lactic acid in the muscle as measured by its concentration in the blood plasma, with which it is in equilibrium, is proportional to the square root of the rate of oxidation of lactic acid, as measured by the rate of oxygen intake, when a steady state has been established. This result agrees with that previously obtained for isolated muscle, and it indicates that the controlling reaction in the re-synthesis of glycogen from lactic acid in the muscle is a bimolecular one.

W. O. Kermack.

Molecular concentration in internal fluids of *Ascidia mentula*, Müll. M. Duval and M. Prenant (Compt. rend., 1926, **182**, 96—98).—The blood of *Ascidia mentula*, Müll., has p_H 7·1, a f. p. (—2·08°) lower than that of the surrounding sea-water (—1·98°), and a higher content of sodium chloride (3·47%) than the sea-water (3·3%).

L. F. Hewitt.

Body fluids of the honey-bee larva. II. Constituents of the blood and their osmotic effect. G. H. Bishop, A. P. Briggs, and E. Ronzoni (J. Biol. Chem., 1925, **66**, 77—88).—As compared with mammalian blood, the blood of the honey-bee larva has a high content of sugar (which falls during pupation); also of fats, amino-acids, potassium, calcium, magnesium, and phosphorus; the proteins, sodium, chlorine, and total salts are low. The depression of the f. p. of larval blood was 0·86° during feeding and 0·75° after pupation; the high values are chiefly due to the large amount of amino-acids, and the difference in the two periods to the above-mentioned reduction of sugar on pupation. Since, on adjusting a synthetic solution of inorganic salts, in similar concentrations, to the p_H of the blood, calcium phosphate was precipitated, it is assumed that, in the blood, part of the calcium is in the form of undissociated compounds of calcium carbonate with amino-acids.

C. R. Harington.

Conservation of red corpuscles *in vitro* and selective sensitivity to poisons. O. Laves (Biochem. Z., 1925, **161**, 416—443).—A solution is recommended in which blood-corpuscles may be kept for some time without hæmolysis. It consists of 2/3 isotonic salt solution (containing 0·9% of sodium chloride; 0·098% of potassium chloride; 0·098% of calcium chloride; 0·049% of sodium hydrogen carbonate) and 1/3 isotonic (9·15%) sucrose solution. The hæmolytic action of morphine, methyl- and ethyl-morphine, quinine, and codeine in solutions containing various anions was investigated.

H. I. Coombs.

Reaction of potassium ferricyanide with blood pigment. M. Nicloux and J. Roche (Compt. rend., 1925, **181**, 823—826).—On treatment of oxyhæmoglobin and carboxyhæmoglobin with potassium ferricyanide in alkaline solution methæmoglobin is formed and oxygen and carbon monoxide, respectively, are liberated in proportions indicating that methæmoglobin contains half the amount of oxygen present in oxyhæmoglobin (cf A., 1925, i, 993).

L. F. Hewitt.

Hæmoglobinogenous pigments. J. Oberzimmer and L. Walker (Virchow's Archiv, 1924, **252**, 33—38; from Chem. Zentr., 1925, II, 310).—By dissolving liver or spleen containing hæmosiderin in 60% potassium hydroxide and subsequently diluting with water, a precipitate consisting principally of ferric hydroxide together with some organic matter is obtained. In amount, it is roughly proportional to the hæmosiderin present. Ferric hydroxide is deposited in living tissues, where it may be adsorbed by protein and lipoid substances. In acid, dying tissues it becomes reduced to ferrous hydroxide, which then becomes diffused as ferrous hydrogen carbonate, from which ferric hydroxide is again formed in the presence of air. Ferric oxide or hæmosiderin is precipitated in large amounts in the superficial portions of fragments of liver containing hæmosiderin.

G. W. Robinson.

Inorganic elements associated with oxyhæmoglobin in horse blood. A. Desgrez and J. Meunier (Compt. rend., 1925, **181**, 1029—1031; cf. A., 1923, i, 409).—Oxyhæmoglobin was obtained from horse blood by defibrination, separation of the red cells at a low temperature after centrifuging, hæmolysis by water at 35°, crystallisation by addition of 25% of ethyl alcohol and cooling to a low temperature, filtration, drying, and recrystallisation in the same manner. After the second recrystallisation, the hæmoglobin dissolved only partly in 25% alcohol, leaving a brown, amorphous residue; the soluble matter was precipitated by addition of more ethyl alcohol. The various fractions were burnt in a hydrogen flame and the flame was examined spectrographically. A considerable amount of potassium together with iron, lithium, calcium, sodium, and traces of manganese were detected in the first crystalline crop of hæmoglobin. In the second crop of crystals, the potassium had decreased considerably in quantity, whilst the amounts of calcium and iron were unchanged. In the insoluble portion of the third crop, lithium, iron, and sodium were detected, but no potassium or calcium. In the portion of the third crop precipitated by alcohol, calcium but no lithium or sodium was detected.

L. F. Hewitt.

Tartarylhæmin. S. Hajdu (Biochem. Z., 1925, **163**, 233—240).—By the action of tartaric acid in methyl alcohol on hæmoglobin, a dark brown, crystalline product, m. p. 250—300° (decomp.), containing C 64·93, H 5·10, N 9·79, Fe 9·77%, has been obtained. By analogy with formylhæmin, this substance is considered to be *tartarylhæmin*,

$$[C_{34}H_{31}O_4N_4MeFeO]_4.$$

E. C. Smith.

Ultrafiltration of serum. B. Brukner and P. Uhlenbruck (Z. Biol., 1925, **83**, 586—592).—The rate of filtration through a Zsigmondy ultra-filter is increased by stirring. A magnetically-operated stirrer is briefly described. The size of the pores in a filter is reduced by prolonged subjection to high pressures, with consequent reduction of the speed of filtration. On this account, the accurate fractionation of proteins by ultrafiltration is very difficult.

H. P. Marks.

Physico-chemical properties of certain serum constituents. F. Vlès and A. de Coulon (Compt. rend., 1925, **181**, 1189—1191).—Human serum is subjected to cataphoresis at various hydrogen-ion concentrations and treated with a mixture of equal parts of ethyl alcohol and acetone. In this manner, flakes and a powdery precipitate are obtained. In the case of healthy men the flakes have two distinct isoelectric points, one in the neighbourhood of p_H 5·5—6·5 and another at p_H 11—12. The points in the case of women vary with their physical condition. In acute infections and cancer, the flakes obtained have different isoelectric points and in some cases only one point is observed. L. F. Hewitt.

So-called anion-deficit in blood-serum. Determination of the dissociation constant and concentration of an unknown acid present in serum. R. Mond and H. Netter (Pflüger's Archiv, 1925, **207**, 515—522; from Chem. Zentr., 1925, II, 315; cf. A., 1924, i, 114).—The alkali of blood at normal reaction is not combined with serum proteins. The deficit of anionic and osmotically active substances in the serum necessitates the assumption of the existence of a hitherto unknown acid. The presence in the ultrafiltrate from ox-serum of an acid, or mixture of acids, of dissociation constant $10^{-3\cdot5}$ and concentration $1/70$—$1/120N$, was indicated by electrometric titration. G. W. Robinson.

Activity of sodium in serum. L. Michaelis and S. Kawai (Biochem. Z., 1925, **163**, 1—7).—The determination of sodium ion in serum by means of a sodium amalgam electrode gives the same value as the determination of total sodium by the Kramer and Gittleman method (A., 1925, i, 180). It is concluded that serum proteins have no effect on the ionisation of sodium. E. C. Smith.

Thiocyanate content of human serum. H. Schreiber (Biochem. Z., 1925, **163**, 241—251).—In women and non-smoking men, the thiocyanate content varies between 0·025 and 0·04 mg.% of the serum. Smoking causes an increase to three times this value. Administration of thiocyanates causes an increase to thirty times the normal value, the level then remaining constant while administration continues. On cessation of treatment, the normal level is attained only after 2—3 weeks. Variations from the normal cannot otherwise be correlated with the condition of the subject. E. C. Smith.

The *pK'* of the Henderson–Hasselbalch equation for blood-serum. G. E. Cullen, H. R. Keeler, and H. W. Robinson (J. Biol. Chem., 1925, **66**, 301—322).—The average value of the term pK' of the Henderson–Hasselbalch equation, determined by observation on the blood-serum from fifteen miscellaneous pathological cases, was 6·095 at 38° and 6·183 at 20°, the temperature coefficient being therefore —0·005 per 1°; similar values were obtained from normal dog's blood-serum; the constancy of the figures derived from the various cases with differing protein and salt contents indicates that variations in the latter have no measurable effect on the value of pK'. The temperature coefficient of $[BHCO_3]$ is —0·1 millimol. per 1° at constant $[H_2CO_3]$ and —0·14 millimol. per 1° at constant p_H.
C. R. Harington.

Charcoals from colloids. R. Ehrenberg (Biochem. Z., 1925, **161**, 339—347).—Blood etc. from animals and diseased human beings was converted into charcoals and the adsorptive power of these measured. H. I. Coombs.

Simple colorimetric method for the determination, and a contribution to the physiology, of the sugar of the blood. I. B. Glassmann (Z. physiol. Chem., 1925, **150**, 16—43).—If excess of resorcinol is added to a solution of dextrose in presence of 20% hydrochloric acid, and boiled for an hour, a yellow solution is obtained, the colour of which, at temperatures above 60°, is a linear function of the dextrose content of the original solution. A method of blood-sugar determination, based on this principle, yields results which are not interfered with by any of the other reducing substances present in blood. Using this method, 45% of blood samples taken from normal, fasting individuals were found to contain no dextrose. The "hypoglycæmic" syndrome following injection of insulin is not due to a lowering of the blood-sugar, but to the production of a toxin which may be neutralised by dextrose. The sugar of the blood is not identical with ordinary dextrose.
H. D. Kay.

Carbohydrate utilisation. I. Rate of disappearance of dextrose from the blood. V. du Vigneaud and W. G. Karr (J. Biol. Chem., 1925, **66**, 281—300).—Rabbits which have fasted for some days show an exaggerated response to administration of dextrose in that the blood-sugar reaches a higher concentration and takes longer to return to the normal level. Administration of fat 18 hrs. previous to the test exaggerates this effect still further, but administration of dextrose, and still more of protein, at the same point increases the tolerance of the animal; a similar increased tolerance is induced by injection of adrenaline and by daily administration of sodium hydrogen carbonate, but insulin has the reverse effect, and morphine, although it raises the blood-sugar to the same extent as adrenaline, has no effect in improving the tolerance of the fasting rabbit.
C. R. Harington.

Normal variations of the inorganic phosphate of blood. R. E. Havard and G. A. Reay (Biochem. J., 1925, **19**, 882—887).—There is a rise of inorganic phosphate during sleep even by day. The seasonal variation in average normal blood was observed to be from 2·9 mg. of phosphorus per 100 c.c. in January to 40 mg. per 100 c.c. in August. The best normal results of the inorganic phosphate of the blood are obtained early in the day when the subject is seated. A micro-adaptation of Briggs' method was employed in this investigation. S. S. Zilva.

Acid-combining power of the blood of healthy and diseased children. J. Csapó and G. Mihalovics (Biochem. Z., 1925, **161**, 459—464).—The acid-combining power of blood and plasma (cf. A., 1925, i, 188) was investigated. In healthy children, the blood has twice the combining power of the plasma, and the combining power varies with the red corpuscle content. In anæmia and icterus the value is low.
H. I. Coombs.

Quantitative changes in blood-sugar and blood lactic acid in canine anaphylaxis. M. McCullough and F. I. O'Neill (J. Infect. Dis., 1925, **37**, 225).—Canine anaphylactic shock is accompanied by a rapid rise in the sugar content of the blood, reaching a maximum in 20 min. of nearly twice the normal value. After the first 15 min. the curve thus obtained is identical with the blood-sugar curve obtained by intravenous injection of a quantity of dextrose equivalent to the estimated glycogen content of the liver. The lactic acid increases during anaphylactic shock, the maximum of twice the normal value being reached within 30 min.

CHEMICAL ABSTRACTS.

Toxicity of serum left in contact with starch. A. LUMIÈRE and H. COUTURIER (Compt. rend., 1926, **182**, 89—91).—The toxicity of serum left in contact with starch is due to a finely-divided suspension which does not turn blue with iodine and which is removed by long centrifuging. L. F. HEWITT.

Immunological properties of alcohol-soluble vegetable proteins. IX. Biological reactions of vegetable proteins. J. H. LEWIS and H. G. WELLS (J. Biol. Chem., 1925, **66**, 37—48).—Complement fixation and anaphylactic tests indicate a close relationship between the alcohol-soluble proteins from the different species of the wheat family on the one hand, and between those from several species of maize on the other, but no inter-relationship between the two groups. C. R. HARINGTON.

Antigenic properties of hæmoglobin. W. ENGELHARDT (Biochem. Z., 1925, **163**, 187—196).—The addition to rabbit serum of dog's hæmoglobin to which the animals have previously been immunised results in the formation of a precipitate in which the hæmoglobin may be determined and thus serve as an index of the amount of antibody in the serum. The values vary between 0·02 mg. and 0·07 mg. of hæmoglobin per 0·1 c.c. of serum. Variation in the method of preparation and repeated crystallisation of the hæmoglobin have very little effect on its action on the immune serum. Heating at 70° for 30 min. has no effect on the power of the immune serum to precipitate hæmoglobin. The action of the immune serum is not rigidly specific, since a small quantity of sheep-hæmoglobin is precipitated.

E. C. SMITH.

Conversion products of the pigments of flesh and blood. VII. Muscle pigment and MacMunn's myohæmatin. O. SCHUMM (Z. physiol. Chem., 1925, **149**, 111—149).—The differences observed by Mörner and Günther between the spectrum of a freshly-prepared aqueous extract of muscle (myochrome solution) and that of an oxyhæmoglobin solution are confirmed. In the muscle of pigeons immediately after death, besides myochrome there is a small quantity of a pigment which gives a similar spectrum to hæmochromogen, with a well-marked absorption band about 550 $\mu\mu$. MacMunn's "dominant band of myohæmatin" is also visible if sections of suitable thickness are employed, but in water extracts the pigment has only been detected if the muscle was kept ½—1 hr. before extracting. The complete spectrum of the pigment, for which the name *myochromogen* is suggested, consists in a very dark, symmetrical band at 549·5 $\mu\mu$ and a weaker one at about 519$\mu\mu$. The altered position of the bands distinguishes the spectrum from that of hæmochromogen. Myochromogen can be converted into myatin (supposed), but the myochromogen spectrum reappears in alkaline solution when hydrazine hydrate is added. The identity of myatin and MacMunn's myohæmatin is not considered proved. Myatin in the presence of much myochrome, oxyhæmoglobin, or methæmoglobin can easily be overlooked, but small quantities incapable of recognition in the spectrum can easily be detected by conversion into myochromogen. It is concluded that muscle from pigeons immediately after death contains very little free myatin or myochromogen, but these are found in increasing quantities in aqueous extracts prepared some time after death. No proof has been found of the presence of myatin or myochromogen in quantity in the living muscle of dogs or pigeons. MacMunn's idea that fresh muscle (breast) of the pigeon contains only or almost only myohæmatin, is erroneous. Myochromogen is found together with other pigments in the flesh juices obtained by the Struve–MacMunn "ether method." The extracts from flesh after leaving it to decompose at 37° or 50° over long periods contain a pigment like hæmochromogen, which gives a spectrum like myochromogen and (for the present) cannot be distinguished from it. Pyridine extracts from the fresh muscle of pigeons give the same hæmochromogen reaction with hydrazine as is given by α-hæmatin. No definite proof has been found of the presence of coprohæmatin in the fresh muscle of pigeons or of calves. A. COULTHARD.

New porphyrin. H. M. FOX (Nature, 1926, **117**, 49—50).—Although the hæmatin of hæmoglobin and that of chlorocruorin both contain iron, the former has a different porphyrin from the latter, the axes of the bands of the two porphyrins obtained by Nencki's method being, respectively, 593, 549, and 613, 553 $\mu\mu$ in dilute (1 : 3) hydrochloric acid. When a modification of Laidlaw's procedure for the preparation of porphyrin was employed, the porphyrin from chlorocruorohæmatin, which is soluble in chloroform, gives bands situated considerably on the red side of those from ooporphyrin or porphyrin from hæmin. A. A. ELDRIDGE.

Ageing process. R. EHRENBERG (Biochem. Z., 1925, **164**, 175—182).—Comparative analysis of human livers and brains of the same and different ages appear to give periodicity with age in the values obtained for the alcohol–ether extract (% dry weight), for the total nitrogen and phosphorus of the extract and of the residue, and for the content of the hydrolysed extract in ammonia, monoamino-nitrogen, melanoidin, total nitrogen of diamino-acids and cystine, arginine, cystine, histidine, and lysine. Similar results are obtained in the comparative analysis of six batches of whole mice of age 0, ½, 1, 3, 8, and 24 months, the material of the mice of the same age being mixed to equalise individual variations. Comparative values are obtained also for the liver, brain, and kidney of a female rabbit and the corresponding organs of its litters of age six weeks and six months.

P. W. CLUTTERBUCK.

Chemical topography of the brain. I. Lipins and total nitrogen of the human cortex. H. Gorodisskay (Biochem. Z., 1925, **164**, 446—480).—The chemical differences between functionally different areas are most marked with regard to cholesterol content, and also the content in alcohol-extractable lipins (cerebrosides and saturated phospholipins), total nitrogen, and the phosphorus of the unsaturated phosphatides. The richest in lipins and total nitrogen is the motor area (ascending frontal gyrus), the poorest is the anterior association centre (frontal pole), occupying an intermediate position are the psycho-sensorial areas (cuneus and ascending parietal gyrus). Corresponding areas of the right and left hemispheres differ considerably in constitution. Above the age of fifty, cholesterol increases and total nitrogen and the phosphorus of the unsaturated phosphatides decrease. Alterations due to sex and age are most pronounced at the occipital pole. E. C. Smith.

Hydrogen-ion concentration and oxidation-reduction potential of the cell-interior before and after fertilisation and cleavage. Micro-injection study on marine eggs. J. Needham and D. M. Needham (Proc. Roy. Soc., 1926, **B**, **99**, 173—198).—Both the p_H and r_H (reduction potential) of certain marine eggs, studied by the method of micro-injection of indicators, show a remarkable constancy, the former being in the neighbourhood of 6·6 and the latter varying from 19 to 22, and both remain constant during fertilisation and also during the initial cell divisions. Asphyxia has no influence on the values found, and although during cytolysis the p_H decreases to between 4 and 5, the r_H does not appear to change. The results do not agree with those obtained by the method of vital staining.

W. O. Kermack.

Physiology of plain muscle. IV. Lactic acid content of plain muscle under various conditions. C. L. Evans (Biochem. J., 1925, **19**, 1115—1127).—Lactic acid is present in small amount in "resting" plain muscle (0·03—0·08%; the larger amounts in mammalian tissue). It increases when the muscle is made to contract, but the maximum is never so high as in skeletal muscle from the same species. Treatment which in skeletal muscle produces rigor raises the lactic acid content in plain muscle. When placed in solutions of phosphates, the lactic acid production is much greater when the p_H of the solution is 9 than when it is 4·5. The rate of lactic acid formation in disodium hydrogen phosphate solutions is accelerated by the presence of arsenates. The rate of acid production is much the same in 0·8% sodium hydrogen carbonate solution as in disodium hydrogen phosphate solution. Lactic acid rapidly accumulates in plain muscle under anaërobic conditions, but scarcely at all in the presence of oxygen. The glycogen content of plain muscle is small. The lactacidogen content of the muscle of the tortoise stomach (autumn) corresponds with about 0·15% of lactic acid.

S. S. Zilva.

Liver function. I. Determination of bile acids and pigments in duodenal contents. C. W. McClure, E. Vance, and M. C. Greene (Boston Med. Surg. J., 1925, **192**, 431—433).—The bile acids are determined colorimetrically by means of furfuraldehyde and sulphuric acid, and the pigments similarly with sodium sulphite and glacial acetic acid. Optimal conditions are given, but neither reaction is specific. Chemical Abstracts.

Elementary composition of hair. Z. Stary (Z. physiol. Chem., 1925, **150**, 202—204).—Human hair which has been previously washed and extracted with alcohol and ether, then treated with pepsin and trypsin to remove any traces of hydrolysable protein, washed and dried, has a very constant carbon, hydrogen, and nitrogen content. There is little difference between men's and women's hair. Average figures are C 50·3, H 6·6, N 16·3%. H. D. Kay.

Keratin substances of human skin. H. Menschel (Arch. exp. Path. Pharm., 1925, **110**, 1—45).—Human nail swells almost equally (25—35%) in water and various acids, but alkalis, especially potassium hydroxide, and the alkali hydrogen sulphides, produce a much increased swelling. Ammonium and calcium hydroxides have only a feeble effect. Similarly, hair is rendered more extensible and less tenacious by the action of alkalis, due to the swelling of the keratin constituents. If the alkali is washed out, the hair returns almost to its original condition. Tanning agents, especially formaldehyde, render hair brittle.

In alkalis skin loses its elasticity, due to the swelling of the keratin constituents. Acids, however, which have little or no action on the keratin constituents, cause rapid swelling and peptisation of the albumoses contained in the reticular layer, and the skin assumes a glassy appearance. H. P. Marks.

I. Colour reaction for disulphides. II. Sulphydryl reaction of skin. E. Walker (Biochem. J., 1925, **19**, 1082—1084, 1085—1087).—I. To the solution to be tested a few drops of 5% aqueous sodium nitroprusside are added, followed by 3—5 drops of 10% aqueous potassium cyanide. If the disulphide is present in high concentration, the colour, a deep magenta, develops immediately; if present in low concentration, there is a delay of a few minutes. The concentration 1 : 10000 is about the limit of sensitivity of the reaction. Sulphydryl compounds give an instantaneous colour. A few illustrations of the applicability of the colour test are given.

II. No evidence could be obtained that the nitroprusside reaction of skin is due to the presence of glutathione (A., 1925, i, 180). It is suggested that the reaction is due to the presence of a substance similar to or identical with the thermostable sulphydryl constituent of muscle. The skin rapidly loses its sulphydryl reaction under the influence of allyl thiocarbimide. S. S. Zilva.

Spermine. H. W. Dudley and O. Rosenheim (Biochem. J., 1925, **19**, 1034—1036).—Spermine is identical with musculamine, neuridine, and gerontine, bases which have been obtained from calf's muscle, human brain, and dog's liver, respectively, by earlier workers. The yields of spermine obtained from various animal tissues and yeast are tabulated. It is absent from bull's semen, ox blood, cow's milk, and hen's egg. Spermine cannot replace vitamin-*B* or the antineuritic vitamin (as tested on pigeons). Spermine phosphate does not function as a co-enzyme in alcoholic fermentation. S. S. ZILVA.

Oils from sharks and rays. A. ROGERS.—See B., 1926, 19.

Solubility of tertiary calcium phosphate in cerebrospinal fluid. L. E. HOLT, jun. [with I. GITTLEMAN] (J. Biol. Chem., 1925, **66**, 23—28; cf. A., 1925, i, 1209).—The reduction in the calcium and phosphorus concentration in human cerebrospinal fluid brought about by prolonged shaking in contact with tertiary calcium phosphate indicates that, as in the case of blood-serum, the fluid is normally supersaturated with this salt to the extent of at least 200%. The true solubility product in cerebrospinal fluid is less than 10^{-28}, being thus much lower than in serum. It is suggested that the lack of agreement between the observed ratios of the diffusible ions of the serum to those of the cerebrospinal fluid with the ratios demanded by the Donnan equilibrium may be due to the fact that the latter theory is concerned, not with stoicheiometric ionic concentrations, but with ionic activities, and that in serum, owing to the relatively high concentration of multivalent protein ions, the activity coefficients, particularly of the multivalent inorganic ions, will be much reduced. C. R. HARINGTON.

Properties and origin of lymph. XI. Influence of specific lymphagogues on the activity of the liver, detected by acetone formation. Y. ABE (Biochem. Z., 1925, **165**, 312—322).—When the surviving liver of rats and guinea-pigs is perfused with blood containing butyric acid, addition of lymphagogues (leech extract, peptone, extract of crab's muscle) causes considerable increase in acetone formation. This favours the view that lymphagogues stimulate the activity of the liver cells. P. W. CLUTTERBUCK.

Influence of certain salts on the yield and composition of milk. A. T. R. MATTICK and N. C. WRIGHT (Biochem. J., 1925, **19**, 915—920).—Calcium chloride, ammonium chloride, sodium hydrogen carbonate, or disodium hydrogen phosphate when administered to cows does not alter the plasma calcium content, nor does such treatment alter the composition of the milk. The administration of ammonium chloride (16 oz.) causes an almost complete suppression of the milk yield, accompanied in its later stages by a temporary increase in the concentration of the constituents of the milk. S. S. ZILVA.

Variation of the amount of nitrogenous material, particularly urea, in the saliva. A. DESGREZ, R. MOOG, and (MME.) L. GABRIEL (Compt. rend., 1925, **181**, 755—757).—Normal saliva contains from 59 to 197 mg. of urea per litre. When the secretion is stimulated, mechanically or chemically (citric acid), the urea content varies from 23 to 164 mg./litre, whilst with people suffering from uræmia the stimulated secretion contains from 330 to 1140 mg./litre. In uræmia, the ratio of nitrogen in the form of urea to total nitrogen in the saliva is about 0·27, compared with 0·16 for normal people. In all cases, the urea is destroyed by enzymic action if the saliva is kept. W. HUME-ROTHERY.

Menotoxin. K. KLAUS (Biochem. Z., 1925, **163**, 41—50).—Choline in sweat is not derived from the breakdown of phosphatides in the glands, but is secreted in the free form. On the first day of menstruation and on the preceding day women excrete nearly fifty times as much choline in the sweat than in the intermediate period. E. C. SMITH.

Presence of rare elements in the food and excretions of man. R. BERG (Biochem. Z., 1925, **165**, 461—462).—Foodstuffs often contain traces of manganese, zinc, nickel, cobalt, copper, and lead. Silicic and titanic acids are always detectable in urine. P. W. CLUTTERBUCK.

Arsenic content of urine. I and II. I. BANG (Biochem. Z., 1925, **165**, 364—376, 377—410).—I. A modification of the author's method (this vol., 39) is found to be satisfactory for the determination of arsenic in urine, the limits being ±0·05 mg. As per litre. The detection by the method of a small amount of arsenic in normal urine is not due to the presence of traces of substances which by using up iodine titrate as arsenic, since Ramberg's micro-method gives the same results. In order to decide whether arsenic is lost during the determination as volatile organic compounds, known amounts of cacodylic acid, atoxyl, and salvarsan were determined both in aqueous solution and in urine. Providing the salvarsan is dried to constant weight, all three substances were determined with the same accuracy as inorganic arsenic. Arsenic in the urine of a large number of hospital patients on the same diet was determined. In 16% of the cases, no arsenic was present; in 43%, 0·01—0·06 mg. As per litre; in 33%, 0·07—0·20; in 8%, 0·21—0·69. In four cases, the physiological variation in urinary arsenic over periods of 4—6 days was from 0 to 0·23 mg. As per litre.

II. Existing knowledge of the arsenic content of a large number of food materials is summarised and greatly amplified by further determination. Arsenic administered by mouth to man and animals quickly appears in the urine and to a greater extent than was previously supposed, the amount excreted varying directly with the dose. The rate at which it leaves the organism varies greatly in different individuals. A considerable amount of arsenic is retained and appears to be absorbed by various organs, chiefly the liver and kidney, and is then very slowly excreted. In acute poisoning, the liver, intestine, and kidney are chiefly affected, but in chronic poisoning chiefly the nervous system. The arsenic content of bone was investigated in one case only, but the quantity found was much greater than expected. P. W. CLUTTERBUCK.

Concentration of chlorides in glomerular urine of frogs. J. T. WEARN and A. N. RICHARDS (J. Biol. Chem., 1925, **66**, 247—273).—By means of the nephelometric method of Richards and Wells (A., 1904, ii, 287), the concentration of chlorides has been determined in the fluid withdrawn directly from the Bowman capsule of the frog's kidney (cf. Amer. J.

Physiol., 1924, **71**, 209). Amounts of chlorine of the order of 0·005 mg. could be determined with an average error of ±2·3%. Comparison of the figures so obtained with simultaneous determinations of the chlorides in the bladder urine indicates that the concentration of the latter is always much lower than that in the glomerular fluid; this affords direct evidence that chlorides are reabsorbed during passage of the urine through the renal tubules; this condition obtains even when the concentration of chlorides in the blood-plasma has been doubled by injection of sodium chloride. The chloride concentration in the glomerular fluid was constantly higher than that in the blood-plasma; the glomerular fluid is therefore not derived from the blood-plasma by a simple process of filtration; it is pointed out that the Donnan equilibrium must play a part in the distribution of ions between plasma and glomerular fluid, and this may account in part for the observed differences.

C. R. HARINGTON.

Melanogen. P. SACCARDI (Atti R. Accad. Lincei, 1925, [vi], **2**, 346—349).—An unstable melanogen has been isolated, by means of its diazo-derivative, from the melanotic urine of rabbits injected with pyrrole. The properties of the melanogen diazo-compound are quite different from those of bisdiazopyrrole, indicating that the pyrrole does not pass unchanged into the urine. The chemical behaviour of the melanogen suggests that it is possibly a polymerised hydroxy-derivative of pyrrole, the oxidation of the pyrrole occurring in the system, and not as a result of the action of enzymes in the urine.

F. G. TRYHORN.

Production of volatile fatty acids in the intestinal tract of calves fed whole milk or cereal gruel. L. C. NORRIS (Cornell Agric. Exp. Sta. Mem., 1925, **90**, 1—32).—Acetic and propionic acids in approximately equal proportions, and very slight traces of butyric acid, were found in the fæces of growing calves; ethyl alcohol, and occasional small quantities of propyl alcohol, were also present. A much greater excretion of acid was observed with the cereal gruel diet than with whole milk.

CHEMICAL ABSTRACTS.

Influence of ethyl ι-hydroxystearate on acidosis. R. WEST and E. M. BENEDICT (J. Biol. Chem., 1925, **66**, 139—144).—The substitution of ethyl ι-hydroxystearate for an equivalent amount of fat, in the diet of normal individuals suffering from artificial fat acidosis, caused a marked fall in the excretion of acetone. This may indicate that the physiological oxidation of this compound involves the intermediate formation of a fatty acid with an odd number of carbon atoms, which, in its further oxidation, would not give rise to acetoacetic acid.

C. R. HARINGTON.

Amyloid. F. PAVLICA (Biol. Listy, 1924, **10**, 256—264; from Chem. Zentr., 1925, II, 318).—The origin of amyloid is attributed to proteins which occur in chronic suppuration, and to the accumulation of sulphuric acid, which appears to be the actual cause of the pathological condition, together with the inability of the tissue to eliminate the accumulated sulphur.

G. W. ROBINSON.

Iron in anæmia. C. S. WILLIAMSON and H. N. ETS (Arch. Intern. Med., 1925, **36**, 333—354).—In the case of rats and dogs, iron lactate given by the mouth, or iron citrate given subcutaneously or intravenously, neither increased the hæmoglobin content of the blood above the normal nor accelerated the return to the normal of artificially reduced hæmoglobin values.

CHEMICAL ABSTRACTS.

Naturally-occurring porphyrins. XVIII. Chemical findings in a case of porphyrinuria. H. FISCHER, H. HILMER, F. LINDER, and B. PÜTZER (Z. physiol. Chem., 1925, **150**, 44—101).—A *post-mortem* examination of a congenital porphyrinic was made, and porphyrins were found in most of the organs. Uroporphyrin was isolated with some difficulty from the bones. In the bone marrow, both copro- and uro-porphyrin were found, the former in larger quantity than the latter, but in the long bones freed from the marrow no definite evidence of the presence of coproporphyrin was obtained. Copper salts of porphyrins were found in various parts of the body. The bile contained large amounts of coproporphyrin. In the blood was found coproporphyrin, but no uroporphyrin. The intestine contained no uroporphyrin, but large quantities of coproporphyrin, which agrees with the *pre-mortem* findings of no uroporphyrin in the fæces. Along with coproporphyrin the spleen contained two other pigments, possibly hitherto undescribed, one of which is volatile. Uroporphyrin was found also in the liver and kidney. The musculature contained pigments in small amounts only. These consisted of coproporphyrin and Kämmerer's porphyrin, but no coprohæmin. The bone marrow appears to be the principal seat of porphyrin formation. Probably normal hæmin is here transformed into Kämmerer's porphyrin, and then into coproporphyrin and uroporphyrin. The relation of these new findings to the physiology and pathology of blood pigments is discussed.

H. D. KAY.

Isolation of methylated guanidines from urine in parathyroid tetany. J. KÜHNAU (Arch. exp. Path. Pharm., 1925, **110**, 76—88).—In two cases of parathyroid tetany, a much increased excretion of methylated guanidines was observed. They consisted of methyl- and dimethyl-guanidines and when injected into mice produced typical fatal symptoms.

H. P. MARKS.

Wild silk-moth, *Dictyoploca japonica*, Moore. I. Chemical development in growth. O. SHINODA (Mem. Coll. Sci. Kyōtō, 1925, *A*, **9**, 225—235).—Caterpillars (*Dictyoploca japonica*) fed on chestnut leaves have a constant chemical composition until becoming pupæ, when the ash content, moisture content, chitin content, and aqueous extract decrease sharply and the total nitrogen content and ether extract increase. When the pupæ become moths the ether extract decreases, whilst the aqueous extract increases.

L. F. HEWITT.

Metamorphosis of insects. II. Apparatus for investigation of the gaseous metabolism of small animals. J. Heller (Biochem. Z., 1925, **165**, 411—419).—The apparatus is described and used for determination of the gaseous metabolism of pupating caterpillars. The oxygen utilisation is, during the restless stage, about 60 c.c./24 hrs., during the next three days falling to 40 c.c., and, after movement stops, decreasing fairly rapidly to 10 c.c.
P. W. Clutterbuck.

Effect of addition of ternary foodstuffs to milk on nitrogen retention during growth. E. F. Terroine and A. M. Mendler (Compt. rend., 1925, **181**, 1176—1179).—Young pigs fed on whole milk show a higher proportional nitrogen retention than those fed on skimmed milk, those fed on whole milk with added cream higher still, and those fed on whole milk with added carbohydrates the highest of all. These effects are intensified if the diets be continued for several weeks. L. F. Hewitt.

Nutritive value of wheat. I. Effect of variation of sodium in a wheat ration. G. A. Olson and J. L. St. John (J. Agric. Res., 1925, **31**, 365—375).—Normal growth and reproduction were not obtained when rats were fed on a basal diet of 100 g. of ground wheat, 10 g. of wheat gluten, and 5 g. of butter fat. The addition of sodium hydrogen carbonate to this diet had its greatest effect when the percentage of sodium in the ration was raised to 0·53; percentages of sodium in the diet greater than 0·785 were detrimental. H. J. Channon.

Rôle of cystine and mineral elements in nutrition. E. Woods (J. Biol. Chem., 1925, **66**, 57—61).—Rats which have been stunted in growth by a deficiency of cystine in their food recover completely on restoration to a normal diet. Whereas whole-milk powder alone is not an adequate diet for rats over long periods, it can be made so by the addition of whole wheat, probably owing to the mineral constituents of the latter.
C. R. Harington.

Effect of zirconium, titanium, and manganese salts on nutrition. C. Richet, Gardner, and Goodbody (Compt. rend., 1925, **181**, 1105—1106).—Administration of daily doses of 0·1 g. per kg. of zirconium or titanium citrates has no physiological effects on dogs. The same daily dose of manganese citrate has a slightly harmful effect, and the same dose every fourth day a slightly beneficial effect on the nutrition of dogs. L. F. Hewitt.

Nitrogen and mineral balances in infants receiving cow's or goat's milk. A. L. Daniels and G. Stearns (Amer. J. Dis. Children, 1925, **20**, 359—366).—Goat's milk leads to a larger urinary excretion of phosphate than cow's milk, and to a considerably smaller retention of nitrogen.
Chemical Abstracts.

Metabolism of the suckling. J. Ellinghaus, E. Müller, and H. Steudel (Z. physiol. Chem., 1925, **150**, 133—148).—The nitrogen metabolism of three healthy human infants of about the same age and weight fed for six-day periods on (1) human milk, (2) cow's milk mixture, (3) human milk, has been followed using Folin's methods, or modifications of these, both for the analysis of the ingesta and of the excreta. The results agree well with those of older investigations using macro-methods. The relatively large excretion of uric acid by infants may be correlated with the relatively larger amount and greater activity of their glandular tissue as compared with adults. Infants also excrete more ammonia nitrogen per kg. than do adults, thereby conserving the fixed base which is necessary for growth. It is concluded that six days is an insufficiently long time to leave between the experimental periods. The metabolism of infants and that of adults is not widely dissimilar considering the amounts and activities of corresponding tissues.
H. D. Kay.

Effect of mineral content of food on fat content of body. K. Onohara (Biochem. Z., 1925, **163**, 61—66).—Administration to rats of 0·1 g. of calcium chloride, 0·2 g. of magnesium chloride, or 0·2 g. of sodium chloride *per diem* for 3 weeks results in an increase of body fat of approximately 1% compared with animals not so treated. Only two out of five animals survived treatment with 0·05 g. of potassium chloride *per diem* for the same period.
E. C. Smith.

Soft pork. I. Formation of fat in the pig. N. R. Ellis and O. G. Hankins (J. Biol. Chem., 1925, **66**, 101—122).—The hardening of the fat of pigs as they reach maturity involves a rise in m. p. and a decrease in refractive index and iodine number, the latter being chiefly due to a decrease in the linoleic acid, since the percentage of oleic acid remains almost constant. The general effect is due to an increase in the rate of deposition of fat, which means (with a diet moderately low in fat) that progressively more of the deposited fat is synthesised in the body and less derived directly from the fat of the food.
C. R. Harington.

Intermediate carbohydrate metabolism. X. Glycolysis. T. Brugsch and H. Horsters (Biochem. Z., 1925, **164**, 191—198).—The authors are unable to detect any glycolytic enzyme in the washed or unwashed dried liver or muscle preparations, and the liver and muscle glycogenase of these preparations is not inhibited by insulin. P. W. Clutterbuck.

Intermediate carbohydrate metabolism. XI. The hexosediphosphatase of muscle and liver and the product of fission, hexosemonophosphoric acid. T. Brugsch, M. Cahen, and H. Horsters (Biochem. Z., 1925, **164**, 199—206).—Dried preparations of muscle and liver of rabbits and dogs contain a hexosediphosphatase which converts hexosediphosphoric acid into a dextrorotatory hexosemonophosphoric acid differing from that obtained from yeast by Robison and possessing a different rotation from that of Neuberg's acid. This acid gives a strong Selivanov reaction and may be determined by the method of Pinoff and Gude (A., 1914, ii, 499). Fresh muscle contains also an α-hexosediphosphatase which converts the hexosediphosphoric acid into phosphoric acid and lævulose, the latter being used for glycogen synthesis. Fresh muscle also contains a hexosemonophosphatase which converts the hexosemonophosphoric acid into phosphoric acid and a *d*-hexose which undergoes glycolysis, giving lactic acid. P. W. Clutterbuck.

Intermediate carbohydrate metabolism. T. Brugsch and H. Horsters. **XIII. Formation of lactic acid in the liver from acetic, tartaric, malonic, and succinic acids.** S. Narita (Biochem. Z., 1925, **164**, 247—256).—Acetic acid does not give rise to lactic acid in the liver either under normal conditions or in pancreatic diabetes, whereas malonic, *l*-tartaric, and succinic acids give lactic acid under both conditions. P. C. Clutterbuck.

Intermediate carbohydrate metabolism. T. Brugsch and H. Horsters. **XIV. Action of insulin on muscle dehydrogenases.** S. Narita (Biochem. Z., 1925, **164**, 257—270).—Insulin is an activator of lactic acid dehydrogenase of washed muscle. The washed muscle of animals treated *in vivo* with insulin shows a dehydrogenase action in presence of galactose, dextrose, lævulose, *d*-fructosediphosphoric acid, and benzaldehyde, but it is probable that these substances act rather as substrata than as activators. P. W. Clutterbuck.

Intermediate carbohydrate metabolism. T. Brugsch and H. Horsters. **XV. Muscle dehydrogenases.** Y. Harada (Biochem. Z., 1925, **164**, 271—278).—Lactic acid dehydrogenase of fresh muscle has an optimum action in a concentration of $M/10$—$M/2$-lactate, and washed muscle (poor in coenzyme) of M—$2M$. The optimum for succinic acid dehydrogenase is M—$M/10$, and is not influenced by washing or by higher concentrations of succinic acid. Malic acid inhibits lactic acid dehydrogenase. Dried muscle contains both dehydrogenases, the succinic acid oxydase being more active. Since malic acid inhibits lactic acid dehydrogenase also in dried muscle, it is concluded that malic acid is probably not decarboxylated to lactic acid. P. W. Clutterbuck.

Physiology of glands. L. Asher. **LXXXIII. Formation of carbohydrates from fat and its dependence on the liver.** V. Calvo-Criado (Biochem. Z., 1925, **164**, 76—96).—Addition of fat to the food of rats, which had been rendered carbohydrate-free by feeding for several days on flesh, Witte's peptone, and thyroid tablets with subsequent injection of phloridzin, causes an increased urinary dextrose excretion, the urinary nitrogen remaining constant or even diminishing, whilst the D/N ratio greatly increased. The sugar thus appearing must have been formed from fat. By the addition of a trace of sucrose to the food, the excretion of dextrose is still further increased, quite out of proportion to the amount added. P. W. Clutterbuck.

Condensation products of ethyl acetoacetate. II. Oxidation and possible relationship to antiketogenesis in the animal body. E. S. West (J. Biol. Chem., 1925, **66**, 63—75).—Condensation products of ethyl acetoacetate with aldehydes (*e.g.*, ethyl benzylidenebisacetoacetate) are much more readily oxidised *in vitro* than ethyl acetoacetate itself; dextrose condenses with ethyl acetoacetate in presence of zinc chloride to give a compound which reduces Fehling's solution in the cold. These results support the theory of Shaffer and Friedemann (A., 1924, i, 1369) regarding the mechanism of the antiketolytic action of dextrose. It is shown that the facts that in the oxidation of acetoacetic acid the α-carbon atom is the point of attack, and that the substitution of a more strongly positive group for one of the hydrogen atoms attached to this carbon yields a more readily oxidisable compound, are in accordance with the electronic relationships involved. C. R. Harington.

Effect of various carbohydrates on the ketosis of starvation in human subjects. M. W. Goldblatt (Biochem. J., 1925, **19**, 948—957).—When administered during starvation ketosis, dextrose, lævulose, sucrose, and maltose have an antiketogenetic action, whilst galactose, mannose, lactose, and glycerol are inert. The rise in respiratory quotient following the injection of a sugar has been shown to occur some time after the maximum blood-sugar is reached. The maximum antiketogenetic action of the sugar, as evidenced by a negative nitroprusside reaction in the urine, has been shown to occur during the period of fall in blood-sugar. Evidence of some deficiency in storage power and oxidation of carbohydrates after starvation is produced. S. S. Zilva.

Distribution of phosphorus and fat in the resting and fatigued muscle of the cat; partition of phosphorus in the blood. D. P. Cuthbertson (Biochem. J., 1925, **19**, 896—910).—In the fatigued muscle there was practically no change in either the total P_2O_5 or the total amount of inorganic plus lactacidogen P_2O_5. There was, however, an increase in the inorganic P_2O_5 of the stimulated muscle, the maximum increase observed being 34%. A decrease in the inorganic P_2O_5 of resting muscles remaining *in situ* during the stimulation (maximum noted was 11%) was also recorded. Little or no effect on the organic acid-soluble P_2O_5 other than lactacidogen was observed. A consistent but small increase (1—2%) in the total acid-soluble fraction was established. There was no alteration in the phosphatide P_2O_5. The effect of fatigue on the phosphorus compounds of the blood was as follows. There was an increase in the inorganic P_2O_5 (100% after 50 minutes' stimulation), in the total acid-soluble P_2O_5 (12—37%), and a decrease in the organic acid-soluble P_2O_5 (17—36%). There was an increase of 4—5% in the water content after stimulation of a muscle for 45 min. The phosphorus-containing proteins of skeletal muscle belong to the nucleoprotein group. S. S. Zilva.

Metabolism of arginine and histidine. II. Arginine and histidine as precursors of purines. C. P. Stewart (Biochem. J., 1925, **19**, 1101—1110).—On a diet deficient in histidine and arginine, young rats lose weight, and their allantoin excretion, but not the total nitrogen excretion, falls almost to half the normal value. Restoration of histidine to the diet is followed by resumption of growth and by increased allantoin excretion. The restoration of arginine to the deficient is, however, not followed either by appreciable growth or by increased allantoin excretion, but by a cessation of both the fall in weight and the allantoin excretion. It is concluded that histidine functions as a precursor of purines in the animal body and that arginine and histidine are not completely interchangeable. Adult rats can live for 28 days without loss of weight or decrease in the allantoin excretion on a diet containing only traces of histidine and arginine. S. S. ZILVA.

Fate in the animal body of phenylsuccinic acid and β-phenylhexoic acid. P. W. CLUTTERBUCK and H. S. RAPER (Biochem. J., 1925, **19**, 911—914).—β-Phenylhexoic acid administered subcutaneously in the dog as the sodium salt is excreted partly unchanged and partly as a glycuronate; 45% of the acid is recovered in this way. No phenylsuccinic acid can be detected as an oxidation product. As it is also shown that phenylsuccinic acid is not easily oxidised in the body, it is concluded that β-phenylhexoic acid does not undergo γ-oxidation. S. S. ZILVA.

Iodine metabolism. W. H. VEIL and A. STURM (Deut. Arch. Klin. Med., 1925, **147**, 166—223; from Chem. Zentr., 1925, II, 1187—1188).—The average iodine content in human blood in late summer and autumn is 0·0128 mg.%, and in winter 0·0083 mg.%. The organic iodine is 65% of the total. The partition of iodine between plasma and corpuscles corresponds approximately with their relative volumes. The iodine of the blood originates principally in the thyroid. Oral administration of 0·5 g. of potassium iodide produced very little effect on the iodine content of the blood after 24 hrs. Up to 68% of the iodine was recovered in the urine. In one case, a decrease in organic iodine in blood occurred after administration of iodine in inorganic form. Resorption of iodine after administration of thyreoidin is similar to that of potassium iodide, except that, owing to digestion, part of the organic iodine is changed to inorganic forms. Absorption takes place partly as organic iodine. Elimination of iodine in the urine takes place more slowly than in the case of administration of potassium iodide. In the urine containing the greatest amount of iodine, 33% of the iodine was in organic form. In untreated goitre, hyperiodæmia was observed. During menstruation, pregnancy, and childbed, marked hyperiodæmia was observed. Stimulation of the sympathic system by means of adrenaline resulted in four cases in a temporary hyperiodæmia followed by hypoiodæmia. In fever, there was no hyperiodæmia corresponding with the sympathicotonic stage, but an actual hypoiodæmia, due probably to increased demand by the tissues and increased excretion of iodine in the urine. G. W. ROBINSON.

Metabolism under reduced atmospheric pressure. II. Behaviour of blood and of liver. W. LAUBENDER (Biochem. Z., 1925, **165**, 427—442).—With normal guinea-pigs, starvation for 48 hrs. and continued subnormal feeding lead to an increase of the residual nitrogen of the liver, the peptone-nitrogen being greatly increased, the urea- and amino-nitrogen only slightly. The residual-nitrogen values are not altered by an oxygen-lack corresponding with a pressure of 430—380 mm., but are increased under pressures of 330—230 mm. up to 15·9—18·8% and in starving animals up to 12·1—14·5%. This increase is due chiefly to an increase of amino- and urea-nitrogen. During oxygen-lack only slight changes occur in sugar and residual nitrogen content of blood. P. W. CLUTTERBUCK.

Effect of radium on metabolism. J. ROSENBLOOM (J. Metabol. Res., 1923, **4**, 75—88).—Intravenous injection of 0·1 mg. of radium in dogs produced an increase in the nitrogen, total sulphur, and neutral sulphur excretion, but not in that of creatinine and uric acid. Local application in carcinoma produced retention of nitrogen, sulphur, calcium, magnesium, and phosphorus. The analytical picture of the urine was normal. CHEMICAL ABSTRACTS.

Biological action of X-rays of different wavelengths. A. DAUVILLIER (Compt. rend., 1925, **181**, 1130—1132).—A criticism of the conclusions of Dognon (Thesis; Strasbourg, 1925), who examined the action of rays of wave-lengths 0·22, 0·70, and 1·54 Å. on the eggs of *Ascaris*, and deduced that the absorption of equal amounts of energy resulted in very different biological action. It is shown, on the contrary, that the results indicate equality of biological action for equal energy absorbed, a conclusion supported by a study of the literature, and from general considerations. S. I. LEVY.

Absorption of electrolytes in small intestine. Z. MALKIEVICZ (Bull. Intern. Acad. Polonaise, 1925, **B**, 259—275).—The absorption of sodium, potassium, and calcium chlorides was studied by introducing isotonic solutions of these salts (0·78% NaCl) into the small intestine of a dog through fistulæ, and later measuring and analysing the unabsorbed residue. The sodium chloride (and calcium chloride) solution is rapidly absorbed, but at the same time potassium and calcium ions pass into the intestine, so that the unabsorbed residue contains all three ions. In the case of potassium chloride, the passage of sodium into the intestine, accompanying the absorption of the potassium, is so considerable that the total volume of fluid in the intestine may actually increase. Ringer's solution and a mixture of the potassium and calcium chloride solutions are uniformly absorbed, but in a mixture of the sodium and potassium chloride solutions, whilst the potassium is rapidly absorbed, sodium either passes into the intestine, or is only slowly absorbed. In general, absorption is accompanied by a readjustment in the concentrations of the ions, tending to bring them into closer conformity with the concentrations in the blood. In all cases, there is a passage of carbonate ions into the intestine, with consequent increase in alkalinity. H. P. MARKS.

Influence of pregnancy on lipins of blood. M. TYLER and F. P. UNDERHILL (J. Biol. Chem., 1925, **66**, 1—14).—During pregnancy, the total cholesterol and lecithin of the whole blood progressively increase in amount from the third month until term; the increase is maintained during the first two weeks *post partum*. The proportion of lecithin to cholesterol is not changed from the normal, but cholesterol esters form a higher proportion of the total cholesterol than in non-pregnant women. C. R. Harington.

Action of choline and of a choline ester on the blood pressure after removal of the suprarenal glands. S. Glaubach and E. P. Pick (Arch. exp. Path. Pharm., 1925, **110**, 212—224).—" Cholazyl " (a preparation described as chloroacetylcholine chloride urea) is ten times as effective in reducing the blood pressure in decerebrate cats as is choline. After atropine, both drugs raise the blood pressure, cholazyl being some five times the more active. Extirpation of the suprarenal glands weakens or destroys the latter effect of the ester, but not of choline.

R. K. Cannan.

Diuretic action of theobromine derivatives. H. Vieth and E. Leube (Biochem. Z., 1925, **163**, 13—26).—The diuretic action of theobromine and theophylline substituted in the 1-position by acyl, alkyl, and carbalkoxyl groups has been investigated. Of these only acetyltheobromine shows a greater diuretic power than theobromine. The diuretic action of purine derivatives is increased by simultaneous administration of salicylates, more particularly of calcium salicylate, but these cause increased heart-rate, whereas theobromine has no action on the heart. Cinnamoyl-, carbomethoxy-, and nitro-theobromine are irritant and cause albuminuria, although the latter is a very active diuretic.

E. C. Smith.

Toxicity of hexosediphosphoric acid. N. Abelles (Biochem. Z., 1925, **163**, 226—229).—Intraperitoneal injection of 0·46 g. of hexosediphosphoric acid as the sodium salt proves fatal to 100-g. rats. The symptoms are those of phosphate poisoning. The toxicity of hexosediphosphoric acid is to that of phosphoric acid (referred to P_2O_5) as 2 : 3, but there is no evidence of detoxication of phosphoric acid in the organism *via* hexosediphosphoric acid.

E. C. Smith.

Toxicity of arsenic under reduced atmospheric pressure. E. Iselin (Arch. exp. Path. Pharm., 1925, **110**, 66—75).—The lethal dose for rabbits of atoxyl and of sodium cacodylate is lowered when the animals are kept under reduced pressure. This is not due to increased retention of the arsenic. Methods of determining arsenic in urine, fæces, and liver are described. H. P. Marks.

Nitrogen metabolism in lead poisoning. A. Tscherkess (Arch. exp. Path. Pharm., 1925, **110**, 174—197).—In sub-acute poisoning there is an intensified nitrogen metabolism. In chronic poisoning two periods may be distinguished. In the first, there is increased nitrogen metabolism. This is followed by a decrease and general distortion of the protein metabolism, suggesting an attempted compensation for an impaired function of the oxidation mechanisms by diminished intake and metabolism.

R. K. Cannan.

Cholesterol in lead poisoning. Kretschmer and Frieder (Biochem. Z., 1925, **164**, 44—46).—The cholesterol content of the serum is reduced and that of the whole blood is increased by lead poisoning. P. W. Clutterbuck.

Transmineralisation in poisoning by mercuric chloride. H. Straub and K. Gollwitzer-Meier (Deut. med. Woch., 1925, **51**, 642—645; from Chem. Zentr., 1925, II, 323).—In the anuric stage of mercuric chloride poisoning there is an increase in the content of nitrogen and salts in the blood corresponding to a retention of these constituents. During recovery, *i.e.*, when the kidneys are again functioning, the nitrogen and sodium chloride balances are markedly negative. The elimination of the debris of toxically degraded tissues and the migration of sodium, chloride, and hydrogen carbonate ions (transmineralisation) from the blood to the tissue in the anuric stage and to the urine in the polyuric stage is not so much the consequence of the pathological condition of the kidneys as of general protoplasmic injury.

G. W. Robinson.

Intravenous silver therapy. VI. Bactericidal action of injections of ionised silver salts. K. von Neergaard (Arch. exp. Path. Pharm., 1925, **110**, 103—120; cf. A., 1925, i, 1212, 1357; this vol., 92).—A discussion of the therapeutic action of colloidal and ionised silver preparations. The maximum silver concentration attainable in the body-fluids by administration of ionisable salts is more than sufficient for bactericidal purposes, but the bactericidal dose lies very close to the tolerance limit of the animal. The latter may be raised slightly by repeated injections, whilst a combination of silver with certain toxic dyes may achieve some diminution of the former. The doses of silver preparations normally employed are too small to be of therapeutic value. H. P. Marks.

[Non-]detoxicating effect of dextrose in guanidine poisoning. J. Bakucz (Arch. exp. Path. Pharm., 1925, **110**, 121—128).—Although the convulsive symptoms following an injection of guanidine are accompanied by a fall in the blood-sugar, they are not relieved by administration of dextrose. H. P. Marks.

Metabolism of the liver in chloroform and phosphorus poisoning. R. Hurthle (Arch. exp. Path. Pharm., 1925, **110**, 153—173).—The accumulation of acetoacetic acid in the perfusion of the rat's liver with this substance was greater in the case of the poisoned animal than in the normal, and was accompanied by an increase in β-hydroxybutyric acid. Both in the normal and in the poisoned liver, the addition of acetoacetic acid to the perfusate led to a considerable production of β-hydroxybutyric acid, whilst addition of the latter gave similar yields of acetoacetic acid. The poisoning would seem to be associated with a diminished capacity to decompose acetoacetic acid together with a possible increase in the metabolism of the unknown precursors of β-hydroxybutyric acid. R. K. Cannan.

Narcotic and toxic effects of halogen derivatives of hydrocarbons. J. Müller.—See B., 1926, 75.

Influence of narcotics on surface tension. E. Czanik (Biochem. Z., 1925, **165**, 443—460).—The surface tension of aqueous solutions against air, paraffin oil, or nitrobenzene is decreased by a number of alkaloids (both stimulating and inhibiting), chloral hydrate, phenol, etc., the amount of decrease increasing with increasing concentration and being much greater against paraffin oil and nitrobenzene than against air. The various pharmacological actions of these substances cannot therefore be attributed simply to an effect on surface tension.

P. W. CLUTTERBUCK.

Intoxication by sulphonal. Localisation of the sulphonal and hæmatoporphyrin. R. FABRE and H. SIMONNET (Bull. Soc. Chim. biol., 1925, 7, 1129—1130).—A rabbit which had received 1 g. of sulphonal per day for 12 days was killed, and the following quantities of sulphonal were recovered from the various organs: brain and cord, 0·057 g.; liver, 0·043 g.; kidneys, 0·018 g.; muscle (24 g.), 0·015 g.; blood (7·5 g.), 0·009 g.; spleen, 0·007 g. Hæmatoporphyrin was definitely detected only in the bile, the urine, and, in very small amounts, in the blood.

C. P. STEWART.

Comparative actions of several local anæsthetics on the heart and intestine. F. LASCH (Arch. exp. Path. Pharm., 1925, **110**, 142—152).—In a series of six local anæsthetics (cocaine and substitutes) no relation was found between the activity on the frog's skin, the isolated frog's heart, and the surviving rat's intestine.

R. K. CANNAN.

Influence of lecithins on the action of drugs. VI. D. M. LAWROW (Biochem. Z., 1925, **161**, 257—274).—If lecithins be injected subcutaneously or intraperitoneally into dogs or rabbits, daily, during a week before an injection of morphia, the effect of the latter is distinctly diminished. This diminution is also evident if the lecithin be injected just after the dose of morphia.

H. I. COOMBS.

Is enzyme action colloido-chemical? (Investigation with pepsin.) H. W. VAN URK (Biochem. Z., 1925, **165**, 358—363).—The changes of viscosity of pepsin solutions with changes of concentration of hydrochloric acid and of various salts may be explained in terms of changes of dissociation. No viscosity difference is caused by anions up to a salt concentration of $M/2$.

P. W. CLUTTERBUCK.

Kinetics of enzyme action. G. E. BRIGGS (Biochem. J., 1925, **19**, 1037—1038).—Theoretical.

S. S. ZILVA.

Do spring-waters containing carbon dioxide and hydrogen carbonates activate amylases? M. LOEPER and A. MOUGEOT (Compt. rend. Soc. Biol., 1925, **92**, 569—571; from Chem. Zentr., 1925, II, 1173).—Spring-waters containing carbon dioxide and hydrogen carbonates have no amylolytic action, but strongly activate the amylase of saliva and pancreatic juice. The effect is not due to the alkali present, since a solution of a hydrogen carbonate does not behave in this way. Removal of carbon dioxide by boiling does not destroy the activating effect. This excludes also the possibility of the action being due to a biological factor. The effect cannot be due to radioactivity nor to the influence of p_H, since the latter is considerably changed on boiling.

G. W. ROBINSON.

Spring-waters containing hydrogen carbonates and the activity of invertase from beer yeast. A. MOUGEOT and V. AUBERTOT (Compt. rend. Soc. Biol., 1925, **92**, 1504—1506; from Chem. Zentr., 1925, II, 1173; cf. preceding abstract).—The effect of spring-waters on invertase depends simply on the p_H of the solution.

G. W. ROBINSON.

Variations of phosphorus-containing lipins during liver autolysis. C. ARTOM (Bull. Soc. Chim. biol., 1925, 7, 1099—1128).—In the liver of normal dogs the fatty acids are present chiefly as phosphatide, and vary only within narrow limits. The chloroform-soluble phosphorus can be divided into three fractions: (1) true phosphatide phosphorus, (2) "carnithin" phosphorus, and (3) acetone-soluble phosphorus. Since the ratio of phosphatide fatty acid to phosphatide phosphorus is almost 18, almost all the phosphatides are to be classed as lecithins or cephalins. During antiseptic autolysis, the phosphatide content of the liver gradually diminishes, more rapidly in the case of dogs killed during digestion or after administration of hydrochloric acid than in the case of fasting dogs, more slowly than usual when an excess of fat has been added to the liver tissue. Since the ratio of phosphatide fatty acid to phosphatide phosphorus usually varies little during autolysis, it seems that there is a complete cleavage of the molecule with liberation of the whole of the fatty acid. Sometimes, however, the ratio is appreciably decreased, indicating an incomplete cleavage, and experimental addition of fat usually leads to a slight increase in the ratio. The "carnithin" phosphorus diminishes more rapidly than that of the phosphatides. The acetone-soluble phosphorus, on the other hand, increases both in absolute amount and relatively to the total chloroform-soluble phosphorus.

C. P. STEWART.

Diastase. II and IIIA. V. SYNIEVSKI (Bull. Intern. Acad. Polonaise, 1925, **A**, 47—50, 51—54).—See this vol., 93.

Enzyme extracted from seeds of *Rhamnus*, rhamnodiastase. M. BRIDEL and C. CHARAUX (Compt. rend., 1925, **181**, 925—926).—It is suggested that the enzyme extracted from seeds of *Rhamnus utilis*, *R. frangula*, etc., which hydrolyses various complex glucosides without breaking down the polysaccharides (A., 1911, i, 391; 1924, i, 659; 1925, i, 336), be named *rhamnodiastase*. A modified method for its preparation is described.

L. F. HEWITT.

Glucosides in plants hydrolysed by rhamnodiastase. M. BRIDEL and C. CHARAUX (Compt. rend., 1925, **181**, 1167—1168).—The effect of rhamnodiastase (cf. preceding abstract) on the rotatory power and reducing power of aqueous extracts of twelve plants has been examined. This provides a method of investigation of the carbohydrates contained in plant glucosides.

L. F. HEWITT.

Fate of invertase in the normal and immune organism. A. Samisslov (Biochem. Z., 1925, **164**, 110—116).—The rate of disappearance from the blood-stream of invertase after its injection into normal rabbits or rabbits which had received preliminary injection of yeast autolysate, is measured. Invertase added to blood of normal or immunised rabbits *in vitro* does not disappear appreciably in 6 hrs. The injected invertase is neither destroyed nor adsorbed by the corpuscles, but is adsorbed by the cells of various organs, *e.g.*, in immunised animals the liver adsorbs 50—60% of the invertase, whilst in normal animals only 20—30%.

P. W. Clutterbuck.

Effect of radioactive radiations and *X*-rays on enzymes. IV. Effect of radiations from radium emanation on solutions of invertase. R. G. Hussey and W. R. Thompson (J. Gen. Physiol., 1925, **9**, 211—215; cf. A., 1923, i, 871; J. Gen. Physiol., 1923—4, **6**, 1, 7).—The inactivation of invertase by β-radiation from radium emanation can be explained quantitatively on the same basis as that of trypsin and pepsin previously reported. Within limits, the rate of inactivation is inversely proportional to the volume of the solution.

C. P. Stewart.

Maltase from barley malt. H. Pringsheim and J. Leibowitz (Biochem. Z., 1925, **161**, 456—458).—A sample of maltase is described which is apparently different from formerly known samples, in that it has not the usual sensitivity to acidity. It is active between p_H 3 and 7·5 and has its optimum between p_H 4·5 and 5. H. I. Coombs.

Enzymic cleavage of cellulose. P. Karrer, P. Schubert, and W. Wehrli.—See B., 1926, 44.

Action of emulsin on amygdalin. L. Rosenthaler (Arch. Pharm., 1925, **263**, 563—566).—When this hydrolysis is followed quantitatively, the amounts of hydrocyanic acid and dextrose formed being determined, results are obtained that agree only with the supposition that the primary products are dextrose and mandelonitrile glucoside, the latter being then hydrolysed itself (cf. Auld, J.C.S., 1908, **93**, 1276). There is no indication that gentiobiose is a direct scission product, but a little is possibly formed. W. A. Silvester.

Perhydridase of milk. B. Sbarsky (Biochem. Z., 1925, **164**, 442—443).—A reply to Hopkins and Dixon (A., 1925, i, 1506). E. C. Smith.

Toxic action of hydrocyanic acid on laccase and its relationship to the reaction of the solution. P. Fleury (Compt. rend. Soc. Biol., 1925, **92**, 596—598; from Chem. Zentr., 1925, II, 1172).—Hydrocyanic acid solution (0·67 mg. per litre) reduces the activity of laccase to 60%. The original activity is restored if the hydrocyanic acid is removed by a stream of air. Hydrocyanic acid acts as a negative catalyst; its effect is not directly proportional to concentration, but shows a logarithmic relationship. The maximum toxicity is shown at the optimum p_H for the action of the enzyme.

G. W. Robinson.

Significance of metallic salts in the action of blood lipases. L. E. Walbum and K. Berthelsen (Z. Immunit., 1925, I, **42**, 467—476; from Chem. Zentr., 1925, II, 307).—The effect of metallic salts in increasing lipolysis by blood lipase, as also their effect on the formation of agglutinins and amboceptors and on the action of bactericidal substances, depends to some extent on the atomic numbers in the individual chemical groups. The effect generally increases with decrease in the atomic number.

G. W. Robinson.

Action of urethanes on serum lipase. P. Rona and A. Lasnitzki (Biochem. Z., 1925, **163**, 197—225).—At low concentrations of urethane, the inhibitory action on serum lipase is directly proportional to the concentration. At concentrations of 0·1*M* and above, the inhibition follows the adsorption isothermal. Methyl-, ethyl-, and propyl-urethanes show increasing inhibition, but do not exactly obey Traube's law. *iso*Propylurethane behaves anomalously, being strongly inhibitory at low concentrations. Inhibition increases with decreasing concentration of the lipase, hence the active surface of the latter must increase on dilution. The inhibitory action of urethane on lipase is reversible. E. C. Smith.

Effect of different preparations of the quinine group on the enzymic functions of the organism. V. Effect of concentration of the substrate on the hydrolysis of triacetin by pancreatic lipase. J. A. Smorodincev and V. A. Danilov (Biochem. Z., 1925, **164**, 394—400; cf. this vol., 94).—Quinine hydrochloride accelerates the hydrolysis of 0·5—1% solutions of triacetin by pancreatic lipase. No effect is shown in 3—5% solutions until the third hour, when a retarding effect is manifested. The velocity of hydrolysis in presence or absence of quinine is independent of the initial concentration of triacetin, and follows the course of a unimolecular reaction. The constant of this reaction is less for higher concentrations of triacetin than for lower.

E. C. Smith.

Nature of so-called serum antipepsin. W. Mozolovski and H. Hilarovicz (Biochem. Z., 1925, **164**, 295—311).—The inhibitory action of serum on peptic digestion, and the phenomena explained by adsorption of pepsin by a serum antipepsin, can be fully accounted for by the change in p_H brought about by the addition of the serum. E. C. Smith.

Buffers in the study of proteases. III. Influence of buffers on the p_H during the digestion of caseinogen by the method of Gross. J. A. Smorodincev and A. N. Adova (Bull. Soc. Chim. biol., 1925, **7**, 1154—1157).—The presence of buffers does not cause any alteration in p_H during the digestion of caseinogen by pepsin.

C. P. Stewart.

Effect of radiations from a mercury arc in quartz on enzymes. I. Effect of ultra-violet radiation on pepsin. R. G. Hussey and W. R. Thompson (J. Gen. Physiol., 1925, **9**, 217—219).—Pepsin in solution is inactivated by the radiations from a mercury arc in quartz, the effective radiations, apparently, being those in the ultra-violet region. The reaction appears to be unimolecular.

C. P. Stewart.

Tryptic digestion with low concentrations of enzymes. III. R. Ehrenberg (Biochem. Z., 1925, **161**, 348—360).—Further evidence is brought forward to support the author's view that enzyme action changes during its course, quantitatively and qualitatively, and the nature of the substrate affects this change. Evidence is also brought to show that a mere change of enzyme concentration qualitatively affects the course of hydrolysis (cf. A., 1925, i, 202).

H. I. Coombs.

Tyrosinase, its action on phenols, tyrosine, and other amino-acids. R. A. McCance (Biochem. J., 1925, **19**, 1022—1031).—Quinol, which is spontaneously oxidised by atmospheric oxygen, reduces methylene-blue only extremely slowly. It reduces dinitrobenzene. In the presence of an amino-acid, however, quinol and pyrocatechol both reduce methylene-blue freely. After complete reduction of the methylene-blue the amino-nitrogen content of the amino-acid is unaltered, and there is no increase in ammonia. *p*-Cresol does not reduce methylene-blue, but does so very slowly in the presence of glycine. The spontaneous oxidation of all the phenols examined was not affected by *M*/500-potassium cyanide, although this treatment inhibits both the aërobic and anaërobic action of tyrosinase. Tyrosine, being both an amino-acid and a phenol, reduces methylene-blue slowly. Tyrosinase catalyses the reduction of methylene-blue by a solution of p_H 8 of *p*-cresol and glycine. The action of tyrosinase on tyrosine depends on the fact that the compound is an amino-acid and a phenol. Additive compounds have been prepared from pyrocatechol and diethylamine (2 : 1 mol.), m. p. 78—79°; resorcinol and diethylamine (2 : 1), m. p. 115°; benzoquinone and *p*-cresol (1 : 2), orange-red, m. p. 63·5°. This compound is not identical with the compound formed by the *p*-cresol–tyrosinase system.

S. S. Zilva.

Formation of acetylmethylcarbinol and βγ-butylene glycol in metabolism of yeast. A. J. Kluyver, H. J. L. Donker, and F. V'T. Hooft (Biochem. Z., 1925, **161**, 361—378).—A method is described for detecting the above compounds in presence of large amounts of impurities. The first-named compound is converted into diacetyl (which can be distilled off and identified) by ferric chloride, and then the second compound can also be oxidised to diacetyl by means of bromine. If suitable hydrogen acceptors are added to fermenting dextrose solutions, both acetylmethylcarbinol and βγ-butylene glycol are formed from the accumulated acetaldehyde. When air is blown through a fermenting sugar solution the oxygen also acts as a hydrogen acceptor.

H. I. Coombs.

Occurrence of an amino-acid containing sulphur in the alcoholic extract of yeast. S. Odake (Biochem. Z., 1925, **161**, 446—455).—From the mother-liquors of adenylthiomethylpentose (cf. A., 1925, i, 338), obtained from the alcoholic extraction of 6000 kg. of yeast, 0·6 g. of a sulphur-containing *amino-acid*, $C_5H_{11}O_2NS$, m. p. 272—273°, was obtained. The aqueous solution had $[\alpha]_D^{16}$ −11·77°, and except for a small variation in this value, the compound has the same properties as that described by Müller (A., 1923, i, 869, 963) from the products of hydrolysis of caseinogen and egg-albumin. The properties and reactions of the acid are described and the *copper* salt and *naphthylcarbimide* derivative, m. p. 187° (uncorr.), were also prepared.

H. I. Coombs.

Volutin in yeast cells. M. Glaubitz.—See B., 1926, 25.

Laboratory pure culture apparatus. F. M. Hildebrandt.—See this vol., 142.

Endo's medium for *Bacillus coli*. N. M. Harris.—See B., 1926, 78.

Salt action. X. Influence of electrolytes on the viability and electrophoretic migration of *Bacillus coli*. H. J. Shaughnessy and K. I. Criswell (J. Gen. Physiol., 1925, **9**, 123—136).—Electrophoretic charge is highest in distilled water adjusted to p_H 6·0 or p_H 8·0; in the presence of salts, p_H 8·0 is somewhat more favourable to electrophoretic charge (although much less so to viability) than p_H 6·0. At p_H 11·0, electrophoretic charge is only slightly decreased, but at p_H 2·0 it may even be reversed. Sodium chloride solutions, in concentrations ranging from 0·0145 to 0·725*M*, were somewhat toxic and tended to decrease electrophoretic charge; calcium chloride in similar concentrations was more toxic; Locke–Ringer solution was slightly toxic (although less so than pure salt solutions) and depressed the migration velocity at all p_H values. It is concluded that the parallelism between viability and electrophoretic charge is not a close one, and that the two effects seem, on the whole, to follow different laws.

C. P. Stewart.

Behaviour of pyrimidine derivatives in organisms. II. Action of *Bacillus coli* on uracil and cytosine. A. Hahn and L. Schäfer (Z. Biol., 1925, **83**, 511—514).—Cytosine is deaminated by *Bacillus coli*, as by yeast (A., 1923, i, 1269). The uracil formed is not further attacked.

H. P. Marks.

***Bacillus pyocyaneus*. Relation of its metabolism to intramolecular respiration.** O. Acklin (Biochem. Z., 1925, **164**, 312—370).—*Bacillus pyocyaneus* is capable of vigorous growth on artificial media containing sodium nitrate and sodium lactate as sole source of nitrogen and carbon, respectively. The reaction becomes more alkaline owing to formation of ammonia from nitrate. Growth can take place from p_H 5·6 to 9·2, the optimum being from p_H 6·4 to 8·1. The reaction of maximum denitrification lies between p_H 7·4 and 9·0. At p_H 6·4 very little denitrification takes place. The character of the source of nitrogen is the determining factor in growth and pigmentation. Of the sources of nitrogen investigated, nitrate, ammonia, and peptone, the last gives maximum growth. In cultures with ammonium salts as the source of nitrogen, pigmentation is absent. The assimilatory reactions consist largely in the formation of ammonia and pyruvic acid, from which alanine and proteins are synthesised. The dissimilatory reactions consist in the breakdown of pyruvic acid to carbon dioxide, acetaldehyde, alcohol, and acetic acid. In peptone–lactic acid media no utilisation of lactic acid occurs. The intracellular respiration, determined colorimetrically by addition of nitroanthraquinone, is at a maximum in 1-day cultures, whereas in most media the maximum rate of growth occurs between the first and third days. The presence of 0·00005M-manganese chloride inhibits growth and reduction in nitrate–lactic acid media. The virulence of the organism is unaltered by 5—10 days' growth on synthetic media, no influence of the nature of the source of nitrogen being observed. The toxicity of sterile cultures is, however, dependent on the source of nitrogen, cultures grown in ammonium chloride media being less toxic than those grown in nitrate media. E. C. Smith.

Lipochromes present in certain bacteria. V. Reader (Biochem. J., 1925, **19**, 1039—1046).—*Sarcina aurantiaca* contains two lipochromes, carotin and lycopin, the latter predominating. The pigment is formed to the same extent whether the organism is grown in the dark or in diffuse light. Direct sunlight impedes growth and prevents the development of colour. Although growth is much more vigorous at 20° than at 37°, pigment formation per mg. of growth is the same whether in light or dark. *Streptothrix corallinus* contains an unknown lipochrome for which the name "coralin" is suggested. The maximum coloration of this pigment appears at 18°. Above 27°, only traces of colour are produced. Growth of this organism is vigorous from 22° to 37° and direct sunlight has no decolorising effect on it. Neither of the above organisms contains appreciable quantities of vitamin-*A*. Yeast contains traces of carotin. *Streptothrix corallinus* contains no cholesterols or phytosterols.

S. S. Zilva.

Utilisation of thiocarbamide by *Aspergillus niger*. A. Rippel (Biochem. Z., 1925, **165**, 473—474).—*Aspergillus niger* oxidises cystine to a much greater extent (40%) than thiocarbamide (4%).

P. W. Clutterbuck.

Chemical composition of the sporangial wall of *Myxomycetes*. A. Kiesel (Z. physiol. Chem., 1925, **150**, 102—117).—The wall substance contains 3·63% of nitrogen, 3·98% of ether-soluble substances, and 2·84% of ash. It contains 50% of complex carbohydrate insoluble in water, which by acid hydrolysis yields, in part, dextrose. Whilst some 27% of the cell-wall material is resistant to 66% sulphuric acid, by heating with alkali to 160—180°, 98—99% goes into solution. In the insoluble portion, neither cellulose nor chitin can be detected. The nitrogen-free polysaccharides may be separated completely from nitrogenous substances by heating on the water-bath with 8% sodium hydroxide, when the former do not go into solution. On longer heating a part of the carbohydrate is gradually destroyed. The name "myxoglucosan" is given to the polysaccharide which is resistant to the action of 8% sodium hydroxide. Previous treatment of the wall substance with 2% hydrochloric acid largely diminishes the yield of polysaccharide insoluble in sodium hydroxide. It is probable that there is protein in the wall material, since a portion of the nitrogen insoluble in hydrochloric acid appears to be soluble in pepsin solutions. No definite protein colour reactions were observed. H. D. Kay.

Effect of p_H on the availability of iron for *Chlorella* sp. E. F. Hopkins and F. B. Wann (J. Gen. Physiol., 1925, **9**, 205—210).—In a phosphate buffered nutrient solution the acid limit for growth of *Chlorella* Sp. was p_H 3·4; the optimum p_H 5·7; and the alkaline limit p_H 6·1. When special precautions—omission of calcium from the medium and addition of sodium citrate—were taken to prevent removal of iron by precipitation or adsorption at the more alkaline reactions, growth was maximal at p_H 7·5.

C. P. Stewart.

Penetration of carbon dioxide into living protoplasm. W. J. V. Osterhout and M. J. Dorcas (J. Gen. Physiol., 1925, **9**, 255—267; cf. A., 1925, i, 1355).—Little or no carbon dioxide enters normal cells of *Valonia macrophysa* except in the form of undissociated molecules. Whenever the interior of a cell is more acid than the surrounding medium (excess of base being the same in both) the internal concentration of total carbon dioxide at equilibrium may be expected to be less than the external. C. P. Stewart.

Accumulation of brilliant-cresyl-blue in the sap of living cells of *Nitella* in the presence of ammonia. M. Irwin (J. Gen. Physiol., 1925, **9**, 235—253).—When living cells of *Nitella* are placed in a solution of brilliant-cresyl-blue containing ammonium chloride, the rate of accumulation of the dye in the sap is less than when ammonium chloride is absent, this decrease occurring without any increase in the p_H of the cell sap. Since the decrease in the rate of accumulation of the dye takes place only when ammonia is present in the sap, and not when the ammonia is confined to the external solution, it is interpreted as being due to competition between the ammonia and the dye for certain substances in the cell. C. P. Stewart.

Protoplasm. Composition of the plasmodium of *Reticularia lycoperdon*. A. Kiesel (Z. physiol. Chem., 1925, **150**, 149—176).—The plasmodium gave the following figures (on the dry weight): fat, 17·85; lecithin, 4·67; cholesterol, 0·58; reducing sugar, 2·74; non-reducing, soluble carbohydrate (not glycogen), 5·32; glycogen, 15·24; difficultly hydrolysable polysaccharide, 1·78; nitrogenous extractives, 12·00; protein (partly nucleoprotein), 20·65; "plastin," 8·42; nucleic acid, 3·68; fat of lecitho-protein (?), 1·20; unknown residue, 5·87%. H. D. Kay.

Cholesterol-synthesising function of the spleen: influence of internal secretion of the spleen on cholesterol in muscle. J. E. Abelous and L. C. Soula (Compt. rend., 1926, **182**, 98—100).—In normal dogs there is more cholesterol in venous than in arterial blood, but this is not the case in the posterior limb when the trunk of the crural and sciatic nerves is severed. When the peripheral ends of the severed nerves are subjected to galvanic stimulation, the venous blood cholesterol content is increased by the tetanus produced. In the splenectomised dog stimulation of the severed nerves does not produce this increase unless an extract of spleen is injected into the opposite saphenous vein. That the influence of the spleen is not direct secretion of cholesterol is shown by the fact that in the above experiments no increase in cholesterol content of the blood in the vein leading directly from the spleen is observed. L. F. Hewitt.

Properties and composition of oocytin. II. G. W. Clark and P. W. Sharp (J. Biol. Chem., 1925, **66**, 123—131).—Oocytin has been prepared by a method similar to that previously described (A., 1918, i, 463) from the blood of all mammalian species so far investigated, and also, in much greater yield, from that of the fowl and the turkey; the latter result suggests that it may be derived from the nuclear material of the red cells; it could not be obtained from an abdominal transudate, but was isolated in undiminished yield from serum which had been kept for 15 months at 4°. The activity of the oocytin, measured by the fertilisation membrane formation in sea-urchin's eggs activated with strontium chloride, was greatest in those preparations derived from adult male animals. Similar membrane formation was observed with nucleic acids from yeast, thymus, and salmon sperm, but these substances were much less active than oocytin. C. R. Harington.

Active principles of pituitary extract. H. H. Knaus (J. Pharm. Exp. Ther., 1925, **26**, 337—346).—When given intravenously, pituitary extract equivalent to 0·01 mg. of fresh posterior lobe per kg. was required to produce an appreciable rise in the blood pressure of the pithed cat, and 0·004 mg. to show an effect on the uterus. With intra-arterial administration, the minimal doses were 0·6 and 0·01 mg. per kg., respectively. These results and those of intramuscular injection are explained by the assumption that there are separate pressor and oxytocic principles in pituitary extract and that the pressor substance is rapidly destroyed by passing through the arterioles. C. P. Stewart.

Mineral metabolism of the lymph following injections of *l*- and *d*-adrenaline, pituitrin, and pilocarpine. W. F. Petersen and T. P. Hughes (J. Biol. Chem., 1925, **66**, 229—246).—Injections into dogs of natural adrenaline and synthetic *l*- and *d*-adrenaline have almost identical effects on the inorganic salts of the lymph; in general, there is observed a preliminary increase and subsequent fluctuation in the concentration of calcium, and a preliminary fall and subsequent rise in that of phosphate; variations in the other inorganic ions are somewhat irregular; following injections of pituitary extract there is an immediate rise in the concentration of phosphate and of sodium and a slight rise in the calcium; pilocarpine causes an increase in the phosphates, and, if the dog has previously been treated with calcium lactate, an increase in the calcium. It is thought that the alterations observed are the result of the action of the drugs directly on the tissues, rather than on the autonomic nervous system. C. R. Harington.

Biocatalysts concerned in carbohydrate metabolism. III. H. von Euler and K. Myrbäck (Z. physiol. Chem., 1925, **150**, 1—15).—Pancreatic insulin cannot replace the co-zymase of yeast. The formation of hexosediphosphate by chopped muscle, without oxygenation, is not greatly increased by pancreatic insulin. H. D. Kay.

Pancreatic hormone. H. Langecker and W. Wiechowski (Klin. Woch., 1925, **4**, 1339—1343; from Chem. Zentr., 1925, II, 1180).—By the methods in use for extracting the pancreatic hormone, substances can be extracted from other organs which have a similar effect on blood-sugar, but their mode of action differs from that of the pancreatic product. Such substances may be also present in the active fraction isolated from the pancreas by existing methods. Using a new method, which consists in salting out the raw insulin with potassium lactate, and after redissolving in water, precipitating with *N*-hydrochloric acid, an active fraction was obtained from the pancreas, but not from other organs. The preparation thus obtained is 2—5 times as active as the preparations hitherto available and must contain the pancreatic hormone free from other substances of similar action. The substance is uncrystallisable and appears to be an albumose rich in sulphur. G. W. Robinson.

Measurement of the action of insulin. H. Langecker and W. Stross (Biochem. Z., 1925, **161**, 295—336).—The action of insulin is dealt with statistically, about 200 rabbits being used in many experiments. The average blood-sugar value for 224 rabbits, starved for 24 hrs., was 96 mg.%; 47 rabbits which had never previously had insulin gave 99 mg.%. The mean value necessary to bring about convulsions was 28 mg.%. Whilst different rabbits show great variations in their sensitivity to insulin —one rabbit being unaffected by sixteen times the dose which brought about convulsions in another—each rabbit seems to have an individual sensitivity which is more or less constant. H. I. Coombs.

Insulin and blood-fat. A. C. White (Biochem. J., 1925, **19**, 921—926).—Hypoglycæmia caused by the administration of insulin is accompanied in the normal dog by an increase in the blood-fat, the increase affecting the fatty acids more than the cholesterol. The administration of dextrose along with insulin, or later, does not seem to affect the changes in blood-fat brought about by insulin. The effect of insulin on the blood cholesterol is not constant. S. S. Zilva.

Fate of blood-sugar after insulin injections in normal animals. A. Hynd (Biochem. J., 1925, **19**, 1095—1100).—The reducing power of plasma is brought down to that of the corpuscles, which is comparatively low, by the administration of insulin. Whilst the sugar of the plasma is not altered to any extent by hydrolysis before or after insulin, the reducing power of the corpuscles increases in both cases. As the increase in the reducing power is greater after insulin, it cannot be due entirely to the interfering action of peptone produced by the hydrolysis. It is suggested that a non-reducing dextrose complex may be formed by the action of insulin and that this complex attaches itself to the tissues including the red blood-corpuscles. About a sixth of the sugar disappearing from the plasma after insulin may be accounted for by the erythrocytes acting in this manner. S. S. ZILVA.

Effect of insulin treatment and nutritional conditions on the fat content of rats on vitamin-free diets. K. ONOHARA (Biochem. Z., 1925, **163**, 51—60).—Normal rats treated with 0·8 unit of insulin per kg. body-weight *per diem* for 2—3 weeks show a slightly greater mean fat content than rats not so treated. Rats fed on vitamin-free diets, either mixed, fat-free, or carbohydrate-free, are considerably poorer in fat. On mixed and carbohydrate-free diets insulin has no effect on the fat content, but on fat-free diet the insulin-treated animals are slightly richer in fat than the controls. E. C. SMITH.

Effect of insulin on the blood-fat level in dogs on a vitamin-free diet. K. ONOHARA (Biochem. Z., 1925, **163**, 67—74).—Insulin has no effect on the blood-fat level of fasting dogs on a vitamin-free diet, nor on the blood-fat curve following the ingestion of a fat meal. E. C. SMITH.

Bio-assay of thyroid. R. HUNT.—See B., 1926, 27.

Physiology of the glands. L. ASHER. **LXXVIII. Effect of the thyroid gland on the growth-promoting properties of blood. Detection of growth-factors in blood.** S. UCHIDA (Biochem. Z., 1925, **163**, 75—94).—A method is described for the determination of the content of growth-promoting substances in rabbit's plasma by addition of the plasma to cultures of chick embryo hearts in Ringer's solution. The plasma of thyroidectomised animals is very deficient in growth-factor, still more so in animals deprived of both thyroid and thymus glands. Animals deprived of thymus show a slight deficiency, but ovariectomy has no effect on the growth-factor content. E. C. SMITH.

Excretion of calcium, magnesium, and phosphorus (*a*) following thyreoparathyroidectomy, (*b*) following injections of calcium chloride, sodium phosphate, or both, (*c*) following injection of parathyroid extract. I. GREENWALD and J. GROSS (J. Biol. Chem., 1925, **66**, 185—199, 201—215, 217—227).—Following parathyroidectomy in dogs, the excretion of calcium became slightly greater in the fæces and considerably less in the urine, the net result being a decrease in the total calcium excreted; the total phosphorus excreted was increased and that of magnesium little changed. When calcium chloride is injected into normal dogs, most of the calcium is retained, the phosphorus excretion is unchanged and that of magnesium slightly reduced; when sodium phosphate and calcium chloride are given together, the extra calcium and phosphorus excreted is approximately equal to that administered; injection of large amounts of sodium phosphate leads to an increased excretion of calcium, phosphorus, and magnesium. Injection of active parathyroid extract increases the excretion of calcium and phosphorus and does not affect that of magnesium; since the calcium excreted could not have been derived from the food and also, since its increased excretion was accompanied by a parallel increase in that of phosphorus, it is assumed that this experiment indicates a mobilisation of calcium phosphate from the bones under the influence of the parathyroid hormone. C. R. HARINGTON.

Parathyroid hormone. II. J. B. COLLIP and E. P. CLARK (J. Biol. Chem., 1925, **66**, 133—137; cf. A., 1925, i, 754).—After acid extraction of the glands, removal of fat, and preliminary removal of inactive proteins by making alkaline and then adding acid to p_H 5·5 and filtering, the filtrate was saturated with sodium chloride; the active material so precipitated was purified by repeated dissolution in dilute hydrochloric acid and precipitation at the isoelectric point (p_H 4·8), and finally washed with alcohol and ether and dried in a vacuum over sulphuric acid. There was thus obtained an amorphous powder (15·5% N) which gave positive reactions for protein, negative for carbohydrate; it contained sulphur and iron, but no phosphorus; it was easily soluble in acid and alkali and in 80% alcohol; insoluble in absolute alcohol, ether, pyridine, and acetone; it did not dialyse. It was inactivated by boiling for an hour with 10% hydrochloric acid or with 5% sodium hydroxide, and also by the action of pepsin and of trypsin; 0·3 mg. was equivalent to 1 unit of physiologically active substance. C. R. HARINGTON.

Vitamin-*A* in beef, pork, and lamb. R. HOAGLAND and G. G. SNIDER (J. Agric. Res., 1925, **31**, 201—221).—The values of beef, pork, and lamb as sources of vitamin-*A* have been studied by following the growth of young rats receiving rations adequate in other respects, but with varying proportions of dried lean meat as the only source of vitamin-*A*. The energy values of the different rations were practically the same. The samples of beef and pork tested were relatively poor in vitamin-*A*. When 50—95% of the ration consisted of the beef, growth was almost normal, but in no case was normal growth obtained with the pork. The samples of lamb differed considerably; some were rather poor in vitamin-*A*, whereas others were richer than any other samples of meat tested. C. T. GIMINGHAM.

Chemical nature of vitamin-*A*. J. C. DRUMMOND, H. J. CHANNON, and K. H. COWARD (Biochem. J., 1925, **19**, 1047—1067).—Vitamin-*A* can be concentrated without loss in the unsaponifiable fraction of cod-liver oil if precautions against oxidation are taken. The concentrate contains no demonstrable traces of iodine or nitrogen, and 50% of this fraction consists of cholesterol which is inactive. Vitamin-*A* is volatile, passing over on distillation mainly between 180° and 220°/2—3 mm. The active distillate contains a saturated alcohol (m. p. about 60°), spinacene, and one or more than one unsaturated alcohol of b. p. about 200°/2—3 mm. The first two constituents are inactive. Whether the vitamin is an unsaturated alcohol could not be established. Oleyl alcohol, selachyl alcohol, and phytol are inactive. Vitamin-*A* is not identical with lycopin or carotin. The claims of Takahashi (J. Chem. Soc. Japan, 1922, **43**, 826; A., 1923, i, 968; 1925, i, 1365), to have isolated vitamin-*A* and identified it as an unsaturated alcohol, $C_{27}H_{46}O_2$ (" biosterin "), are criticised.

S. S. Zilva.

Technique of testing for the presence of vitamin-*A*. J. C. Drummond, K. H. Coward, and J. Handy (Biochem. J., 1925, **19**, 1068—1074).—Rats kept on deficient basal diet from which fat is excluded receive small quantities of irradiated cholesterol to supply the antirachitic vitamin. When the weight curve declines owing to the exhaustion of the animal's store of vitamin-*A*, the substance to be tested is administered to the animal. In a positive test, the rats resume growth. If vitamin-*A* is absent from the substance the decline in weight continues.

S. S. Zilva.

Biochemical colour test. III. Colour reactions associated with vitamin-*A*. W. R. Fearon (Biochem. J., 1925, **19**, 888—895).—Phosphorus pentoxide produces a deep violet colour when added to oils containing vitamin-*A*. The pigment giving this colour can be separated by adsorbing it with phosphorus pentoxide and centrifuging. On hydrolysing the deposit and extracting the pigment, the extract did not give the colour tests, nor did it possess any growth-promoting properties. Active oils depigmented by the above procedure lose their growth-promoting activity. In the presence of a 12% solution of trichloroacetic acid in dry light petroleum, pyrogallol and other polyphenols interact with oils containing vitamin-*A*, giving a stable coloration. Oils inactivated by aëration, inactive vegetable oils, irradiated cholesterol, "oxycholesterol," irradiated hardened fat, and " ostelin " give no colour with pyrogallol. This reaction could not be reproduced by adding the commoner aldehydes and ketones, with and without cholesterol, to medicinal petroleum, aërated liver oil, or vegetable oil.

S. S. Zilva.

Fat, cholesterol, and sterol metabolism of growing rats in the presence and absence of vitamin-*A*. B. Liang and L. Wacker (Biochem. Z., 1925, **164**, 371—393).—Rats fed on fat-free diet lacking vitamin-*A* are incapable of laying down fat, but on diets poor in fat and vitamin-*A* they synthesise large amounts of cholesterol. The cholesterol content may be greater than when fed on diets containing sufficient vitamin-*A* and rich in cholesterol. Vitamin-*A* and lipochrome may act as carriers of the endogenous oxygen derived from carbohydrate in process of conversion into fat. Vitamin-*A* is also concerned with the formation of neutral fat from fatty acid and glycerol. Much more sterol is formed in the organism than is contained in the diet, but as most of these substances are excreted in the fæces, very little increase in sterol content is found on normal diets, and none on fat-free diet. E. C. Smith.

Antirachitic value of irradiated cholesterol and phytosterol. IV. Factors influencing biological activity. A. F. Hess, M. Weinstock, and E. Sherman (J. Biol. Chem., 1925, **66**, 145—160).—Whereas irradiated vegetable oil retains its antirachitic activity for at least a year, irradiated cholesterol loses a part of its activity during storage for a month; the loss is greatest if it is stored dry and least if kept in olive oil. The inactivation produced by prolonged irradiation of activated cholesterol (cf. A., 1925, i, 1020) is an irreversible process. Cholesterol can be activated by irradiation in an atmosphere of nitrogen and does not lose its activity in a vacuum or on prolonged contact with acetone, chloroform, or benzene; on recrystallisation from alcohol, it becomes less active; if the crystallisation be repeated, the soluble portion recovered from the mother-liquor is found to be progressively less active; none of the recrystallised products could be completely reactivated by irradiation, and the more soluble portions could not be reactivated at all. Cholesterol isolated from egg-yolk and from bone-marrow was devoid of antirachitic activity (before irradiation); no change in elementary composition could be detected in cholesterol which had been activated by irradiation for 1 hr.

C. R. Harington.

Mammary secretion. VI. Vitamin-*B* and the lactating rat's diet. 1. The quantitative relation of vitamin-*B* to protein. 2. Vitamin-*B* requirements of the lactating and non-lactating rat. G. A. Hartwell (Biochem. J., 1925, **19**, 1075—1081).—There is a quantitative relation between the protein and vitamin-*B* in the lactating rat's diet. On a synthetic diet containing 20% of caseinogen, 6—8 g. of marmite per 20 g. of caseinogen are needed for the mother to rear her young normally. On a synthetic diet containing 20% of caseinogen, the lactating rat requires at least four times as much vitamin-*B* as does the young, growing animal. The lactating rat can rear some of her young on a synthetic diet free from vitamin-*B*, but conditions are not normal. In a synthetic diet 10% of caseinogen is insufficient for the lactating rat. S. S. Zilva.

Technique for studying vitamin-*B*. A. H. Smith, G. R. Cowgill, and H. M. Groll (J. Biol. Chem., 1925, **66**, 15—21).—The importance is emphasised, when using rats as subjects of vitamin-*B* experiments, of eliminating the possibility of the animals eating their fæces. C. R. Harington.

Glycogen reserves and arterial sugar (free and combined with protein) in experimental scurvy. L. Randoin and A. Michaux (Compt. rend., 1925, **181**, 1179—1181).—Guinea-pigs fed on a diet deficient in vitamin-*C* have the normal blood-sugar level (both free and combined sugar), and although the liver glycogen reserves are somewhat diminished, some glycogen remains in the liver and muscles of animals dying of scurvy. L. F. Hewitt.

Synthesis of vitamins by yeasts. R. Zajdel and C. Funk (Compt. rend. Soc. Biol., 1925, **92**, 1527—1528; from Chem. Zentr., 1925, II, 1178).—Vitamin-*D* is shown to be indispensable for the growth of yeast in nutrient solutions. On addition of unpurified sugar, growth takes place. The authors suggest that there are several components in vitamin-*D*, one of which occurs in ordinary unpurified sugar. In one case where yeast grew apparently in the absence of vitamin-*D*, it is supposed that there was a synthesis of the vitamin by wild yeast. G. W. Robinson.

Reproduction, growth, and alimentary equilibrium. L. Randoin, J. Alquier, Asselin, and Charles (Compt. rend., 1926, **182**, 94—96; cf. A., 1925, i, 210, 1002).—The diets most favourable for the growth of white rats are not the most favourable for reproduction. Butter (or milk) is an essential part of the diet to ensure fertility, caseinogen (or milk) is necessary for the rearing of the young, and a balance between mineral constituents and carbohydrates in the diet is necessary for reproduction and growth. L. F. Hewitt.

Assimilation of carbon dioxide by plants. F. J. Nellensteyn.—See B., 1926, 35.

Controlling influence of carbon dioxide. V. Production of ethyl alcohol and acetaldehyde by cells of the higher plants in relation to concentration of oxygen and carbon dioxide. M. Thomas (Biochem. J., 1925, **19**, 927—947).—In the absence of oxygen, ethyl alcohol and traces of acetaldehyde accumulate in apple cells. This is due to respiration of a zymasic type (anaërobic zymasis). Neither of these compounds accumulates as intermediate or end-product of the respiration of apple cells in air; nor can they be oxidised by the apple tissue. When carbon dioxide is present, zymasic respiration takes place even in the presence of abundance of oxygen (carbon dioxide zymasis). In carbon dioxide zymasis, the ratio of ethyl alcohol to acetaldehyde is 2 : 1, whilst in anaërobic zymasis it is 50 : 1. Mixtures of carbon dioxide and oxygen may therefore be more injurious to apples than anaërobic conditions, owing to the toxicity of the acetaldehyde, which is produced in greater quantities in carbon dioxide zymasis. S. S. Zilva.

Influence of electrolytes in medium on gaseous exchange of mosses. A. Mayer and L. Plantefol (Compt. rend., 1925, **181**, 1094—1095; cf. A., 1924, i, 809; 1925, i, 1120).—Mosses were soaked in dilute solutions of various salts and acids, withdrawn, dried in the air, and their gaseous exchanges studied. Practically all salts in low concentrations increased the oxidation intensity of the mosses and in higher concentrations retarded it. Different salts of the same anion or cation produced very different effects. Some salts, *e.g.*, calcium chloride, retarded the respiration without increasing it at any concentration. Acids exert their influence in much more dilute solutions, and if the concentration is large enough to inhibit respiration the inhibition period is followed by an accelerated respiration; the other effects described last for several days. The respiratory quotient increases or decreases with the increase or decrease in respiration intensity. L. F. Hewitt.

Equilibrium of cellular constituents and cellular oxidation intensity. Imbibition and oxidation in seeds. R. Jacquot and A. Mayer (Compt. rend., 1925, **181**, 931—933; cf. A., 1924, i, 809; 1925, i, 1120).—Until the seeds of the broad-bean, maize, and pea-nut have absorbed a certain amount of moisture, no carbon dioxide is liberated; when this limiting value is exceeded, the oxidation increases rapidly to a maximum value as more water is absorbed, and then decreases rapidly from that maximum. The water content necessary for oxidation to commence, the maximum value of carbon dioxide liberation per 100 g. of the moist seeds, and the water content of the seeds at this maximum, are characteristics of each of the seeds examined. The maximum amount of carbon dioxide liberated per 100 g. of water in the seeds is the same for all the seeds (*i.e.*, 17 c.c. of carbon dioxide per 100 g. of water per hour). The hydrobiotic yield has also a maximum value and is approximately the same in each case. L. F. Hewitt.

Coupled fat and carbohydrate metabolism. H. von Euler (Biochem. Z., 1925, **164**, 18—22).—The development of carbon dioxide by the press juice of sterilised seeds of *Brassica Napus* is increased during the early period of observation by the addition of cozymase solution, but no further increase is observed after 3½ hrs. P. W. Clutterbuck.

Effect of light on tannin formation. Michel-Durand (Compt. rend., 1925, **181**, 1171—1173; cf. A., 1924, i, 477).—Chestnuts and acorns were allowed to germinate and grow in washed sand in darkness and others in sunlight, and in every case from 5% to 23% of tannins was found in the plants. Less acetone-soluble tannins were found in every part, and less water-soluble tannins in every part but the leaves, of chestnut plants grown in darkness than in those grown in sunlight. The same but less marked differences were found in the case of oak plants. L. F. Hewitt.

Effect of light on the alkaloid content of *Lupinus luteus*, L. T. Sabalitschka and C. Jungermann (Biochem. Z., 1925, **164**, 279—287; cf. this vol., 99).—The alkaloid content of seedlings grown on a nitrogen-free substrate for 14 days from germination, in the dark, is 74%, that of seedlings grown in daylight is 81%, of the original content of the seeds. When brought into the light for a further 14 days, the alkaloid content increase is 30% more than the corresponding increase in the normal plants. Again placed in the dark for 14 days, the alkaloid content decreases to 60%. Plants grown for 13 weeks in the light when placed in semi-darkness for 1 week show no increase in alkaloid content, whereas normal plants show a 25% increase during that time. E. C. Smith.

Donnan membrane equilibrium in connexion with living cells. W. S. Butkevitsch and W. W. Butkevitsch (Biochem. Z., 1925, **161**, 468—487).—The phenomena connected with the Donnan membrane equilibrium are important in plant cells—particularly in the root system. In experiments with collodion membranes where silicic acid is present, the diffusion of diffusible anions is promoted. In this way, silicic acid influences the absorption of phosphate, and thus has a beneficial effect on the development of the plant when phosphates are present only in small concentration. The indiffusible sodium ions also affect the absorption of the diffusible potassium ions in the plant. H. I. Coombs.

Isoelectric points for plant-tissue. W. J. Robbins and I. T. Scott (J. Agric. Res., 1925, **31**, 385—399).—When potato-tuber tissue was placed in small volumes of dilute buffer solutions and the reaction determined electrometrically, solutions of p_H 6·15 or greater became more acid, those of p_H 6·14 or less, more alkaline. The isoelectric points of potato-tuber tissue and of soya-bean root tips are p_H 6·4 and p_H 6·2—6·44, respectively, of the mycelia of *Gibberella saubinettii*, *Fusarium lycopersi*, and *F. oxysporum*, 6·2, 5·5, and 4·9, respectively.

H. J. Channon.

Tolerance of barley for alkali salts in soil. R. E. Neidig and H. P. Magnuson.—See B., 1926, 24.

Iron solubility tests in culture solutions at different p_H values. R. P. Marsh (New Jersey Agric. Exp. Sta. Ann. Rep., 1923, 252—256; Chem. Abstr., 1925, **19**, 3558).—The solubility of ferric glycerophosphate, soluble ferric phosphate, ferric tartrate, and ferrous sulphate in culture solutions is influenced by the hydrogen-ion concentration of the solutions. When the hydrogen-ion concentration is kept high, ferric glycerophosphate can be used as a source of iron for plants; when it approaches the neutral point, ferric tartrate is preferable.

A. A. Eldridge.

Lignification. I. Nature of lignin: its physiological significance and its determination in timbers. II. Histological studies on the polysaccharides and aromatic constituents of the cell wall. M. M. Mehta (Biochem. J., 1925, **19**, 958—978, 979—997).—I. Lignin, m. p. 170°, occurs in wood in the free condition, but the major part is in combination with polysaccharides. Free lignin can be extracted from the wood by alcohol. The combined lignin can be obtained by resolving lignocellulose into its constituents completely by heating with 4% sodium hydroxide at 10 atm. for 1 hr. This treatment does not decompose the lignin, which can be precipitated by acidifying the alkaline liquid and isolated in pure condition quantitatively by extraction with alcohol. This method can be utilised as a gravimetric method for the determination of lignin. The combined and free lignin was thus determined in a number of timbers. A microchemical colorimetric method is described. It is based on the fact that lignin gives a blue coloration with phosphotungstic and phosphomolybdic acids in phosphoric acid in presence of sodium carbonate solution. A study of the distribution of lignin in different parts of Scotch fir by the colorimetric method shows its presence in young twigs as well as in leaf and buds. It is assumed that lignin occurs in chemical combination with cellulose and related polysaccharides as an aromatic glucoside. The aromatic constituent just before lignification is not of the nature of "hadromal" described by Czapek (cf. A., 1899, i, 560). Pure, resistant α-cellulose is obtained when lignocellulose is resolved by the above method and can be determined accurately in this way.

II. α-, β-, and γ-Cellulose, α-, β-, and γ-oxycellulose, hydrocellulose, mannan, galactan, pectin, amylohemicellulose, hemicellulose, gums, starch, lichenin, and chitin have been isolated in the purest possible condition and their staining capacities determined. β- and γ-Cellulose show a greater affinity for stains than α-cellulose. Oxycelluloses, unlike α-, β-, and γ-celluloses and hydrocellulose, are stained by ruthenium-red. Two kinds of hydrocellulose can be differentiated by the coloration given by one of them with iodine in potassium iodide solution. Resins react in some respects like lignin and are associated with gums in different parts of the same plant. Lignification sets in very early in the life-history of the plant and occurs in ground-tissue, fibro-vascular bundles, medulla, and cuticularised cells. The relative amounts of different cellulosic constituents vary widely, according to the cultural conditions, general environment, and the nature of the plant. The middle lamella in young stems of pine is composed of neutral pectic substance, whilst in old timber it is composed of lignin, gums, and hemicellulose, pectin being absent.

S. S. Zilva.

Microchemical identification of potassium [in plants] as picrate. N. Patschovsky (Ber. deut. Bot. Ges., 1925, **43**, 489—496).—The presence of potassium in botanical sections may be detected by placing on the slide one drop of an alcoholic solution of picric acid, and observing the formation of crystals of potassium picrate. The calcium, sodium, and ammonium salts are much less likely to separate, on account of the greater solubilities, but confirmation may be obtained by placing on the crystals a drop of sodium cobaltinitrite or of perchloric acid solution; potassium picrate is transformed by these into the characteristic cobaltinitrite or perchlorate. Plant organs may be immersed in a solution of picric acid in petroleum, the potassium picrate crystals then developing at the surface. If the test is negative or uncertain, the plant organ may be incinerated, and the ash similarly tested; it is suggested that potassium observed in the ash but not detected by the test in the organ may be present in some organic combination and not as a salt.

S. I. Levy.

Chemical characteristics of green, yellow, and red leaves. H. Colin and A. Grandsire (Compt. rend., 1925, **181**, 1168—1170).—In red leaves, the reducing and non-reducing sugars are increased in amount, and the electrical conductivity is increased, but the ash, water, potassium, and calcium contents are decreased, whilst in yellow leaves the reducing sugar content, water and ash, and calcium content are appreciably higher, the electrical conductivity is slightly higher, and the non-reducing sugar and calcium content lower than in green leaves.

L. F. Hewitt.

Influence of manures on yield and morphine content of latex of opium poppy. H. E. Annett and H. D. Singh.—See B., 1926, 74.

Oil content of seeds of opium poppy. H. E. Annett and M. N. Bose.—See B., 1926, 66.

Ash constituents of Indian opium. H. E. Annett and M. N. Bose.—See B., 1926, 74.

Root of *Gentiana lutea*, L. R. Binaghi and P. Falqui.—See B., 1926, 106.

Phytochemistry [1. Mannitol in jalap; 2. sucrose in belladonna root; 3. the cyanophoric glucoside in the bark of *Pyrus aucuparia*, Gaertn.; 4. a cyanophoric glucoside in *Achillea millefolium*, L.; 5. hydrocyanic acid in *Chloris petræa*]. L. Rosenthaler (Arch. Pharm., 1925, **263**, 561—563).—1. (Cf. Buchner's "Repertorium für die Pharmazie," **54**, 221.) When an aqueous extract of the drug is evaporated to dryness, and an alcoholic solution of the residue is allowed to crystallise, mannitol (m. p. 165—166°) is obtained.

2. Crystals of sucrose separate from an alcoholic extract of belladonna root.

3. When the stem bark of *Pyrus aucuparia*, Gaertn., is extracted by the author's method ("Grundzüge der chem. Pflanzenuntersuchung," 2nd edition, p. 32) there is eventually obtained, by crystallisation from chloroform, a glucoside having the enzymolytic index of 560, determined by Bourquelot's method. This, and the fact that on hydrolysis the substance yields *l*-mandelic acid, indicates that a mandelonitrile glucoside is present.

4. The author (Biochem. Z., 1922, **134**, 219) has already shown that *Achillea millefolium*, L., is a cyanophoric plant. Determinations of the enzymolytic index indicate that a benzaldehyde cyanohydrin glucoside, possibly new, is present.

5. The South African grass *Chloris petræa* contains 0·002% of hydrocyanic acid; it also yields on distillation a little acetone. W. A. Silvester.

Occurrence of methyl mercaptan in fresh *Raphanus* roots (Daikon, *Raphanus sativus*, L.). N. Nakamura (Biochem. Z., 1925, **164**, 31—33).—Methyl mercaptan is isolated as the mercury compound from the distillate from the pulp of the fresh roots. P. W. Clutterbuck.

Constituents of the tegument of the seeds of *Anagyris fœtida*. P. Condorelli (Annali Chim. Appl., 1925, **15**, 426—431).—The tegument of these seeds contains, not dextrose (cf. Reale, A., 1888, 188), but galactose, together with a mucilaginous substance, termed *podalirin*, which yields galactose and arabinose on hydrolysis and exhibits the characters of paragalacto-araban (cf. Schulze, A., 1891, 1179). T. H. Pope.

Phytobiochemical studies. II. A. Zlatarov (Biochem. Z., 1925, **161**, 379—389).—The peas of *Cicer arietinum*, L., contain 1·61% lecithin (by phosphorus analyses). The following *compounds* were isolated from 70 kg. of the meal and analysed: $C_{43}H_{80}O_9NP(C_5H_8O_4)_2$, a lecithin-pentosan, $C_{43}H_{80}O_9NP(C_6H_{12}O_6)$, a lecithin-glucose, and $C_{43}H_{80}O_9NP$, a lecithin. They were easily oxidised and were kept in an atmosphere of carbon dioxide. When hydrolysed with 2% sulphuric acid they yielded no purine compounds, but gave a good yield of betaine. (Cf. A., 1916, i, 620.) H. I. Coombs.

Nitrogen constituents of celery plants in health and disease. G. H. Coons and L. J. Klotz (J. Agric. Res., 1925, **31**, 287—300).—Two necrotic diseases of the leaves of celery, caused by the fungi *Cercospora apii*, Fres., and *Septoria apii*, Chester, have been investigated from a chemical point of view. In both cases, there is distinctly less total nitrogen in diseased than in healthy leaves; diseased tissue contains less nitric, amino-acid, and acid amide nitrogen, and more ammonia, "humin," and protein nitrogen. Nitrites are present in diseased but not in healthy leaves. The results are interpreted on the basis of the metabolism of fungi in cultures. It is considered that when the purely carbonaceous food supply is exhausted, the parasite must decompose nitrogenous constituents to obtain the requisite carbon and that a stage is reached when there is more nitrogen available than is required for protein synthesis etc., the excess appearing as ammonia and being lost in this form. C. T. Gimingham.

Glucosides of indigenous orchids. P. Delauney (Bull. Soc. Chim. biol., 1925, **7**, 1144—1147).—See A., 1925, i, 487.

Presence of loroglossoside (loroglossin) in *Listera ovata*, R. Br., and *Epipactis palustris*, Crantz. C. Charaux and P. Delauney (Bull. Soc. Chim. biol., 1925, **7**, 1148—1150).—See A., 1925, i, 874.

Bromine-containing gland cells (bromuques) in *Antithamnion*, Naeg. C. Sauvageau (Compt. rend., 1925, **181**, 1041—1043).—The colourless, highly refractive "gland cells" of *Antithamnionella sarniensis*, Lyle, *A. plumula*, Thur., *A. refractum*, Thur., *A. boreale*, Kjellm., *A. Pylaisœi*, Kjellm., and *A. Butleriæ*, Coll., contain bromine in such a form that on treatment with fluorescein, eosin, identified spectrometrically, is produced. This property does not disappear when the plant is dead and dried. It is suggested that the bromine is dissolved in a carbohydrate in the plant. L. F. Hewitt.

Formation of resin in conifers. I. Formation of resin in the needles of *Pinus cembra*. G. V. Pigulevski and V. V. Vladimirova (J. Russ. Phys. Chem. Soc., 1925, **56**, 325—334; cf. *ibid.*, 1924, **55**, 1).—The needles of *Pinus cembra* contain up to 10% of resin, the accumulation of which starts immediately the buds burst, follows a course parallel to that of the development of the needles, and has its greatest intensity when the increase of the dry matter of the needles is most rapid. The formation of ethereal oil in the needles occurs later than that of resin, and is at its maximum only after the accumulation of dry matter has begun to fail. Some increase in the resin content occurs during the second and third years of the life of the needles, and evidently occurs at the expense of the ethereal oil, of which the high-boiling constituents gradually disappear. The resin contains considerable proportions of acid and esters; the content of acid is less in the early than in the later stages of development of the needles, but diminishes in needles aged one or two years. T. H. Pope.

Formation of resin in conifers. II. Formation of resin in *Pinus cembra*. G. V. Pigulevski (J. Russ. Phys. Chem. Soc., 1925, **56**, 335—348; cf. preceding abstract).—Confirmation is obtained of the view that the bulk of the secretion of the needles of *Pinus cembra*, composed of the resin and of part of the ethereal oil, is formed during the period of growth of the needles, and is a function of the accumulation of dry matter. After severe frost, a marked increase in the secretion is observed on cutting the points of the needles; this phenomenon depends, not on increased secretion, but on increase in the pressure on the walls of the resin ducts, this producing compression of the tissues. After frost, the secretion contained 33% of ethereal oil. T. H. Pope.

Formation of resin in conifers. III. Formation of resin in *Abies sibirica*. G. V. Pigulevski and V. F. Grigorieva (J. Russ. Phys. Chem. Soc., 1925, **56**, 349—358; cf. preceding abstracts).—The needles of *Abies sibirica* contain up to 14% of resin, the formation of which proceeds parallel to that of dry matter and precedes that of ethereal oil. The resin contains esters and acid, the latter tending to diminish in amount during the period of vegetation. The ratio of ethereal oil to resin in the secretion is 1 : 2·7, so that the secretion contains 27·6% of the former. T. H. Pope.

Formation of ethereal oil in conifers. VII. Formation and transformation of ethereal oil in *Pinus strobus*. G. V. Pigulevski and V. V. Vladimirova (J. Russ. Phys. Chem. Soc., 1925, **56**, 359—366).—The dry needles of *Pinus strobus* contain up to 1% of ethereal oil, which accumulates as the needles grow and reaches its maximum development after the formation of dry matter has begun to fail. The higher-boiling components of the oil gradually diminish in quantity, possibly owing to transformation of the sesquiterpenes into non-volatile products. With this tree, the secretion consists of 15·9% of ethereal oil and 84·1% of resin. T. H. Pope.

Apparatus for the rapid evaporation of unstable solutions [sera etc.]. W. Gäde and W. Straub (Biochem. Z., 1925, **165**, 247—249).—The apparatus, which can be evacuated, consists of a vessel containing the solution, heated in a water-bath, connected with a second vessel containing sulphuric acid, cooled in a cooling bath. P. W. Clutterbuck.

Micrometer syringe. J. W. Trevan (Biochem. J., 1925, **19**, 1111—1114).—The principle of the instrument is based on the displacement of a volume of fluid by the well-fitting piston of a glass syringe. The displacement is measured by a Starret micrometer. The degree of accuracy of the instrument is demonstrated by a series of titration experiments; 0·01 c.c. of fluid is measurable with an error of less than ±1%. S. S. Zilva.

General principle for the determination of different substances in body-fluids. L. Lorber (Biochem. Z., 1925, **162**, 354—358).—In order to avoid precipitation methods, the amount of any substance in a body-fluid is determined directly in the whole fluid before and after addition of a known amount of that substance, when, by use of an equation, the actual amount of substance in the fluid is calculable. The way in which this principle might be applied to titrimetric, colorimetric, nephelometric, fermentative, and eudiometric determinations is indicated. P. W. Clutterbuck.

Modification of the method of isothermic distillation for the determination of the molecular concentration of blood serum. C. Hrynakovski and A. Rychter (Bull. Soc. Chim. biol., 1925, **7**, 1131—1138).—Barger's method for the determination of mol. wt., as modified by Rast, has been further modified to allow of the attainment of equilibrium and the measurement to be carried out at a constant temperature of 36·5° (±0·3°). Comparison under these conditions with a standard solution of urea shows human blood-serum to have a concentration of 0·292—0·302*M*. C. P. Stewart.

Preservation of blood samples for analysis. A. T. Cameron and J. E. Williamson (Can. Med. Assoc. J., 1925, **15**, 393—394).—Sander's method (J. Biol. Chem., 1923, **58**, 1) is satisfactory for 4 days' preservation for analysis of dextrose, urea, creatinine, non-protein nitrogen, and cholesterol, but not of uric acid. Chemical Abstracts.

Micro-determination of dextrose by Bang's method. E. Cohn and A. Wagner (Biochem. Z., 1925, **160**, 43—51).—A large number of determinations of blood-sugar by Bang's second reduction method indicate that this method fulfils all its author's claims in regard to accuracy. P. W. Clutterbuck.

Determination of proteins in human blood-serum. I, II, III. W. Starlinger and K. Hartl (Biochem. Z., 1925, **160**, 113—128, 129—146, 147—154).—A very full, critical study of the gravimetric, Kjeldahl, quantitative precipitation, refractometric, polarimetric, nephelometric, diaphanometric, colorimetric, and viscosi-refractometric methods for the determination of proteins in human serum. P. W. Clutterbuck.

Comparison of methods of protein precipitation. H. Wunschendorff (Bull. Soc. Chim. biol., 1925, **7**, 1158—1167; cf. A., 1925, i, 1346).—Metaphosphoric acid fails to precipitate proteins completely. The precipitate obtained by the use of trichloroacetic acid contains the whole of the protein, but appears to adsorb some non-protein material, depending on the concentrations of the acid and protein. Tungstic acid gives complete precipitation with less adsorption, but filtration is so slow that there may be appreciable hydrolysis of the protein. The use of colloidal ferric hydroxide, as previously described by the author, is recommended. C. P. Stewart.

Micro-determination of chloride in blood and other media containing proteins. M. Claudius (Acta med. Scand., 1924, **61**, 4—7; from Chem. Zentr., 1925, II, 1198).—Twenty c.c. of blood or serum are treated with 0·2 c.c. of 0·04*N*-silver nitrate and 4—5 drops of strong nitric acid. The liquid is heated until the coagulum dissolves and finally concentrated by boiling to 0·25 c.c. One drop of 4% potassium permanganate is added and the precipitated manganese dioxide dissolved by addition of a drop of nitric acid. After cooling, one drop of 4% ferric nitrate and 5 c.c. of ethyl alcohol are added, and the solution is titrated with 0·01*N*-potassium thiocyanate in ethyl-alcoholic solution. G. W. Robinson.

Colorimetric micro-method for the determination of lactic acid in blood. B. Mendel and I. Goldscheider (Biochem. Z., 1925, **164**, 163—174).—After removal of protein with metaphosphoric acid and of carbohydrate with copper sulphate and lime, the blood filtrate is treated with concentrated sulphuric acid and the acetaldehyde produced gives with veratrol a red colour. The determination takes 1½ hrs., and requires 1 c.c. of blood. The limiting concentration of lactic acid is about 5 mg.%. Acetone, β-hydroxybutyric acid, acetoacetic acid, urea, uric acid, creatine, creatinine, glycine, alanine, and propionic acid do not give the red colour. Acetaldehyde, formaldehyde, and pyruvic acid give the colour before heating (distinction from lactic acid), but are present in blood only in negligible amount.
P. W. Clutterbuck.

Application of phosphotungstic and phosphomolybdic acids to the determination of uric acid in milk and blood. G. Reif (Biochem. Z., 1925, **161**, 128—138).—A phosphotungstic–phosphomolybdic acid reagent is used for the production of a violet coloration with uric acid solutions which has the advantage of being permanent. Substances other than uric acid occurring in blood and interfering with this reaction may be removed from the solution by extraction with chloroform. C. Rimington.

Micro-determination of urea in 0·1 c.c. of blood. B. Pohorecka-Lelesz (Bull. Soc. Chim. biol., 1925, **7**, 1085—1088).—The urea contained in 0·1—0·2 c.c. of a fluid containing that substance in a concentration similar to that in which it occurs in blood is hydrolysed by urease at 38—40° in a special apparatus. The mixture is rendered slightly alkaline by means of borate, and the ammonia is removed by a current of air and collected in dilute sulphuric acid. It is then determined by neutralising the sulphuric acid and adding an excess of sodium hypobromite. The excess of hypobromite is determined by adding potassium iodide and hydrochloric acid and the iodine liberated is titrated with sodium thiosulphate.
W. O. Kermack.

Micro-Kjeldahl method without distillation. B. Pohorecka-Lelesz (Bull. Soc. Chim. biol., 1925, **7**, 1038—1043).—To 1 c.c. of urine diluted twenty times are added 1 c.c. of sulphuric acid and 1 c.c. of a 30% solution of potassium oxalate, the use of this salt being preferable to that of copper sulphate. After the combustion is complete, 2 c.c. of approximately 0·1*N*-sodium hypobromite are added to the mixture, which has been previously made neutral to methyl-red.

To determine the excess of hypobromite, excess of potassium iodide solution and 2 c.c. of *N*-hydrochloric acid are added. The iodine liberated is titrated with 0·02*N*-sodium thiosulphate. Allowance is made for the ammonium sulphate in the sulphuric acid used, as determined by a blank test. W. O. Kermack.

Simple micro-determination of diastase in body-fluids. L. Lorber (Biochem. Z., 1925, **163**, 480—487).—The application is described of the author's sugar micro-determination (cf. A., 1925, i, 852) to the determination of the diastatic activity of body-fluids. The method claims to permit the comparison of the activities of different fluids by making experimental allowance for the differences, *e.g.*, p_H, between the various fluids. R. K. Cannan.

Determination of free acid in gastric juice. H. E. Büttner (Klin. Woch., 1925, **4**, 877—879; from Chem. Zentr., 1925, II, 1078).—In the titration of the hydrochloric acid in gastric juice, using alkali, combined hydrochloric acid is set free and the original free hydrogen ions are thus not determined. This may be avoided by colorimetric determination, using 0·1% methyl-violet. The values thus obtained are 50% lower than those obtained by direct titration.
G. W. Robinson.

Nephelometric determination of various substances. Determination of sulphate in urine. L. Lorber (Biochem. Z., 1925, **163**, 476—479; see A., 1925, i, 852).—The turbidity produced by the direct addition of barium chloride and acid to urine containing a known addition of sulphate is reduced by dilution to the same intensity as that produced in the urine without addition. From the dilution the urinary sulphate concentration can be calculated. An accuracy of 5% is claimed. R. K. Cannan.

Determination of total sulphates in tissues. W. Denis and S. Leche (J. Biol. Chem., 1925, **65**, 561—563).—The tissue is autoclaved for 1 hr. at 200° with 5 parts of *N*-hydrochloric acid and the sulphuric acid determined in the filtered solution by precipitation as barium sulphate. The error of the method is ±5%. C. R. Harington.

Volumetric determination of phosphoric acid in yeast. Staiger (Brennereiztg., 1924, **41**, 209—210; from Chem. Zentr., 1925, II, 1105).—The solution of the ash from 5 g. of yeast (which should not contain more than 0·07 g. P_2O_5), after removal of silica, is titrated by the Pfyl method.
G. W. Robinson.

Measurement of fluids in perfusion experiments. M. Kochmann (Arch. exp. Path. Pharm., 1925, **109**, 358—361).—Apparatus for the automatic measurement of volume and rate of flow in perfusions is described. S. I. Levy.

Pharmacological evaluation of atropine and scopolamine solutions, and of their stability. G. Kühl (Arch. exp. Path. Pharm., 1925, **109**, 295—299).—The effect of injected solutions on the blood pressures of cats treated with acetylcholine hydrochloride has been found to be a suitable pharmacological method for determination of atropine and scopolamine solutions. No diminution in effect was observed after heating the solutions to 100° for 30 min. in presence of either acids or alkalis.
S. I. Levy.