

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Spectrum of hydrogen. A. SOMMERFELD and A. UNSÖLD (*Z. Physik*, 1926, **38**, 237—241).—Recent measurements of the intensities of the lines in the fine-structure of H_α are not in agreement with the calculations in the former paper (this vol., 549), but are found to be in agreement with calculations based on Schrödinger's equations. The values for H_α and He^+ are tabulated and also represented graphically.

E. B. LUDLAM.

Method for producing a discharge in hydrogen. R. W. LUNT (*Phil. Mag.*, 1926, [vii], **2**, 743).—The attention of Gill and Donaldson (*ibid.*, 129) is directed to two prior papers by the author (*A.*, 1925, ii, 579, 616) on the production of discharges in gases at frequencies of the order of 10^7 cycles per sec.

A. E. MITCHELL.

Spectroscopic study of the discharge in helium. T. TAKAMINE (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 55—61).—When helium is electrically excited by the method of exploding wires (Anderson, *Astrophys. J.*, 1920, **51**, 37) a depression of intensity in the middle of the line for 4922, 4472, and 3203 (ionised helium line) is observed. This is ascribed to the interatomic electric field produced by the very closely packed atoms at high current densities and not to self-reversal (cf. Holtmark and Trumphy, *A.*, 1925, ii, 338). A similar phenomenon is observed in the condensed discharge at pressures from 0.5 to 1 atm. for lines 6678, 5876, and 3889. It is probable that in this case also the effect may be due, at least in part, to the interatomic field (cf. Merton, *Proc. Roy. Soc.*, 1918, **A**, 95, 30).

M. S. BURR.

Intensity relations of the components of the helium doublets. D. BURGER (*Z. Physik*, 1926, **38**, 437—439).—The so-called doublets have a ratio of intensities 1 : 8, instead of 1 : 2 as is to be expected for doublets; probably they are triplets with a ratio 1 : 3 : 5, but not easily separated. E. B. LUDLAM.

Absorption and resonance radiation in excited helium and the structure of the 3889 line. W. H. MCCURDY (*Phil. Mag.*, 1926, [vii], **2**, 529—538).—See this vol., 549.

Series spectra of beryllium, Be I and Be II. I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1926, [ii], **28**, 256—258).—Tabulated data concerning the intensity, frequency, designation, and term values are given of 20 lines of Be II (14 being new) between 842.03 and 5274.28 Å., and 20 lines of Be I (6 being new) between 1943.60 and 3322.30 Å. The

frequencies of series terms for stripped atoms Li I to C IV are compared.

A. A. ELDRIDGE.

Oxygen spectral line 5577.35 Å. J. C. McLENNAN, J. H. McLEOD, and W. C. McQUARRIE (*Nature*, 1926, **118**, 441).—The line is obtainable with pure oxygen, but not in its absence; conditions for maximal intensity are described. The intensity is enhanced by the presence of helium, neon, or argon, the enhancement factors being, respectively, 1.7, 4.6, and 84.2. No fine structure was observed. A study of the Zeeman effect suggests that the line has an atomic origin; it probably originates in an electron transition between atomic levels for oxygen provided by one or other of two new singlet-triplet schemes based on Hund's theory.

A. A. ELDRIDGE.

Intensity variations in the spectrum of neon. (MRS.) M. R. JOHNSON and R. C. JOHNSON (*Phil. Mag.*, 1926, [vii], **2**, 593—611).—The effects on the intensity, of the visual spectrum of neon, of current density, condensed and "bulb" discharge, high and low pressure, admixture of hydrogen, helium, argon, and carbon dioxide have been examined, together with the intensity distribution as a function of the distance from a flat cathode. The examination is limited chiefly to a comparison of the various principal series amongst themselves.

A. E. MITCHELL.

Width of the absorption lines in sodium vapour. W. KUHN (*Z. Physik*, 1926, **38**, 440—442).—Light which was dispersed but not absorbed by sodium vapour was passed through the vapour and the width of the absorption of the D-line simultaneously observed. There was no widening of the absorption line such as would have resulted if the dispersed light had been able to raise the sodium atom to a higher energy level. E. B. LUDLAM.

Optical spectra of different atoms of the same electronic structure. II. Aluminium-like and copper-like atoms. D. R. HARTREE (*Proc. Camb. Phil. Soc.*, 1926, **23**, 304—326; cf. *A.*, 1925, ii, 2).—The calculation of the relations between corresponding terms of different atoms of the same electronic structure has been extended and more general formulæ have been derived. Values of the polarisability of the Al^+ and Si^{++} ions are calculated from terms of Al I and Si II, respectively, corresponding with non-penetrating orbits, and are shown to be very much greater than the values of the polarisability of the neon-like ions Al^{+++} and Si^{++++} . The quantum

defect of a penetrating orbit can be expressed as the sum of the contributions from the electrons in groups of core orbits of different principal quantum number. For corresponding terms of different atoms of the same structure, the reciprocal of the quantum defect tends asymptotically to be linear in C , the core charge. Somewhat similar relations hold for the variation of quantum defect within a sequence. Comparison with values deduced from observed spectra show fair agreement, even although the value of C is only small.

E. B. LUDLAM.

Intensity measurements in the iron spectrum. J. B. VAN MILAAN (Z. Physik, 1926, 38, 427—436).—Tables are given of the relative intensities of the lines from 6136 to 6411 and from 5208 to 5506, also from 3680 to 3800 Å. for two different strengths of current for the arc and for the spark, which show very considerable differences. The observations for the multi-

plets $f'-d^2$, $p'-d^2$, $\bar{f}-d^2$ were in good agreement with the summation rule; those for $\bar{d}-d$ and $\bar{f}'-f'$ showed a divergence.

E. B. LUDLAM.

Interferometer measurements of the pressure-shift of lines in the arc spectrum of nickel. B. T. BARNES (Astrophys. J., 1926, 63, 127—132).—The wave-lengths of 72 lines in the nickel spectrum when emitted by an arc operated at a pressure of 760 mm. are compared with those for 60 mm. Most of the lines had a pressure-shift of less than 0.005 Å. per atm.; a greater shift in some cases is attributed to an unsymmetrical broadening of the lines.

A. A. ELDRIDGE.

Comparison of the red cadmium line in the vacuum arc and in the discharge tube. F. L. BROWN (J. Opt. Soc. Amer., 1926, 13, 183—192; cf. A., 1923, ii, 2).—The wave-length of the red cadmium line emitted by the vacuum arc has been compared with that of the same line emitted by the discharge tube, using a Fabry-Perot interferometer. They differ by less than 0.001 Å. The vacuum arc can be used as a safe source for all but the most precise work, and probably even then if the current density is not too great and the pressure is kept below 10 mm.

A. B. MANNING.

Structure of cadmium and zinc resonance lines. R. W. WOOD (Phil. Mag., 1926, [vii], 2, 611—612).—The fine structure of the $1S-2p_2$ and $1S-2P$ lines of cadmium and zinc, analogous to the mercury lines 2536 and 1849 Å. previously examined (A., 1925, ii, 1015), has been determined. The cadmium line at 2288 Å. is double with a wave-length separation of 0.021 Å. The cadmium line at 3261 Å. consists of a strong and easily reversed line accompanied by a faint companion on the shorter wave-length side; the wave-length separation is 0.019 Å. The zinc line at 2138.6 Å. was found to be double and that at 3075.9 single.

A. E. MITCHELL.

Fine structure of certain lines and energy levels of cadmium. W. A. MCNAIR (Phil. Mag., 1926, [vii], 2, 613—621; cf. preceding abstract).—The Lummer-Gehrcke plate method of Wood (A., 1925, ii, 1015) has been applied to the examination

of the fine structures of a number of cadmium lines and the observations have been applied to the arrangement of the fine structure of the electron orbits of cadmium. One such arrangement is similar to that suggested by Joos (A., 1925, ii, 612), except that the separations assigned to the p levels are slightly different and that the $2p_2$ level is more complex.

A. E. MITCHELL.

Effect of electric field on the spectral lines of zinc and cadmium. Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, 5, 45—53).—The Stark effect for zinc and cadmium has been examined by the ordinary Lo Surdo method, and many combination lines, such as pp , pb , pe , and pf , have been observed up to $2p-7q$. The results are similar to those obtained by the new method of Schüller (this vol., 215). The lines of diffuse series are displaced towards the less refrangible side in the electric field. Many anomalous lines appearing in the electric field have been observed and approximate measurements made of the intensities of these relative to the intensities of the lines of the diffuse series. Several new energy levels have been determined.

M. S. BURR.

Intensity distribution in the fine-structure of the cadmium triplet $2p_1-2s$. J. L. SNOEK and T. BOUMA (Z. Physik, 1926, 38, 368—369).—The intensity of the satellites has been measured, using a vacuum cadmium arc, which made an exposure of several hours necessary with the high dispersion used. The separation of the lines is about half that of the corresponding mercury lines, but the distribution of intensities is much the same. No satellites have yet been discovered for zinc.

E. B. LUDLAM.

Arc spectrum of europium. Measurements between 3500 and 3100 Å. under normal pressure. S. PINA DE RUBIES (Compt. rend., 1926, 183, 385—387).—Examination of the arc spectra, under normal pressure, of pure preparations of europium and of europium-gadolinium and europium-samarium mixtures has disclosed all the lines described previously by Exner and Haschek and by Urbain. The six lines between 3204.37 and 3443.81 Å., attributed by Eder to europium, were not observed. Seventy-nine lines between 3485.8 and 3105.2 Å. were obtained and measured. These have not been described previously and are identified with the spectrum of europium.

A. E. MITCHELL.

Arc spectrum of lead. N. K. SUR (Phil. Mag., 1926, [vii], 2, 633—642).—The heavy-arc method has been applied to a reinvestigation of the spectrum of lead with a view to obtain the higher members of the Rydberg sequence in the series spectrum of lead. Several members of the series $2s-mp_{1,2}$ and $2x-mp_{1,2}$ have been obtained. The results indicate that the arc spectrum of lead contains negative terms similar to those described by Russell and Saunders (A., 1925, ii, 911) in the arc spectrum of calcium. Two combination lines at 7330.12 and 4618.21 Å., being intercombinations of the $^3p_1-^1D_2$ and $^3p_1-^1S_0$ terms, respectively, have been obtained.

A. E. MITCHELL.

Theory of the absorption of X-rays. R. A. HOUSTON (Phil. Mag., 1926, [vii], 2, 512—520).—Mathematical. The author's previous deductions (A., 1920, ii, 462) that one electron is concerned in the *K*-absorption and more than one in the *L*-absorption are elaborated. A mechanism is suggested whereby within the region of the *K*-absorption all but one of the electrons of an atom are absorbing energy from the incident radiation and scattering it to lose it by resonance radiation, whilst the remaining electron absorbs energy from a narrow region situated somewhere between the head of the band and infinite frequency. Most of this latter energy is transmitted to another hypothetical system. A. E. MITCHELL.

Scattered X-rays. The *J*-phenomenon. IV. C. G. BARKLA and S. R. KHASTGIR (Phil. Mag., 1926, [vii], 2, 642—656; cf. A., 1925, ii, 456; this vol., 217).—It is shown that whilst the secondary differs from the primary radiation when its absorptibility is examined in certain substances, it is precisely like the primary when its absorptibility is measured in other materials. Experimental evidence shows that there is no change of wave-length of *X*-radiation either in the process of re-emission or in the subsequent transmission through matter. No gradual variation of absorptibility of a scattered radiation with the angle of scattering, as required by Compton's quantum theory of *X*-ray scattering, was found. Where any differences were found, these were characteristic of "*J*-discontinuities" and corresponded with the differences between two well-defined absorption levels. A. E. MITCHELL.

X-Ray levels of the elements copper (29) to lanthanum (57). D. COSTER and F. P. MULDER (Z. Physik, 1926, 38, 264—279).—New measurements have been made of the absorption edges and emission lines in the *L* region of the elements from rubidium (37) to cadmium (48), from which the energy levels can be calculated with greater accuracy than hitherto. The most trustworthy results for the elements from copper to lanthanum are tabulated and curves given. In conjunction with data from the optical spectra, the sub-grouping of the electrons is discussed.

E. B. LUDLAM.

X-Ray spectra and chemical combination. E. BÄCKLIN (Z. Physik, 1926, 38, 215—226; cf. A., 1925, ii, 914).—The effect on an atom of combination with other atoms is to displace the *K* level nearer to the nucleus and the *K* lines in the spectrum are displaced towards shorter wave-lengths. There is difficulty arising from overlapping of the lines when the compound is decomposed by the electronic bombardment, as both the free element and the combined element give rise to lines. Measurements have been made on the so-called spark lines, $K\alpha_3$ and $K\alpha_4$ (which bear the same relation to $K\alpha_1\alpha_2$ as do spark lines to arc lines in optical spectra). Barium sulphate and sulphur are compared and silica with silicon; the latter has the advantage that none of the element is liberated; in both cases the displacement is easily measurable. With silicon, a strong $K\beta_1$ line was obtained and a weaker $K\beta_2$; with silica, no $K\beta_1$ line appeared, but $K\beta_2$ was present. As the four *M*

electrons have gone to the oxygen atom, this may account for the absence of β_1 , but leaves β_2 unexplained.

E. B. LUDLAM.

Absorption of X-rays in crystalline compounds. R. J. HAVIGHURST (Proc. Nat. Acad. Sci., 1926, 12, 477—479).—Since an empirical formula due to A. H. Compton (Bull. Nat. Res. Council, 1920, [4]) represents within about 5% the *X*-ray absorption of all elements of atomic number greater than 5 as a function of the atomic number *N* and the at. wt. *A* of the absorber, an approximate expression for the absorption by a compound may be obtained by substituting ΣN and ΣA for *N* and *A*, respectively, the summations being taken over each atom in the molecule. In the case of polar compounds where electrons pass from one ion to the other, *N* is the nuclear charge on the atom, and not the actual number of electrons which reside in the ion. The measured linear absorption coefficients for sodium chloride, sodium fluoride, calcium fluoride, and calcium carbonate for radiation of wave-length 0.71 Å. are in satisfactory agreement with those calculated from the extended Compton formula. The agreement fails for lithium fluoride. The atomic absorption of lithium (*N*=3) is probably not accurately represented by the simple atomic absorption formula and hence the lack of agreement is not surprising.

J. S. CARTER.

Zeeman effect for the spectrum of fluorine. G. H. CARRAGAN (Astrophys. J., 1926, 63, 145—159).—The Zeeman patterns of 20 of the brighter lines of fluorine between 6239.63 and 7573.32 Å. have been determined, whence a first-order quartet system is indicated. The term combinations of the principal and diffuse series have been located, and those of other lines proposed. The possible existence of the fluorine ion and of higher order spectra is suggested.

A. A. ELDRIDGE.

Stark effect of the second order for hydrogen and the Rydberg correction for the spectra of helium and Li^+ . I. WALLER (Z. Physik, 1926, 38, 635—646).—Schrödinger's equation is developed by means of parabolic co-ordinates and the Stark effect of the second order calculated for hydrogen-like atoms. Equations are obtained which give successive approximations to the energy values. Good agreement is obtained for the helium atom and the ionised lithium atom.

E. B. LUDLAM.

Schrödinger's quantum theory and the Stark effect. P. S. EPSTEIN (Nature, 1926, 118, 444—445).—Schrödinger's theory of atomic oscillations is satisfactorily applied to the Stark effect in hydrogen.

A. A. ELDRIDGE.

Second order Stark effect. J. S. FOSTER (Astrophys. J., 1926, 63, 191—195).—The observed average second order Stark effect for six perpendicular components of H_2 in a field of 65 kilovolts/cm. is 0.40 Å., and for the central perpendicular component of H_2 0.79 Å., in agreement with values calculated from Epstein's formula. The displacement of the central perpendicular component of the helium group 4009 Å. is 0.35 Å. in a field of 60 kilovolts/cm. Although there is some evidence of a possible Doppler

effect, none was observed for neutral helium lines from a mixture of hydrogen and helium in a field of 50 kilovolts/cm. A. A. ELDRIDGE.

Compton effect and the reflexion of X-rays by crystals. E. J. WILLIAMS (Phil. Mag., 1926, [vii], 2, 657—674).—The laws applicable to the reflexion, by a crystal, of modified radiation scattered by its own electrons are derived by considering an electron lattice moving with a velocity which would give as a Doppler effect the wave-length change required by the quantum theory of scattering. The results so obtained differ appreciably from those of Bragg, and since the reflected radiation obeys Bragg's law, it is concluded that either no modified radiation is scattered in the directions concerned, or modified radiation is scattered but not regularly reflected. The bearing of the Compton effect on the theory of the intensity of reflexion by crystals is considered in the light of the second alternative, and the recalculated "*F* curves" are compared with the classical and observed curves. The recalculated curves agree much more closely with observations on the intensity of reflexion than do the classical ones, which should be the case, since they are little influenced by contributions from the outer electrons, as these electrons scatter very little unmodified radiation. The correction for the Compton effect, being a function of $\sin \beta/\lambda$, resembles the other factors entering into the theory. The capacity of a crystal to reflect modified and unmodified radiation is discussed.

A. E. MITCHELL.

Radiation produced by the passage of electricity through gases. (SIR) J. J. THOMSON (Phil. Mag., 1926, [vii], 2, 674—701).—Experiments on the character of the radiation produced when electric currents are passed through gases at low pressures are described. The method is based on a determination of the rate of emission of electrons due to the photo-electric effect when a disc of metal is placed in the path of the radiation and the emission is retarded by an electric field tending to inhibit the escape of electrons. The radiation produced by the passage of cathode and positive rays through hydrogen, oxygen, helium, and argon at different pressures is discussed. It is found that the frequencies of by far the greater part of the radiation are comparable with those corresponding with quanta of the order of the ionising and resonance potentials of the gas. Radiations due to cathode rays are mixed with others of a higher frequency. In general, the radiation is a mixture of radiation comparable with that of the ionising radiation and another of higher frequency. In a few cases it is homogeneous. The electrodeless ring discharge is found to be a ready source of this type of radiation, and various experiments for demonstrating its existence and examining its properties are described.

A. E. MITCHELL.

Emission of electrons and positive ions at the m. p. of metals. A. WEHNELT and S. SEILIGER (Z. Physik, 1926, 38, 443—464).—In the liquid as contrasted with the solid state, both for negative and positive emission, the work of escape is smaller and the number emitted at the m. p. is greater. By passage into the fluid state the number of free electrons

in the metal is diminished in approximately the same ratio as the resistance increases. The metals used were copper and silver. E. B. LUDLAM.

Series and ionisation potentials in the iron spectrum. O. LAPORTE (Proc. Nat. Acad. Sci., 1926, 12, 496—503; cf. Walters, A., 1924, ii, 285; Laporte, *ibid.*, 364; 1925, ii, 4; Hund, *ibid.*, 912).—A more detailed discussion in which the action of Pauli's equivalence principle (A., 1925, ii, 339) is demonstrated. The lowest term in the iron arc spectrum is a 5D term. J. S. CARTER.

Excitation potentials of the spectra of argon II and neon II. F. L. MOHLER (Science, 1926, 63, 405).—Argon exhibits sharp increases in photo-ionisation at 32.2 ± 0.2 , 34.8 ± 0.5 , and 39.6 ± 0.5 volts, corresponding respectively with a spark excitation potential, the work required to remove two electrons, each from a 3_2 orbit, and, probably, the work required to remove one 3_1 electron. Neon shows critical potentials at 48.0 ± 1 and 54.9 ± 1 volts; the latter measures the work required to remove two 2_2 electrons, and the former probably that required to remove one electron and displace another to a 3 quantum orbit of energy 26.5 volts.

A. A. ELDRIDGE.

Application of Pauli's method of co-ordination to atoms having four magnetic parts. G. BREIT (Physical Rev., 1926, [ii], 28, 334—340).—The origin of spectral terms of an arc spectrum obtained by adding a highly excited electron to a certain term of the spark may be understood in terms of an application of the principle of mechanical transformability made by Pauli.

A. A. ELDRIDGE.

Thermionic and adsorption characteristics of caesium on tungsten and oxidised tungsten. J. A. BECKER (Physical Rev., 1926, [ii], 28, 341—361).—The electron emission from a tungsten or an oxidised tungsten filament carrying adsorbed caesium is maximal for a monatomic layer of the alkali metal, which has its atomic rather than its ionic diameter. The positive ion emission was also studied. Practically all the adsorbed caesium is removed by drawing away positive ions at 1040° Abs.; it appears that below 650° Abs. every atom that strikes the filament adheres until the optimum activity is reached. Caesium on oxidised tungsten is apparently partly ionised, for the number of atoms forming the monatomic layer is 10% greater than on tungsten alone; it is held more firmly by the oxidised metal. The caesium can evaporate either as atoms or as ions; the atomic rate depends only on the temperature and on the fraction of the surface covered, rapidly increasing with the latter for a given temperature. On the other hand, the isothermal ion evaporation rate increases only up to a point at which 1% of the surface is covered, thereafter decreasing as the fraction becomes larger. The results indicate that the work necessary to remove a positive ion can be appreciably decreased by applying large negative potential gradients. It is suggested that the new method for determining quantitatively how the concentration of adsorbed atoms is affected by surface temperature, surface potential gradient, and rate of arrival of

atoms may be applied in the elucidation of the nature of the forces which cause one atom to stick to another.

A. A. ELDRIDGE.

Scattering of electrons in ionised gases. F. M. PENNING (Nature, 1926, 118, 301).—Contrary to the observations of Langmuir (this vol., 3) oscillations were observed in mercury-vapour discharges with a hot cathode. It seems possible that the observed scattering of primary electrons is always accompanied and caused by these oscillations.

A. A. ELDRIDGE.

Scattering of electrons in helium. E. G. DYMOND (Nature, 1926, 118, 336–337).—A study of the angular distribution of scattering of electrons, which have suffered inelastic encounters and have lost 20 volts energy, in helium; results are given for initial velocities of 50–400 volts.

A. A. ELDRIDGE.

Transmission of low-velocity electrons through thin metallic foils. T. KURCHATOV and K. SINELNIKOV (Physical Rev., 1926, [ii], 28, 367–371).—Hartig's observations (A., 1925, ii, 921) on the permeability of aluminium foil to electrons having a velocity of at least 2 volts are confirmed when the foils exhibit no holes in transmitted light, but not with foils showing no holes on being tested in water.

A. A. ELDRIDGE.

Secondary electron emission from tungsten, copper, and gold. R. L. PETRY (Physical Rev., 1926, [ii], 28, 362–366).—When a stream of electrons from a hot filament, accelerated by a field of 0–1500 volts, struck a plate of tungsten, copper, or gold, the maximum values for the number of secondary electrons emitted per primary electron striking the plate were 1.45 (700 volts), 1.32 (240 volts), and 1.14 (330 volts), respectively. Critical primary potentials were observed as follows: tungsten, 11.0, 17.1, 25.2, 29.3, 40.5, 46.0, 89.5, and 271.5 volts; copper, 7.8, 12.6, 16.8, 19.5, 23.8, 39.0, 56.9, and 73.5 volts; gold, 15.5, 21.0, 23.2, 31.5, and 43.7 volts.

A. A. ELDRIDGE.

Mean free path of electrons in mercury vapour. L. R. MAXWELL (Proc. Nat. Acad. Sci., 1926, 12, 509–514).—The mean free path of slow electrons in mercury vapour has been examined over the range 0.5–3000 volts. The mean free path increases with the accelerating potential, there being, however, changes in the direction of the curve at 4.9 and 6.7 volts and a slight minimum value at about 40 volts.

J. S. CARTER.

Energy of high-velocity electrons. M. W. WHITE (Physical Rev., 1926, [ii], 28, 247–255).—Up to 25,000 volts, all the energy supplied to a Coolidge tube is ultimately transformed into heat; any source or sinks of energy which may exist have an effect of less than 0.2%. No radiations involving an absorption of energy at the cathode could be detected. Hence all of the energy input into an X-ray tube goes into the moving electrons and their fields, and only a negligible part of the current in a Coolidge tube is furnished by positive ions reaching the cathode.

A. A. ELDRIDGE.

Determination of effective cross-section towards slow electrons. M. RUSCH (Ann. Physik, 1926, [iv], 80, 707–727).—A new method has been developed for determining the effective cross-section of gas particles towards slow electrons in a longitudinal magnetic field. For argon, the effective cross-section has been plotted against values of \sqrt{v} , in the range 3.5–29 volts for the electron velocity. The curve resembles closely that of Ramsauer (A., 1923, ii, 529) for the transverse field, although the cross-section is always a little greater in the earlier work.

R. A. MORTON.

Work of escape of electrons from oxide cathodes. H. ROTHE (Z. Physik, 1926, 38, 410).—A reply to Katsch (*ibid.*, 407), who described cases of three-electrode valves in which a grid current was obtained with a negative potential on the grid. The beginning of a grid current is due to the contact difference of potential between the cathode and the grid. The oxide cathode slowly disintegrates and some of it deposits on the grid, thereby reducing the contact difference of potential.

E. B. LUDLAM.

Dissociation of nitrogen by electron impact. V. KONDRATJEV (Z. Physik, 1926, 38, 346–352).—Nitrogen was submitted to electron bombardment and the velocity of the electrons determined at which, in addition to the band spectrum of nitrogen, the atomic lines first appeared. The necessary voltage was found to be 32 ± 2 . The nitrogen molecule can break down in one elementary action into excited atoms, $N_2 \rightarrow N' + N'$ or $N_2 \rightarrow N' + N^+ + \ominus$.

E. B. LUDLAM.

High-voltage cathode rays outside the generating tube. W. D. COOLIDGE (Science, 1925, 62, 441–442).—Cathode rays, obtained through an aluminium window from a vacuum tube operated at 200,000 volts and several milliamperes, had a range of 46 cm. in air, causing luminosity. Calcite crystals are caused to fluoresce in the orange, and remain luminous for several hours after exposure. The high-voltage electrons affect gases in a manner similar to radium emanation; acetylene yields large quantities of a yellow substance, castor oil solidifies, and an aqueous solution of sucrose becomes acid. The effect on organised tissues is very pronounced.

A. A. ELDRIDGE.

Method of demonstration of phenomena in discharge tubes. (FRL.) A. KATSCH (Z. tech. Physik, 1925, 6, 595–598; from Chem. Zentr., 1926, I, 1600).—Excitation phenomena resulting from electron collision at very low pressures (10^{-4} – 10^{-5} mm.) are used as indicators of electron movements in evacuated discharge tubes. The nature of the phenomena has been investigated over a wide range of potential and it is concluded that there are three distinct methods of excitation, viz., by electrons, by positive ions, and by negative ions.

J. S. CARTER.

Mobility of acetylene ions in air. H. A. ERIKSON (Physical Rev., 1926, [ii], 28, 372–377).—As in air, carbon dioxide, hydrogen, and argon, α -rays from polonium produce in acetylene only one negative

ion having the same mobility in air as those formed in the other gases. Like the initial positive ion of hydrogen, the positive ion of acetylene has a mobility slightly less than that of the negative ion, but, up to an age of 1 sec., is not converted into a more stable ion of smaller mobility. When acetylene is admitted into ionised air or nitrogen it takes up the charge of the final positive ions by means of an electron exchange.

A. A. ELDRIDGE.

Ions of inert gases as catalysts. S. C. LIND and D. C. BARDWELL (*Science*, 1926, **63**, 310—311).—The velocity of polymerisation of acetylene, cyanogen, or hydrogen cyanide, mixed with xenon or krypton and irradiated with α -particles, is of the same order as with helium, neon, and argon, although the ionisation potentials of xenon and krypton are lower than those of the reactants. Hence it is indicated that the effect is due to clustering about both kinds of ions as reaction centres, although exchange of charge may also take place. This view is supported by the fact that some of the xenon is removed by occlusion in the polymeride.

A. A. ELDRIDGE.

Magnetic properties of atoms. J. KUNZ, J. B. TAYLOR, and W. H. RODEBUSH (*Science*, 1926, **63**, 550—551).—Gerlach and Stern's results (*Z. Physik*, 1921, **8**, 110) for the deflexion of a beam of atomic rays in a powerful, heterogeneous magnetic field were confirmed for silver; similar results were obtained for sodium and potassium. The calculated magnetic moment is within 10% of the value of the Bohr magneton.

A. A. ELDRIDGE.

Infra-red absorption of brucite and some sulphates. Isotopic effect. E. K. PLYLER (*Physical Rev.*, 1926, [ii], **28**, 284—290).—Maximal absorption for brucite, $\text{Mg}(\text{OH})_2$, is at 2.48μ ; small maxima occur at 2.40 , 2.30 , and 2.14μ . The first three values correspond with Mg^{24} , Mg^{25} , and Mg^{26} , respectively; the small band at 2.14μ corresponds in position with Mg^{28} , but no such isotope has been observed by other investigators. Reflexion spectra of nickel sulphate exhibit maxima at 9.15 and 9.5μ , probably due to Ni^{58} and Ni^{60} ; with potassium sulphate, maxima appear at 9.1 and 9.4μ , representing K^{39}SO_4 and $\text{K}^{39}\text{K}^{41}\text{SO}_4$. The complexity of the bands of barium, strontium, and magnesium sulphates cannot definitely be ascribed to an isotopic effect.

A. A. ELDRIDGE.

Homogeneous disintegration and half-period of mesothorium-2. O. HAHN and O. ERBACHER (*Physikal. Z.*, 1926, **27**, 531—533).—Eka-caesium (87) does not exist in amount greater than $1/10^7$ in preparations of mesothorium-2. The half-period of mesothorium-2 is found to be 6.13 hrs., which is 3% greater than the value of Widdowson and Russell (*A.*, 1925, ii, 463).

R. A. MORTON.

Anomalous scattering of α -particles. W. HARDMEIER (*Physikal. Z.*, 1926, **27**, 574—576).—Earlier work (this vol., 450) is more rigidly considered. The polarisability of the nucleus of aluminium is 0.5×10^{-36} , a value smaller than that found before.

R. A. MORTON.

Number of particles in β -ray spectra. II. Thorium-B and thorium-C+D. R. W. GURNEY (*Proc. Roy. Soc.*, 1926, **A**, **112**, 380—390; cf. this vol., 5).—The determination of the number of β -particles emitted with different velocities in β -ray spectra is extended to thorium-B and thorium-C+D. The total number of particles in the continuous thorium-C+D spectrum between $\text{H}\nu$ 4040 and 10,080 is in agreement with the view that they contain nuclear electrons. A law of " β -ray disintegration" is suggested, viz., no γ -rays of high energy can be emitted by those radioactive substances which expel their nuclear electrons with low energies. The probability that a γ -ray of 150,000 volts energy emitted by thorium-B is converted into a β -ray instead of escaping from the atom is at least 1 in 4 in the *K* level. For the γ -ray of 40,500 volts emitted by thorium-D, the probability of conversion in the *L* level is more than 1 in 5.

S. K. TWEEDY.

Pleochroic haloes in biotite. Probable independent origin of the actinium series. S. IIMORI and J. YOSHIMURA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 11—23).—The pleochroic haloes in a number of Japanese biotites have been examined. A biotite from Ishigure contains a new group of haloes, designated as *Z*-haloes, which can be ascribed neither to the uranium nor to the thorium series. They may be subdivided into Z_1 , Z_2 , and Z_3 , but all possess a common ring, Z_3 , of mean radius 18.2μ . This approximates to the value to be expected for radium-*F*, radiothorium, or protoactinium, but the fact that the Z_3 haloes may occur without the accompaniment of uranium or thorium rings suggests that they are due to protoactinium. On this assumption, it appears that the independent origin of the actinium series is probable. The *Z*-haloes sometimes include very small inner rings of radius 10.0μ and 5.9μ , or a small bleached crest, corresponding with α -radiators of half-life periods of 10^{12} and 10^{23} years, respectively, which is in agreement with Piccard and Stahel's view that two α -radiators precede protoactinium (*A.*, 1922, ii, 185).

M. S. BURR.

Electrolysis of radium-D and -E. J. P. McHUTCHINSON (*J. Physical Chem.*, 1926, **30**, 1112—1115; cf. von Hevesy, *A.*, 1913, ii, 174; Curie, this vol., 5).—Radium-D or -E could not be extracted from nitric acid solution under the electrolytic conditions required respectively for their isotopes. Traces of lead or bismuth make extraction possible, however, but the active matter obtained on any one electrode is due to adsorption as well as to electrolytic deposition.

L. S. THEOBALD.

Method of separating radium and barium. I. BASHILOFF.—See B., 1926, 742.

Extracting radium from radium-barium salts and the like. H. FLECK.—See B., 1926, 743.

Absorption by scattering of hydrogen positive rays by passage through hydrogen. R. CONRAD (*Z. Physik*, 1926, **38**, 465—474; cf. this vol., 106).—The experimental results are in approximate agreement with the formula earlier deduced, when, in addition to the scattering produced by the nuclei

of the two atoms and the electrons, the repeated scattering and discharge are taken into account.

E. B. LUDLAM.

Selective radiation pressure and the accelerated motion of Ca^+ vapour in eruptive prominences. R. K. SUR (*Astrophys. J.*, 1926, 63, 111—121).

Law of radiation. G. GIANFRANCESCO (*Nature*, 1926, 118, 302).

Orbits and radiation of hydrogen electrons. T. ENGSET (*Ann. Physik*, 1926, [iv], 80, 823—828).—Mathematical (cf. Schrödinger, *ibid.*, 79, 361).

Quantum theory of vibration-rotation bands. J. R. OPPENHEIMER (*Proc. Camb. Phil. Soc.*, 1926, 23, 327—335).—The energies and frequencies of states of the diatomic molecule are calculated on the new quantum mechanics. The terms of the rotational energy are $A(m^2 - \frac{1}{4})$, where $m = \pm\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$; the weights of the corresponding states are $2m$. The frequencies differ from the classical ones by an amount too small for experimental detection. The intensities are valid only for the fundamental branch. The central line vanishes; the positive branch is only slightly stronger than the negative. E. B. LUDLAM.

Quantum theory of tri- and poly-atomic molecules. F. LUTGEMEIER (*Z. Physik*, 1926, 38, 251—263).—The rotational energy of molecules having three different moments of inertia is calculated on the older quantum mechanics. If two of the moments of inertia are nearly equal, two formulæ are obtained according as the third is greater or less than the other two. Where there are no two moments of inertia equal, the spectra will be complicated, but one or other of the two formulæ will give the first quantum value.

E. B. LUDLAM.

Kaufmann's experiment and the spinning electron. L. C. JACKSON (*Nature*, 1926, 118, 263).—If the force, $1/c(\mu[vX])$ (where μ is the magnetic moment of the spinning electron, v is the velocity, and X the magnetic field), introduced by Wentzel, has a real existence, Kaufmann's experiment shows that the free electron cannot possess any spin comparable with that required by Goudsmit and Uhlenbeck's theory.

A. A. ELDRIDGE.

Dynamical model for complex atoms. J. C. SLATER (*Physical Rev.*, 1926, [ii], 23, 291—317).—As a model for a complex atom, the author employs the conception of a number of electrons, each moving in a central orbit, and exerting torques on one another dependent only on the angle between their angular momentum vectors, and not on their phase in their respective orbits. For two electrons and a nucleus, this model leads to a multiply periodic system which can be solved completely, whereas that in which the electrons instantaneously influence each other reduces to the astronomical three-body problem. The dynamical equations are solved and the quantum conditions applied; these agree with the quantum conditions previously set up empirically, and yield new quantum numbers relating to the orientation of electrons. The formula for the energy in terms of the quantum numbers leads to an explanation of inverted

multiplets, of the fact that relativity doublets follow the same formula as alkali doublets, but are inverted, and of the fact that doublets and triplets both fit on the same "relativity" doublet curve.

A. A. ELDRIDGE.

Gyromagnetic electrons and a classical theory of atomic structure and radiation. L. V. KING (*Science*, 1926, 63, 504).—A mathematical consideration of the fields due to a spinning electron moving with uniform velocity, taking into account the deformation of the electron boundary into an ellipsoid. Planck's constant is a fundamental characteristic of a rotating electron.

A. A. ELDRIDGE.

Nitrogen afterglow spectra. R. C. JOHNSON and H. G. JENKINS (*Phil. Mag.*, 1926, [vii], 2, 621—632).—The spectrum is best produced by the presence of only a little nitrogen in a large quantity of oxygen. The most prominent point is the continuous spectrum above 4300 Å., and the absence of the mercury line at 2536, which places an upper limit of 4.86 volts to the energy of the afterglow molecule. No variation of the intensity of the β - and γ -groups was found in the presence of helium and argon. This is not in agreement with the observations of Rayleigh (*A.*, 1923, ii, 45). The cyanogen tail bands obtained when the gas tube was contaminated with a small amount of carbon have been examined.

A. E. MITCHELL.

Absorption spectra of some gases and vapours in the Schumann region. S. W. LEIFSON (*Astrophys. J.*, 1926, 63, 73—89).—A study of the absorption in the Schumann region of oxygen, nitrogen, nitrous oxide, nitric oxide, nitrogen peroxide, carbon monoxide, carbon dioxide, ammonia, methane, water, carbon tetrachloride, and ethyl alcohol, the continuous spectrum of hydrogen in the region 2000—1600 Å. and the secondary spectrum of hydrogen in the region 1600—1250 Å. serving as a background. Fluorite transmits the hydrogen line 1215.67 Å. Formulæ are given for the heads of the bands in terms of frequency for oxygen, carbon monoxide, carbon dioxide, and ethyl alcohol. The approximate value $11.2 \times 10^{-4} \text{ g.cm.}^2$ is obtained from the double bands for the moment of inertia of the nitric oxide molecule.

A. A. ELDRIDGE.

Absorption spectrum of hydrogen iodide in the ultra-violet. K. F. BONHOEFFER and W. STEINER (*Z. physikal. Chem.*, 1926, 122, 287—292).—The absorption spectrum of hydrogen iodide in the spectral region between 2300 and 3000 Å. has been examined and is found to be continuous, the absorption increasing with decreasing wave-length. It is therefore probable that the primary photochemical decomposition of the iodide involves a dissociation of the molecule into uncharged atoms, not into ions (cf. Stern and Volmer, *A.*, 1920, ii, 461).

R. CUTHILL.

Carbon monoxide bands. D. C. DUNCAN (*Science*, 1926, 63, 382—383).—Three band systems previously designated the second negative and fifth and seventh positive bands of nitrogen (this vol., 549) actually belong to carbon, and are probably due to carbon monoxide. Support is afforded to the view that the structure of the carbon monoxide

molecule is very similar to that of the nitrogen molecule. Since a difference of 2% would be expected for the vibrational shifts of corresponding systems, the differences in the forces in the two molecules apparently compensate for the difference in mass.

A. A. ELDRIDGE.

More refrangible band system of cyanogen as developed in active nitrogen. W. JEYONS (Proc. Roy. Soc., 1926, A, 112, 407—441).—The modifications of the 3590 Å. ($n''-n'=-1$) group of cyanogen bands and of some of the "tail" bands, as developed in the afterglow of active nitrogen in comparison with the arc, are discussed. Data for the (1, 0) and (2, 1) bands of this group are identified in Kayser and Runge's arc list (Abh. Akad. Wiss. Berlin, 1889). The modifications in the 4216 and 3883 groups and the interpretations of them given by Birge and by Mulliken are discussed (cf. Strutt and Fowler, A., 1912, ii, 214; Mulliken, *ibid.*, 1925, ii, 1020). Like these groups, the 3590 group is shortened in the low wave-length direction, but unlike these groups, it is prolonged in the high wave-length direction in the afterglow as compared with the arc, and also consists of headless bands. Grating measures of the 3590 afterglow group are recorded and compared with the arc data for the same region. Each source develops some lines which the other does not.

S. K. TWEEDY.

Emission of light by the decomposition of chloroazoimide. K. GLEU (Z. Physik, 1926, 38, 176—201).—Chloroazoimide was prepared by mixing solutions of sodium hypochlorite and sodium azide and slowly adding sulphuric acid. The gas was led through a capillary tube into a wider tube heated at 400°, and kept at a pressure of 2 mm. The decomposition then took place without explosion, producing a red glow and exciting fluorescence in the glass. The spectrum shows a new band system in the red, consisting of four groups of bands. It is suggested that this is due to a molecule containing both nitrogen and chlorine. In the ultra-violet, the spectrum shows the continuous bands with maxima at 3060 and 2570 Å. of the emission spectrum of chlorine. This spectrum is not emitted in the decomposition of chlorine dioxide. The addition of hydrogen produces an intense white glow, which is identical in the visible region with the α -band of ammonia; a new band is produced in the ultra-violet with maxima at 3742 and 3752 Å., consisting of a few well-separated lines and ending at 3240 and 3610 Å., respectively. They are ascribed to a molecule containing both nitrogen and hydrogen. No nitrogen bands are observed.

E. B. LUDLAM.

Validity of Beer's law in dilute solutions of electrolytes. H. VON HALBAN and J. EISENBRAND (Z. physikal. Chem., 1926, 122, 337—348).—The very large apparent deviations from Beer's law, in the region 248.2—365.5 μ , reported by Suhrmann and Huppert (A., 1925, ii, 773) to be exhibited by dilute solutions of potassium nitrate in water and of salicylic acid in alcohol, are due to an unsuitable method of investigation. Ebert's experimental results for potassium nitrate in water (A., 1924, ii, 824) are corroborated, and hence the applicability of

Beer's law. A comparatively small deviation from Beer's law occurs with alcoholic solutions of salicylic acid, the extinction coefficients decreasing with increasing dilution (10—20% per tenfold dilution). The light absorption data of Winther (A., 1923, ii, 519) and of Henri ("Études de Photochimie," Paris, 1919) for salicylic acid in alcohol are confirmed, in contradistinction to those of Suhrmann and Huppert.

L. F. GILBERT.

Absorption spectra of quinones. Relations of quinones to α -diketones. L. LIGHT (Z. physikal. Chem., 1926, 122, 414—454).—The absorption spectra of *p*-benzoquinone in alcohol and ether, of toluquinone in hexane and alcohol, and of *p*-xyloquinone in hexane, alcohol, and ether have been investigated over the range 5000—2000 μ , approximately. Similarities and differences between these absorption spectra are discussed with special reference to chemical constitution. The absorption spectra of vaporised *p*-benzoquinone and diacetyl have also been investigated and are compared with that of glyoxal (cf. Lüthy, A., 1924, ii, 80). Each of these latter spectra can be expressed by the equation $1/\lambda = N + n\alpha + p\beta + q\gamma$.

L. F. GILBERT.

Fluorescence, phosphorescence, chemiluminescence, and the activation of molecules. N. R. DHAR (Z. anorg. Chem., 1926, 155, 303—310).—It is suggested that fluorescence is due to molecules which have been activated by absorbed radiation returning to their normal state (cf. A., 1924, ii, 746). The effect is destroyed by the presence of other molecules which take the energy from the active molecules. Phosphorescence is essentially similar to fluorescence, but the life of the active molecules seems to be in some way lengthened. In chemiluminescence, *e.g.*, the slow oxidation of phosphorus, the molecules are activated by the ions formed in the reaction.

R. CUTHILL.

Band fluorescence of potassium and sodium. P. PRINGSHEIM (Z. Physik, 1926, 38, 161—175).—The metals were purified with great care, heated at about 300° in a glass bulb, and illuminated with light from a powerful carbon arc. In addition to the red bands of potassium and the bluish-green and orange bands of sodium, yellow bands were observed for a mixture of sodium and potassium which can also be obtained as absorption bands. These bands cannot be due to the presence of hydrogen or organic impurities and must be ascribed to molecules Na_2 , K_2 , and NaK .

E. B. LUDLAM.

Excitement of fluorescence by short-wave ultra-violet light. O. OLDENBERG (Z. Physik, 1926, 38, 370—377).—Light in the ultra-Schumann region was employed, necessitating the production of the light in the tube containing the gas of which the fluorescence was being studied. A spark between aluminium or copper electrodes was produced in front of a narrow aperture in a block of copper connected to a copper tube; this was enclosed in a tube through which the gas was streaming. For hydrogen, the line spectrum of the atom was emitted; for nitrogen, the bands of the neutral and ionised molecules.

E. B. LUDLAM.

Phosphorescent sulphides of zinc. A. A. GUNTZ (Ann. Chim., 1926, [x], 6, 5—55; cf. this vol., 558, 885).—The intensity I of the phosphorescence of zinc sulphide containing a trace of copper and various proportions of cadmium sulphide diminishes with time t according to Becquerel's exponential law $I^m/(t+c)=K$, where m depends on the composition of the material and on the temperature, but is always greater than 0.5 at the ordinary temperature. A rise of temperature or an increase in the concentration of the phosphorogen (copper) causes the intensity (and the value of m) to increase, but an optimum point is observed with respect to each of these variable factors. The optimum temperatures for blende and wurtzite are different. From photometric observations of the intensity of phosphorescence the energy involved is calculated to be a fraction (0.42—0.11) of a quantum per atom of phosphorogen at the ordinary temperature and one or two quanta at the optimum temperature. The yield of energy as light varies between 60 and 77%. The magnetic susceptibility of the various mixtures used has been determined, but no relation is apparent between this and the phosphorescence, nor does the susceptibility vary during the luminescence.

G. M. BENNETT.

Phosphorescence excitation by means of moderately rapid cathode rays. R. STADLER (Ann. Physik, 1926, [iv], 80, 741—778).

Heat of dissociation of non-polar molecules. R. T. BURGE and H. SPONER (Physical Rev., 1926, [ii], 28, 259—283).—The limiting value of the vibrational energy of a diatomic molecule is given by $E_n = h\nu_0^* \omega^n / n$, where ω^n is the frequency of vibration as a function of the vibrational quantum number n , and n_0 is the value of n for $\omega^n = 0$. For non-polar molecules n_0 is finite, and extrapolation of the linear $\omega^n - n$ curves to $\omega^n = 0$ gives values of E_n (± 0.5 volt). Since the heat of dissociation of a diatomic molecule is the energy necessary to separate the normal molecule into two stable atoms, allowance must be made for any resulting excitation. The following values are tabulated: O_2 7.02 volts (162,000 cal.); O_2^+ 6.5 volts (150,000 cal.); N_2 11.9 volts (274,000 cal.); N_2^+ 9.1 volts (210,000 cal.); CO 11.2 volts (258,000 cal.); CO^+ 9.8 volts (226,000 cal.); NO 7.9 volts (182,000 cal.). The possibility of adiabatic dissociation of a molecule by light absorption, and the difference in behaviour of oxygen and nitrogen in positive-ray analysis are discussed.

A. A. ELDRIDGE.

Ionisation potential of methane. G. GLOCKLER (J. Amer. Chem. Soc., 1926, 48, 2021—2026).—Consideration of certain physical properties leads to the assumption that methane has a rare-gas structure, occupying a position intermediate between argon and krypton, whence its ionisation potential is predicted by Eve's rule (A., 1922, ii, 364) to be 13.7 volts. The value obtained experimentally by Lenard's method was 14.4—15.2 volts, special precautions being taken to avoid errors due to the effect of mercury vapour and to the possible thermal decomposition of the gas by the hot filament.

S. K. TWEEDY.

Photo-ionisation experiment with hydrogen. F. L. MOHLER (Proc. Nat. Acad. Sci., 1926, 12, 494—496).—By the method employed with monoatomic gases (this vol., 877), it is found that hydrogen emits no radiation capable of ionising the normal molecule, a result in harmony with spectroscopic evidence. The excitation potentials and the ionisation potential of H_2^+ are less than 15.9 volts.

J. S. CARTER.

Influence of absorbed gases on the magnitude of the photo-electric effect. A. PREDVODITELEV and G. JOFFE (Z. Physik, 1926, 38, 280—288).—The influence of adsorbed air on the photo-electric current from coconut charcoal has been determined, and the effect of temperature examined. With increasing quantity of gas, the current rises, reaches a maximum, at which it remains for a while with further increase of gas, afterwards diminishing. Equations are derived from considerations of the electrical moment of the medium and of the gas which represent the results of the experiments satisfactorily.

Dielectric constant of diatomic dipole-gases on the new quantum mechanics. R. DE L. KRONIG (Proc. Nat. Acad. Sci., 1926, 12, 488—493).—Mathematical. A treatment of the dielectric constant of a diatomic dipole-gas, based on the methods of Heisenberg's quantum mechanics (Z. Physik, 1925, 33, 879), leads to an expression which under appropriate temperature conditions is identical with that of Debye, derived on the classical theory. The expression for the transition probabilities of absorption in the pure rotation spectrum is given.

Temperature-sensitivity of the dielectric constant for methane, methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride vapours. R. SÄNGER (Physikal. Z., 1926, 27, 556—563).—Debye's theory for the temperature-sensitivity of the dielectric constant has been successfully applied to vapours. The symmetrical skeleton of methane is strongly distorted when methyl chloride is formed, and as successive hydrogen atoms are displaced the asymmetry increases, until with complete chlorination to the tetrachloride there is a return to symmetry of the molecule. The values of the electrical dipolar moments of methyl chloride, methylene dichloride, and chloroform are 1.9, 1.5, and 0.9×10^{-18} c.g.s.u., respectively.

R. A. MORTON.

Dielectric constant of diatomic dipolar gases according to "wave" mechanics. C. MANNEBACK (Physikal. Z., 1926, 27, 563—569).—Theoretical. The Schrödinger-Born and the Heisenberg-Born mechanics both lead to the result that the dielectric constant of an ideal diatomic gas with rigid molecules, in which the resulting electron impulse moment is nil (accounting for the non-existence of paramagnetism in the normal state of the molecule), approaches the value indicated at high temperatures by the classical theory of Langevin and Debye. At the ordinary temperature the deviations are small.

R. A. MORTON.

Fundamental constants of nature. H. COLLINS (Chem. News, 1926, 133, 161—162).—A theoretical

summary of the author's papers on the relative volumes of the elements. A. R. POWELL.

Gyration of light by multiplet lines. C. G. DARWIN (Proc. Roy. Soc., 1926, A, 112, 314—336).—A theoretical investigation of the dispersive effect of the rotation of polarised light by a vapour possessing a multiplet spectrum (cf. this vol., 216). Frenkel's treatment is considered to be in error because the intensity changes of the Zeeman lines were not calculated (Z. Physik, 1926, 36, 215; cf. this vol., 554).

S. K. TWEEDY.

Theory of optically active isotropic media. V. BURSIAK and A. TIMOREV (Z. Physik, 1926, 38, 475—484).—Born's theory based on a purely general model of a molecule needs expansion for the actual optically active isotropic substance. In addition to the periodic electric polarisation, a mean periodic magnetic moment must be considered. Consequently a different result for the numerical value for the rotation is obtained, and Maxwell's equations satisfy the principle of energy. E. B. LUDLAM.

Rotatory dispersion of the esters of lactic acid. II. Isomeric butyl esters. C. E. WOOD, J. E. SUCH, and F. SCARF (J.C.S., 1926, 1928—1938).—Comparison of the optical rotation of *n*-butyl *l*-lactate with its isomerides shows that isobutyl *l*-lactate exhibits an increased rotation, whilst the tertiary and inactive secondary esters exhibit a considerable decrease. The presence of two asymmetric carbon atoms of the same sign in the molecule causes an enhanced rotation, whereas a decrease takes place when the asymmetric centres are of opposite sign. *d*-sec.-Butyl *d*-lactate shows anomalous rotatory dispersion. C. J. STILL.

Anomalous dispersion of excited gases. R. LADENBURG, H. KOPFERMANN, and (FRL.) A. CARST (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1926, 255—273).—Exact dispersion measurements have been made in the neighbourhood of series lines of electrically excited helium, neon, mercury vapour, and hydrogen. Anomalous dispersion was observed in hydrogen only for currents above 100 milliamperes, but in the others for a fraction of a milliamperé. It was most evident in the *s*—*p* lines of neon lying in the yellowish-red, and in the lines 5876 and 6678 of helium and 5461 Å. of mercury. The dependence of anomalous dispersion on current strength, pressure, and temperature has been studied. The relative value *A* of the probability of transformation of the excited states for certain combinations has been determined, and also the *p*-value, and calculation has been made of the number of atoms in the *s*-states of neon and of the absolute value of *A*. M. S. BURR.

Electric double refraction in colloids. Y. BJÖRNSTÅHL (Phil. Mag., 1926, [vii], 2, 701—732).—Measurements of the electric double refraction in mercury, gold, and sulphur hydrosols are described. The Kerr effect in all these sols is negative, whilst for pure water it is positive. In the case of gold sols, at least, the phase difference approaches saturation with increasing intensity of the electric field. It is concluded that the approach to saturation is accom-

panied by an approach to completion of the orientation of the particles in the electric field.

A. E. MITCHELL.

Spectro-chemistry of compounds containing nitrogen. II. K. VON AUWERS and W. ERNST (Z. physikal. Chem., 1926, 122, 217—249; cf. A., 1925, ii, 847).—Densities and refractivities are recorded for pyrazoles, isooxazoles, oxazoles, thiazoles, isothiazoles, and glyoxalines. With all the unsaturated heterocyclic compounds so far examined, the closing of the ring involves a reduction in the refractivity and dispersive power to such an extent that the usual optical effect of double linkings does not appear. Such optical depression may be reduced or even converted into exaltation by substituents. The pronounced optical sensitivity of nitrogen makes the analysis of the available data extremely difficult, but in a few cases at least, e.g., the pyrazoles, certain relations between structure and optical properties emerge. R. CUTHILL.

Birefringence of crystalline carbonates, nitrates, and sulphates. C. V. RAMAN (Nature, 1926, 118, 264—265).—The observation that the light scattered by dust-free nitric acid is nearly unpolarised, whilst that from concentrated or aqueous sulphuric acid is nearly completely polarised, supports Bragg's explanation (A., 1924, ii, 373; 1925, ii, 92) of the strong birefringence exhibited by the crystalline carbonates and nitrates. A. A. ELDRIDGE.

Rotation of molecules. D. M. DENNISON (Physical Rev., 1926, [ii], 28, 318—333).—Mathematical. The application of Heisenberg's new theory of quantum mechanics to the system of a particle moving in a plane at a fixed distance from a centre is reconsidered from the point of view of a system involving a restraint, and is extended to a particle moving in space at a fixed distance from a centre, and to the motion of molecules having an axis of symmetry. A. A. ELDRIDGE.

Atomic volumes of carbon and hydrogen. W. F. SHORT (Nature, 1926, 118, 445).—Ingold's value (115.3°) for the angle between the carbon to carbon valencies in a polymethylene chain (J.C.S., 1921, 119, 305) is criticised; the value 116° 34' is deduced, the ratio of the atomic volumes of carbon and hydrogen being taken as 4 : 1. A. A. ELDRIDGE.

Atomic numbers and the properties of ions in the crystal lattice. III. The metallic state. A. F. SCOTT (J. Physical Chem., 1926, 30, 1009—1030; cf. this vol., 662).—The relationship connecting the distance between ions in the crystal lattice of a metal and the chemical forces of the element is considered in an attempt to correlate more closely the qualitative relationships existing between the chemical and physical properties of the elements. It is concluded that: (a) the lattice distance varies linearly with the constraint, *k*, acting on the valency electron, which is a measure of the forces of chemical affinity; (b) the relation between *k* and *f*, the constraint acting on the outer group of electrons of an ion (this vol., 662), is also linear and possibly represents a condition necessary for the existence of a crystal lattice; (c) the effect of changes in the nuclear charge on *f*

is uniform for different series of isoelectronic ions. Evidence is also advanced for the view that the valency electrons in a crystal are not "free" in the classical sense, but remain as integral components of individual atoms and, further, the determining factors in group properties lie in the characteristics of ions as well as in the number of valency electrons.

L. S. THEOBALD.

Electronic structure of the elements based on their chemical properties. H. LUX (Z. angew. Chem., 1926, 39, 953—955).—From a consideration of the stability of the oxides of the elements, it is shown that in groups II—VIII of the periodic system two valency electrons must have elliptical n_1 orbits and the number having more or less circular n_2 orbits increases from 0 to 6. As the atomic number increases, the charge on the nucleus also increases and causes the n_1 orbits to become more elliptical and the valency electrons on these orbits to become more firmly bound; hence the stability of the highest oxides of these elements is reduced and the oxide corresponding with a valency reduction of 2 is the most stable. This is particularly marked in group III; boric anhydride and alumina are very stable, indium has an unstable monoxide and a fairly stable trioxide, and thallium a very stable monoxide and an unstable trioxide. These and other chemical considerations substantiate Stoner's grouping of the elements, arrived at by purely physical methods (cf. A., 1925, ii, 85).

A. R. POWELL.

Crystal structure and chemical constitution of basic beryllium acetate and its homologues. G. T. MORGAN and W. T. ASTBURY (Proc. Roy. Soc., 1926, A, 112, 441—448).—The crystal structures of the basic acetate, isobutyrate, *n*-butyrate, and pivalate of beryllium were investigated by X-ray methods (cf. Morgan and Bragg, *ibid.*, 1923, A, 104, 437). The acetate crystals belong to the space-group T_h^4 . The pivalate forms monoclinic crystals (m. p. 163°; d 1.05) of bipyramidal habit, having a nearly orthorhombic face-centred cell containing 8 molecules and of dimensions: $a=19.3$, $b=12.4$, $c=35.4$ Å., $\beta=91^\circ 21'$. The space-group is either C_2^2 or C_{2h}^2 , probably the former. The acetate and pivalate have similar structures; the differences can be attributed to the replacement of the $\cdot\text{Me}$ group by the $\cdot\text{CMe}_3$ group, which probably cannot be arranged in a dyad axis, so that the four trigonal axes present in the acetate are not apparent in the pivalate. A complete change in crystal type occurs on passing to the isobutyrate, which has a triclinic pinakoidal unit. The *n*-butyrate crystals were unsuitable for complete X-ray investigation.

S. K. TWEEDY.

Relative intensities of reflexion of X-rays from the principal atomic planes of powdered sodium chloride. L. HARRIS, S. J. BATES, and D. A. MACINNES (Physical Rev., 1926, [ii], 28, 235—239).—Measurements of the relative intensities of reflexion of the α -doublet of characteristic molybdenum X-rays (*a*) filtered, and (*b*) reflected from a calcite crystal, from powdered sodium chloride give results in agreement with those of Bragg, James, and Bosanquet (A., 1921, ii, 477) as corrected for "extinction."

A. A. ELDRIDGE.

Crystal structure of olivine. W. L. BRAGG and G. B. BROWN (Z. Krist., 1926, 63, 538—556).—An olivine having the composition $9\text{MgSiO}_4 \cdot \text{Fe}_2\text{SiO}_4$ has been examined by the spectrometer and rotation methods. There are 4 molecules to the cell, space-group V_h^6 , $a=4.755$, $b=10.21$, $c=5.985$ Å. The arrangement of the atoms resembles that of chrysoberyl. Co-ordinates are given for the magnesium, silicon, and oxygen atoms. The last-named stand very nearly in the close-packed hexagonal arrangement. Each silicon atom is surrounded tetrahedrally by four oxygen atoms, between which there is a minimum distance of 2.3—2.7 Å. W. A. CASPARI.

Parameters in crystal structure. [Structure of] mercurous halides. R. J. HAVIGHURST (J. Amer. Chem. Soc., 1926, 48, 2113—2125).—The formulæ hitherto proposed for calculating the intensities of X-ray reflexion for a crystal powder are shown to be unsatisfactory owing to the uncertain value of the structure factor, which is usually calculated on the invalid assumption that the atomic structure factors of the component atoms vary similarly with the angle of reflexion. Another method of determining crystal parameters is described based on the fact that the distribution density of diffracting power ("electron density") may be represented by a Fourier series (Allison and Duane, A., 1925, ii, 930), the coefficients of which may be evaluated from the measured reflexion intensities. The method is illustrated by an application to the mercurous halides for which $u=0.116$ and $v=0.347$, the unit cell containing 2 molecules and having mercury atoms at $(0, 0, u; 0, 0, \bar{u})$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u)$, and halogen atoms at $(0, 0, v; 0, 0, \bar{v})$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+v; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-v)$.

S. K. TWEEDY.

Crystal structure of bivalent chlorides. G. BRUNI and A. FERRARI (Atti R. Accad. Lincei, 1926, [vi], 4, 10—13).—Laue photographs for magnesium, manganous, and cadmium chlorides show that these have a rhombohedral structure with axial ratios 2.45, 2.34, and 2.20, respectively (cf. this vol., 236). Zinc chloride, examined by the Debye method, has probably a rhombohedral cell of 2 molecules, axial ratio 2.36, $a=5.27$ Å., $d_{\text{calc.}}$ 3.10, or a hexagonal cell, $a_1=3.77$, $c_1=8.90$ Å.

E. W. WIGNALL.

[Crystal] structure of manganous oxide. C. FONTANA (Gazzetta, 1926, 56, 396—397).—The determinations of Levi (A., 1924, ii, 862) are repeated, using a chromium instead of a copper anticathode, with the improved results: for $\lambda_\alpha=2.287$, $a=4.409$ Å. and $d_{\text{calc.}}=5.429$; for $\lambda_\beta=2.080$, $a=4.407$ Å. and $d_{\text{calc.}}=5.436$.

E. W. WIGNALL.

Change of crystal structure of some salts when crystallised from silicic acid gel. Structure of silicic acid gel. H. A. FELS and J. B. FIRTH (Proc. Roy. Soc., 1926, A, 112, 468—474).—The separation of sodium chloride, bromide, iodide, and nitrate crystals from silicic acid gels occurs usually in the form of blades with a straight fibrous habit. The fibres are flexible and somewhat elastic. X-Ray examination of the sodium chloride crystals showed them to be of cubic structure. Transverse and longitudinal cleavages are present; the former

are inclusions, probably bubbles, and, being parallel to the cube, indicate that the needles are elongated parallel to the cubic axis. The longitudinal cleavages are negative crystals. Sodium bromide crystallised in six-sided prisms elongated parallel to the principal axis and showing a perfect basal cleavage. Aniline and toluene hydrochlorides yielded distorted plates, but no distortion occurred in the case of sodium tartrate. The results are considered to support a capillary structure for silicic acid gels, the pores being centres of crystal growth, which is controlled by the continuous accumulation of salt at the pore.

S. K. TWEEDY.

Crystal structure of ruthenium and osmium.

G. R. LEVI and R. HAARDT (Gazzetta, 1926, 56, 369—375; cf. Hull, A., 1922, ii, 624).—X-Ray photographs, photomicrometer curves, and tabulated data are given for powders of ruthenium and of osmium (cf. this vol., 693). For the close-packed hexagonal lattice $a=2.680$, $c=4.261$ Å., axial ratio 1.59, for ruthenium, and $a=2.714$, $c=4.316$ Å., axial ratio 1.59, for osmium are found, giving $d_{\text{calc.}}$ 12.71 and 22.98, respectively, somewhat higher than observed values. The structure is the same whether or not the metals are cooled slowly after the initial heating at 1050°.

E. W. WIGNALL.

Lattice structure of calcium chromate. K. HERRMANN, M. HOSENFELD, and N. SCHÖNFELDT (Wiss. Veröff. Siemens-Konz., 1926, 5, 119—127).—The lattice structure of calcium chromate, forming rhombic bipyramidal crystals, has been determined. The crystal unit contains 4 molecules, $a=7.45$, $b=10.3$, $c=5.88$ Å. The most probable space-group is B_h^{12} , and symmetry C_i . The parameters of the molecules are $(\frac{1}{4}, \frac{1}{4}, 0; \frac{3}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0; \frac{3}{4}, \frac{3}{4}, 0)$ or $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}; \frac{3}{4}, \frac{3}{4}, \frac{1}{2})$.

C. J. SMITHELLS.

Crystal structure of cobaltous oxide and hydroxide. G. NATTA and A. REINA (Atti R. Accad. Lincei, 1926, [vi], 4, 48—54).—Cobaltous oxide is of the sodium chloride type with 4 molecules to the cell; $a=4.22$ Å., from which the diameter of the Co^{++} ion is 2.92 Å., $d_{\text{calc.}}$ 6.62, agreeing well with the value found for the sample used. Cobaltous hydroxide has a uniaxial rhombohedral structure (cf. De Schulten, A., 1889, 1114), the unit cell of one molecule, of the brucite type, having co-ordinates $\text{Co}(0, 0, 0)$, $\text{O}(\frac{2}{3}, \frac{1}{3}, u)$, $(\frac{1}{3}, \frac{2}{3}, \bar{u})$, where u is $\frac{1}{4}$ — $\frac{1}{3}$, and dimensions $a=3.19$, $c=4.66$ Å. Hydroxides of cobalt and nickel precipitated together give lines intermediate between those of the pure substances, a proof that they are isomorphic. E. W. WIGNALL.

X-Ray examination of metallic hydrides.

Copper hydride. A. QUILICO (Atti R. Accad. Lincei, 1926, [vi], 4, 57—62; cf. Müller and Bradley, this vol., 889).—X-Ray photograms of preparations by various methods fail to indicate the existence of copper hydrides. The action of hydrogen on heated copper or cupric oxide, and that of zinc on an acid copper sulphate solution, gives products consisting of copper with a small quantity of occluded hydrogen. The reduction of copper sulphate by hypophosphorous acid gives below 40° a black substance consisting of

amorphous copper with varying amounts of occluded hydrogen; at about 70°, mainly cuprous oxide containing occluded hydrogen; and at the b. p., copper either alone or mixed with cuprous oxide.

E. W. WIGNALL.

Crystal structure of tiemannite and coloradoite. W. F. DE JONG (Z. Krist., 1926, 63, 466—472).—From X-ray rotation photographs, with special reference to intensities, it is concluded that these minerals crystallise like sphalerite in space-group T_d^2 . For tiemannite $d_{100}=6.04$ Å., whence $d=8.41$ and distance $\text{Hg—Se}=2.62$ Å. For coloradoite $d_{100}=6.43$ Å., whence $d=8.20$ and distance $\text{Hg—Te}=2.78$ Å.

W. A. CASPARI.

Crystal structure of telluric acid. L. M. KIRKPATRICK and L. PAULING (Z. Krist., 1926, 63, 502—506).—The cubic modification of $\text{Te}(\text{OH})_6$, crystallising in octahedra, has been examined by the spectrometer and Laue methods. The lattice is found to be face-centred, with $d_{100}=15.48$ Å. The Laue photograph results indicate O_h^8 as space-group.

W. A. CASPARI.

Micro-structure of mercury. W. ROSENHAIN and A. J. MURPHY (Nature, 1926, 118, 261).—A photograph showing the typical micro-structure of solid mercury is reproduced.

A. A. ELDRIDGE.

Morphology of graphite. J. BRUNNER and H. HAMMERSCHMID (Z. anorg. Chem., 1926, 155, 255—256).—In incomplete combustion of laminated graphite numerous regular hexagons are seen with the microscope, indicating an uptake of oxygen according to a certain orientation. In graphite, the carbon atoms lie in planes, and in each plane are arranged in regular hexagons; the planes lie so that the middle of a hexagon side coincides with the angle of the next. That this structure explains the phenomena observed when graphite is burnt is proved by microscopic comparison of partly burnt crystalline and amorphous graphite. In the latter case, no orientation is observed.

M. CARLTON.

Structure and isotrimorphism of the tervalent metallic acetylacetonates. W. T. ASTBURY (Proc. Roy. Soc., 1926, A, 112, 448—467).—X-Ray investigation of ten metallic acetylacetonates shows that the α -acetylacetonates are monoclinic-prismatic crystals of space-group C_{2h}^2 , β -acetylacetonates are rhombic-pyramidal crystals of space-group C_{2v}^2 , both types containing 4 molecules per unit cell, and γ -acetylacetonates are rhombic-pyramidal crystals of space-group C_{2v}^2 with 4 groups of 4 molecules in each cell; none of the three forms is pseudo-hexagonal. The nature of the isotrimorphism exhibited by the crystals is explained from the results, which also confirm the assumptions that the univalent acetylacetonate radical in these compounds is a chelate grouping functioning in the co-ordinated complex as a two-fold associated unit, and that 3 such groups are arranged symmetrically around the central tervalent atom (cf. Morgan and Moss, J.C.S., 1914, 105, 189).

S. K. TWEEDY.

[X-Ray analyses. II.] V. M. GOLDSCHMIDT (Z. physikal. Chem., 1926, 122, 250—253).—A criticism of Günther and Wilcke's analysis of a

gadolinite (this vol., 663) on the ground that in analysis by X-ray spectroscopy the possibility of a line of a particular element being reinforced by the coincidence with it of a line of another element must be taken into account.

R. CUTHILL.

[X-Ray analyses. II.] P. GÜNTHER and G. WILCKE (Z. physikal. Chem., 1926, 122, 254—256).—A reply to Goldschmidt (cf. preceding abstract).

R. CUTHILL.

Parallelism between the phenomena of magnetostriction and magnetic hysteresis in nickel. B. WVEDENSKI and J. SIMANOV (Z. Physik, 1926, 38, 202—214).—A nickel wire of 0.5 mm. diameter was suspended from a lever, passed through the vertical core of an electromagnet, and stretched by a weight. The striction curves as a function of the applied tensile stress follow the same course as the hysteresis curves, and it is concluded that they are related. There is no simple parallelism between magnetostriction and magnetisation, remanence, or coercitive force. The hysteresis curves as a function of the strength of field have a quite different course from those of striction.

E. B. LUDLAM.

Distortion of iron crystals. G. I. TAYLOR and C. F. ELAM (Proc. Roy. Soc., 1926, A, 112, 337—361).—Experiments on the stretching and compression of single iron crystals are described (cf. Taylor and Farren, *ibid.*, A, 111, 529). Unlike other metals, the iron particles adhere along a certain crystallographic direction, so that the resulting distortion resembles that of a collection of rods sliding over one another in groups of irregular cross-section. The slip lines apparent on the crystal surface are the traces of these groups in the surface. When the distortion is a uniform shear, the groups stick together in the form of plates of irregular thickness, which are more or less parallel to the plane of slip and have no immediate directional relationship with the crystal axes. This theory requires that the slip lines in a crystal section parallel to the direction of slip should be all straight; experiment confirmed this prediction.

S. K. TWEEDY.

Pure zinc at normal and elevated temperatures. J. R. FREEMAN, jun., F. SILLERS, jun., and P. BRANDT (U.S. Bur. Standards Sci. Paper 522, 1926, 20, 661—695).—The properties of pure cast zinc (99.997%) were studied from the ordinary temperature to the m. p. No evidence of any allotropic modifications was found (cf. Bingham, B., 1920, 660A). The following values were obtained for cast metal: coefficient of linear expansion from 20° to 100° 0.0000395, Brinell hardness 31, decreasing to 6.5 at 200°, tensile strength 4000 lb./sq. in., d 7.131. X-Ray measurements showed no change in structure between 20° and the m. p. The length of the side of the elementary prism is 2.65 Å., d_{calc} 7.19. Strain-free cast zinc does not recrystallise on annealing up to 390°. Three types of fracture were obtained in tensile tests depending on the temperature: 20—100° brittle, 100—220° oblique, 220—350° wedge. These are explained with reference to stages in recrystallisation and the development of a preferred orientation in the stressed specimens.

C. J. SMITHELLS.

Behaviour of single crystals of aluminium under reversed torsional stresses. H. J. GOUGH, S. J. WRIGHT, and D. HANSON (Inst. Metals, July, 1926, advance copy, 16 pp.; cf. this vol., 666).—Single crystals of aluminium are subjected to alternating torsional stressing. The resulting distortion under this complex type of straining action is observed using slip-band measurements, and is related to the atomic spacing by means of X-ray analysis. The observed system of slip bands is shown to be in agreement with the simple law that slip is confined at any point of the surface of the crystal to one of the octahedral planes, and in the direction of the most highly stressed principal lines of atoms. The progressive hardening during a long endurance test is studied, and the phenomena attending the last stages of the test are isolated from those of the earlier stages. It is shown that no slip occurs in the stages immediately preceding fracture. Some quantitative data on hardening are deduced from ball indentation tests on cross-sections of the specimens.

C. J. SMITHELLS.

Deformation of tungsten crystals. C. J. SMITHELLS, H. P. ROOKSBY, and W. R. PITKIN (Inst. Metals, July, 1926, advance copy, 9 pp.).—When metals are rolled or drawn, the crystal fragments tend to take up a definite orientation with respect to the direction of working. It is shown that the same effect is produced during the swaging of tungsten rods. The micro-structure and X-ray diffraction pattern at various stages in the swaging of tungsten rods have been examined with a view to understand the mechanism by which this "preferred" orientation is attained. When large crystals are deformed, they are first broken up into fragments with random orientation. It is shown that the percentage reduction necessary to develop a given degree of preferred orientation is less the finer the original grain size. The results are discussed in connexion with Goucher's work on the deformation of tungsten single crystals (A., 1924, ii, 818). It is suggested that the size of the crystal fragments, rather than the amount of work done, determines their ability to assume the preferred orientation.

C. J. SMITHELLS.

Determination of the mol. wt. of fatty acids. M. TRAUTZ and W. MOSCHEL (Z. anorg. Chem., 1926, 155, 13—20).—Determinations of the mol. wt. of the five lowest fatty acids by the Beckmann cryoscopic method in benzene and nitrobenzene solution give values varying from two to three times the normal value, no definite constant being obtained. Vapour-density measurements were of no value with formic acid owing to its decomposition, but with the next four acids almost exactly dimeric equivalents were obtained and dimeric heats of 13—18 cal. The step-rule was not followed, but there were indications of it in cryoscopic measurements with nitrobenzene.

M. CARLTON.

Electrical conductivity of liquid cyanogen bromide. G. GLOCKLER (Proc. Nat. Acad. Sci., 1926, 12, 522—523).—According to the theory of "pseudo-atoms" put forward by Grimm (A., 1925, ii, 1123), the cyanogen radical resembles sodium, and

hence fused cyanogen halides should conduct electricity. This is found to be the case, the specific conductance of liquid cyanogen bromide at 55° being 0.02 mho/cm. cube. Observations on the electrolysis in a cell with platinum electrodes are recorded.

J. S. CARTER.

Dual theory of metallic conduction. E. H. HALL (Physical Rev., 1926, [ii], 28, 392—417).—The theory is considered in relation to the Peltier effect within metallic crystals, the Volta effect, Richardson's formula for thermionic emission, and the "equation" connecting the Peltier and Volta effects. A theory of heat conduction is derived, and the effect of high pressure on the characteristic constants of metals is considered. Generally, compression of a metal reduces the latent heat of the ionisation process within it, and increases the ratio of free-electron conductivity to total electric conductivity. The evidence supports the suggestion that the free electrons may pass through, and not necessarily between, the atoms in their progress through a metal. Possibly, in the superconductive state, the distinction between "free" and "associated" electrons disappears.

A. A. ELDRIDGE.

Temperature relations of photoelectric emission and thermionic emission of electrons. E. H. HALL (Proc. Nat. Acad. Sci., 1926, 12, 486—488; cf. preceding abstract).—The total work done against resisting forces in the photo-electric emission of electrons is practically independent of temperature. This is not the case with thermionic emission.

J. S. CARTER.

Electrical and photo-electric properties of thin films of rubidium on glass. H. E. IVES and A. L. JOHNSRUD (Astrophys. J., 1925, 62, 309—319).—An invisible film of rubidium, spontaneously deposited on a glass surface in an exhausted cell, is an electrical conductor (for a plate 19×40 mm. the resistance was 1.3×10^8 ohms) and is photo-electrically active. In the dark, the resistance is ohmic, but on illumination it is decreased on account of the added current formed by the liberated photo-electrons under a potential gradient.

A. A. ELDRIDGE.

Electrical polarity of molecules. C. V. RAMAN and K. S. KRISHNAN (Nature, 1926, 118, 302).—Electrically polar molecules generally exhibit a Kerr effect which is very large in relation to their optical anisotropy, indicating that the orientative action of the field on the molecule is in such cases chiefly due to the permanent electric doublet present in it. The permanent electric moment can be calculated for molecules having an axis of optical symmetry to which the electric doublet is parallel or is inclined at a known angle; thus for hydrogen chloride the moment is 1.06 or 1.04×10^{-18} e.s.u., according as the orientative couple or the induced doublet is not, or is, taken into account.

A. A. ELDRIDGE.

Thermomagnetic and galvanomagnetic effects in arsenic. N. C. LITTLE (Physical Rev., 1926, [ii], 28, 418—422).—The following coefficients (in absolute e.m.u. at 20°) are recorded: specific resistance, 4.60×10^4 ; thermal conductivity, 3.68×10^6 ; Peltier heat against lead, 3.80×10^5 ; Thomson heat, 3.33×10^3 ;

Hall coefficient, 4.52×10^{-2} ; Nernst coefficient, 2.25×10^{-3} ; Ettingshausen coefficient, 1.75×10^{-7} ; Righi-Leduc coefficient, 4.15×10^{-7} . The results are compared with Bridgman's corresponding values for antimony and bismuth. The temperature coefficient of resistance is 0.00435 per 1° and the thermal *E.M.F.* against copper is $(7.91t + 0.051t^2) \times 10^{-6}$ volt between 0° and 170°. None of the coefficients varies with the strength of the magnetic field. When the plate of arsenic was subjected to a temperature gradient of 10° per cm., a field of 8000 gauss caused a fall in temperature of 0.4°. The value of the coefficient, provisionally defined by the equation: temperature change = coefficient \times (temperature gradient)² \times (field strength)², is for arsenic -6.25×10^{-10} at 20°.

A. A. ELDRIDGE.

Magnetic analysis of hydroxides. (MILLER) S. VEIL (Rev. Scient., 1926, 64, 8—10; from Chem. Zentr., 1926, I, 2220).—The magnetic properties of ferric hydroxide are largely dependent on the method of preparation and the oxide obtained on calcination is usually much less magnetic than the original hydroxide. If the precipitated hydroxide is heated with water in sealed vessels at high temperatures, a brick-red, less-hydrated, strongly magnetic product is obtained, which does not lose its magnetic properties on ignition. The product is soluble only in hot concentrated hydrochloric acid. Reprecipitation with ammonia and repetition of the heating process cause a further increase in magnetic properties. Continued repetition leads to a product which is about thirty times as magnetic as the original hydroxide. The reverse is true of chromium hydroxide, the magnetic properties of which appear to fall to a lower limiting value on repeated precipitation from hot solutions. The magnetic character of cupric hydroxide is independent of temperature and of the conditions of precipitation. Nickelous hydroxide from cold solutions is about six times as magnetic as the corresponding oxide. On treatment with hot water and reprecipitation, the hydroxide becomes less magnetic, whilst the magnetic properties of the corresponding oxides reach a maximum and then decrease. Nickelic hydroxide behaves similarly. Nickelous hydroxide in contact with solutions of hydrogen peroxide becomes continually less magnetic as the peroxide decomposition proceeds. The magnetic properties of the corresponding oxides pass through a maximum value.

J. S. CARTER.

Polishing of surfaces. J. M. MACAULAY (Nature, 1926, 118, 339).—It is suggested that in the process of polishing, surface layers of molecules are really melted by the communication to them of heat vibrations.

A. A. ELDRIDGE.

Specific heats of silver and diamond in the region of high temperatures. A. MAGNUS and A. HODLER (Ann. Physik, 1926, [iv], 80, 808—822).—The mean specific heats of silver and of diamond have been measured between the ordinary temperature and a temperature extending from 500° to 900°. On the basis of the results the true atomic heat of silver is satisfactorily expressed by a formula employing three constants. The more complicated results for

diamond require an expression containing at least five constants. If C_p (diamond) is reduced to C_v and the values are compared with those calculated from Debye's theory (A., 1912, ii, 1134), when the characteristic temperature is taken as 1909° satisfactory agreement is obtained. It was found that Born's elasticity constants could not be evaluated trustworthily. R. A. MORTON.

Lattice dynamics of melting. W. BRAUNBEK (Z. Physik, 1926, 38, 549—572).—It is assumed that the crystal model consists of two partial lattices and that thermal agitation consists in their mutual vibration. The potential energy of the lattice has a threshold value which the two halves must overcome in their mutual displacement; by the elimination of this value, the following thermal relationships are obtained in satisfactory agreement with experimental data: the proportionality between the latent heat of fusion and the absolute m. p., the divergence of the atomic heat from $3R$ at high temperatures, the relation between the m. p. and the variation in the temperature coefficient of the atomic heat at high temperatures, the connexion between m. p. and infra-red specific vibration frequency. A relationship is also found between the m. p. and the lattice constant. E. B. LUDLAM.

Normal densities of gases. (Miss) M. S. BLANCHARD and S. F. PICKERING (U.S. Bur. Standards, Sci. Papers 529, 1926, 20, 141—177).—A review of the literature relating to the densities of forty-eight different gases. A table gives the most probable value for the weight of a normal litre of each gas under standard conditions, and the deviation from the ideal value is plotted against the b. p. In general, the deviation diminishes with b. p., but there are some marked exceptions. M. S. BURR.

Preparation and determination of the weight of a normal litre of hydrogen iodide. E. MOLES and R. MIRAVALLS (Anal. Fis. Quím., 1926, 24, 356—399; cf. this vol., 340).—Hydrogen iodide was prepared by the following methods: (1) direct synthesis over platinised asbestos at 300° and solution of the resultant hydrogen iodide in water; (2) hydrolysis of the phosphorus iodide obtained by the action of a suspension of iodine in water on red phosphorus; (3) reduction of iodine with hydrogen sulphide; (4) action of metaphosphoric acid on sodium iodide or on a mixture of sodium iodide and ammonium iodide. The hydrogen iodide solution was freed from water by allowing the solution to drop on excess of phosphoric oxide, and after further drying, was condensed and distilled. The last is considered the best method. The density results obtained with the first and third methods are in good agreement, but the results with the second method are in disagreement with the results by other methods. The value obtained, as the mean of twenty measurements, for the weight of a normal litre of hydrogen iodide is 5.78882. The corresponding figure for the gas obtained by the second method is 5.7976. From measurements made at pressures lower than atmospheric pressure the coefficient of compressibility of hydrogen iodide is given as 0.000113 per mm. G. W. ROBINSON.

Absolute density and coefficient of expansion of silicon tetrachloride. P. L. ROBINSON and H. C. SMITH (Nature, 1926, 118, 303).—Previously published values of the absolute density and coefficient of expansion of silicon tetrachloride (cf. this vol., 771), when corrected for the expansion of the "durosil" glass, become 1.481461 ± 0.000020 and 0.0014048 ± 0.0000022 , respectively. The value of the at. wt. of silicon is not affected. A. A. ELDRIDGE.

Dependence of the density of a liquid on the temperature. A. BATSCHEVSKI and K. SCHAPOSCHNIKOV (Z. Physik, 1926, 38, 573—574).—Polemical (cf. Predvoditelev, this vol., 669). The claim of Predvoditelev to have deduced Saslavsky's formula from the van der Waals equation of state is not justified. E. B. LUDLAM.

Density measurements at high temperatures.

VIII. Density and expansion of white and grey pig iron in the liquid and solid states. F. SAUERWALD and E. WIDAWSKI (Z. anorg. Chem., 1926, 155, 1—12).—Changes in the specific volume of white iron up to the m. p. and above are normal and correspond with known structural changes. The contraction between 900° and 1000° noted in previous experiments with grey iron was confirmed dilatometrically, whereby it was possible to determine the amount of contraction due to pearlite solution. The specific volumes of molten grey and white iron agree to within 1%, the value of dv_s/dt for grey iron being 0.31×10^{-4} and for white iron 0.30×10^{-4} . The hypothesis was confirmed that the contraction of solid grey iron was due to solution of graphite and also that cementite is formed when grey iron is melted. No change in the volume of molten iron at constant temperature could be detected. M. CARLTON.

Halochromy. III. Densities of some molecular compounds. S. SKRAUP and M. EISEMANN (Annalen, 1926, 449, 1—14; cf. A., 1923, i, 667).—Of 33 molecular compounds only 6 showed contraction, i.e., a molecular volume smaller than additive, whilst 16 showed dilatation, and 11 were approximately additive. This characteristic does not run parallel with the "stability constant, G " (Dimroth, A., 1925, ii, 36), but the most stable complexes show dilatation, and the metastable show contraction. Compounds of trinitro-benzene, -toluene, and -xylene with amines and indole show appreciable dilatation, whilst in the compounds with hydrocarbons the molecular volume is simply additive. On the other hand, compounds of picric acid with both classes equally show a small or no dilatation. The preparation of the following molecular compounds is detailed: trinitrobenzene-indole; trinitrotoluene-anthracene, m. p. 162°; trinitrotoluene-indole, m. p. 121°; trinitrotoluene- α -naphthol, m. p. 125°; trinitroxylene-indole, m. p. 126°. C. HOLLINS.

Vapour pressure of ethane near the normal b. p. A. G. LOOMIS and J. E. WALTERS (J. Amer. Chem. Soc., 1926, 48, 2051—2055).—The vapour pressure of ethane between 0.0245 and 2.1441 atm. is given by: $\log_{10} p(\text{atm.}) = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T - 238)^4$, from which the

normal b. p. is $184.46(7)^{\circ}$ Abs. and the molar heat of evaporation at the b. p. 3642.4 cal.

S. K. TWEEDY.

Vapour pressures and specific volumes of saturated ethane vapour. F. PORTER (J. Amer. Chem. Soc., 1926, 48, 2055—2058; cf. preceding abstract).—The vapour pressures of saturated ethane vapour between 203.49 and 288.26° Abs. are given by $\log_{10} p(\text{atm.}) = -(780.24/T) + 4.2563 - 0.0001037T + 1.4 \times 10^{-11}(T-238)^5$; the observed specific volumes of the vapour and the (calculated) latent heats of evaporation of the liquid are tabulated for some intermediate temperatures. The normal density of ethane at 25° is 0.0012383 .

S. K. TWEEDY.

High vapour pressures of nitrogen. F. PORTER and J. H. PERRY (J. Amer. Chem. Soc., 1926, 48, 2059—2060).—The vapour pressures of nitrogen between 90.12 and 121.47° Abs. are given by the equation: $\log_{10} p(\text{atm.}) = -(302.34/T) + 3.94127 - 0.00274T + 1.116 \times 10^{-6}(T-100.5)^3$, which, when extrapolated to low pressures, agrees fairly well with the data of von Siemens (A., 1913, ii, 1023).

S. K. TWEEDY.

Isotherms of helium, hydrogen, and neon below -200° . L. HOLBORN and J. OTTO (Z. Physik, 1926, 38, 359—367).—Determinations of the isotherms of the three gases were made at -208° up to 100 atm. and for helium also at -252.8° and -258.0° . The correction of the gas thermometer to the thermodynamic scale is calculated.

E. B. LUDLAM.

Internal pressure and coefficient of expansion. W. HERZ (Z. anorg. Chem., 1926, 155, 323—326).—The internal pressures of a number of liquids have been calculated from their densities and critical data, and are found to decrease with increasing temperature, whilst at the same time the expansion coefficients increase in such a way that the product of the two quantities is approximately constant, independently of the temperature.

R. CUTHILL.

Entropy of amorphous substances. F. SIMON and F. LANGE (Z. Physik, 1926, 38, 227—236).—The problem of the entropy of crystalline and amorphous substances at absolute zero is discussed. Measurements of the specific heats of fused silica and super-cooled glycerol have been made at temperatures as low as 10° Abs. It is obvious from the curves for glycerol that extrapolation to absolute zero from the temperature of liquid air would lead to quite untrustworthy conclusions; from 10° Abs. downwards the specific heat is so small that the experimental error is large. It is calculated that for silica the amorphous form has an entropy 0.9 ± 0.3 cal./degree per mol. greater than that of the crystalline; for glycerol the difference is 4.6 ± 0.3 .

E. B. LUDLAM.

Viscosities and densities of anhydrous methyl alcohol and of solutions of some halides of sodium and potassium in this solvent. F. K. EWART and H. R. RAIKES (J.C.S., 1926, 1907—1912).—Pure methyl alcohol was prepared by the method of Hartley and Raikes (A., 1925, i, 498). The effect of small quantities of both water and acetone on the

viscosity was determined, and this property used for testing the dryness of the material. The values obtained for the pure alcohol were d_4^{25} 0.78641 and viscosity 0.00545 c.g.s.u., which agree closely with accepted values. The influence of concentration on the density and viscosity of solutions of potassium iodide, potassium bromide, potassium chloride, sodium iodide, and sodium bromide in methyl alcohol was determined. The results display no irregularities.

C. J. SMITHELLS.

Dielectric constants of binary mixtures. J. W. WILLIAMS and I. J. KROHMA (J. Amer. Chem. Soc., 1926, 48, 1888—1896).—The dielectric constants of the pure liquids and of mixtures of benzene and toluene, chlorobenzene and bromobenzene, and carbon tetrachloride and benzene were measured at 25° by an improved resonance method. Evidence is quoted in support of the value found for chlorobenzene, 5.610 , which is about half the accepted value (Veley, Phil. Mag., 1906, [vi], 11, 73). The results for the first-named mixture do not agree with those of Grützmacher (A., 1925, ii, 263). Each system is discussed from the point of view of departure from the ideal solution.

S. K. TWEEDY.

Surface tension and vapour pressure of binary mixtures. N. A. YAJNIK, R. K. SHARMA, and M. C. BHARADWAJ (J. Indian Chem. Soc., 1926, 3, 63—72).—The variation of surface tension with composition has been examined at three temperatures. For the mixtures benzene-ethylene dichloride, ethylene dibromide-propylene dibromide, bromobenzene-toluene, and chlorobenzene-toluene the variation is linear. The observed values for the mixtures acetic acid-pyridine, chloroform-acetone, and methyl alcohol-ethyl iodide are greater than those calculated from a simple mixture law, whilst the converse is the case for ethyl acetate-carbon tetrachloride, ethyl acetate-ethyl iodide, ethyl iodide-carbon tetrachloride, and acetone-carbon disulphide. The conclusions reached are similar to those of Worley (J.C.S., 1914, 105, 273).

G. M. BENNETT.

Total and partial vapour pressures of aqueous ammonia solutions. T. A. WILSON (Univ. Ill. Eng. Exp. Sta. Bull., 1925, [146], 1—47).

CHEMICAL ABSTRACTS.

Nitric acid. III. Partial pressures of aqueous nitric acid solutions at 12.5° and 30° . Partial pressure of hydrochloric acid at 12.5° . A. KLEMENC and A. NAGEL (Z. anorg. Chem., 1926, 155, 257—268).—The partial pressure of nitric acid in its aqueous solutions at 12.5° and 30° was determined by a dynamic method in which a measured amount of nitrogen was led through the aqueous solution. The nitric acid carried over by the gas was determined by absorption in standard alkali and the total increase in weight of the absorption apparatus gave the aqueous vapour pressure. Comparison experiments were made with aqueous solutions of hydrochloric acid and the results are tabulated. Hydrochloric acid has a much greater partial pressure at higher concentrations than nitric acid, but in dilute solution the reverse is the case.

Of the hydrates of nitric acid the vapour-pressure

curve shows only a dihydrate at about 14N; there is, however, some evidence for a monohydrate at 18N.

M. CARLTON.

Critical solution temperature of acraldehyde and water. A. BOUTARIC and S. CORBET (Compt. rend., 1926, 183, 42—44).—Mixtures of acraldehyde (stabilised with 0.004 of its weight of quinol) and water were heated in sealed tubes until completely mixed, and were then allowed to cool until opalescence just occurred. The effect of acraldehyde resin on the critical temperature suggests that this has a high mol. wt. Confirmation of this view is obtained from cryoscopic measurements with acraldehyde resin in acetic acid, which give a mol. wt. of about 545, in rough agreement with the formula $(\text{CH}_2\cdot\text{CH}\cdot\text{CHO})_{10}$.

L. F. GILBERT.

Thermal anomalies of certain solid solutions. P. CHEVENARD (Inst. Metals, Sept., 1926. Advance copy).—Certain feebly magnetic solid solutions show transformations similar to those of ferromagnetic substances in that they occur without change of phase or of the space lattice. They exist over a large range of temperature and give rise to anomalies in various physical properties. It is shown that such transformations occur in α -copper-aluminium, nickel-chromium, and copper-nickel solid solutions. Their effects on the dilatation of the first two groups of alloys and on the resistivity of the last have been studied in detail.

C. J. SMITHELLS.

Method for investigating binary systems. IV. The "thaw-melt" diagram as a micro-method. H. RHEINBOLDT and M. KIRCHHEISEN (J. pr. Chem., 1926, [ii], 113, 348—354; cf. this vol., 908).—A method is described for the investigation of the m. p. of binary mixtures, requiring about 15 mg. of each component, and illustrated by results obtained for the systems *d*- and *l*-carvoximes, α -naphthol- β -naphthylamine, and β -naphthylamine-*s*-trinitrobenzene.

F. G. WILLSON.

Heterogeneous systems of biological interest.

I. Distribution of saline compounds between immiscible solvents. J. HOLLÓ and D. DEUTSCH (Biochem. Z., 1926, 173, 298—309).—Various indicators were shaken up with a two-phase mixture of ether and water and the amount and extent of dissociation of the indicators determined in each phase. With basic dyes (methylene-blue, fuchsin, Nile-blue sulphate, Bismarck-brown) in alkaline solution both phases are almost equally coloured, whereas in acid solution the ether phase is not coloured. Acid dyes (methyl-red, phenol-red, *m*-nitrophenol) are distributed almost equally in acid solution, whereas in alkaline solution they are present almost exclusively in the water phase. When other anions are added in acid solution to the system and are placed in order of their effect on the distribution of the dyes, the Hofmeister series is obtained.

P. W. CLUTTERBUCK.

Absorption of gases by charcoal. I. R. A. SMITH (Proc. Roy. Soc., 1926, A, 112, 296—303).—Extracts from a paper, now important historically, which was summarised in Proc. Roy. Soc., 1863, 12, 424.

S. K. TWEEDY.

Adsorptive power of charcoals. M. SURUN (Compt. rend., 1926, 183, 44—46).—The adsorptive power was measured by shaking known volumes of various 0.01N-solutions (mercuric chloride, chloral, citric acid, phenol, resorcinol, antipyrine, and pyrimidone) for 30 min. with the charcoal under examination, and systematically increasing the quantity of charcoal until, after filtration, none of the solute could be detected by tests of known sensitivity.

L. F. GILBERT.

Adsorption. IX. Adsorption of gases by wood charcoal at low pressures. A. MAGNUS and L. CAHN (Z. anorg. Chem., 1926, 155, 205—219).—The adsorption of ammonia and carbon dioxide at pressures down to below 0.001 mm. at different temperatures by wood charcoal which had been variously treated as regards degree of gas extraction was investigated. The results with ammonia are not very definite, but on the whole confirm and extend Titov's measurements. The power of adsorption of carbon dioxide by charcoal between 0° and 300° diminishes constantly with the increase in amount of gas absorbed. The more strongly heated the charcoal before adsorption the stronger is its adsorptive power, especially for small quantities of gas, and the greater is the deviation from proportionality between the volume adsorbed and the gas pressure, especially at low pressures. Large deviations from Henry's law are met with, although carbon dioxide at 300° and at pressures of 0.001 mm. behaves as if it were a perfect gas. The greater deviations from Henry's law depend more on the nature of the adsorption medium than on the properties of the adsorbed gas.

M. CARLTON.

Adsorption. X. Wood charcoal as adsorption medium for gases. A. MAGNUS (Z. anorg. Chem., 1926, 155, 220—224; cf. preceding abstract).—Equations are deduced to show that increase of the adsorption potential by roughening the surface is to be expected only if the cavities formed are comparable in their dimensions with the molecular diameter of the adsorbed gas. Formation of such small holes can be produced only by chemical disintegration in the charcoal surfaces. Whereas strong heating may bring this about, a lower temperature will liberate only adsorbed gases or vapours from a somewhat smooth surface. Thus for less strongly heated charcoal Henry's law is nearly fulfilled, whilst stronger heating leads to greater deviations in the ratio of gas adsorbed to gas pressure.

Adsorption in strongly outgassed charcoal in which the places of highest adsorption potential are already filled gives a better approximation to Henry's law than adsorption in the initial stages. This is explained by the equalisation of the charcoal surface as regards its adsorption potential when the finer pores are occupied.

M. CARLTON.

Adsorption of gases by platinum-black. A. F. BENTON (J. Amer. Chem. Soc., 1926, 48, 1850—1861).—The adsorption of hydrogen, oxygen, and carbon monoxide at 1 atm. pressure by the same specimen of platinum-black was measured at 25° by a method designed to eliminate the errors of previous work. The 25° isotherm for hydrogen was also

determined. Hydrogen and carbon monoxide are adsorbed to equal extents; the adsorption of oxygen is little more than half as great, but it is inferred that at somewhat higher temperatures the amounts of hydrogen and carbon monoxide adsorbed would be unchanged, whereas the amount of oxygen would increase. The results with the two former gases support the hypothesis of unimolecular adsorbed films.

S. K. TWEEDY.

Adsorption of gases by glass walls. II. Ammonia. M. CRESPI and E. MOLES (Anal. Fis. Quím., 1926, 24, 210—221).—The adsorption of ammonia by the walls of glass vessels at different pressures was measured by means of an apparatus which is described in detail. The results obtained may be expressed by the equation $A = k \times 10^{-6} \cdot p^{1/4}$, where A is the weight of ammonia adsorbed per cm.² and k is a constant (0.071 for blown glass and 0.045 for drawn glass). The weight of ammonia adsorbed by flasks of different capacity is calculated.

G. W. ROBINSON.

Adsorption of acids, bases, and salts by freshly-precipitated silicic acid. M. R. MEHROTA and N. R. DHAR (Z. anorg. Chem., 1926, 155, 298—302).—Inorganic bases are very readily adsorbed by silicic acid, and tend to cause peptisation, whereas with organic and inorganic acids the reverse is the case. It is therefore probable that peptisation is conditioned by the affinity between the colloid and the peptising agent.

R. CUTHILL.

Absorption of ammonia by chromic, ferric, and aluminium oxides. N. NIKITIN (Z. anorg. Chem., 1926, 155, 358—360).—The above oxides when prepared by ignition of the precipitated hydroxides possess at the ordinary temperature a considerable absorptive power for ammonia, which increases in the order given. With ferric oxide, this is much reduced by increasing the temperature of ignition of the hydroxide, but with the other oxides this is not so. Calcium oxide is much less active than any of the above.

R. CUTHILL.

Adsorption mechanisms. M. L. HUGGINS and J. FIELD (Science, 1926, 63, 454—455).—An attempt to classify types of adsorption by reference to the commonest sources of affinity: (a) an unpaired electron in the valency shell of an atom, e.g., probably amorphous carbon and the fresh surfaces of some metals; (b) a positive atomic kernel not surrounded by electron-pairs; (c) a lone electron-pair in the valency shell of a negative atom; (d) double and triple linkings, three- or four-membered rings, etc., in which one or more of the linking electron-pairs is not near the line joining the centres of the two atoms it unites. Adsorption of the types *ab*, *ad*, *ac*, *bc*, *dd*, *bd*, and *cd* is considered; *bd* is "polar," whilst *dd* is probably "apolar."

A. A. ELDRIDGE.

Interpretation of adsorption isotherms and isosteres. A. S. COOLIDGE (J. Amer. Chem. Soc., 1926, 48, 1795—1814).—The discontinuity in adsorption isotherms at saturation pressure is not adequately explained by the capillary-condensation theory (McGavack and Patrick, A., 1920, ii, 417) or by the appearance of a new phase, but is not contrary to

Póányi's adhesion theory (A., 1916, ii, 474). The conditions are discussed under which forces which are continuous functions of distance can give rise to potentials which are discontinuous functions of the volume of adsorbed gas, and the author considers that the observed discontinuities are not incompatible with the hypothesis that the observed vapour is in the liquid state. The Clausius-Clapeyron equation applies to adsorption within a few per cent., the discrepancy being attributed to the presence of air in the vapour. The heat of adsorption in unsaturated systems is mainly the work performed by the attraction of the adsorbent plus the latent heat of condensation of the vapour; in saturated systems, the heat may be the work of compression (cf. Harkins and Ewing, A., 1922, ii, 123, 197). The evidence for and against the existence of a high pressure due to adsorption suggests that the liquid does not obey the ordinary equations of state and that adsorption may be considered as a special case of solution (Homfray, A., 1910, ii, 771, 1041).

S. K. TWEEDY.

Structure of thin films. VIII. Expanded films. IX. Dibasic substances. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1926, A, 112, 362—375, 376—380; cf. this vol., 348, 468).—VIII. The "expanded" state of surface films and the relation of such films to condensed and gaseous films have been examined. When a definite surface vapour pressure exists between the expanded and the gaseous film such that the transition between the two is discontinuous, the former is regarded as "liquid." The present results on the expanded state of films of some organic compounds containing one and more chains in the molecule indicate the existence of "vapour" expanded films in the case of esters and methyl ketones. These are expanded films which neither behave as liquid films nor show the phenomena of surface evaporation; they pass without discontinuity into gaseous films as the surface pressure is decreased. There is a definite limit to the area occupied by liquid expanded films at no compression; this is about 48 Å.²/mol. in the case of fatty and bromo-acids and 21 Å.²/mol. in that of methyl ketones. It is independent of the length of the chain and of the nature of its head. The long chains in liquid expanded films may assume the form of helices with vertical axes in a close-packed arrangement. Hysteresis, due to the slowness of the molecules in assuming their final packings, probably occurs, even with a simple fatty acid. It becomes apparent with hydrolecithin in the condensed state, which takes some minutes to reach its final pressure in the films. Acid potassium permanganate solution affects ethylenic linkings in the middle of the chain so as to make the films gaseous.

IX. Films of the acids $[\text{CH}_2]_n(\text{CO}_2\text{H})_2$ where $n=16, 20, 24, 32$, of the diethyl esters where $n=10, 11, 16, 20, 32$, and of the monoethyl ester with $n=16$ were investigated. They are all unimolecular and of the gaseous and condensed types. The films of the esters in which $n=10$ or 11 represent the closest approach to the perfectly gaseous state yet found with insoluble films. The transition from the condensed to the gaseous films is of the same nature as that from the condensed to the expanded films

described in previous papers (cf. A., 1925, ii, 195, 658); in all cases, the condensed films expand to films of the "vapour" type. S. K. TWEEDY.

Distribution and orientation of molecules. I. LANGMUIR (Third Colloid Symposium Monograph, 1925, 48—75).—As a first approximation, the field of force about a group or radical in a large organic molecule is independent of the rest of the molecule. From the Boltzmann equation it is calculated that the probability that in the surface layer the hydroxyl group is immersed in the liquid phase is 300—100,000:1. The evaporation of pure substances, the vapour pressures of binary mixtures, the mutual solubilities of liquids, and the orientation of molecules in liquids and interfaces are considered mathematically. The author considers that in expanded films only the heads of the molecules behave as a two-dimensional gas. Such molecules of palmitic acid as are free must lie flat on the surface; the substance therefore does not expand beyond a certain definite area. CHEMICAL ABSTRACTS.

Thermal synthesis of colloids. II. Colloidal selenium. A. GUTBIER [with R. KÖHLER] (Z. anorg. Chem., 1926, 155, 199—204; cf. this vol., 574).—Superheated selenium vapour was passed into water free from air. Only under the most favourable conditions were the colloidal solutions obtained clear yellowish-red, or deep red in colour; usually they were rose-coloured and at first of a blue tint and cloudy. All showed the Tyndall phenomenon and the Brownian movement. Under the cardioid ultra-microscope the yellowish-red solution is the most highly dispersed, but in all solutions there is evidence of the polydisperse character of the sols. The blue sols are exceedingly stable and may be kept in closed vessels for months at the ordinary temperature.

Non-dialysed solutions decompose after a few days, and in these selenious acid may be detected, but no other compounds; there is no trace of this in the yellowish-red preparation. Dialysed sols may be frozen to an almost colourless ice; these slowly thaw at the ordinary temperature, but quickly decompose.

Coagulation by electrolytes sets in readily with chlorides. Under the influence of a *P.D.* of 110—220 volts, the selenium particles migrate to the anode, the system containing 0.003—0.01% of selenium. The presence of protective colloids leads occasionally to the formation of the yellowish-red variety. The amount of colloid is only slightly increased; the stability is the same as with water. M. CARLTON.

Reactions taking place in the preparation of colloidal copper by Bredig's method. V. PODROUŽEK (Chem. Listy, 1926, 20, 403—406).—When an arc is struck between two copper electrodes under water, cupric hydroxide appears to be first formed on the electrodes. Under the action of the heat of the arc, dehydration takes place and cupric oxide is the final product of the action. The ratio $\text{Cu}(\text{OH})_2:\text{CuO}$ decreases with the time the arc is in operation and increases with the alkalinity of the medium. A small quantity of hydrogen peroxide is formed during the process, and this produces a

small quantity of copper peroxide, which, however, soon decomposes into cupric hydroxide or oxide.

A. R. POWELL.

Number of electrical quanta on colloid particles. W. KISTAKOVSKI (Kolloid-Z., 1926, 39, 329).—An error in a previous paper (this vol., 679) is corrected. N. H. HARTSHORNE.

Shear modulus and relaxation of sols. E. HATSCHKE and R. S. JANE (Kolloid-Z., 1926, 39, 300—313).—Measurements have been made by Schwedoff's method of the shear modulus of a number of sols of gelatin, ammonium oleate, mercuric sulphosalicylate, cotton-yellow, and benzopurpurin. With the exception of the very labile ammonium oleate, the moduli increase with age. With rising temperature they fall rapidly, and at 40—45° the shear elasticity is scarcely measurable. In some cases, the time in which the tension required to maintain a certain deformation falls to the e^{th} part of its initial value was determined. From the relaxation times and the moduli, the viscosity coefficients were calculated, and found to be of the order of magnitude of 10^2 — 10^4 absolute units. Some observations were also made on the decrease of torsion in the wire with time. An equation is derived, giving the viscosity as a function of the time and the small difference in the angle of torsion, and from this equation the viscosity coefficient can be calculated at extremely small shear gradients of the order of magnitude 10^{-4} — 10^{-6} sec.⁻¹ The values so obtained show moderate agreement with those calculated from the Maxwell formula. The elasticity of a sol is strongly dependent on its previous history. Thus, benzopurpurin sols of 0.2, 0.3, and 1%, prepared in the cold, show no elasticity and low viscosity; heated to boiling, on the other hand, they show a high shear modulus and viscosity. L. L. BIRCUMSHAW.

Consistency measurements of solutions of rubber in benzene. W. H. HERSCHEL and R. BULKLEY (Kolloid-Z., 1926, 39, 291—300).—Various equations for the streaming of a plastic material through a capillary tube are considered, and it is found that the expression $d^4/L \cdot (P-k)^n/q = I$ (where I is an empirical constant, d the capillary diameter, L the effective length, P the total effective pressure, k the initial pressure, and q the velocity of streaming) is the most suitable for a solution of raw rubber in benzene up to a concentration of 1.2%. This equation yields applicable values for all practical streaming velocities, and avoids the necessity of using very high pressures. A simple experimental method can be used, and the errors caused by the uncertainty in the application of the kinetic energy correction are avoided. By using the logarithmic streaming-pressure diagram, better agreement can be obtained for capillaries of different dimensions than by the determination of shear modulus, rigidity, or mobility. The material constants n and I can be obtained from the logarithmic curve, and both increase with the concentration. In comparison with the shear modulus and mobility, both these constants have the advantage that they influence the streaming in the same direction. The initial pressure k vanishes with large capillary tubes and low concentrations, or is too small to be deter-

mined. When measurable, its value increases with decrease of the capillary diameter.

L. L. BIRCUMSHAW.

Stability of colloidal solutions. V. Effect of similarly charged ions as a factor in electrolyte antagonism in the coagulation of sols and the mechanism of stabilisation. K. C. SEN (J. Indian Chem. Soc., 1926, 3, 81—90; cf. this vol., 122).—The antagonistic effect of potassium oxalate, tartrate, or citrate and of sodium oxalate in the coagulation of sols of copper ferrocyanide by potassium or sodium chloride has been examined. The oxalate or tartrate has a stabilising effect, and the consequent antagonistic action is greater if the coagulating salt does not contain a common ion with the stabiliser, this being attributed to the depressing effect of the common ion on the ionisation of the stabiliser. The mechanism of stabilisation in presence of two electrolytes is discussed. G. M. BENNETT.

Stability of suspensoids under influence of electrolyte mixtures. H. R. KRUYT and P. C. VAN DER WILLIGEN (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 484—491).—The concentrations of various salt mixtures have been determined which induce coagulation of sols of arsenious and mercuric sulphides and of selenium. The addition of lithium chloride, potassium ferrocyanide, and to a less extent of potassium chloride makes the concentration of magnesium chloride necessary for coagulation much larger than would be the case in their absence—an effect classified as antagonistic action. Cataphoretic velocities for these sols afford independent evidence of the increased charge on the particles. Potassium hydroxide does not cause antagonistic action in gold, platinum, and silver sols, but has rather a sensitising effect with both magnesium and barium chlorides. The charge on the metal particles cannot be due to adsorbed hydroxyl ions, but probably involves a double layer built up by complex compounds of the metals which are unstable in the presence of alkalis. G. M. BENNETT.

Anomalous flocculation of clay. N. M. COMBER (Nature, 1926, 118, 412).—Polemical (cf. Joseph and Oakley, this vol., 576). The significance of the results is entirely dependent on what is meant by a "highly purified clay," i.e., on the complete removal of adventitious and absorbed calcium.

A. A. ELDRIDGE.

Adsorption. VI. Influence of the hydrolysis of sols and precipitating electrolytes on the coagulation of colloids. S. GOSH and N. R. DHAR (Kolloid-Z., 1926, 39, 346—361).—Hydrolysable sols such as arsenic and antimony trisulphides, Prussian-blue, copper ferrocyanide, mastic, gamboge, and dammar resin, if coagulated with a mixture of an acid and a salt, require a much smaller quantity of the salt than the calculated value. The addition of acids, by preventing hydrolysis, makes the sols unstable, for the weak acids produced by hydrolysis have a markedly stabilising effect. Hydrochloric acid is a much better coagulator for mastic, gamboge, and dammar resin sols than is potassium chloride at an equivalent concentration. With arsenic and

antimony trisulphides and Prussian-blue, the difference between hydrochloric acid and potassium chloride is not so great, because these sols are not so strongly hydrolysed. If hydrolysable sols are coagulated with hydrolysable salts such as potassium hydrogen carbonate, potassium acetate, and potassium nitrite, greater quantities of them are required than of potassium chloride, since the hydroxyl ions formed increase the hydrolysis and the stability of the sols. The abnormal behaviour of these sols on dilution, viz., that they require a greater quantity of electrolyte for coagulation than when concentrated, cannot be explained solely by the adsorption of similarly charged ions; the greater degree of hydrolysis must be taken into account. Thus the results show that the more hydrolysable the sol the greater the abnormality, whilst if acids are used and the hydrolysis is thus suppressed, the coagulation values tend to become normal.

The strong coagulative power of hydroxyl ions for hydroxide sols depends more on the fact that they destroy the stabilising electrolytes present than on their high migration velocity. N. H. HARTSHORNE.

Adsorption of similarly charged ions as stability factor in the dilution of sols, the acclimatisation, and the antagonistic action of electrolytes on the coagulation of colloids. K. C. SEN (Kolloid-Z., 1926, 39, 324—328; cf. A., 1925, ii, 664, 665).—Data relating to the coagulation of various sols and emulsions are quoted in support of the author's theory that the phenomena of acclimatisation and of stabilisation by dilution or by a mixture of electrolytes, are related, and are to be explained by the adsorption of similarly charged ions. In the action of electrolytes on a suspension, a non-solvated emulsoid, or a solvated emulsoid there will always be abnormal behaviour on dilution, marked acclimatisation, and antagonistic electrolytic action if similarly charged ions are adsorbed in greater quantities. L. L. BIRCUMSHAW.

Anomalous precipitation series. H. MAYANAGI (Kolloid-Z., 1926, 39, 319—322).—By the addition of increasing quantities of strongly adsorbable ions of high valency to a sol, four zones are to be distinguished: the lower non-precipitation zone, the lower precipitation zone, the upper non-precipitation zone, and the upper precipitation zone. The ionic concentrations at the three boundary points, where precipitation just begins or ceases, are designated as the first, second, and third swelling values. A consideration of the mechanism causing the lowering of *P.D.* of the colloid particles on addition of electrolytes shows that the relation between the colloid concentration and the electrolyte concentration necessary for precipitation can be predicted from the adsorbability of the electrolyte concerned. In the first precipitation zone the concentrations should be proportional, whereas in the second the salt concentration should be constant and independent of the colloid concentration. The author's views are supported experimentally by observations of the three swelling values in the case of mastic sol (coagulator, ferric chloride), gold sol (coagulator, ferric chloride), ferric hydroxide sol

(coagulator, potassium ferrocyanide), and albumin sol (coagulator, ferric chloride). L. L. BIRCUMSHAW.

Rapid and slow coagulation of polydisperse systems. P. TUORILA (Koll. Chem. Beihefte, 1926, 22, 191—344).—From von Smoluchowski's theory (cf. A., 1917, ii, 297) it is shown that the rate of "rapid" coagulation of monodisperse systems is comparatively slow if the initial number of particles is small, but if this number is large, the rate is high, and after a time is independent of the original number of particles. The coagulation curves of all monodisperse systems ultimately approach each other, and the number of particles tends to a value which does not depend on the original number of particles. Müller's theory (this vol., 242) leads to the conclusion that after a short time the rapid coagulation of systems containing two sizes of particles closely resembles that of monodisperse systems unless the initial number of larger particles lies between 10^7 and 10^{10} and the number of smaller particles is as great or greater, in which case the two systems behave differently. Even then the difference is appreciable only if the radius of the larger particles is at least 20 times that of the smaller particles. After a time, the coagulation curves of both types of system approximate to each other and the number of particles reaches a value which is independent of the dispersity of the system.

The above deductions have been confirmed by experiments with gold sols. In the slow coagulation of polydisperse systems, the amicros coagulate much more slowly than the submicros, whilst for monodisperse submicroscopic gold sols the rate of coagulation after a time becomes rather less than is calculated from von Smoluchowski's theory. The coagulative power for gold sols of the chlorides of lithium, sodium, potassium, rubidium, caesium, and hydrogen increases in this order. In respect of rapid coagulation, monodisperse suspensions of clay and kaolin behave like gold sols, but polydisperse suspensions coagulate more rapidly than the theory indicates, probably owing to the influence of stirring and sedimentation. A direct ultra-microscopic method of observing the continuous decrease in the number of particles during coagulation is described. R. CUTHILL.

Influence of lyophilic colloids on the precipitation of insoluble salts. Gelatin and silver chromate. I and II. T. R. BOLAM and (MISS) M. R. MACKENZIE (Trans. Faraday Soc., 1926, 22, 151—161, 162—177).—See this vol., 678.

Formula for the electrolytic swelling value of gold sol and iron hydroxide sol. K. HAKOZAKI (Kolloid-Z., 1926, 39, 316—319; cf. Tsuji, this vol., 795).—Investigations have been made with gold and ferric hydroxide sols to discover if Tsuji's formula (*loc. cit.*) for the swelling value of the coagulation concentration of electrolytes for mastic sol is also applicable to other hydrophobic colloids. The concentration of sodium chloride at which precipitation of gold sol began in 24 hrs. was found to be independent of the colloid concentration. The swelling value of sodium chloride at different hydrogen-ion concentrations was then determined, using acetate buffer and phosphate buffer. By introducing into Tsuji's

formula the values so obtained for the sodium-ion concentration (including that of the buffer) and the hydrogen-ion concentration, which must be combined for the precipitation of the gold sol, the value $10^{-5.3}$ is obtained for K . The experimental results are in good agreement with those calculated from the formula. Similar experiments with ferric hydroxide sol, using acetate buffer, yielded the value $10^{-9.3}$ for K . The observed values agree moderately well with those calculated. L. L. BIRCUMSHAW.

Reactions of colloidal gold with proteins. R. WERNICKE and F. MODERN (Rev. Soc. Argentina Biol., 1926, 2, 143—156).—Electrically dialysed serum-albumin from the horse precipitates gold sols obtained by reduction with formaldehyde or dextrose and purified by prolonged electro-dialysis. The precipitating action is less marked with undialysed sols. When appropriate amounts of electrolytes are added, the precipitating action is changed to a protective action. G. W. ROBINSON.

Colloid chemistry of urine. F.-V. VON HAHN (Kolloid-Z., 1926, 39, 329).—A brief reply to Bechhold (this vol., 902). N. H. HARTSHORNE.

Ebullioscopic determination of the equilibrium constant relative to the formation of complexes with mercuric cyanide. F. BOURION and E. ROUYER (Compt. rend., 1926, 183, 390—392).—Ebullioscopic examination has shown that at 100° mercuric cyanide does not combine to a great extent with alkali halides in aqueous solutions. When the ordinary method of mixtures is used to interpret the results, these indicate that in solutions containing 1 mol./litre of each constituent potassium bromide-mercuric cyanide mixtures are combined to the extent of 40.5%, whilst in potassium chloride-mercuric cyanide mixtures only 30% combined. When calculated on the basis of the b.p. elevations per unit weight of water, the results indicate that only 27% of the potassium bromide-mercuric cyanide mixture is combined. The observations lead to no conclusions regarding the rule to apply for the calculation of the equilibrium constant from the b.p. elevations of the single salts. A. E. MITCHELL.

Empirical viscosity formula. M. KUNITZ (J. Gen. Physiol., 1926, 9, 715—725).—The expression $\eta = (1 + 0.5\phi)/(1 - \phi)^4$, where η is the relative viscosity of the suspension and ϕ the fraction of the total volume occupied by the dispersed substance, represents very closely the relation between the volume of the solute and the viscosity of the solution. The formula was found to hold for solutions of sugars, glycogen, caseinogen, and rubber up to 50% concentration. In the case of sugar solutions and sulphur suspensions, the volume of the solute calculated from viscosity values agrees with the actual volume of the substance in the dry state; for solutions of rubber in benzene, the values of ϕ calculated from viscosity measurements fit the equation for the osmotic pressure. W. ROBSON.

Viscosities of solutions in ethyl and methyl alcohols. H. GOLDSCHMIDT and H. AARFLOT (Z. physikal. Chem., 1926, 122, 371—382).—The viscosity changes caused by the addition of water to solutions

of electrolytes in methyl and ethyl alcohols and the neutralisation of acids dissolved in these solvents by bases of different strengths have been investigated. Measurements of the viscosities of mixtures of the two alcohols and of the densities of the various solutions have also been made. The results obtained are correlated with existing conductivity data.

L. F. GILBERT.

Viscosities of aqueous solutions of organic substances and the polymerisation of water. H. M. CHADWELL (J. Amer. Chem. Soc., 1926, 48, 1912—1925).—The densities and viscosities at 25° of solutions of some organic substances in water and of water in methyl and ethyl acetates and in benzene are recorded. Although the organic constituents are all less viscous than water, the solutions have a viscosity higher than that of water. The viscosity decrease due to depolymerisation of water is thus more than balanced by other effects causing a viscosity increase; the volume of the solute molecules is probably the most important factor in this respect. The effect may also be due to the volume contraction accompanying solution, since the contraction and the viscosity increase run parallel. For normal solutes, the larger the molecular volume the larger is the relative viscosity.

S. K. TWEEDY.

Viscosities of univalent salts of the higher fatty acids in aqueous solution. K. S. MALIK (Kolloid-Z., 1926, 39, 322—324; cf. Yajnik and Malik, A., 1925, ii, 779).—The viscosities of aqueous solutions of sodium stearate and sodium palmitate at 60°, 70°, and 80° and at various concentrations have been employed to test whether or not the viscosities of colloidal electrolytes follow any of the known equations connecting viscosity and concentration. The observed values of η_s/η_0 are considerably higher than those calculated from Einstein's formula, but the logarithmic formula of Arrhenius is applicable to aqueous solutions of the salts in question. Calculation of the Arrhenius constant shows that it deviates strongly from the value 0.01086 given by Arrhenius and increases with increasing concentration of the salt.

L. L. BIRCUMSHAW.

Theory of concentrated solutions. I. Theory of hydration. II. Thermodynamics of binary mixtures. W. HEITLER (Ann. Physik, 1926, [iv], 80, 629—671).—I. The assumption of complete dissociation of moderately concentrated solutions of strong electrolytes and the recognition of inter-ionic attractions have been admitted to require solvation or hydration in one form or another before they can provide agreement with experience. The molecules of solvent and solute are regarded as arranged on a space lattice. Such deviations from the laws obtaining in dilute solutions as can be traced to solvation arise from certain positions in the sphere of influence of a solute molecule being forbidden to solute, but not to solvent molecules. The solvent molecules held fast in this way undergo no permanent change which would differentiate them from the rest of the medium. Interchanges of solvent molecules are permitted only with other solvent molecules and not with the solute. The forces operating between solute and solvent exert

no direct influence on the medium, their effect being confined to distortion of the space lattice.

II. The assumption of oriented molecules is carried over to a quite distinct investigation of the potential energy between two molecules, and of the statistical conditions under which molecules of the same or of different kinds occur in close proximity one to another. A simple set of expressions is advanced which accounts in a fairly complete manner for the behaviour of a mixture, e.g., its vapour pressure and miscibility. The heat of mixing is the important quantity for the theoretical reasoning, and the experimental data agree in respect of sign and order of magnitude with the results deduced.

A note is appended on the velocity of sound in mixtures as a basis for the determination of characteristic frequency in relation to the specific heat.

R. A. MORTON.

Milner and Debye theories of strong electrolytes. G. SCATCHARD (Phil. Mag., 1926, [vii], 2, 577—586).—It is claimed, contrary to the conclusions of Pike and Nonhebel and of Nonhebel and Hartley (A., 1925, ii, 1061), that Debye's theory of strong electrolytes offers a better representation of observed facts than does Milner's. It is shown that, when the complete Debye equation is applied to an electrolytic cell comprising a methyl alcohol solution of hydrochloric acid, the *E.M.F.* values obtained are more constant and show less deviation from the experimental values over a much wider range of concentration than those given by Milner's formula.

A. E. MITCHELL.

Milner and Debye theories of strong electrolytes. G. NONHEBEL and H. HARTLEY (Phil. Mag., 1926, [vii], 2, 586—587; cf. preceding abstract).—The authors disagree with Scatchard in the choice of the constant E_0 in the equation $E = E_0 - 0.1183 \log cf$ and claim that the value assumed is incompatible with that obtained by a simple extrapolation without resource to any theory. An extract from a communication from Milner indicates that the numerical differences obtained in the application of the two theories are attributable to greater approximations in the Milner as compared with the Debye formula.

A. E. MITCHELL.

Inter-ionic attraction theory of ionised solutes. VI. Ionisation and ionisation constants of moderately ionised acids. M. S. SHERRILL and A. A. NOYES (J. Amer. Chem. Soc., 1926, 48, 1861—1873).—The ionisation constants of moderately ionised acids are calculated from the relation $\alpha = \Lambda/\Lambda_\infty$, where Λ_∞ is corrected for the mobility decrease of the ions due to their higher concentration. This decrease is calculated as a function of ionic strength (Lewis and Randall, A., 1921, ii, 427). The method is used to calculate the first ionisation constants of orthophosphoric acid (0.0083 at 18°) and sulphurous acid (0.012 at 25°), and the second ionisation constant of sulphuric acid (0.0115 at 25°). S. K. TWEEDY.

Recognition and separation of mono- and polybasic acids. E. WERTZ (Leopoldina, 1926, 2, 160—165).—The solubility in water of the ammonium salts of monobasic organic and inorganic acids increases in

presence of ammonia, whereas the solubility of the ammonium salts of polybasic acids diminishes (cf. Gaus, A., 1901, ii, 7). The increase is probably due to the formation of ammonia-ammonium salt complexes; the decrease is probably a salting-out effect which occurs when no complexes are formed. Graphical representation of the results indicates that ammonium persulphate and perchlorate both form solutions with ammonia which are completely miscible with water. The polymerised hydrofluoric, iodic, and periodic acids behave as polybasic acids; dithionic and persulphuric acids behave as monobasic acids. The two last-named acids can probably be regarded as "doubly monobasic," $(\text{HSO}_3)_2$ and $(\text{HSO}_4)_2$, there being two separate nuclei in the molecule, each containing an acid hydrogen atom. Only two dibasic organic acids behave thus, viz., isophthalic and benzene-*m*-disulphonic acids. It is considered that the reciprocal influence of the carboxyl groups in isophthalic acid is much smaller than in the normally-behaving phthalic and terephthalic acids, so that their rôles are separately conserved and the acid reacts as doubly monobasic. The order of increase of solubility in ammonia solution of some ammonium salts of monobasic and doubly monobasic acids places the latter in a series identical with Hantzsch's series for the strength of acids (A., 1923, ii, 475), which is compatible with the view that the solubility increase is due to complex formation. Mixtures of ammonium salts of monobasic acids with a similar salt of a polybasic acid may often be separated by passing ammonia into the aqueous solution of the mixture, when the latter salt is precipitated.

S. K. TWEEDY.

Electrolytic dissociation of dibasic acids. III. Determination of the second dissociation constant from solubility experiments. E. LARSSON (Z. anorg. Chem., 1926, 155, 247—254).—A method is described for calculating the second dissociation constant of dibasic acids from the solubility of a sparingly soluble monobasic acid in the solution of a neutral salt of the dibasic acid. The applicability of the method to oxalic, succinic, fumaric, *l*-malic, and *d*-tartaric acids is shown; the results are in good agreement with those obtained electrometrically.

M. CARLTON.

Foundation of the expressions $r_{(m)}$ and $r_{(p)}$. A. F. RICHTER (Biochem. Z., 1926, 174, 271—275; cf. Giribaldo, *ibid.*, 1925, 163, 8; A., 1925, ii, 325).—Theoretical.

E. C. SMITH.

Equilibrium point in the reaction between iodic and hydrobromic acids. A. SCHWICKER and G. SCHAY (Z. physikal. Chem., 1926, 122, 482—484).—The mass law constant corresponding with the equilibrium $2\text{IO}_3' + 10\text{Br}' + 12\text{H}' \rightleftharpoons \text{I}_2 + 5\text{Br}_2 + 6\text{H}_2\text{O}$, as determined from analyses of the equilibrium products of mixtures of solutions of iodic and hydrobromic acids, is, approximately, 1.6×10^{-22} at 25° .

L. F. GILBERT.

Electrolyte-free water-soluble proteins. VI. Acid glutins and the Donnan equilibrium. W. PAULI and H. WIT (Biochem. Z., 1926, 174, 308—332).—Measurement of the conductivity and hydrogen-

ion concentration of solutions of glutin in hydrochloric acid solutions shows that with increasing concentration of the acid, the activity and conductivity of glutin hydrochloride increase to a maximum in 0.01—0.03*N*-hydrochloric acid. Similar results are obtained with sulphuric acid. At the maximum point, the apparent normality of the glutin hydrochloride also diminishes, which would indicate that hydrogen ions previously attached to the protein are again liberated by further addition of acid. The anomaly indicates the inapplicability of the Debye-Hückel formula to this system. The effect of doubling the glutin concentration is to increase the maximal normality 100%, but the maximal activity and conductivity increase only 97%. At constant temperature and hydrogen-ion concentration the charge on the glutin particle appears to be independent of the glutin concentration, and at the point of optimal activity of the hydrochloride and of the sulphate the charge carried is of the same magnitude. The viscosity curves follow those of conductivity very closely, the maxima being, however, at a slightly higher p_{H} . The difference is probably due to the greater degree of hydrolysis resulting from the higher temperature at which the viscosity measurements were made.

E. C. SMITH.

Volatility and dissociation of borax. H. V. A. BRISCOE and P. L. ROBINSON (Nature, 1926, 118, 374).—The volatility of borax is well established (cf. Kolthoff, this vol., 813). Moreover, a silica muffle used for the fusion of borax acquired an interior enamel produced by interaction with the volatilised material (cf. A., 1925, ii, 619).

A. A. ELDRIDGE.

Dissociation pressures and the transition point of sodium sulphate decahydrate. M. MATSUI, E. NANAI, S. ITO, and S. FUKUSHIMA (J. Soc. Chem. Ind. Japan, 1926, 29, 161—167).—The dissociation pressures of sodium sulphate decahydrate (mixed with the anhydrous salt) were measured dynamically by Partington's method (J.C.S., 1911, 99, 467). The curve of $\log p$ against $1/T$ was fairly concordant with that of Baxter and Lansing (A., 1920, ii, 286). The dew-point method of Cumming (J.C.S., 1909, 95, 1772) was also used. The transition point, established from the intersection of the two curves so obtained, was 32.6° , in agreement with Cohen's result (Z. physikal. Chem., 1897, 14, 53). The transition point was also estimated by the tensimeter (32.33°) and the dilatometer (32.436°), respectively.

K. KASHIMA.

Decomposition of the double ammonium fluorides of the elements of the titanium group. S. HARTMANN (Z. anorg. Chem., 1926, 155, 355—357).—The thermal dissociation in a current of nitrogen of the double compounds of the fluorides of hafnium, titanium, and zirconium with ammonium fluoride has been examined. The hafnium compound decomposes rather more readily than the zirconium compound (cf. Wolter, A., 1908, ii, 701), whilst the titanium salt occupies an intermediate position. The solubility of the last named in 0.125*N*-hydrofluoric acid is 1.344 g.-mol./litre. Scandium ammonium fluoride commences to decompose at 125° .

R. CUTHILL.

Heat of vaporisation and surface tension. W. HERZ (Z. anorg. Chem., 1926, 155, 348—350).—The empirical relation $\log L = a + b \log \gamma$, where L is the heat of vaporisation, γ is the surface tension, and a and b are constants, is valid for water and certain organic liquids over considerable temperature ranges. Near the critical point irregularities occur.

R. CUTHILL.

Association of liquids and a relation between the capillary constant and the heat of vaporisation. N. DE KOLOSOVSKI (Z. anorg. Chem., 1926, 155, 351—354).—Combination of the relation between the molecular elevation of the b. p. and the b. p. previously deduced (this vol., 791) from van 't Hoff's expression for the molecular elevation and Kistiakowski's rule (A., 1913, ii, 837) leads to the conclusion that the ratio between the heat of vaporisation of a liquid and its capillary constant is independent of the temperature, and for non-associated liquids has the value 18. This is confirmed by an examination of available data, liquids known to be associated giving values for the constant as high as 36.

R. CUTHILL.

Free energy of hydration of ions. T. J. WEBB (Proc. Nat. Acad. Sci., 1926, 12, 524—529).—Previous calculations of the heat of hydration of gaseous ions (Born, A., 1920, ii, 527; Latimer, this vol., 684) assume that the ions are spherical and that the heat of hydration is equal to the energy obtained from discharging the spheres in a vacuum and subsequently charging them in water. Consideration of the principles involved leads to the conclusions that: (a) the above energy change is a free energy change; (b) the dielectric constant of a molecular medium is not constant in the immediate vicinity of an ion (Sack, this vol., 456); (c) the effective ionic radius is that of the cavity surrounding the ion, in which there are no solvent molecules; (d) there is an energy change due to the compression of the solvent in the vicinity of the ion. Starting from these premises, the effective radii and the free energies of hydration of a number of ions have been calculated, details of the calculations, which are rather complex, being promised later. The following numbers represent the free energies of hydration (Cal./mole) of the ions of sodium, bromine, hydrogen, and zinc, respectively, the figures in parentheses being the corresponding effective radii in Å.: 99.0, (1.505); 66.2, (2.38); 250, (<0.5); 525, (1.04). The effective radii are in general about 0.5 Å. higher than those given by Wasastjerna (A., 1923, ii, 593) and Bragg (Proc. Roy. Inst., 1925, 24, III, 614) for the radii of ions in crystals. The electron affinities of the halogens have been calculated.

J. S. CARTER.

Residual affinity and co-ordination. II. Thermal measurements on derivatives of cupric iodide. G. T. MORGAN, S. R. CARTER, and W. F. HARRISON (J.C.S., 1926, 2027—2030).—The heat of formation of *ethanolbisethylenediamminocupric iodide*, $[\text{Cu}_2\text{en}_2\text{Et}\cdot\text{OH}]_2$, m. p. 235° (decomp.), has been found to be +55.28 cal., whilst the heats of formation of the mono- and di-hydrated bisethylenediamminocupric iodides (cf. this vol., 1027) are +53.78

and 55.55 cal., respectively. The heat of formation of the monoalcoholate from cuprous iodide, iodine, and aqueous ethylenediamine is +22.12 cal.

C. J. STILL.

Heats of mixing of water with acetic acid and isopropyl alcohol. C. SANDONNINI (Atti R. Accad. Lincei, 1926, [vi], 4, 63—68).—The heat evolved on mixing water with acetic acid at 15—18° rises to a maximum of 48 cal. per 100 g. of mixture at 14% acetic acid and falls through zero above 34% to a minimum of -192 cal. at 79%. The specific heats and heats of mixing for water-isopropyl alcohol mixtures have been determined. The former are always higher than those calculated by the mixture rule, and the latter have a maximum of 871 cal. per 100 g. of mixture at 25% alcohol, falling to a minimum of -32.5 cal. at 95%.

E. W. WIGNALL.

Moving-boundary method for determining transference numbers. V. Constant current apparatus. D. A. MACINNES, I. A. COWPERTHWAIT, and K. C. BLANCHARD (J. Amer. Chem. Soc., 1926, 48, 1909—1912; cf. A., 1925, ii, 542).—An automatic device is described which maintains a constant current through a moving-boundary transport apparatus, the resistance in which increases steadily during a determination. The transport number of the cation in 0.1N-potassium nitrate solution at 25° is 0.5122 (cf. Denison and Steele, A., 1906, ii, 68).

S. K. TWEEDY.

Theory of electrolytic ions. XXXIII. Transport numbers of anions of chlorides of sodium, potassium, and lithium and of potassium bromide and iodide. R. LORENZ and J. WESTENBERGER (Z. anorg. Chem., 1926, 155, 273—280; cf. this vol., 910).—From Lorenz's theory of transport numbers it is shown that if the transport number of the anion of an electrolyte is plotted against the cube root of the concentration, the resulting graph will be in general, not a straight line, but a hyperbolic curve. This is shown to be true by an examination of published data for the above salts.

R. CUTHILL.

Oxidation-reduction. IX. Potentiometric and spectrophotometric study of meriquinones of the *p*-phenylenediamine and benzidine series. W. M. CLARK, B. COHEN, and H. D. GIBBS (U.S. Pub. Health Ser., 1926, Suppl. 54, 1—61).—Potentiometric measurements have been conducted on solutions containing meriquinones (partly oxidised products), the normal potentials being calculated by means of a relation developed on the assumption that a meriquinone consists of equal parts of oxidant and reductant. The curves connecting electrode potential with p_H of solution show points of inflexion corresponding with the first and second ionic dissociations of reductants, the dissociation constants being evaluated for both oxidants and reductants. Calculations of the concentrations of meriquinone are found to be roughly in accord with spectrophotometric and colorimetric methods of determination. The instability of the systems in question causes great experimental difficulties.

C. H. D. CLARK.

Oxidation-reduction. X. Reduction potentials in cell suspensions. R. K. CANNAN, B. COHEN, and W. M. CLARK (U.S. Pub. Health Ser., 1926, Suppl. 55, 1—34).—Measurements of the electrode reduction potentials of suspensions of rat liver, dried yeast and tissue, and of growing bacterial cultures indicate that these may be advantageously employed in place of reversible indicators in the study of biological reactions. The unimolecular reduction of methylene-blue by yeast-cell suspensions is decreased by washing the cells. Possibly on account of the influence of hydrogen donors within the cells, the reduction of methylene-blue by boiled, washed yeast-cells is accelerated by glutathione.

P.D. measurements made with bacterial cultures using platinum electrodes are somewhat uncertain. In considering the problem of oxygen catalysts in biochemistry, it appears that account should be taken of a characteristic oxidation-reduction potential of aerated suspensions of different cultures in the region marked by the indophenol indicators.

The cell suspensions, in the absence of oxygen, develop increasing negative potential, and a small quantity of active material appears to be continuously produced from a large reserve. The behaviour of cell-enzymes in presence of oxidants such as methylene-blue is discussed in the light of electronic theories.

C. H. D. CLARK.

Increase in potential when some reducing agents are added to certain oxidants. W. S. HENDRIXSON (Proc. Iowa Acad. Sci., 1924, 31, 319—323).—When added to dilute solutions of oxidants in sulphuric acid, ferrous iron seems to cause a rise in the potential of electrodes by accelerating the rate at which they take up their full charges. In all but extremely dilute solutions, the electrodes reach saturation after several hours, and normal falls of potential are then produced by the addition of ferrous sulphate. Other similar instances are cited.

CHEMICAL ABSTRACTS.

Location of the *E.M.F.* in a photo-active cell containing a fluorescent electrolyte. C. C. MURDOCK (Proc. Nat. Acad. Sci., 1926, 12, 504—508).—Goldmann (Ann. Physik, 1908, [iv], 27, 449) has reported that it is necessary to illuminate the actual boundary between electrode and solution in order to obtain an *E.M.F.* from the arrangement, Pt|fluorescent solution|Pt. Grumbach, on the other hand (A., 1923, ii, 108; 1925, ii, 549), has pointed out that by working with very dilute solutions (Goldmann used concentrated alcoholic solutions of dyes) an effect may be obtained merely by illuminating a portion of the solution. He concludes that the total *E.M.F.* when the electrode is illuminated is due in part to an effect in which the electrode is not directly concerned. In the present investigation, measurements have been made using Goldmann's type of semi-transparent film-electrodes on glass and a 3% solution of rhodamine-B in absolute alcohol, under such conditions that the solution flows along the surface on which the electrode is deposited and may be illuminated through, or on either side of, the electrode. An effect is observed even when the only light falling on the electrode is that due to scattering and fluorescence

in the neighbouring illuminated solution; the maximum effect is observed when the electrode is completely bathed in light. The results indicate that the photo-active *E.M.F.* in the Goldmann cell is partly due to some action of light on the electrolyte in which the electrode plays no active part. There is, however, a residual *E.M.F.* for the production of which illumination of the electrode appears to be necessary.

J. S. CARTER.

Determination of the velocity constant of a unimolecular reaction. E. A. GUGGENHEIM (Phil. Mag., 1926, [vii], 2, 538—543).—It is shown that if $v_1 \dots v_i \dots v_n$ are n readings taken at times $t_1 \dots t_i \dots t_n$ and $v'_1 \dots v'_i \dots v'_n$ those for times $t_1 + \tau \dots t_i + \tau \dots t_n + \tau$, then the gradient of the straight line obtained by plotting $\log_{10} (v'_i - v)$ against t will be $-k \log_{10} e$, where k is the velocity constant. This method of determining k is considered to be more accurate than the usual one depending on an extrapolated value of v_∞ , since each measurement is employed once only.

A. E. MITCHELL.

[Radiation] theory of the velocity of chemical reactions. J. K. SYRKIN (Z. anorg. Chem., 1926, 155, 317—322).—It is shown that the application of the quantum theory to the theory of the velocity of chemical reactions necessitates the assumption that the cross-section of the light quanta is proportional to the square of the wave-length, which conflicts with the results of light absorption measurements. Further, the decomposition of sulphuryl chloride (Smith, A., 1925, ii, 876) takes place at a higher speed than is accounted for by the radiation theory.

R. CUTHILL.

Interaction (coaction) of molecules in termolecular reactions. H. J. PRINS (Chem. Weekblad, 1926, 23, 389—393).—The conditions under which termolecular reactions may occur are considered, and it is concluded that such reactions will occur most readily where one or more pairs of molecules are able to form intermediate aggregates in virtue of their electronic configurations.

S. I. LEVY.

Expression of equations of chemical actions as functions of time. S. G. BOTELLA (Anal. Fís. Quím., 1926, 24, 400—412).—The equations showing the relationship between the quantity of substance changed and the time in homogeneous unilateral reactions may be transformed into direct functions of the time. For example, the ordinary equation $dx/dt = k(a-x)$ becomes $x = a(1 - e^{-kt})$. The equations obtained in different cases are discussed. In the case of multimolecular reactions, solutions are possible only when the reacting substances are initially present in equal concentration. From the author's analysis, it would appear that the hypothesis of Damianovitch (Anal. Asoc. Quím. Argentina, 1913, 1, 289) that there are alternate maxima and minima in the reaction velocity-time curve for bimolecular and higher reactions is untenable.

G. W. ROBINSON.

Kinetics of the reaction between iodic and hydriodic acids. E. ABEL and F. STADLER (Z. physikal. Chem., 1926, 122, 49—80).—The above reaction has been investigated at 25°, since Dushman's

work (A., 1904, ii, 718) appears to be marred by numerous errors. The complicating effect of the tri-iodide equilibrium is eliminated by keeping the solution saturated with iodine, or else removing it as it is formed with benzene, and in this way the reaction is found to be quinquemolecular. In sulphuric acid solutions, the velocity constant decreases with increasing concentration of acid, or on addition of potassium sulphate, whilst in solutions containing acetic acid-acetate mixtures change in the concentration has very little effect. This effect can be accounted for in a satisfactory manner by applying Brönsted's theory of reaction velocity, but not by means of the classical theory of electrolytic dissociation. The experimental results have also been worked out in terms of Debye's theory of strong electrolytes.

R. CUTHILL.

Decomposition of formaldehyde by heat.

S. S. MEDVEDEV and E. A. ROBINSON (Trans. Karpov Inst. Chem., 1925, No. 4, 117—125).—The effect of temperature, duration of heating, and concentration of formaldehyde in gaseous mixtures on the speed of decomposition of formaldehyde ($\text{H}\cdot\text{CHO}=\text{CO}+\text{H}_2+22,300\text{ cal.}$) was determined by passing dry carbon dioxide first through a U-tube containing trioxymethylene at various temperatures from 60° to 150° , and then through an electrically heated glass tube. Undecomposed formaldehyde was absorbed by water and determined iodometrically. For a formaldehyde concentration of 39.7% and time of heating 29 sec., the amounts of decomposition were: 450° , 10.21; 500° , 38.6; 550° , 44.7; 600° , 87.5; 650° , 94.9; 700° , 97.6%. The quantity of formaldehyde decomposed thus increases proportionally to the rise of temperature; it also increases proportionally to the time of heating. The original concentration of formaldehyde in the gaseous mixture, however, has no influence on the rate of decomposition; apparently the reaction takes place only at the surface of contact of the formaldehyde with the glass tube. The catalytic effect is apparently peculiar to glass, since the increase of surface by introducing asbestos or aluminium phosphate does not perceptibly increase the decomposition.

CHEMICAL ABSTRACTS.

Reaction velocity of chloral hydrate and permanganate. A. BUZAGH (Mat. Term. Ertesito, 1923, 40, 134—143).—Between 30° and 40° , no chloroform is formed, and the progress of the reaction can be followed by determining the decrease in concentration of the permanganate. The reaction is bimolecular. The velocity constants are: 0° , 0.00116; 8.5° , 0.00254; 25° , 0.0112; 40° , 0.0474; 60° , 0.289.

CHEMICAL ABSTRACTS.

Velocity of hydrolysis of acid anhydrides in aqueous solutions of electrolytes and non-electrolytes. R. SZABÓ (Z. physikal. Chem., 1926, 122, 405—413).—The velocity of hydrolysis of acetic and succinic anhydrides in presence of various acids, salts, and non-electrolytes in iso-osmotic solution was determined by means of an optical (refractive index) method at 14° and 18° . The viscosities of the solutions were also determined. In the presence of salts the velocity coefficient is roughly inversely proportional to the viscosity. The hydrolysis of acetic

and succinic anhydrides is catalysed by hydrogen and acetate ions, and by hydrogen and succinate ions, respectively. The influences of the non-electrolytes employed are specific.

L. F. GILBERT.

Velocity of hydrolysis of the simplest formals.

A. SKRABAL and H. H. EGER (Z. physikal. Chem., 1926, 122, 349—356).—The velocities of the acid (hydrogen chloride) hydrolysis of the formals of ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *isobutyl*, and *sec*-butyl alcohols in dilute aqueous solutions have been measured at 25° . A connexion between chemical constitution and velocity coefficient is apparent which is similar to that obtaining for the acid saponification of the esters.

L. F. GILBERT.

Velocity of hydrolysis of mixed acyl acetals.

A. SKRABAL and I. SAWIUK (Z. physikal. Chem., 1926, 122, 357—370).—The velocities of the acid and alkaline hydrolysis of the diacetate, dipropionate, and acetate-propionate of ethylidene glycol have been measured. The velocity coefficients of the last-named compound are approximately the arithmetic means of those of the other compounds (cf. A., 1924, ii, 666). The factors underlying the velocity of hydrolysis of acetals, generally, are analysed, and systematic numerical relations between the influences of the chemical groups concerned are deduced.

L. F. GILBERT.

Kinetics of the change of halogenalkylamines into heterocyclic compounds. IV.

H. FREUNDLICH and H. KROEPELIN (Z. physikal. Chem., 1926, 122, 39—48; cf. A., 1914, ii, 448; 1922, ii, 489).—The affinity constant of bromoethylamine is found by conductivity measurements to be 3×10^{-7} at 20° . There is in neutral aqueous solution no true equilibrium between this substance and dimethyleneimine hydrobromide owing to side reactions of the latter. The velocity constants for the closing of the chain have been determined for γ -bromopropylamine, and for ζ -chloro- and ζ -bromo-hexylamine. Of the monobromoalkylamines with 2—6 carbon atoms and having the bromine atom at the opposite end of the chain to the amino-group, δ -bromobutylamine has the greatest constant, and γ -bromobutylamine the least. The closing of the chain of bromoethylamine in alkaline aqueous solutions of methyl alcohol has also been investigated. This reaction is of the first order, the velocity constant, k , decreasing with increasing concentration of methyl alcohol, although there is no simple relation between the two magnitudes except for alcohol concentrations below 25%, when $\log_e k$ is a linear function of the alcohol concentration in g.-mol. %.

R. CUTHILL.

Calcination rates of limestone. W. A. GILKEY.—See B., 1926, 707.

Rate of solution of aluminium. M. CENTNERSZWER and W. ZABLOCKI (Z. physikal. Chem., 1926, 122, 455—481).—The rate of solution of aluminium in dilute hydrochloric acid has been determined from measurements of the amount of hydrogen evolved. An induction period, during which the rate of solution increases, is followed by normal solution. It is considered that metallic aluminium is covered with a passive film which is continuously

transformed to active metal (in the presence of acid), and of thickness, as determined from the surface area and the volume of hydrogen evolved during the induction period, 30–84 μ . The (normal) velocity coefficient is increased by increasing the concentration of hydrochloric acid; this is explained on the hypothesis that the reaction occurs between aluminium atoms and non-ionised molecules of acid. Other data presented as confirming this hypothesis are: (a) The addition of chlorides increases and the addition of sulphates and nitrates decreases the velocity of solution (in consequence of the decrease and increase, respectively, of the ionisation of hydrochloric acid thereby caused); (b) the velocity of solution in other acids (sulphuric, hydrobromic, hydriodic) has no apparent connexion with their degrees of ionisation. The values of the temperature coefficients for the reaction between aluminium and hydrochloric acid, and the slight effect of the velocity of rotation of the aluminium samples on the rate of solution are also in accordance with the view that the reaction velocities measured are those of the reaction which takes place directly between acid and metal, and are not determined by the velocity of diffusion of the acid through an adhering liquid film. The rate of solution of aluminium in alkali increases as the concentration of the alkali decreases, and can thus be explained as a reaction between metallic aluminium and hydroxyl ions.

L. F. GILBERT.

Kinetics of carbon dioxide assimilation. J. HOLLUTA (Z. physikal. Chem., 1926, 121, 429–438).—Theoretical. An expression for the rate of assimilation of carbon dioxide by plants is derived which agrees approximately with Warburg's results (Naturwiss., 1925, 13, 985). Stoichiometric equations for the assimilation processes in presence of light are advanced which accord with Einstein's law of photochemical equivalence.

L. F. GILBERT.

Kinetic laws of homogeneous catalysis. E. SPITALSKY (Z. physikal. Chem., 1926, 122, 257–286).—A development of a theory of the velocity of catalysed reactions, including enzyme reactions, starting from the assumption that the function of the catalyst is to convert the substrate into a reactive form by combining with it. The rate of the reaction as a whole is proportional to the concentration, not of the substrate, but of the intermediate compound, which is formed by a practically instantaneous reversible reaction to an extent dependent on the affinity of the catalyst for the substrate. It is then deduced by application of ordinary mass law considerations that the apparent order of such a catalysed reaction is determined by the magnitude of this affinity, and may have any value from zero upwards either integral or fractional. This apparent order bears in general no relation to the true order of the reaction as a whole, which is that of the relatively slow decomposition reaction of the intermediate compound. Change of temperature may, by altering the equilibrium concentration of the intermediate compound, change the apparent order of the reaction. Hydroxyl or hydrogen ions, if present, may influence the reaction either by entering into the composition of the intermediate compound, or by affecting the rate of its

decomposition. In the former case, but not in the latter, the order of the reaction may be changed. A further complication is the possibility of the formation of more than one compound of catalyst and substrate, which differ in stability, in which case the reaction velocity may pass through one or more maximum or minimum values. If at the same time hydroxyl or hydrogen ions play a part, the phenomenon of an optimum concentration may manifest itself. When several catalysts are present together, the state of affairs is very complex, as the substrate may form compounds with two or more of the catalysts simultaneously, as well as with each of them singly. In such a case, therefore, there is usually no question of a simple addition of the effects of the individual catalysts. The above theory is supported by numerical examples.

R. CUTHILL.

Catalytic action of copper ions in the evolution of hydrochloric acid [from chloride solutions evaporated with sulphuric acid]. J. BODNÁR and L. E. ROTH (Z. angew. Chem., 1926, 39, 1101–1102).—Prolonged evaporation of a 1% solution of sodium chloride with sulphuric acid on the water-bath removes only 10–15% of the hydrochloric acid; addition of 1 mg. of copper sulphate per 100 c.c. causes, under the same conditions, a loss of more than 80% of the chlorine. This action is much more marked if the heating is carried out in a Kjeldahl flask over a small gas flame; in 3 hrs., no hydrochloric acid is lost from a mixture of 10 c.c. of 10% sodium chloride solution and 5 c.c. of concentrated sulphuric acid when copper is absent, whilst the whole of the hydrochloric acid disappears in the presence of 1 mg. of copper sulphate.

A. R. POWELL.

Oxidation of oxalic acid by iodic acid. O. WARBURG (Biochem. Z., 1926, 174, 497–499).—The effect of hydrocyanic acid on the oxidation of oxalic acid by iodic acid is not the destruction of the catalytic action of iron by the formation of un-ionised cyanide, but the destruction of the catalytic action of iodine, formed in the first stage of the reaction, by conversion into cyanogen iodide.

E. C. SMITH.

Transfer of excited energy from ozone to hydrogen and nitrogen. A. C. GRUBB (Science, 1926, 63, 460–462).—When a mixture of hydrogen and nitrogen (3 : 1 vols.) is passed over a platinum anode at which ozonised oxygen is being rapidly evolved, ammonia is produced. In the dark, the yield is decreased but slightly; no light phenomena were observed. Neither nitrate nor any decomposition product of the aqueous sulphuric acid electrolyte was found. The formation of ammonia probably results from cumulative excitation of the second kind. The ozone appears to transfer its excitation to the hydrogen.

A. A. ELDRIDGE.

Decomposition of potassium chlorate in the presence of iron oxide. F. E. BROWN and W. C. O. WHITE (Proc. Iowa Acad. Sci., 1924, 31, 291–298).—The minimum temperature (approx. 324°) for the "spontaneous decomposition" of potassium chlorate in the presence of ferric oxide does not vary between the limits $32\text{KClO}_3 : \text{Fe}_2\text{O}_3$ and $\text{KClO}_3 : 4\text{Fe}_2\text{O}_3$. The

history of the ferric oxide affects the temperature, which is lowered by water of hydration. The presence of ammonium chloride in the ferric oxide may lower the temperature to 120°. CHEMICAL ABSTRACTS.

Mechanism of poisoning of catalysts. N. BAKH (Trans. Karpov Inst. Chem., 1925, No. 4, 11—40).—An examination of the reaction $\text{NaH}_2\text{PO}_3 + \text{H}_2\text{O} = \text{NaH}_2\text{PO}_4 + \text{H}_2$, catalysed by palladium, to determine whether definite or infinitesimal quantities of poisons are required to destroy the activity of the catalyst. With palladium-black, the quantities of various poisons required for 1 mol. of palladous chloride were: potassium cyanide, 1.75 mol., mercuric chloride, 1 mol., thiocarbamide, 1.5 mol., quinine hydrochloride, more than 10 mols. Alkaloids generally have a relatively weak action on catalysts. The poisoning effect is due partly to chemical combination between the palladous chloride and the poison, yielding a compound which cannot be reduced by sodium hypophosphite, and partly to adsorption on the surface of the palladium-black. With colloidal palladium, the effect is one of adsorption, and again a definite number of mols. of the poison is required to saturate the surface of the palladium particles and paralyse their action.

CHEMICAL ABSTRACTS.

Catalytic action considered as a surface action. G. R. LEVI and R. HAARDT (Gazzetta, 1926, 56, 424—429).—The first quantitative results relating catalytic action to the surface of unit mass of catalyst are obtained by the help of a new method of regulating the size of platinum particles.

The edge of particles, supposed cubic, obtained by reducing potassium chloroplatinate in acid solution at 60° with aluminium is found to have the value 5.05μ (cf. this vol., 365). When such preparations are heated for 12 hrs. at different temperatures from 60° to 215°, particles of edge ranging from 5.05 to 20.3μ can be obtained, with corresponding surface per 0.01 g. decreasing from 5588 to 1385 cm^2 .

Using this mass of platinum to catalyse the decomposition of hydrogen peroxide solutions, it is found that the extent of the decomposition in unit time increases with increasing surface up to a limiting value; above 3000 $\text{cm}^2/0.01 \text{ g.}$, increase of surface has comparatively little effect. E. W. WIGNALL.

Mechanism of the inhibition of the respiration model by hydrogen cyanide. H. BLASCHKO (Biochem. Z., 1926, 175, 68—78).—The inhibition by hydrogen cyanide of a number of oxidations in presence of charcoal can be reversed by simple physical means. Thus inhibition of the oxidation of leucine is completely reversed by washing for a short time. Inhibition of the process of decomposition of hydrogen peroxide by palladium is also readily reversible, whereas palladium-black, poisoned by hydrogen cyanide, only regains its power to oxidise alcohol extremely slowly. The oxidation of laevulose in alkaline phosphate solution (p_{H} 8.3) is inhibited by hydrogen cyanide, but recovers on evacuating and warming until the solution attains p_{H} 4.5. P. W. CLUTTERBUCK.

Catalytic dissociation of carbon monoxide. J. CLEMINSON and H. V. A. BRISCOE (J.C.S., 1926, 2148—2154).—The reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ does not proceed at or below 400° when glass forms the only contact surface. The minimum temperatures of reaction with various catalysts were: carbon, 300°; magnesium oxide, 290°; aluminium oxide, 250°. The percentages of carbon monoxide decomposed in presence of alumina were: 5.35 at 250°; 8.50 at 270°; and 12.25 at 290°. S. K. TWEEDY.

Activation of the inert varieties of calcium sulphate. P. BUDNIKOV (Compt. rend., 1926, 183, 387—388).—The influence of various catalysts on the rate of rehydration of gypsum calcined between 600° and 700° for 4 hrs. has been examined. Of the substances examined, sodium and potassium hydrogen sulphates in concentrations of 1 and 2%, respectively, were the most effective. Plasters made with their aid from material passing 4900 meshes/ cm^2 set in 15 min. and acquired tensile strengths of 49 and 50 kg./cm^2 , respectively, after 21 days. The variation of tensile strength with time is not regular. In the case of sodium hydrogen sulphate, the strength reaches a maximum after 8 hrs., and the subsequent variation is attributed to recrystallisation of the plaster. A. E. MITCHELL.

Inhibiting agents in the oxidation of unsaturated organic compounds. O. M. SMITH and R. E. WOOD.—See B., 1926, 713.

Catalytic oxidation of methane. II. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1925, No. 4, 117—125).—On oxidation of methane by atmospheric oxygen with tin phosphate or borate as catalyst the activity of the latter soon decreases, whereas hydrogen chloride originally present is gradually removed. It is now shown that in the absence of hydrogen chloride only about 2% of the methane was decomposed, whereas the addition of 4% of hydrogen chloride to the gaseous mixture caused the decomposition of 27% of methane. Small concentrations of hydrogen chloride afford formaldehyde as the principal product; larger concentrations give chiefly carbon monoxide. The best catalyst for the production of formaldehyde is a mixture of aluminium, tin, and iron phosphates at 600°; employing a mixture of methane, 58.2; oxygen, 26.1; nitrogen, 8.7; hydrogen, 6.96; hydrogen chloride, 0.13%, half of the total quantity (6.7%) of methane decomposed is converted into formaldehyde, by way of the liberation of chlorine and chlorination of the methane. The maximum oxidation of formaldehyde by excess of hydrogen chloride is reached when 90% of the methane is converted into carbon monoxide. The yield of formaldehyde is increased by operating in a series of communicating tubes. Thus, in a 2-tube system the total yield of formaldehyde was 8.8% of the amount of methane taken, 15% of the methane remaining undecomposed, but by passing the mixture through the system twice, the yield of formaldehyde was increased to 15.2%.

CHEMICAL ABSTRACTS.

Catalysis by metallised silica gel. L. H. REYERSON and K. THOMAS (Third Colloid Symposium Monograph, 1925, 99).—Silica gel, prepared by

Patrick's method, was evacuated by heating for 2 hrs. at 250°, cooled to -20°, saturated with hydrogen, and metallised with 0.1*M*-solutions of platinum, palladium, copper, gold, or nickel. Using palladium and platinum, ethylene was hydrogenated to the extent of 60.9% at 0°, 98.9% at 95°; with nickel at 180°, 50–60% of phenol was converted into cyclohexanol; aniline gave ammonia and, probably, phenylamino-cyclohexane. The metallised gels also catalyse oxidations.

CHEMICAL ABSTRACTS.

Cathodic sputtering. A. VON HIPPEL (Ann. Physik, 1926, [iv], 80, 672–706).—The particles of metal emitted in the process of cathode sputtering consist primarily and predominantly of uncharged atoms. The particles collide with electrons and ions in the glow discharge, and excitation follows with consequent emission of the resonance lines of the cathode metals. This forms the basis of a quantitative method for the spectroscopic measurement of vapour pressure. An independent check was provided by a method for determining the vapour pressure from the thickness of the metallic film. The somewhat elaborate conditions which must be observed in the spectroscopic work are discussed in detail. The decisive experiments were carried out with a cadmium cathode; zinc and silver were used in confirmatory work. A special absorption effect was observed in the sputtering of cadmium.

R. A. MORTON.

Cathodic sputtering. II. A. GÜNTHER-SCHULZE (Z. Physik, 1926, 38, 575–588; cf. this vol., 693).—The sputtering of silver in hydrogen has been investigated at a cathode fall of potential of 1000 volts. The quantity of silver sputtered was found to be inversely proportional to the distance apart of the electrodes and also to the pressure of hydrogen; it had been shown previously (*loc. cit.*) to be directly proportional to the fall of potential. A table of values for other metals, and for oxygen as well as hydrogen, is given.

E. B. LUDLAM.

Electrolytic separations by graded potentials. A. LASSIEUR (Bull. Soc. chim., 1926, [iv], 39, 1167–1183; cf. A., 1925, ii, 159, 711).—Zinc can be deposited from an acid solution of p_H between 4.5 and 5.0, or from a solution of the complex cyanide, provided that only sufficient potassium cyanide is added to form the complex salt. To separate tin from zinc, hydrochloric acid and hydroxylamine hydrochloride are added to the solution, and the tin is separated with an auxiliary potential of 480 millivolts; the zinc is then deposited from the neutral cyanide solution. Cadmium is separated from zinc by using an auxiliary potential of 650 millivolts and a solution of such acidity that it turns thymol-blue a cherry-red. A method is described of separating antimony, copper, lead, tin, cadmium, and zinc.

R. CUTHILL.

Electrolysis of sodium chromate with a mercury cathode. I. STSCHERBAKOV and O. ESSIN.—See B., 1926, 712.

Theory of photophoresis. G. HETTNER (Z. Physik, 1926, 37, 179–192).—Mathematical. A theory is developed in which photophoresis is regarded

as a radiometer effect and its variation with pressure is calculated. The photophoretic force for molecules of the usual radius has a maximum at a pressure about equal to that of the atmosphere, and this explains the fact that change of pressure in this region of pressure makes very little difference. For higher pressures, the theory is in satisfactory agreement with experiment. Independence of the effect on the nature of the gas is also satisfactorily accounted for within certain limits.

E. B. LUDLAM.

Photolysis of gaseous hydrogen iodide in the light of the quartz mercury-vapour lamp. M. TRAUTZ and B. SCHEIFELE (Z. wiss. Phot., 1926, 24, 177–216).—In the direct light of a quartz lamp running at 350 watts and at 10–50 cm. distance, hydrogen iodide, in a quartz cell at ordinary or decreased pressure, is decomposed at a velocity which can be readily measured manometrically. The reaction proceeds to complete decomposition of the hydrogen iodide; no decomposition in the dark or re-formation of hydrogen iodide in the light was observed. The active wave-lengths lie between 300 and 220 μ . The reaction velocity is apparently independent of temperature up to 120°, of the interposition of hydrogen, water, or 10% copper sulphate solution between the lamp and the cell, of the admixture of nitrogen with the hydrogen iodide, and of placing a palladium mirror behind the cell. The reaction velocity falls if a glass plate or an iodine filter is interposed between lamp and cell, if iodine vapour is mixed with the gas, and apparently if an excess of hydrogen is added. At first, the reaction velocity is for a time constant; it then falls to that of a unimolecular reaction (constant = 10^{-4} sec.⁻¹ for lamp at 15 cm. distance), and later falls again. These results indicate that at the start the active wave-lengths are strongly absorbed, but in the region where the unimolecular law is followed, only very weakly so. An approximate value is derived for the absorption constant. The falling off in reaction velocity towards the end of the reaction starts the sooner the higher is the initial pressure of hydrogen iodide and the lower the temperature. At 120°, it is very small. The initial reaction velocity appears to increase approximately proportionally to the initial concentration of hydrogen iodide. Exposure to the neon arc lamp or to a high candle-power Wotan lamp resulted in practically no decomposition. Simultaneous exposure to these sources and to the mercury lamp gave results no different from those obtained with the mercury lamp alone. The effect of varying the distance of the lamp from the cell was in accordance with the inverse square law. There is no appreciable absorption of the active wave-lengths by air.

W. CLARK.

Photosensibility of selenium. I. A. KASARNOVSKII (Trans. Karpov Inst. Chem., 1925, No. 4, 93–97).—The potential of selenium becomes more positive on illumination; hence the difference between illuminated and non-illuminated selenium cannot be ascribed to the formation of a new allotropic modification, and the cause of the photosensibility is not a reversible photochemical reaction.

CHEMICAL ABSTRACTS.

Photochemical properties of chromates and of other compounds. J. PLOTNIKOV and M. KARSCHULIN (Z. Physik, 1926, 38, 502—510).—The fact that the authors had found a different position for the maximum absorption for chromated collodion from that found by Eder (this vol., 774) is attributed to different medium and the difference in the distribution of energy in the light from different sources. The spectrographic and photochemical absorption have been determined for potassium and ammonium chromates, iron carbonyl, iodine, potassium iodide, solutions of iodine in potassium iodide, and bromine. The photochemical absorption in each case shows a position of maximum effect, but the slope of the rise and fall varies. Mixtures of chromate and potassium iodide show the photochemical absorption of each substance separately. E. B. LUDLAM.

Decomposition of potassium manganioxalate in plane polarised, circularly polarised, and ordinary light. J. C. GHOSH and A. N. KAPPANNA (J. Indian Chem. Soc., 1926, 3, 127—140; cf. this vol., 366).—The molecular extinction coefficients of potassium manganioxalate in aqueous solution have been measured for all visible regions of the spectrum. It absorbs light throughout, but a maximum occurs at about 4870 Å. Beer's law is obeyed for light of 5790 Å. The decomposition of the salt is a unimolecular reaction which proceeds spontaneously in the dark, the temperature coefficient of the velocity being 2.13 per 10°. White light more than trebles the velocity of decomposition, its effect having a temperature coefficient of 1.30 per 10°. Ordinary and plane polarised light are equivalent in effect, but circularly polarised light has a slightly greater efficiency. Addition of oxalic acid to the solution diminishes the velocity of the reaction. From measurements of the velocity in approximately monochromatic light (4880 Å.) it is calculated that one molecule is decomposed per quantum of energy absorbed. G. M. BENNETT.

Thiocarbamide fog and a suggested explanation of a Waterhouse reversal. S. O. RAWLING. —See B., 1926, 721.

Photographic solarisation. H. BELLIOU.—See B., 1926, 721.

Nature of optical sensitisation and desensitisation. H. H. SCHMIDT.—See B., 1926, 772.

Optical sensitisation. II. Water as sensitizer. G. KÖGEL and A. STEIGMANN.—See B., 1926, 772.

Effect of concentration of sensitizer on speed, and fog corrections. S. E. SHEPPARD.—See B., 1926, 773.

Primary action of photochemical absorption. Optical photochemical transformation of radiation. G. KÖGEL (Z. wiss. Phot., 1926, 24, 216—218).—*o*-Nitrobenzaldehyde is very sensitive to light, whereas *o*-nitrocinnamaldehyde is insensitive, and the reactivity of the aldehyde group as oxygen acceptor is very different in the two substances. The action of the aldehyde group is not specific, either chemically or photochemically. The *o*-nitro-

groups in *o*-nitrobenzaldehyde and also in *o*-nitrocinnamaldehyde are exceedingly sensitive to light in presence of pyrogallol. The influence of substituents disappears under these conditions. The fact that such an apparently inactive substance, exposed with or without acceptor, shows the same spectral absorption, indicates that the thermal, photoinactive absorption and the photochemically active absorption are alike. The light does not undergo a particular form of absorption determined by the presence of conditions favourable to a particular chemical reaction. It is possible that the light-sensitive group can be influenced favourably by some internal change (e.g., loosening of linkings) brought about by the presence of an acceptor, without requiring any specifically different absorption of light. W. CLARK.

Yield of photochemical reactions with complex light in comparison with that obtained with the component lights. III. M. PADOA and N. VITA (Gazzetta, 1926, 56, 375—388).—A more detailed account of work previously published (this vol., 584). In the bromination of cinnamic acid the amount of reaction does not at first decrease to the extent demanded by the inverse square law as the light source is removed. To the previous results are added those of an experiment in which hydriodic acid is decomposed by white light and by the same filtered through an ammoniacal copper sulphate solution. In the latter case, although only 47% of the luminous energy was available, the iodine formed was increased by 25%. E. W. WIGNALL.

Lithium chlorate. L. BERG (Z. anorg. Chem., 1926, 155, 311—316).—Attempts to prepare the hemihydrate of the above salt described by previous authors (cf. Bruhl, A., 1913, ii, 50) have been fruitless, but a hydrate, $3\text{LiClO}_3 \cdot \text{H}_2\text{O}$, which loses its water when heated to about 55°, has been obtained.

R. CUTHILL.

Action of organic compounds on sodium hydrogen sulphate. H. B. DUNNICLIFF and S. SINGH (J. Indian Chem. Soc., 1926, 3, 91—100; cf. J.C.S., 1920, 117, 649; 1923, 123, 476).—Trisodium hydrogen disulphate, like the corresponding ammonium salt, is unaltered by prolonged extraction with alcohol or ether. Methyl, ethyl, *n*-propyl, isopropyl, butyl, isobutyl, and isoamyl alcohols extract sulphuric acid from sodium hydrogen sulphate with diminishing readiness, leaving ultimately a residue of trisodium hydrogen disulphate. Acetone and methyl ethyl ketone have a similar effect, but aromatic ketones are without action. Since the hydrogen sulphates of sodium and ammonium thus yield two thirds of their acidity to solvents, a termolecular formula is suggested for them, whilst the hydrogen sulphates of potassium, rubidium, and caesium, which are not affected by solvents, are regarded as unimolecular. The relative effects of alcohol and acetone on sodium hydrogen sulphate do not appear to be connected with their relative electrical conductivities. The specific conductivities are recorded for three series of mixtures of alcohol with acetone, alcohol with ether, and acetone with ether, respectively. G. M. BENNETT.

Reaction between sodium phosphates and calcium hydroxide. H. HAYASHI and M. MATSUI (J. Soc. Chem. Ind. Japan, 1926, 29, 175—179; cf. *ibid.*, 1925, 101).—Trisodium phosphate was agitated with calcium hydroxide for a definite time, the solution filtered, and its content of phosphoric acid determined. The amount of reaction increases with time and rise of temperature. At 70—90° and 1·5 hrs., the quantity of calcium hydroxide necessary to precipitate the total phosphoric acid is 137·5% of the theoretical. Trisodium phosphate is more active than disodium hydrogen phosphate towards calcium hydroxide; the amount of the calcium hydroxide is almost constant so long as the amount of free alkali is less than 20%. When the solution of sodium phosphates is diluted with water, the amount of the calcium hydroxide above given is sufficient up to a dilution of 150%. The action of quick, slaked, and weathered limes is in the above order. The grains of lime passing through 90—150-mesh sieves give the same result. When other salts are present, the reaction is retarded owing to increasing solubility of calcium phosphate formed. K. KASHIMA.

Separation of copper and ferrous sulphates by crystallisation. G. AGDE and H. BARKHOLT.—See B., 1926, 707.

Displacement of caesium and of rubidium by iron. L. HACKSPILL and H. PINCK (Compt. rend., 1926, 183, 388—389).—The previous work of Hackspill and Grandadam (A., 1925, ii, 233), where it was shown that, in a vacuum and at temperatures where the vapour pressure of the alkali metal was of the order of 1 cm., iron would readily displace sodium and potassium from most of their salts, has been extended to a number of salts of caesium and rubidium with corresponding results. A. E. MITCHELL.

Gold from mercury. E. DUHME and A. LOTZ (Wiss. Veröff. Siemens-Konz., 1926, 5, 128—151).—See this vol., 930.

Reported transmutation of mercury into gold. M. W. GARRETT (Proc. Roy. Soc., 1926, A, 112, 391—406).—Unsuccessful experiments designed to bring about the above transformation are described (cf. Miethe and Stammreich, this vol., 367, 493).

S. K. TWEEDY.

Alleged preparation of artificial gold from mercury. A. SMITS (Z. anorg. Chem., 1926, 155, 269—272).—A reply to Haber, Jaenicke, and Matthias (this vol., 699) giving a detailed account of the purification of lead from the last traces of mercury.

M. CARLTON.

Constitution of cement. E. JÄNECKE.—See B., 1926, 747.

Fluoroborates. H. FUNK and F. BINDER (Z. anorg. Chem., 1926, 155, 327—332).—The fluoroborates of the following metals have been prepared by the action of the acid on the carbonate or oxide: magnesium, $\text{Mg}(\text{BF}_4)_2 \cdot 7\text{H}_2\text{O}$; calcium, $\text{Ca}(\text{BF}_4)_2 \cdot 5\text{H}_2\text{O}$; strontium, $\text{Sr}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$; zinc, $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$; cadmium, $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$; mercury, $\text{HgBF}_4 \cdot \text{HF} \cdot \text{H}_2\text{O}$. The ferrous salt, $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, is obtained by the action of the acid on the metal. R. CUTHILL.

Saccharification of starch by Japanese acid clay. K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1926, 29, 95—102).—On heating starch with Japanese acid clay under pressure, the former is hydrolysed and consequently saccharified. The saccharifying action of the clay towards starch is proportional to the "acidity" of the clay as previously shown to be the case with the inversion of sucrose. An aqueous extract of the acid clay gives no acid reaction, but on contact with water, a double layer is formed on its surface. Thus the acid clay itself is not an acidic substance, but an arrangement may result on the surface of the clay as in the scheme: $\text{H}^+[\text{OH}(\text{acid clay})]^-$. The saccharifying action of Japanese acid clay seems to be due to these "bound hydrogen ions." K. KASHIMA.

Carbon suboxide. O. DIELS (Z. angew. Chem., 1926, 39, 1025—1028).—A summary of the properties and reactions of the suboxide C_3O_2 , from which the conclusions are reached that the allene formula $\text{OC}:\text{C}:\text{CO}$ is most probable and that other oxides, C_4O_2 , C_5O_2 , etc., may be found capable of existence.

S. I. LEVY.

Reduction of carbon monoxide under ordinary pressure. A. JAEGER and H. WINKELMANN.—See B., 1926, 698.

Complex iodates of tin and antimony. P. RÂY and S. N. RAY (J. Indian Chem. Soc., 1926, 3, 110—117).—Stannic chloride reacts with iodic acid in dilute nitric acid solution to produce *dihydroxy-tetraiodatostannic acid*, $[\text{Sn}(\text{IO}_3)_4(\text{OH})_2]\text{H}_2$, and if the iodic acid be in large excess *stanni-iodic acid*, $[\text{Sn}(\text{IO}_3)_6]\text{H}_2$, which on ignition leaves a residue containing iodine. The potassium, ammonium, rubidium, caesium, sodium, and lithium salts of this acid are obtained by the action of iodic acid on the corresponding chlorostannates. Addition of potassium iodate to a solution of potassium chlorostannate, however, yields a double compound of the composition $\text{K}_2\text{Sn}(\text{IO}_3)_6 \cdot \text{K}_2\text{Sn}(\text{IO}_3)_5\text{OH}$, and stannic chloride with an excess of sodium iodate in dilute nitric acid solution gives a precipitate of *tetrahydroxydi-iodatostannic acid*, $[\text{Sn}(\text{IO}_3)_2(\text{OH})_4]\text{H}_2$. Antimony pentachloride and an excess of iodic acid furnish *trihydroxytri-iodoantimonic acid*, $[\text{Sb}(\text{IO}_3)_3(\text{OH})_3]\text{H}$.

G. M. BENNETT.

Double sulphates of the rare-earth and alkali metals. VI. (Cerous) cerium and potassium sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1926, [vi], 4, 5—10).—In the system $A-B\text{H}_2\text{O}$, where A is $\text{Ce}_2(\text{SO}_4)_3$, and B is K_2SO_4 , the following crystalline double sulphates are obtained at 25°: $A, B, 2\text{H}_2\text{O}$, stable in a solution containing 4·9—6·7% A , 0·07—0·04% B ; $2A, 3B, 8\text{H}_2\text{O}$, obtained from solutions in which A and B have equal concentrations; $2A, 9B$ and $A, 5B$, stable in solutions of 1·2—5·0 and 5—9% B , respectively.

E. W. WIGNALL.

Heterogeneous lead complexes. Iodothiocyanates. A. C. VOURNAZOS (Z. anorg. Chem., 1926, 155, 241—246; cf. this vol., 371).—The following salts have been prepared: Sodium and

potassium lead iodothiocyanate, $X_4[PbI_2(SCN)_4] \cdot 2H_2O$; on electrolysis the complex ion yields lead iodide, sulphur, and the compound $(SCN)_2$. *Ammonium lead iodothiocyanate*, $(NH_4)_8[PbI_2(SCN)_8] \cdot 2H_2O$; white needles readily decomposed by moisture. *Lead aniline iodothiocyanate*, $[PbI_2 \cdot C_6H_5 \cdot NH_2 \cdot HSCN]$, yellow, exists in amorphous and prismatic forms. *Lead guanidine iodothiocyanate*, $PbI_2 \cdot CH_5N_3 \cdot HSCN$, yellow.

M. CARLTON.

Action of stannous chloride on nitrous acid.

F. RASCHIG (Z. anorg. Chem., 1926, 155, 225—240).—Reduction of nitrous acid by excess of stannous chloride gives a solution which decolorises more potassium permanganate than can be accounted for by the excess of stannous chloride determined by iodine. This is due to formation of hydroxylamine and hyponitrous acid. These together with nitrous oxide are the only products of the reduction. The course of the reaction is explained thus: $O:N \cdot OH + 2H = O:NH + H_2O$, the nitroxyl then yielding nitrous oxide. Then $HO:N \cdot O + 2H = HO \cdot NH \cdot OH$ (dihydroxyammonia, which is known to be an intermediate product), which breaks up into hyponitrous acid and on reduction gives hydroxylamine.

The ratio of amount of hydroxylamine formed to hyponitrous acid changes with the conditions of experiment. About 90% of nitrous acid is converted into nitrous oxide, and the remaining 10% into hyponitrous acid and hydroxylamine. This division, which is unaffected by external conditions, is suggested to be due to difference in constitution of nitrous

acid: $H \cdot N < \begin{smallmatrix} O \\ \parallel \end{smallmatrix}$ and $HO \cdot N \cdot O$. The acid solution of hyponitrous acid is only slowly neutralised by sodium hydroxide and is stable in acid and alkaline solution. If, however, the acid solution be suddenly made alkaline by soda, it is at once decomposed. If the neutralisation be slowly performed, the acid is only partly decomposed. The stability of hyponitrous acid is greatest in strongly acid or strongly alkaline solution.

M. CARLTON.

Sulphurous acid and its salts. III. Behaviour of sulphurous acid towards thiosulphuric acid. F. FÖRSTER and R. VOGEL (Z. anorg. Chem., 1926, 155, 161—191).—The following equilibria arise when thiosulphate solutions are acidified: $S_2O_3^{2-} + H^+ \rightleftharpoons HS_2O_3^-$; $HS_2O_3^- \rightleftharpoons HSO_3^- + S$; i.e., $S_2O_3^{2-} + H^+ \rightleftharpoons HSO_3^- + S$ (i), since (a) hydrogen sulphite as well as thiosulphate on acidification gives sulphur and sulphurous acid; thus hydrogen sulphite dissolves sulphur, forming thiosulphate, with increasing acidification; (b) changes in concentration of the substances taking part in the equilibrium move this in the direction anticipated, e.g., increasing the hydrogen-ion concentration moves the equilibrium to the right, increasing the hydrogen sulphite concentration (and consequently diminishing the hydrogen-ion concentration) moves it to the left, sometimes so far that separation of sulphur ceases; (c) in thiosulphate solutions which are decomposed by such weak acids as acetic, formic, etc., the equilibrium constant expected from the law of mass action, $[S_2O_3^{2-}][H^+]/[HSO_3^-] = k$ is about 13×10^{-2} at 11° .

That the addition of excess of sulphurous acid to thiosulphate solutions gives yellow solutions without separation of sulphur was already known. The assumption that these solutions contain free colloidal sulphur is here disproved, the colour being rather due to complex anions in which sulphur dioxide is coordinately linked through thiosulphate ions. The possibility of such anions existing is suggested by the existence of numerous other similar anions (cf. Ephraim, this vol., 36) and was confirmed by preparations of the yellow solid compounds $K_2S_2O_3 \cdot SO_2$ and $Rb_2S_2O_3 \cdot SO_2$, which are prepared from anhydrous thiosulphate and liquid sulphur dioxide at low temperatures and give clear yellow solutions with a little water in which the equilibrium $S_2O_3^{2-} + SO_2 \rightleftharpoons [S_2O_3(SO_2)]^-$ (ii) exists. Among the components of this equilibrium the following may also exist: $H^+ + HSO_3^- \rightleftharpoons H_2SO_3 \rightleftharpoons SO_2 + H_2O$ (iii); thus by sufficiently acidifying the thiosulphate solutions, equilibrium (ii) can set in, with consequent yellow coloration of the solution. Since by appearance of (ii) the concentration of thiosulphate is diminished, the separation of sulphur in (i) may be hindered by sufficiently lowering the hydrogen-ion concentration or increasing hydrogen sulphite or sulphurous acid concentration, i.e., the ratio of the concentration of sulphurous acid to that of thiosulphate must be somewhat greater than 1. According to (ii), it must be the greater the smaller is the thiosulphate concentration; such solutions are yellow and remain completely clear for some time.

Solutions (i) and (ii) are subject to slow change, during which polythionates are formed; penta- or tri-thionates are formed: $5S_2O_3^{2-} + 6H^+ \rightarrow 2S_5O_6^{2-} + 3H_2O$ (iv) or $S_2O_3^{2-} + 4HSO_3^- + 2H^+ \rightarrow 2S_3O_6^{2-} + 3H_2O$ (v); also $S_5O_6^{2-} + HSO_3^- \rightarrow S_4O_6^{2-} + S_2O_3^{2-} + H^+$ (vi); $S_4O_6^{2-} + HSO_3^- \rightarrow S_3O_6^{2-} + S_2O_3^{2-} + H^+$ (vii) give rise to the anions of all three polythionic acids on conversion of the components of (i) and (ii).

Since the trithionate anion is not stable: $S_3O_6^{2-} + H_2O \rightarrow SO_4^{2-} + S_2O_3^{2-} + 2H^+$ and thiosulphate and hydrogen ions again enter in equilibrium (i), finally the acidified thiosulphate solution passes into sulphate, sulphur, and sulphurous acid. Moreover, in the thiosulphate solution coloured yellow by sulphur dioxide, this, and with it the yellow coloration, can completely vanish before large amounts of free sulphur are precipitated from the trithionate.

M. CARLTON.

Precipitation of metals from non-aqueous solutions. I. R. MÜLLER, A. SCHIMKE, and N. M. FARMAKIDES (Z. anorg. Chem., 1926, 155, 333—347).—Experiments have been made on the precipitation of nickel by zinc from solutions of nickel chloride in 98% ethyl alcohol. The rate of the reaction is much greater than in aqueous solution, and very little nickel hydroxide is formed (cf. Kremann, Angelberger, Bakalarz, Röhrich, and Stöger, A., 1923, ii, 866), but the deposit of metal is chiefly in the form of a loose powder. The reaction is more nearly complete at 18° than at 77° , and the completeness also increases with increase of the ratio of metallic zinc to nickel in solution, and with increase in the surface of the zinc, i.e., it is greater with the zinc in the form of

turnings than in the form of small cylinders. Examination of the turnings after the reaction has occurred shows them to consist of a nucleus of unchanged zinc, surrounded by a thin layer of zinc-nickel alloy, with a powdery external coating of nickel.

R. CUTHILL.

Palladium oxides. G. R. LEVI and C. FONTANA (*Gazzetta*, 1926, 56, 388—396; cf. Levi and Tacchini, A., 1925, ii, 424).—X-Ray examination shows that partial oxidation of finely-divided palladium gives a mixture of the metal and palladous oxide, PdO, no suboxide Pd₂O being formed (cf. Wöhler and König, A., 1905, ii, 722). Palladous oxide has a face-centred tetragonal symmetry; for the unit cell of 4 molecules $a=4.23$, $c=5.20$ Å., axial ratio 1.23, $d_{\text{calc.}} 8.73$, $d_{\text{obs.}} 8.70$. From the hydrated peroxide, PdO₂· x H₂O, no X-ray spectrum was obtained.

E. W. WIGNALL.

Hydrogen from water-gas. R. M. EVANS and W. L. NEWTON.—See B., 1926, 698.

Preparation of a chromium carbonyl through the intermediary of a magnesium compound. A. JOB and A. CASSAL (*Compt. rend.*, 1926, 183, 392—394).—When an ethereal solution of magnesium phenyl bromide is added drop by drop to an ether-benzene suspension of chromium chloride in the presence of carbon monoxide maintained below 10°, hydrolysis results. On distilling away the ether, white crystals of chromium carbonyl, Cr(CO)₆, are obtained. The carbonyl is not attacked by hot or cold potassium hydroxide, hydrochloric acid, concentrated sulphuric acid, or bromine, but is attacked immediately by cold fuming nitric acid, forming chromic nitrate and evolving carbon monoxide.

A. E. MITCHELL.

Preparation of colloidal lead. W. STENSTRÖM and M. REINHARD (*J. Biol. Chem.*, 1926, 69, 607—612).—Repetition and extension of the work of Bell (*Brit. Med. J.*, 1926, i, 537) shows that more concentrated and more stable lead sols can be obtained by the use of potassium chloride as a stabilising salt instead of the calcium chloride recommended by him.

C. R. HARRINGTON.

Iodometric determination of chloride and the determination of chloride, bromide, and iodide in the presence of cyanide. R. BERG (*Z. anal. Chem.*, 1926, 69, 1—15).—For the determination of iodide alone or in the presence of chloride and bromide, the solution is treated with 5—10 c.c. of *N*-potassium cyanide solution and then with phosphoric, sulphuric, or hydrochloric acid to an acidity of 30, 15, or 5—10%, respectively. After addition of starch solution, the liquid is titrated at the rate of one drop per second with 0.1*N*-potassium bromate; the reaction is as follows: $\text{HBrO}_3 + 3\text{HI} + 3\text{HCN} = 3\text{CNI} + \text{HBr} + 3\text{H}_2\text{O}$. Bromide is determined in the absence of iodide by a somewhat similar process; the solution is treated with 10 c.c. of *N*-potassium cyanide and hydrochloric acid is added until the solution contains 10—15% of free acid. The 0.1*N*-bromate solution is dropped in slowly until no further yellow colour appears, a mixture of 20 c.c. of 10% aniline hydro-

chloride and 10 c.c. of 0.1*N*-potassium bromide solutions is added, followed by 1 g. of potassium iodide, and the liberated iodine is titrated with thiosulphate. The aniline solution destroys the excess of bromate required to complete the reaction: $\text{HBrO}_3 + 2\text{HBr} + 3\text{HCN} = 3\text{CNBr} + 3\text{H}_2\text{O}$, and the iodine liberated is a measure of the cyanogen bromide formed in the first reaction thus: $3\text{CNBr} + 6\text{HI} = 3\text{I}_2 + 3\text{HBr} + 3\text{HCN}$. The reaction between chloride and bromate in the presence of cyanide takes place only in a strongly acid solution according to the equation $\text{HBrO}_3 + 2\text{HCl} + 3\text{HCN} = 2\text{CNCl} + \text{CNBr} + 3\text{H}_2\text{O}$. The following is the procedure: The chloride solution (20—30 c.c.) is treated with an excess of *N*-cyanide solution (measured exactly) in a glass-stoppered flask and 1:1-sulphuric acid is added to 30% acidity, whereby the temperature rises to 30—35°. Without cooling, 8—10 times the requisite quantity of *N*-bromate solution is added and the flask is kept at 35—40° for 20—30 min. After cooling, the contents of the flask are poured in a thin stream into a mixture of 50—100 c.c. of 10% aniline hydrochloride solution, 10 c.c. of *N*-potassium bromide solution, and 20 c.c. of 1:1-sulphuric acid. The content of cyanogen chloride and bromide formed is then determined by adding potassium iodide (1% of the total volume) and titrating the liberated iodine with thiosulphate. A blank test must be carried out on the same volume of cyanide solution as that used in the analysis, as most samples of commercial cyanide contain small amounts of chloride. For the determination of the three halogens in the presence of each other the iodide is determined by the first of the above methods, and the same solution is used for the determination of the sum of the bromide and iodide by the second method, allowance being made for the bromide introduced in the first titration. In a second portion of the original solution, the sum of the three halides is determined by the third procedure.

A. R. POWELL.

Determination of small quantities of halogen compounds, especially of perchloric acid. F. KÖNIG (*Z. anal. Chem.*, 1926, 68, 385—387).—Perchloric acid is reduced in sulphuric acid solution by boiling with excess of titanous sulphate, the excess oxidised cautiously in the cold by means of ammonium persulphate, and the filtered solution titrated with mercuric nitrate, using sodium nitroprusside as indicator, and employing the Tyndall effect to observe the end-point. Small quantities of bromides, chlorides, cyanides, and thiocyanates may be titrated directly with mercuric nitrate if heavy metals are absent.

S. I. LEVY.

Combined determination of oxygen absorbed and albuminoid ammonia in sewages and effluents. J. W. H. JOHNSON.—See B., 1926, 726.

Analysis of sulphur dioxide in presence of excess of air. E. D. RIESS and L. E. CLARK.—See B., 1926, 706.

Decomposition of standard sodium thio-sulphate solutions. E. SCHULEK (*Z. anal. Chem.*, 1926, 68, 387—397).—Hydrogen sulphide is nearly

always present in thiosulphate solutions, and may be determined colorimetrically by addition of sodium hydroxide and lead acetate. No suitable method was found for the detection of traces of sulphite. Tetra-thionate was determined by the cyanide method, and was always present. Bacteriological examination showed the presence of some twenty different kinds of bacteria; several of these were selected, and cultures added to sterile thiosulphate solutions. Two found to be most powerful caused considerable diminutions in the values of the solutions, with relatively high development of sulphide and tetrathionate.

S. I. LEVY.

Rapid electrolytic determination of tellurium by the use of a reduced potential. J. LUKAS and A. JILEK (Chem. Listy, 1926, 20, 396—403).—For the determination of tellurium in a preparation of the element, 0.3 g. is dissolved by heating with 3 c.c. of concentrated sulphuric acid. The cold solution is diluted with water and 0.5 g. of tartaric acid added, followed by ammonia until neutral to methyl-red; the solution is acidified with 3 g. of malonic acid, cooled to 18°, treated with 10 g. of ammonium sulphate, diluted to 120—150 c.c., and electrolysed with a rotating anode in a platinum dish at 2 volts. The current, originally 0.03—0.09 amp., falls to 0.004—0.007 amp. when the tellurium is completely deposited. Without shutting off the current, the deposit is washed first with water, then with alcohol, dried at 100°, and weighed; it should possess a bright, silvery lustre and be firmly adherent to the dish.

A. R. POWELL.

Electrometric titration of phosphates. S. BODFORSS (Svensk Kem. Tidskr., 1925, 37, 296—300; from Chem. Zentr., 1926, I, 1675—1676).—The volumetric method for the determination of phosphates by titration with a solution of a uranyl salt in presence of acetic acid may be followed potentiometrically. In presence of a small amount of a quadrivalent uranium salt, the equilibrium $\text{UO}_2^{++} + 4\text{H}^+ - 2\text{F}^- \rightleftharpoons \text{U}^{++++} + 2\text{H}_2\text{O}$ is set up and the potential E of the solution with respect to a platinum electrode is given by the formula $E = E_0 + RT/2F \cdot \log_e [\text{UO}_2^{++}][\text{H}^+]^4/[\text{U}^{++++}]$. If the hydrogen-ion concentration remains constant, the potential is altered only when an excess of uranyl salt has been added. In order to obtain a sharper end-point, it is advisable to add quinol or potassium ferrocyanide. A more suitable method is to use a mercury electrode and add a known amount of mercurous sulphate, the titration being carried out at 70°. The fall in voltage at the end-point is extremely sharp. On further addition of uranyl salt, the voltage, after passing through a minimum, increases to an almost constant value. This behaviour is interpreted as resulting from the equilibrium relations involved in the formation and dissociation of a complex mercury uranyl phosphate. The accuracy is of the order 0.3—0.4%.

J. S. CARTER.

Titration of hypophosphorous acid and its salts with permanganate. I. M. KOLTHOFF (Z. anal. Chem., 1926, 69, 36—38).—Titration of neutral or alkaline hypophosphite solutions with permanganate at 100° usually yields slightly high results owing

to partial decomposition of the permanganate (cf. Köszei, this vol., 702). The reaction between hypophosphite and permanganate in acid solution at the ordinary temperature is slow and does not go to completion unless a large excess of the oxidising agent is present. Accurate results may be obtained, however, as follows: The hypophosphite solution is acidified with half its volume of 4*N*-sulphuric acid, treated with about 2.5 times the theoretical quantity of 0.1*N*-permanganate, and set aside over-night in a stoppered flask. The excess of permanganate is then determined iodometrically. A blank test on the reagents is necessary in order to allow for any slight decomposition of permanganate. A similar procedure serves for the determination of various organic acids, alcohols, and sugars, whilst hydrazine and sulphites may be titrated similarly, using an alkaline solution for the oxidation process.

A. R. POWELL.

Effect of cellulose on arsenic determinations. T. J. WARD (Analyst, 1926, 51, 457).—If glass wool be substituted for filter-paper and cotton wool in the purifying tube of the Gutzeit or Marsh arsenic apparatus, the life of the tube may be considerably prolonged, since the small amounts of acid present in the evolved gas cause cellulose to retain arsenic.

D. G. HEWER.

Destruction of filter-papers by alternate oxidising agents applied to quantitative analysis. R. POGGI and A. POLVERINI (Atti R. Accad. Lincei, 1926, [vi], 4, 55—57).—Cellulose is oxidised completely by treatment alternately with nitric acid, *d* 1.5, and with hydrogen peroxide (15 vol.-%) intermediately evaporating to dryness. This enables filter-papers to be used and destroyed in the gravimetric determination of arsenic, in which they may not be burnt.

E. W. WIGNALL.

Detection and colorimetric determination of carbon monoxide. H. KAST and H. SELLE (Gas- u. Wasserfach, 1926, 69, 812—815).—A review of the various methods that have been proposed for the detection and determination of carbon monoxide is given together with comparative data on their limits of sensitivity. Accurate quantitative results are obtained, in the absence of other combustible gases, only by the combustion method. With practice, however, the time required to produce a reaction in a solution of ammonium chloropalladite or of ammoniacal silver nitrate gives a sufficiently accurate idea of the concentration of the gas in the air. Thus, the first visible darkening is noticed in 350 sec., when 100 c.c. of air containing 0.05% of carbon monoxide are shaken with 10 c.c. of the chloropalladite solution, and in 80 sec., when shaken with 10 c.c. of the silver nitrate solution; the corresponding figures for air containing 0.4% of the gas are 50 and 20 sec., and, for air containing 1.6%, 20 and 7 sec., respectively.

A. R. POWELL.

Carbonic acid content of distilled water and its determination. I. M. KOLTHOFF (Chem. Weekblad, 1926, 23, 381—384).—The high values found by titration for the carbonic acid concentration of distilled water are due to improperly neutralised indicators and the slowness with which distilled water

reaches equilibrium with the atmosphere. Water freshly distilled from tap water contains a large excess of carbon dioxide, which does not escape for more than a week; if washed air is drawn through the water, equilibrium is attained in 10 hrs. By calculation, the p_H after titration corresponding with the theoretical concentration of carbon dioxide, $1.5 \times 10^{-5} M$, should be about 8.0; hence the indicator must be neutralised to this point before use. With these conditions, and keeping the flasks and vessels used always full of liquid, the theoretical value is confirmed by titration. This value is so small that it may be neglected for most purposes. S. I. LEVY.

Determination of potassium in the presence and absence of sulphate. M. A. HAMID (Analyst, 1926, 51, 450—453).—The cobaltinitrite method is recommended for general use in the determination of potassium, both in the presence and absence of sulphate. The precipitate was found to be dipotassium monosodium cobaltinitrite monohydrate, $K_2NaCo(NO_2)_6 \cdot H_2O$. Results by this method agree well with those by the perchloric acid method in the absence of sulphate, whilst the perchloric acid method breaks down in the presence of sulphate.

D. G. HEWER.

Gravimetric determination of sodium. E. CREPAZ (Annali Chim. Appl., 1926, 16, 219—224).—Blanchetière's method (A., 1923, ii, 579; Kling and Lassieur, Chim. et Ind., 1924, 12, 1012) involving the precipitation of sodium magnesium uranyl acetate is too inexact for the determination of sodium, but when applied in the presence of alcohol it is of value in the detection of small quantities of sodium in the presence of potassium and magnesium.

R. SANSONE.

Detection of small amounts of silver and cadmium. W. GEILMANN (Z. anorg. Chem., 1926, 155, 192—198).—Silver in ores is detected by microchemical reactions as rubidium silver gold chloride, $Rb_6Ag_2Au_3Cl_{17}$. In 0.1—0.2 g. of ore, 0.005% of silver may be recognised. Cadmium is detected by the dry method of Biewend (Berg- und Hüttenmännische Ztg., 1902, 61, 401). In zinc ores, 0.002% of cadmium could be detected. In glasses, the limit of detection is 0.0002%.

M. CARLTON.

Absence of mirror formation in Vortmann's method of separating silver and lead. G. VORTMANN (Analyst, 1926, 51, 456—457; cf. this vol., 262).—To ensure the absence of a mirror, the liquid should not be heated above 70—80°, and only a slight excess of ammonia should be added after addition of tartaric acid or ammonium tartrate. D. G. HEWER.

Determination of total alkalinity in presence of alkaline earths. R. BÜRSTENBINDER.—See B., 1926, 742.

Determination of zinc as acetate. (Miss) H. J. RAVENSWAAY (Chem. Weekblad, 1926, 23, 375).—Zinc acetate on ignition gives widely varying proportions of residue, and cannot be quantitatively converted into oxide. When the substance is heated in a distilling flask, the condensate collected below 100° contains zinc.

S. I. LEVY.

Oxidation of manganese to permanganate. Application to the determination of manganese. A. TRAVERS (Ann. Chim., 1926, [x], 6, 56—86).—A more detailed account of work already published (this vol., 704).

Colorimetric determination of ferric iron and some remarks on known reactions. H. W. VAN URK (Pharm. Weekblad, 1926, 63, 1101—1107; cf. Heczko, B., 1926, 791).—In the examination of battery acid for iron, a large excess of thiocyanate should be used to compensate for the high concentration of acid. This reaction is somewhat more sensitive than the pyramidone test, and considerably more sensitive than the ferrocyanide test. The ferric thiocyanate may be extracted by means of ether or amyl alcohol, but is insoluble in other organic solvents; the colour is more intense in dry than in moist ether. Oxidation of ferrous to ferric iron is readily accomplished by boiling with potassium persulphate.

S. I. LEVY.

Determination of ferro- and ferri-cyanides. W. M. CUMMING and W. GOOD (J.C.S., 1926, 1924—1928).—Insoluble ferrocyanides may be determined by the gravimetric method previously described, provided the heavy metal is first removed, either as carbonate or sulphide (cf. Cumming, A., 1924, ii, 353). The volumetric method is modified; a measured quantity of standard benzidine dihydrochloride solution is added to a neutral solution of the ferrocyanide after removal of the heavy metal, and the filtrate titrated with standard alkali, using phenolphthalein as indicator: $3[B_2HCl] + M_4Fe(CN)_6 = 3B_2H_4Fe(CN)_6 + 4MCl + 2HCl$. Both methods are applicable to the determination of ferricyanides, provided a large excess of the benzidine dihydrochloride solution is used. In each case, the same sample of salt may be determined both gravimetrically and volumetrically.

S. K. TWEEDY.

Separation of zirconium from titanium. L. MOSER (Z. anal. Chem., 1926, 68, 468).—An acknowledgment of Schröder's correction (this vol., 705) of a statement erroneously made in an earlier paper by Moser and Lessnig (A., 1925, ii, 718).

A. R. POWELL.

Microchemical detection of germanium. E. M. CHAMOT and H. I. COLE (Mikrochem., 1926, 4, 97—102).—Although a large number of organic and inorganic reagents were tried, no characteristic micro-reaction for the detection of germanium was discovered, and only those tests which are available for the detection of silicon (complex fluorine and molybdenum compounds) are practicable for germanium. Since the fluogermanates and germanomolybdates closely resemble the corresponding compounds of several other elements, a preliminary separation is essential. The material to be tested is placed in a small crucible, moistened with concentrated hydrochloric acid, and warmed over a micro-burner. Volatile germanium chloride condenses on a cooled celluloid object-slide covering the crucible and is converted into sodium fluogermanate or rubidium germanomolybdate for microscopical examination. The former compound is obtained by warming the

distillate with sodium chloride and ammonium fluoride. On cooling, crystals begin to appear at the circumference of the drop as hexagonal plates or as skeletal six-pointed stars. Later, hexagonal prisms may appear. The crystals are feebly double-refracting, and since their refractive index is almost that of water, they are seen only with difficulty. The sensitivity is $0.1\text{ }\mu\text{g}$. Rubidium germanomolybdate is obtained by warming with nitric acid and ammonium molybdate, evaporating to dryness twice with nitric acid, dissolving in water, and precipitating with rubidium chloride. Pale yellow octahedral or dodecahedral isotropic crystals are obtained. The sensitivity is $0.02\text{ }\mu\text{g}$. It is obvious that fluorides must be absent from the original material tested, otherwise silicon fluoride may appear in the distillate.

J. S. CARTER.

Detection of vanadic acid by means of hydrogen peroxide. J. MEYER and A. PAWLETTA (Z. anal. Chem., 1926, 69, 15—20).—Vanadic acid dissolves in a solution of hydrogen peroxide, giving a pale yellow solution which appears to contain vanadic acid in a colloidal form; at the same time, the hydrogen peroxide is catalytically decomposed. With sulphuric acid, the yellow solution yields an almost colourless solution containing the compound $(\text{VO})_2(\text{SO}_4)_3$, which is oxidised by hydrogen peroxide to the reddish-brown substance $(\text{VO}_2)_2(\text{SO}_4)_3$. Further, hydrogen peroxide causes the colour to fade to yellow, but the reddish-brown colour is restored by adding more sulphuric acid. These changes are due to hydrolysis according to the scheme: $(\text{VO}_2)_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{VO}_2(\text{OH})_3 + 3\text{H}_2\text{SO}_4$. In concentrated sulphuric acid solution, however, hydrogen peroxide reduces vanadic acid to vanadyl sulphate. In view of these results, the most satisfactory procedure for detecting and determining vanadium by the colorimetric method is as follows: The alkaline solution obtained by fusion is treated with sufficient sulphuric acid to give a 15—20% solution of the acid and, after a short time, 3% hydrogen peroxide is added drop by drop until the colour ceases to increase in intensity. In this way, 1 part of vanadium may be detected in 160,000 parts of solution.

A. R. POWELL.

Action of potassium iodide on vanadophosphoric acid. T. HECZKO (Z. anal. Chem., 1926, 68, 461—468).—A solution of vanadic acid in phosphoric acid reacts with potassium iodide with the liberation of iodine and reduction of the vanadium from the quinquevalent to the quadrivalent form. For every 0.1 g. of vanadic acid, 7 c.c. of 83% phosphoric acid are required for solution; after heating gently for a few minutes, the liquid is cooled, diluted with 3—4 times its volume of water, and treated with an excess of potassium iodide. The liberated iodine is titrated with 0.1N-thiosulphate solution. The method is adapted to the determination of very small quantities of vanadium.

A. R. POWELL.

Determination of antimony by electrolysis in hydrochloric acid solution. A. SCHLEICHER [with L. TOUSSAINT and P. H. TROQUAY] (Z. anal. Chem., 1926, 69, 39—47).—The deposit of metallic antimony obtained by electrolysis of a solution

of the chloride in 1—1.5N-hydrochloric acid, maintaining a cathode potential of 0.28—0.35 volt against the normal calomel electrode, always contains chlorine, the amount varying from 0.04 mg. for a deposit weighing 0.05 g. to 0.77 mg. for a deposit weighing 0.5 g. No hydrogen or antimony hydride appears to be adsorbed by the metal, but a minute trace of the hydride is evolved at the end of the electrolysis if the cathode potential is allowed to rise above 0.5 volt. When hydrazine sulphate is used as the anode depolariser, only slightly more than the theoretical quantity required to combine with the liberated chlorine, i.e., 0.2 g. for 0.2 g. of antimony, is required, provided that the solution is thoroughly stirred by mechanical means. Addition of ammonium persulphate towards the end of the electrolysis is recommended to guard against loss of antimony as hydride; no reaction takes place between the hydrazine sulphate and the ammonium persulphate. Engelenburg's modification of Classen's method is recommended as a standard procedure (cf. A., 1923, ii, 260).

A. R. POWELL.

X-Ray spectrograph. J. T. NORTON (J. Opt. Soc. Amer., 1926, 13, 231—233).—An X-ray spectrograph of the rotating crystal type is described. It is of simple construction, is easy to set up, and gives results of considerable precision.

A. B. MANNING.

High-vacuum X-ray spectrometer. M. SIEGBAHN and R. THORÆUS (J. Opt. Soc. Amer., 1926, 13, 235—242).—The details of construction and method of operation of a vacuum X-ray spectrometer are described. The spectrometer and X-ray tube are mounted together, and can be evacuated to the same low pressure. The plate holder can be turned to make any desired angle with the tube up to 35° while still maintaining the vacuum. The required range of wave-lengths, using reflexion angles not exceeding 35° , is obtained by choosing suitable crystal gratings, e.g., calcite up to $3.5\text{ }\text{\AA}$, mica up to $11.0\text{ }\text{\AA}$, and palmitic acid up to $40.0\text{ }\text{\AA}$.

A. B. MANNING.

Direct-reading ionisation gauge. C. F. FOUND and N. B. REYNOLDS (J. Opt. Soc. Amer., 1926, 13, 217—222; cf. A., 1924, ii, 586).—An ionisation gauge is described which can be operated directly from a 125 volt supply, and is independent of small fluctuations in the voltage. The electron current to the grid of the three-electrode tube forming the gauge is automatically maintained constant at 10 milliamps. The voltage drop across a high resistance in the plate circuit, which is proportional to the positive ionisation current, is amplified by a "push-pull" amplifier circuit, the plate current in which is recorded by a milliammeter. The milliammeter reading is then directly proportional to the pressure in the gauge.

A. B. MANNING.

Simple spectral apparatus of high light intensity. I. Spectral photography of weak luminescence phenomena. K. SCHAUM and W. KRAEMER (Z. wiss. Phot., 1926, 24, 219—223).—A Seibert direct-vision spectroscope was provided with a specially calculated two-lens achromat of aperture 0.07 as collimator and a three-lens achromat of aperture 0.11 as resolving objective, and with a

small camera. The luminescence of vapours was studied, at atmospheric pressure, in a Kauffmann "elektrisor" (ozoniser) (Z. physikal. Chem., 1898, 26, 719; 1899, 28, 673), using a Tesla discharge, and at low pressures in a Tesla tube using a high-frequency field. A Geissler tube could not be used owing to rapid decomposition of the substances studied. Observed lines and bands are tabulated for aniline, dimethylaniline, α -naphthylamine, *o*-phenetidine, and "tetralin" in the "elektrisor," and for aniline, dimethylaniline, and α -naphthylamine in the Tesla tube.

W. CLARK.

Lens-polariscopes. H. SCHULZ (Z. tech. Physik, 1925, 6, 614—618; from Chem. Zentr., 1926, I, 1674—1675).—The substitution of lenses for prisms in polariscopes is recommended. Using lenses of calcite, observations may be made in the ultra-violet region. By using a combination of a calcite and a glass lens the relation of focal length for the ordinary and extraordinary rays can be adjusted to have any value, and a system suitable for a variety of purposes obtained.

J. S. CARTER.

Stirring apparatus for use in potash analysis according to the tartaric acid method of Przibylla. G. MÜLLER (Kali, 1926, 20, 31; from Chem. Zentr., 1926, I, 1859).—The individual stirrers are arranged in a circular fashion round a central driving pulley under such conditions that each stirrer may be used at will. The solutions are contained in wide-necked, weighted flasks of about 160 c.c. capacity which stand in two semi-circular water-baths.

J. S. CARTER.

Weighing by hydrostatic compensation. M. GUICHARD (Bull. Soc. chim., 1926, [iv], 39, 1113—1115; cf. A., 1925, ii, 427).—A balance is described in which the pan which normally carries the weights is replaced by a plunger dipping into a vessel of oil. By means of an attached burette, the amount of oil can be regulated so that the apparent weight of the plunger balances a body placed in the other pan. After the balance has been once calibrated, the weight required can be determined from the burette reading. Such a balance is dead-beat.

R. CUTHILL.

Improvement in MacMullin's automatic apparatus for determining the m. p. of organic compounds. H. F. PALMER and G. H. WALLACE (J. Amer. Chem. Soc., 1926, 48, 2230—2232; cf. this vol., 593).—An arrangement is described whereby the

maximum thermometer is raised automatically from the bath at the moment the substance melts.

F. G. WILLSON.

Differential method for the measurement of the vapour pressure of liquids. V. G. JOLLY and H. V. A. BRISCOE (J.C.S., 1926, 2154—2159).—The liquid is contained in a sealed U-tube the limbs of which are maintained at different constant temperatures. The liquid itself behaves as the manometer liquid, and from a knowledge of the vapour pressure at one temperature the values at other temperatures are readily obtained. The method, which may be used in dealing with intensively dried liquids, has the advantage that the presence of a foreign gas is not involved (cf. Campbell, A., 1915, ii, 516). The vapour pressures of water, benzene, and bromine are recorded; the values for bromine agree well with those of Ramsay and Young (J.C.S., 1886, 49, 453).

S. K. TWEEDY.

Ignition of firedamp by momentary flames. N. S. WALLS and R. V. WHEELER.—See B., 1926, 730.

Ignition of firedamp by momentary flames. W. RINTOUL and A. G. WHITE.—See B., 1926, 730.

Laboratory electric furnace for temperatures up to 1400°. S. REINER (Chem.-Ztg., 1926, 50, 578).—A simple furnace formed by placing suitably shaped blocks of refractory material about an iron or quartz tube is described.

S. I. LEVY.

Apparatus for production of gases. H. HERBST (Chem.-Ztg., 1926, 50, 579).—A cylinder containing the solid reagent is provided with a side tube sealed on near the bottom, and connected to a higher level vessel for the liquid reagent, the latter vessel being provided with a seal. The cylinder has a stopper carrying a three-way cock, which delivers the gas directly as required, or to a graduated measuring vessel provided with a pressure-equalising connexion.

S. I. LEVY.

Earliest human knowledge of copper. P. E. SPIELMANN (Nature, 1926, 118, 411).—Where copper and petroleum occur in close proximity (as in the Caucasus, whence the earliest Egyptian immigrants may have come), ignition of the oil would produce metallic deposits liable to early discovery and use.

A. A. ELDRIDGE.

Mineralogical Chemistry.

Phosphate content of sea water in relation to the growth of the algal plankton. III. W. R. G. ATKINS (J. Mar. Biol. Assoc., 1926, 14, 447—467).—The maximum concentration of phosphate as P_2O_5 in the English Channel is 40 mg. per cub. m. and the minimum 5.1 mg. for the depth 0—70 m. The deep water of the ocean is a reservoir of phosphate, containing 50—80 mg. per cub. m. In tropical waters, the intense light normally results in the utilisation of all phosphate down to at least 50 m. and the winter

cooling never suffices to effect mixing with the deep water; further north, the mixing is more complete, and the seasonal phosphate cycle becomes more pronounced (cf. this vol., 42).

W. THOMAS.

Precipitation of calcium and magnesium from sea water. L. IRVING (J. Mar. Biol. Assoc., 1926, 14, 441—446).—Calcium and magnesium may be precipitated under possible conditions of natural sea-water alkalinity. The same conditions governing

precipitation outside of the organism may explain the excess of calcium over magnesium in organic "formed" precipitates, as alkalinity necessary for magnesium precipitation is much more difficult for the organism to attain, especially within its tissues.

W. THOMAS.

Occurrence of iodine in Nature. X. **Geochemistry of iodine.** T. VON FELLEBERG and G. LUNDE (Biochem. Z., 1926, 175, 162—171).—The amounts of iodine and bromine contained in various rocks and minerals are tabulated.

P. W. CLUTTERBUCK.

Cornuite. F. V. VON HAHN (Zentr. Min. Geol., 1925, A, 353—356; from Chem. Zentr., 1926, I, 1787—1788).—The green diatomite of Neu-Ohe contains inclusions of an amorphous, transparent yellow mineral to which the name cornuite is given. The mineral contains about 97% of water and 0.08% of ash, and appears to be a protein, since it gives a number of reactions characteristic of albumin.

W. A. CASPARI.

Lead hydrogen arsenate as a mineral. L. J. SPENCER (Nature, 1926, 118, 411—412).—Colourless monoclinic plates ($a:b:c=0.8643:1:0.7181$, $\beta=84^\circ 36'$) from Tsumeb, South-West Africa, were found to have the composition PbHAsO_4 . They are identical with the crystals prepared by de Schulten (A., 1905, ii, 174), and the new mineral is named "schultenite."

L. J. SPENCER.

Stibiobismuthinite. E. QUERCIGH (Atti R. Accad. Lincei, 1926, [vi], 4, 68—72).—Koenig (A., 1917, ii, 487) described stibiobismuthinite as a new mineral $(\text{Bi,Sb})_4\text{S}_7$. Artificial preparations of antimony and bismuth sulphides by the method of Geitner (Annalen, 1864, 129, 359) contain included sulphur, as do mixed sulphides $(\text{Bi,Sb})_2\text{S}_3$, to which type it is suggested that the mineral belongs.

E. W. WIGNALL.

New Russian occurrence of vanadium and uranium minerals. S. KURBATOV (Bull. Acad. Sci. St. Pétersbourg, 1925, 315; from Chem. Zentr., 1926, I, 1789).—A yellow mineral containing about 33% of vanadium pentoxide, 52% of cupric oxide, and 0.59% of uranium oxide occurs near copper mines in Minusinsk. The mineral consists of a mixture of calcium volborthite with allophane, opal, and brown hæmatite.

W. A. CASPARI.

Pectolites from Russian Lapland. E. KOSTY-LEVA (Bull. Acad. Sci. St. Pétersbourg, 1925, 383; from Chem. Zentr., 1926, I, 1788).—Three specimens of pectolite from the Chibinsk Tundra contained 49.00—53.80% SiO_2 , 0.68—2.06% Al_2O_3 , 0.95—1.39% Fe_2O_3 , 32.04—32.46% CaO , 0.55—2.17% MnO , 1.09% MgO , 7.38—8.99% Na_2O , 0.53—0.60% K_2O , and 2.85—4.08% of water. A new mineral, *juxporite*, $(\text{HNaK})_2(\text{CaMgMn})\text{SiO}_3$, is found accompanying the above; it forms pink fibres and scales of silky lustre, fusible in the blowpipe.

W. A. CASPARI.

Organic Chemistry.

Thermal decomposition of methane by a glowing filament. G. M. SCHWAB and E. PIETSCH.—See this vol., 918.

Production of propylene. L. J. BONHAM (J. Amer. Pharm. Assoc., 1925, 14, 114—118).—*n*-Propyl alcohol, b. p. 96—98°, is vaporised in a glycerol bath at 125—130° and passed through a hard glass tube containing a catalyst prepared by precipitating aluminium hydroxide from the sulphate with ammonia, washing by decantation until free from ammonium sulphate, drying in pans at 80—90°, and breaking into pellets which were subsequently dried in a slow stream of air at 510°. At 510°, 25 c.c. of the alcohol gave 8200 c.c. of gas; at 365°, the product was purer and the catalyst could be used repeatedly. On regeneration of the catalyst, then containing carbon, by heating for 30 min. at a high temperature, it exhibited increased activity, and the product was purer.

CHEMICAL ABSTRACTS.

Photolysis of alcohols. VOLMAR.—See this vol., 920.

Formation of carbon dioxide from alcohols. W. A. LAZIER and H. ADKINS.—See this vol., 918.

Mechanism of the catalytic dehydration of methyl alcohol. H. C. HOWARD, jun.—See this vol., 918.

Synthetic manufacture of alcohol and acetic acid [and acetone]. P. PASCAL.—See B., 1926, 767.

Action of sodium acetate on isobutylene dibromide and trimethylethylene dibromide. K. KRASSOORSKY and F. SCHENDEROWITCH (Ukraine Chem. J., 1925, 1, 633—637).—On heating isobutylene dibromide for 3 hrs. with acetic acid and sodium acetate, 33% of the theoretical quantity of isobutenyl acetate, $\text{CH}_2:\text{CMe}\cdot\text{CH}_2\cdot\text{OAc}$, b. p. 120—123°, was obtained.

Trimethylethylene dibromide treated in the same way gave β -methyl- Δ^2 -buten- γ -yl acetate, $\text{CMe}_2\cdot\text{CMe}\cdot\text{OAc}$, b. p. 133—139°. It probably contains some of the isomeric acetate, $\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{OAc}$.

S. BOTCHARSKY.

Natural methylheptenone. II. **Alcohols, dienes, and cyclogeraniolones.** I. R. ESCOURROU (Bull. Soc. chim., 1926, [iv], 39, 1121—1138).—Natural methylheptenone, b. p. 173—174°, d^{20}_4 0.8691, n^{20}_D 1.44345, prepared from citral, gives good yields of tertiary alcohols when treated with magnesium alkyl halides. The following are obtained in this way: β -dimethyl- Δ^2 -hepten- ζ -ol, b. p. 77—78°/13 mm., d^{10}_4 0.8564, n^{10}_D 1.45197 (acetate, b. p. 184—186°/740 mm., d^{11}_4 0.883, n^{11}_D 1.44235); β -dimethyl- Δ^2 -octen- ζ -ol, b. p. 92.5°/13 mm., d^{17}_4 0.8572, n^{15}_D 1.45658 (acetate, b. p. 214°/738 mm., d^{12}_4 0.8841, n^{15}_D 1.44606); [β -di-

methyl- Δ^8 -nonen- ζ -ol, b. p. 102—103°/13 mm., d^{20}_4 0.8592, n^{20}_D 1.45727 (acetate, b. p. 112—113°/13 mm., d^{20}_4 0.8863, n^{20}_D 1.45247); $\beta\zeta\eta$ -trimethyl- Δ^8 -octen- ζ -ol, b. p. 97—98°/12 mm., d^{20}_4 0.8717, n^{20}_D 1.46295; $\beta\zeta$ -dimethyl- Δ^8 -decen- ζ -ol, b. p. 95—96°/5 mm., d^{20}_4 0.8603, n^{20}_D 1.45997 (acetate, b. p. 122—123°/13 mm., d^{20}_4 0.8903, n^{20}_D 1.45177); $\beta\zeta$ -trimethyl- Δ^8 -decen- ζ -ol, b. p. 123—124°/14 mm., d^{20}_4 0.8566, n^{20}_D 1.45657; ζ -phenyl- β -methyl- Δ^8 -hepten- ζ -ol, b. p. 155—156°/19 mm., d^{20}_4 0.9679, n^{20}_D 1.52316; β -methyl- ζ -benzyl- Δ^8 -hepten- ζ -ol, b. p. 153—154°/10 mm., d^{20}_4 0.9654, n^{20}_D 1.52632. On redistillation, and especially if a trace of acid be present, these alcohols tend to decompose, yielding methylheptenone and the hydrocarbon corresponding with the alkyl radical present in the original magnesium alkyl halide. R. W. WEST.

Ethers derived from $\beta\beta'$ -dihalogenated *iso*-propyl alcohols and halogenated propylene glycols. L. BLANCHARD (Bull. Soc. chim., 1926, [iv], 39, 1119—1121).—A mixture of trioxymethylene and $\alpha\alpha'$ -dichlorohydrin, saturated with hydrogen chloride, yields *chloromethyl dichloroisopropyl ether* $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$, b. p. 95—96°/17 mm. (cf. Hamonet, A., 1905, i, 403). In similar manner, α -monochlorohydrin yields the *ether*, $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{CH}_2\text{Cl})\cdot\text{CH}_2\text{Cl}$. These substances react with magnesium alkyl halides, yielding ethers of the type $>\text{CH}\cdot\text{O}\cdot\text{CH}_2\text{R}$ (cf. Hess and Fink, A., 1916, i, 158). R. W. WEST.

Addition of methyl hypobromite and methyl hypochlorite to certain ethylene derivatives. E. L. JACKSON (J. Amer. Chem. Soc., 1926, 48, 2166—2174; cf. A., 1924, i, 962).—The presence of water is unnecessary for the addition of methyl hypobromite to ethylene derivatives when their methyl-alcoholic solutions are treated with bromine. In absolute methyl-alcoholic solution, phenyl styryl ketone yields in this way α -bromo- β -methoxy- β -phenylpropionophenone, together with ketone dibromide; cinnamic acid affords methyl esters of the corresponding additive products, which are also obtained similarly from methyl cinnamate; whilst stilbene yields stilbene dibromide and α -bromo- β -methoxy- $\alpha\beta$ -diphenylethane, m. p. 115.5—116.5°. The action of bromine on cinnamic acid in 50% aqueous methyl-alcoholic solution brings about the simultaneous addition of bromine, hypobromous acid, and methyl hypobromite. Treatment of phenyl styryl ketone in absolute methyl alcohol with chlorine affords two isomerides of α -chloro- β -methoxy- β -phenylpropionophenone, m. p. 69—70° and 98—99°, respectively, the former predominating. Cinnamic acid affords similarly the dichloride, together with α -chloro- β -methoxy- β -phenylpropionic acid, m. p. 163—164°, and its methyl ester, m. p. 54—55°, the latter being obtained analogously from methyl cinnamate. Reaction between chlorine, cinnamic acid, and methyl alcohol proceeds similarly, but less smoothly, in carbon tetrachloride solution. Treatment of stilbene with chlorine in methyl-alcoholic solution affords two isomerides of α -chloro- β -methoxy- $\alpha\beta$ -diphenylethane, m. p. 96—97° and 55—57°, respectively, together with stilbene dichloride. An analogous reaction with iodine was not observed.

F. G. WILLSON.

Varying valency of platinum with respect to mercaptanic radicals. III. P. C. RÂY, B. C. GUHA, and K. C. BOSE-RÂY (J. Indian Chem. Soc., 1926, 3, 155—160; cf. A., 1925, ii, 1121).—The molecular compound of platinous chloride and ethyl sulphide is decomposed by ammonia with formation of tetrammineplatinous dichloride, whilst pyridine yields a mixture of the corresponding tetrapyridine compound with the non-electrolyte dipyridine-platinous chloride. The same platinotetrammine is produced by the action of ammonia on the compound $\text{PtCl}_3\cdot 2\text{Et}_2\text{S}$. The platinic chloride compound $\text{PtCl}_4\cdot 2\text{Et}_2\text{S}$ is decomposed by ammonia, yielding tetramminedichloroplatinic dichloride and by pyridine to give dipyridinetetrachloroplatinum.

G. M. BENNETT.

Triethylene trisulphide and 1:4-dithian. P. C. RÂY and K. C. BOSE-RÂY (J. Indian Chem. Soc., 1926, 3, 73—74).—The identification of "triethylene trisulphide" with 1:4-dithian (cf. Bennett and Berry, A., 1925, i, 695) is confirmed, but the authors prefer, notwithstanding the evidence as to the mol. wt. of the substance both in solution and as vapour, to retain the formula $(\text{C}_2\text{H}_4\text{S})_3$, mainly on the ground of the isolation of a compound, $(\text{C}_2\text{H}_4)_3\text{S}_2\text{PtCl}_3$, by the action of aqueous platinic chloride solution.

G. M. BENNETT.

Lengthened chain compounds of sulphur. P. C. RÂY and K. C. BOSE-RÂY (J. Indian Chem. Soc., 1926, 3, 75—80).—The "polymeride" of dithian prepared as described by V. Meyer (A., 1887, 228) is found to contain substances of high mol. wt. of the general formula $\text{Br}(\text{C}_2\text{H}_4\text{S})_n\cdot\text{C}_2\text{H}_4\text{Br}$ isolated by extraction with solvents such as nitrobenzene. The following compounds are described: $n=48$, m. p. 163°; $n=40$, m. p. 170°; $n=32$, m. p. 157—159°; $n=26$, m. p. 145—155°; $n=24$, m. p. 147°; $n=16$, m. p. 162°; $n=12$, m. p. 100°; and $n=10$, m. p. 120°. The mol. wt. of the first of these ($n=48$) in boiling ethylene dibromide is half that expected, the reason suggested being that the solvent reacts with the substance to yield the compound having $n=24$.

G. M. BENNETT.

Action of aluminium selenide, telluride, and arsenide and of magnesium arsenide on alcohols and ethers. G. NATTA (Giorn. Chim. Ind. Appl., 1926, 8, 367—370).—Analogues of alkyl mercaptans, sulphides, and disulphides are obtained by passing the vapour of alcohols over analogues of aluminium sulphide heated at 250—300° (cf. A., 1924, i, 952). Aluminium selenide (prepared without explosion if the mixed elements are ignited by a hot wire; cf. Chikashige and Aoki, A., 1918, ii, 114) gives, with ethyl alcohol, ethyl selenol, selenide, and diselenide; with isopropyl alcohol, isopropyl selenol, b. p. 70—75°, accompanied at higher temperatures with isopropyl diselenide, b. p. 210°, and some isopropyl selenide. Ethers react less readily than alcohols: ethyl ether yields ethyl diselenide and selenide, with hydrogen selenide and unsaturated hydrocarbons. Aluminium telluride with methyl alcohol gives dimethyl telluride and with ethyl alcohol perhaps ethyl telluro; ethers scarcely react at their decomposition point. Aluminium arsenide gives with methyl alcohol trimethyl-

arsine, some dimethylarsine, and a black substance, probably $(\text{CH}_3\text{As})_x$ (cf. A., 1906, i, 150). With ethyl alcohol, an analogous substance, perhaps $(\text{C}_2\text{H}_5\text{As})_x$, is obtained, but at temperatures giving stable products the reaction is very feeble. Magnesium arsenide, prepared in a very violent reaction on igniting the mixed elements, reacts with ethyl alcohol at the b. p. to give arsine and organo-magnesium compounds, and at 280–295° to give ethyl- and diethyl-arsine, with a trace of triethylarsine. E. W. WIGNALL.

Determination of the mol. wt. of fatty acids. M. TRAUTZ and W. MOSCHEL.—See this vol., 997.

Diagnosing potential optical activity. II. Optical activity of chlorobromoacetic acid. J. READ and A. M. McMATH (J.C.S., 1926, 2183–2191).—Chlorobromomalonic acid, m. p. 83° (cf. Vanderstichele, *ibid.*, 1923, 123, 1225), is produced by the successive action of bromine and sulphuryl chloride on a solution of malonic acid in anhydrous ether; the normal *brucine* salt and *brucine hydrogen* salt, $[\alpha]_D^{20}$ –15.2°, are described. When heated at 130°, chlorobromomalonic acid is converted quantitatively into chlorobromoacetic acid, which can be resolved into optically active components by crystallisation of the *l*-hydroxyhydrindamine salt. *l*-Hydroxyhydrindamine *dl*-chlorobromoacetate has m. p. 165° (decomp.), $[\alpha]_D^{20}$ –20.2° in dry methyl alcohol, –56° in acetone (with slow mutarotation). *l*-Hydroxyhydrindamine *d*-chlorobromoacetate, m. p. 157° (decomp.), is readily racemised when dissolved in methyl alcohol or acetone; the racemising action of methyl alcohol is somewhat retarded by dilution with chloroform, transformation to the *dl*-compound occurring on heating. *l*-Hydroxyhydrindamine *dichloroacetate* has m. p. 139°, $[\alpha]_D^{20}$ –24.6° in methyl alcohol, $[\alpha]_D^{20}$ –24.7° in glacial acetic acid, $[M]_D^{20}$ –195° in acetone, with slow mutarotation. *Brucine chlorobromoacetate* has $[\alpha]_D^{20}$ –17.0° in chloroform. C. J. STILL.

Kinetics of chemical reactions. IV. Velocity equation of the hydrolytic decomposition of α -bromopropionic acid. V. α -Bromobutyric acid. J. ZAWIDZKI.—See this vol., 914.

Higher aliphatic compounds. II. Hydration of stearolic acid. G. M. ROBINSON and R. ROBINSON (J.C.S., 1926, 2204–2209).—*l*-Ketostearic acid has been synthesised by an application of the method previously described. By reference to the f.-p. curve for mixtures of *l*-ketostearic and *k*-ketostearic acids, it is shown that the product obtained by treating stearolic acid with sulphuric acid and then with water consists of a mixture of 42.4% of *l*-ketostearic acid and 57.6% of *k*-ketostearic acid. *8-Ketomyristic acid*, m. p. 87° (*oxime*, m. p. 74°), *k*-ketononadecic acid, m. p. 86–87° (*amide*, m. p. 83°), and *k*-ketobehenic acid, m. p. 94° (*amide*, m. p. 99°), are described. C. J. STILL.

Configurational relationships of α -, β -, and γ -hydroxy-acids. P. A. LEVENE and H. L. HALPER (J. Biol. Chem., 1926, 69, 165–173; cf. this vol., 597).—Methyl *d*- β -hydroxybutyrate, $[\alpha]_D^{25}$ +8.6°, on reduction with sodium and glacial acetic acid gave *d*- $\alpha\gamma$ -dihydroxybutane, $[\alpha]_D^{25}$ +7.5°, which, in turn, gave the *d*- $\alpha\gamma$ -diphenylcarbamate, $[\alpha]_D^{25}$ +20°. *d*- γ -Hydroxy-

valeric acid, $[\alpha]_D^{25}$ +14.0°, yielded, by the method of Hofmann, *d*- α -amino- γ -hydroxybutane (hydrochloride, $[\alpha]_D^{25}$ +13.3°), which, on deamination, gave *d*- $\alpha\gamma$ -dihydroxybutane. *d*- γ -Hydroxyvaleric acid is therefore related configuratively to *d*- β -hydroxybutyric acid and hence to *d*-lactic acid. C. R. HARRINGTON.

Hydrolysis of ethyl acetoacetate by acids. A. SKRABAL and A. ZAHORKA.—See this vol., 914.

Configuration changes in substitution reactions. W. HÜCKEL (Z. angew. Chem., 1926, 39, 842–851).—In an endeavour to determine which type of structure influences the configuration changes, in the sense of causing the Walden inversion, when substitution is effected in a group not directly attached to the asymmetric carbon atom, the author reviews a large number of reactions in which these changes take place. As a result, it appears that inversion almost invariably occurs when the molecule contains a $\cdot\text{CH}\cdot\text{C}\cdot\text{O}$ group, the first carbon atom of which is asymmetric. This is particularly noticeable in the case of *cis-trans*-isomerides containing double linkings. Substitution reactions involving hydrolysis of the $\text{C}\cdot\text{O}$ group, when the carbon atom is asymmetric, usually result in configuration changes, although the asymmetric atom is apparently undisturbed. In certain other cases, racemisation of an optically active substance is effected by substitution in a position very remote from the asymmetric atom, e.g., hydrogenation of optically active ricinoleic acid with the formation of inactive hydroxystearic acid. The author considers that reactions of this type need further investigation to determine whether true racemisation takes place or whether the product is really only very slightly optically active. A. R. POWELL.

Derivatives of ethyl β -aceto- α -methylsuccinate; constitution of hæmatoporphyrin. W. KÜSTER, H. MAURER, and A. PALM (Z. physiol. Chem., 1926, 156, 1–34; cf. A., 1925, i, 992; this vol., 713).—A detailed account of work already published. The following is new. Oxidation of hæmatoporphyrin dimethyl ether, which has previously been reduced with zinc dust and acetic or hydrobromic-acetic acid, still gives only 1 mol. of the imide, $\text{C}_8\text{H}_{11}\text{O}_3\text{N}$, and 2 mols. of hæmamic acid, one pyrrole nucleus of the prosthetic group being destroyed. Ethyl hydrogen β -aceto- α -methylsuccinate, m. p. 66–67° (silver salt) and *barium* β -aceto- α -methylsuccinate are described. $\alpha\gamma$ -Dimethylparaconic acid (Fichter and Rudin, A., 1904, i, 472) when brominated with phosphorus and bromine and then boiled with water, gives the *lactone*, m. p. 110° (indef.), of hydroxydimethylitaconic (β -hydroxy- Δ^5 -pentene- $\gamma\delta$ -dicarboxylic) acid (fumaroid). Reduction of ethyl β -aceto- α -methylsuccinate with sodium amalgam in the cold gives ethyl hydrogen α -methyl- β -(α -hydroxyethyl)succinate, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, m. p. 81°, from which α -methyl- β -(α -hydroxyethyl) succinic acid, m. p. 105°, is obtained on hydrolysis. C. HOLLINS.

Synthesis of triacetolactone-5-carboxylic acid. R. MALACHOWSKI (Rocz. Chem., 1926, 6, 23–26).—Ethyl γ -acetylacetone- $\alpha\gamma$ -dicarboxylate, b. p. 120–122°/5 mm. (copper salt, m. p. 124.5–125.5°), is prepared from the potassium salt of acetonedicarboxylic acid.

oxylic ester by the action of acetyl chloride. This is converted by hydrolysis into the γ -ethyl ester, m. p. 96—98° (decomp.), which is condensed by sulphuric acid to *ethyl triacetolactone-5-carboxylate*, m. p. 63—65° (copper salt, m. p. 182°), and this on hydrolysis yields triacetolactone-5-carboxylic acid, m. p. 180° (pyridine salt, m. p. 117—118°). R. TRUSZKOWSKI.

Oxidation of tartaric acid by solutions of silver salts. D. R. MAXTED (J.C.S., 1926, 2178—2182).—When tartaric acid is oxidised with an excess (6—8 mols.) of silver nitrate in ammoniacal solution, 6 atoms of silver are deposited for each molecule of tartaric acid. Oxalic acid, formic acid, carbon dioxide, and water are formed in quantities agreeing with the equations: $C_4H_6O_6 + 3Ag_2O \rightarrow (a) 2(CO_2H)_2 + 6Ag + H_2O$; $(b) (CO_2H)_2 + H \cdot CO_2H + CO_2 + 6Ag + H_2O$; $(c) 2H \cdot CO_2H + 2CO_2 + 6Ag + H_2O$.

The proportion of oxalic acid is increased when the solution is more alkaline. C. J. STILL.

Complex bismuthotartrates. R. PORTILLO (Anal. Fís. Quím., 1926, 24, 420—431; cf. this vol., 939).—By dissolving bismuthoditartaric acid, $H[Bi(C_4H_4O_6)_2] \cdot 3H_2O$, in hot, dilute sulphuric acid, a crystalline compound is obtained to which the formula $H_2[BiC_4H_2O_6] \cdot 0.5H_2SO_4 \cdot 3H_2O$ is assigned. By a similar method, the author has prepared the compounds: $H_2[BiC_4H_2O_6]Cl \cdot 3H_2O$; $H_2[BiC_4H_2O_6]ClO_4 \cdot 4H_2O$; $H_2[BiC_4H_2O_6]NO_3 \cdot 5H_2O$; $H_2[BiC_4H_2O_6]NO_3 \cdot 8H_2O$. Except in the case of the chlorine compound, the combined water is completely given up in a vacuum over sulphuric acid. In the case of the second compound, the combined water is only given up with decomposition above 120°. G. W. ROBINSON.

Natural occurrence of aconitic acid and its isomerides. O. A. BEATH (J. Amer. Chem. Soc., 1926, 48, 2155—2158).—Samples of aconitic acid obtained from six species of delphiniums, from two species of *Aconitum*, and from the *columbianum*, had m. p. 172—173° in each case, identical with that of commercial aconitic acid. The m. p. was unchanged after esterification and hydrolysis. It is concluded that these acids are identical with the acid of the same m. p. described by Bland and Thorpe (J.C.S., 1912, 101, 1490), and that the variations in m. p. recorded for naturally occurring aconitic acids are due to the samples being mixtures of isomerides.

F. G. WILLSON.

Structure of lactones from simple sugars. Trimethyl- γ -arabonolactone and the supposed β -gluconolactone and β -mannolactone. W. N. HAWORTH and V. S. NICHOLSON (J.C.S., 1926, 1899—1902).—Trimethyl- γ -arabinolactone, prepared from the γ -arabonolactone obtained by oxidation of *l*-arabinose, is identical with the product previously prepared by oxidation of trimethyl- γ -arabinose with nitric acid, thus confirming the presence of the butylene oxide ring in trimethyl- γ -arabinose. The unstable β -gluconolactone and β -mannolactone described by Nef (A., 1914, i, 490) are in reality δ -lactones containing a six-membered ring corresponding with the normal or amylenoxide type.

C. J. STILL.

Lactone formation from gluconic acids and the structure of dextrose. P. A. LEVENE and H. S. SIMMS (J. Biol. Chem., 1926, 68, 737—749).—Gluconic and $\beta\gamma$ -dimethylgluconic acids, on keeping in aqueous solution, form lactones with both five- and six-membered rings; $\gamma\epsilon\zeta$ -trimethylgluconic acid forms only one lactone with a five-membered ring, whilst $\beta\gamma\delta$ -trimethyl- and $\beta\gamma\delta\zeta$ -tetramethylgluconic acids each form only one lactone with a six-membered ring; since the last two acids were derived from methylglucoside and the $\gamma\epsilon\zeta$ -trimethylgluconic acid was derived from diisopropylidene-glucose, it appears that the ring structure of the derivatives of dextrose does not indicate the structure of dextrose itself. In the present series of acids, the rates of lactone formation and hydrolysis are higher, and the equilibria are situated more to the acid side than in the series previously described. C. R. HARRINGTON.

Optical resolution of chlorosulphoacetic acid. J. READ and A. M. McMATH (J.C.S., 1926, 2192—2198).—By fractional crystallisation of the normal salt of chlorosulphoacetic acid with *l*-hydroxyhydrindamine, there is obtained *l*-hydroxyhydrindamine *d*-chlorosulphoacetate, m. p. 203° (decomp.), $[\alpha]_D -18.0^\circ$ in methyl alcohol. *Brucine d*-chlorosulphoacetate has m. p. 196° (slight decomp.), $[\alpha]_D -2^\circ$ in methyl alcohol; *ammonium d*-chlorosulphoacetate, $[\alpha]_{5461} +16.3^\circ$, $[\alpha]_D +13.8^\circ$, rotatory dispersion Hg_{5461}/Na_D 1.177 in water; *benzidine d*-chlorosulphoacetate, decomp. 245°, $[\alpha]_{5461} +15.7^\circ$. Impure *l*-hydroxyhydrindamine *l*-chlorosulphoacetate, *brucine l*-chlorosulphoacetate, and *ammonium l*-chlorosulphoacetate were also isolated. C. J. STILL.

Formation of formaldehyde by reduction of carbonic acid by hydrogen peroxide. E. RUPP and H. SCHLEE (Biochem. Z., 1926, 172, 373—378).—From a mixture of sodium hydrogen carbonate, hydrogen peroxide, and an iron salt, carbon dioxide escapes and formic acid and formaldehyde are found in the liquid. The first product is probably formic acid, which is then converted into formaldehyde and carbonic acid by a Cannizzaro reaction.

C. RIMINGTON.

Process of making crotonaldehyde. F. W. LOMMEN.—See B., 1926, 770.

Action of organo-magnesium compounds on nitriles. Ketone cyanohydrins. J. GEURDEN (Bull. Soc. chim. Belg., 1926, 35, 253—260).—The principal product of the action of magnesium alkyl, phenyl, and benzyl halides on the cyanohydrin of an aliphatic ketone is in each case the tertiary alcohol which would be obtained if the ketone itself were used in the reaction. Gauthier (A., 1911, i, 415, 513) mistook these tertiary alcohols for the ketonic alcohols which he expected to be produced. The true ketonic alcohol, β -methylpentan- γ -on- β -ol, b. p. 154°, d_{20}^{20} 0.9326 (*semicarbazone*, m. p. 129°), is also produced in small quantity in the action of magnesium ethyl bromide on acetone cyanohydrin, and from the corresponding reaction between magnesium methyl bromide and the cyanohydrin of methyl ethyl ketone the *semicarbazone* (m. p. 140°) of γ -methylpentan- δ -on- γ -ol is obtained. G. M. BENNETT.

Dynamic isomerism. XXII. Methyl alcohol as an amphoteric solvent for the mutarotation of the sugars. I. J. FAULKNER and T. M. LOWRY (J.C.S., 1926, 1938—1943).—Purified methyl alcohol, which gave a velocity coefficient of 0.00018 when used as a solvent for the mutarotation of tetramethylglucose, gave a maximum value for k of 0.0018 when mixed with three times its weight of cresol, and of 0.035 when mixed with two thirds its weight of pyridine. In purified ethyl alcohol, $k=0.00016$, a value about one eightieth of the velocity in water.

C. J. STILL.

Oxidation of methylated glucoses. H. SOBOTKA (J. Biol. Chem., 1926, 69, 267—275).—Since the reducing power of dextrose towards alkaline solutions of cupric salts is greater than can be accounted for by the oxidation of the aldehydic group of dextrose to carboxyl, it must be assumed that the hydroxyl groups also play some part in the reduction. In agreement with this, it is found that all methylated glucoses have less reducing power, as measured, e.g., by the method of Bertrand, than dextrose itself. $\beta\gamma$ -Dimethylglucose has less reducing power than $\gamma\epsilon\zeta$ -trimethylglucose, which is ascribed to the fact that the free hydroxyl group on the β -carbon atom in the latter substance facilitates enolisation. The reducing power of pentamethylglucose towards alkaline copper solutions approximates to its reducing power towards hypoiodite; the latter, being a measure of the reducing power of the aldehydic group only (cf. Willstätter and Schudel, A., 1918, ii, 337), is equal for dextrose itself and all its methyl ethers.

C. R. HARRINGTON.

Pentamethylglucose and its dimethylacetal. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1926, 69, 175—180).—Methylation of diethylmercaptoglucose, first with methyl sulphate and then further by Freudenberg's method, yielded *pentamethyldiethylmercaptoglucose*, b. p. $152^{\circ}/0.6$ mm., $[\alpha]_D^{20} +19.2^{\circ}$ in methyl alcohol; this, on treatment with mercuric chloride, gave *pentamethylglucose*, b. p. 108 — $110^{\circ}/0.4$ mm., $[\alpha]_D^{20} -35.1^{\circ}$ in tetrachloroethane; $[\alpha]_D^{20} -33.5^{\circ}$ to $+11.5^{\circ}$ in 18 hrs. in methyl alcohol; in methyl alcohol containing 0.25% of hydrochloric acid, $[\alpha]_D^{20} +15.5^{\circ}$ immediately. The *dimethylacetal* had b. p. $95^{\circ}/0.8$ mm., $[\alpha]_D^{20} +15.09^{\circ}$ in methyl alcohol.

C. R. HARRINGTON.

Action of aniline on dextrose in acetic acid solution. C. N. CAMERON (J. Amer. Chem. Soc., 1926, 48, 2233—2238).—Aniline reacts with dextrose in acetic acid with formation of a *product*, apparently identical with that obtained by the action of acetic acid on glucoseanilide. Conversion of dextrose into the anilide is incomplete unless excess of aniline and acetic acid is present. Glucoseanilide has $[\alpha]_D^{20} -53.01^{\circ}$ in alcohol, in presence of excess of aniline to suppress hydrolysis (cf. Irvine and Gilmour, J.C.S., 1908, 93, 1429).

F. G. WILLSON.

Reaction of paraldehyde applicable to carbohydrates. P. BRUÈRE (Bull. Soc. Chim. biol., 1926, 8, 462—463).—Carbohydrates which furnish laevulose on hydrolysis give, with concentrated sulphuric acid and guaiacol, a colour almost identical with that

given by paraldehyde; others give a bright red colour.

C. P. STEWART.

Molecular dimensions of cellulose. H. BRUNSWIG (Cellulosechem., 1926, 7, 118—121).—A graphic representation of the relations between the percentage of nitrogen in a cellulose nitrate and the percentage solubility at 1% concentration in ether-alcohol 2:1 by vol. shows a region of the graph between 10.2 and 12.8% N where the solubility may reach 100%. On both sides of this region, the line of solubility falls very abruptly to negligible proportions. For instance, a cellulose nitrate with 10.0% N has a solubility of 90%, and one with 13.0% N already contains 40—60% of insoluble cellulose nitrate. Hence it follows that the two cellulose nitrates representing the higher and lower limits of the region of 100% solubility must be single individuals of uniform composition. This was demonstrated in the case of the cellulose nitrate with 10.2% N by fractional precipitation of its acetone solution. The solubility in ether-alcohol is a direct function of chemical composition and does not depend on dispersion. The percentage of nitrogen in any cellulose nitrate may be varied upwards or downwards by re-immersion in another nitrating mixture of appropriate composition, and the solubility in ether-alcohol is modified strictly in accordance therewith. The simplest expressions for the two limiting cellulose nitrates which are 100% soluble are represented by the heptanitate with 10.18% N and the decanitate with 12.75% N, calculated on a cellulose molecule which is not smaller than $4C_6H_{10}O_5$.

J. F. BRIGGS.

Constitutional formula for cellulose. H. LE B. GRAY (Ind. Eng. Chem., 1926, 18, 811).—Chemical evidence (E.P. 231800 and 231811; cf. B., 1925, 913, 914) indicates that, in the cellulose molecule, one hydroxyl group per C_{24} is different from the other eleven, and to account for this a formula for cellulose consisting of four dextrose residues, three of which contain the amylen oxide ring and the fourth the butylene oxide ring, is proposed. This formula is in agreement with known data concerning the degradation products of cellulose.

J. W. BAKER.

Esterification of alkali-cellulose. I and II. G. KITA, T. MAZUME, T. NAKASHIMA, and I. SAKRADA (Cellulosechem., 1926, 7, 125—130, 130—133).—When alkali-cellulose is treated with stearyl chloride, the proportion of acid combining with the cellulose is diminished greatly by the presence of phosphoryl chloride and hydrochloric acid, and slightly by excess of alkali. Alkali-cellulose from 1 g. of cellulose requires about 3 g. of stearyl chloride to obtain maximum combination; additional stearyl chloride has little effect. The amount of combination is slightly increased by lowering the temperature at which the alkali-cellulose is prepared, but it is not affected by the temperature of esterification, or by the age of the alkali-cellulose; drying the alkali-cellulose prevents combination. The amount of stearyl chloride combining increases with the concentration of the sodium hydroxide up to 15 vol. %; it then remains constant to 35%, after which a further increase takes place. The curve thus obtained is similar to that of Vieweg for the amount

of alkali combining with cellulose. With naphthoyl chloride the amount of combination is constant from 20 to 45% of sodium hydroxide, but with benzoyl chloride there is a continuous increase up to 45%.

The addition of small quantities of sodium chloride to 13 or 15% sodium hydroxide, used in preparing alkali-cellulose, slightly increases the ability of the latter to combine with stearyl chloride. More sodium chloride has the reverse effect, but this is probably due to its influence on the esterification reaction. The addition of sodium carbonate to 15% sodium hydroxide increases the amount of combination. The addition of alcohol to sodium hydroxide of any concentration results in increased combining power, but the form of the curve, concentration-% combination, remains similar. It is concluded that the addition of alcohol causes further alkali to combine with the cellulose both chemically and physically.

A. GEAKE.

Action of organo-magnesium compounds on nitriles. α -Aminonitriles. M. VELGHE.—See this vol., 1044.

Basis for the physiological activity of certain -onium compounds. V. Mobilities of the -onium ions. II. I. BENCOWITZ and R. R. RENSCHAW (J. Amer. Chem. Soc., 1926, 48, 2146—2155; cf. this vol., 497).—From conductivity measurements of aqueous solutions of tetramethylammonium bromide, tetraethylammonium chloride, and tetrapropylammonium iodide, values for the Λ_{∞} of the tetramethyl-, tetraethyl-, and tetrapropyl-ammonium ion of 46.90, 34.09, and 23.57, respectively, are calculated. The Λ_c/\sqrt{C} graphs of the above three alkylammonium salts, as well as those of two alkylsulphonium salts (cf. A., 1925, ii, 872), form straight lines.

F. G. WILLSON.

Residual affinity and co-ordination. XXVIII. Ethylenediammine copper salts. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1926, 2018—2027).—The stabilising effect of ethylenediamine in preventing the change from cupric to cuprous compounds containing the iodide and cyanide radicals has been investigated. Cuprous iodide in the presence of aqueous ethylenediamine is rapidly oxidised by air to give *diaquobisethylenediamminocupric iodide*, $[2H_2O, Cu, 2en]I_2$, which is stable in moist air; desiccation of this compound over sulphuric acid yields *monoquobisethylenediamminocupric iodide*, $[H_2O, Cu, 2en]I_2$, which reverts to the monoquo-compound in a moist atmosphere. *Methanolbisethylenediamminocupric iodide*, $[MeOH, Cu, 2en]I_2$, m. p. 225—230° (decomp.), separates on addition of methyl alcohol to a concentrated aqueous solution hydrated compound. Other complex co-ordination compounds are described. *Monoquobisethylenediamminocupric cuprocyanide*, $[Cu, 2en, H_2O][Cu(CN)_2]_2$, which on heating passes into *bisethylenediamminocupric dicuprocyanide*, $[Cu, 2en][Cu_2(CN)_3]_2$; *monoquobisethylenediamminodicupric cuprocyanide*, $[en \cdot Cu \cdot OH_2 \cdot Cu \cdot en][Cu(CN)_2]_2$; a compound, $Cu_5(CN)_6 \cdot 9C_2H_4(NH_2)_2 \cdot H_2CO_3 \cdot 3H_2O$; *ethylenediammonium tricuprocyanide*, $[CH_2 \cdot NH_3]_2[Cu_3(CN)_5]$ in

hemihydrated and anhydrous forms; *ethylenediammonium cuprocyanide* and *cuprobromide*, $[CH_2 \cdot NH_3]_2[CuX_2]_2$. *Tetra-aquoethylenediamminocupric perchlorate*, $[Cu, 4en, 4H_2O][ClO_4]_2$, and *bismethanolbisethylenediamminocupric cyanate tetrahydrate*, $[Cu, 2en, 2MeOH](CNO)_2 \cdot 4H_2O$, are also described.

C. J. STILL.

Optical activity of cysteine. J. C. ANDREWS (J. Biol. Chem., 1926, 69, 209—217).—The most complete reduction of cystine to cysteine was obtained by the use of tin and hydrochloric acid in large excess or by electrolytic reduction; in the latter case, racemisation occurred unless the solution was well cooled. Starting with *l*-cystine having $[\alpha]_D^{20} -215.5^\circ$, preparations of cysteine were obtained with $[\alpha]_D^{20} +9.7^\circ$.

C. R. HARRINGTON.

Urethanes. I. Mono- and di-carbethoxyguanidines: dicarbethoxyethylisocarbamide. S. BASTERFIELD and L. E. PAYNTER (J. Amer. Chem. Soc., 1926, 48, 2176—2179).—Dicarbethoxyguanidine has m. p. 165°, and monocarbethoxyguanidine m. p. 98° (hydrated) or 114° (anhydrous) (cf. Nencki, Ber., 1874, 7, 1588). The former is practically inert pharmacologically, but the latter, when injected intravenously in aqueous solution, produces mild central depression with muscular hypertonus. Dicarbethoxyethylisocarbamide (cf. Dains, A., 1899, i, 592) produces complete muscular relaxation in 20 min.

F. G. WILLSON.

Production of formamide and hydrocyanic acid. BADISCHE ANILIN- U. SODA-FABR.—See B., 1926, 770.

Action of organo-magnesium compounds on nitriles. Benzoyl cyanide. A. DE COSTER (Bull. Soc. chim. Belg., 1926, 35, 235—238).—Magnesium phenyl, benzyl, and ethyl bromides act on benzoyl cyanide to give a good yield of triphenylcarbinol, phenyldibenzylcarbinol, and phenyldiethylcarbinol, respectively. In the last case, there is also produced a little of the *hydrocyanide* (m. p. 117—119°) of α -imino- α -benzoylpropane (corresponding *hydrochloride*, m. p. 137—139°).

G. M. BENNETT.

Trimeric crotononitrile. P. BRUYLANTS and L. MATHUS (Bull. Soc. chim. Belg., 1926, 35, 239—253; cf. A., 1923, i, 311, 762).—The action of magnesium ethyl bromide on β -ethoxybutyronitrile, β -chlorobutyronitrile, β -dimethylaminobutyronitrile, or the isomeric crotononitriles produces a viscous mixture of polymeric crotononitriles from which is obtained a small yield of the trimeride, m. p. 174°. This substance is saturated, being converted by bromine into a monobromo-compound, $C_{12}H_{14}N_3Br$, m. p. 131°; it is also neutral and is inert towards alkyl iodides, picric, chloroplatinic, and nitrous acids. Hydrolysis with concentrated hydrochloric acid yields the acid, $C_{11}H_{15}N_2 \cdot CO_2H$, m. p. 109°, which is converted by potassium permanganate in alkaline solution into the dibasic acid, $C_{10}H_{15}N(CO_2H)_2$, m. p. 179°, but is oxidised by nitric acid to the acid, $C_8H_{16}(CO_2H)_2$, m. p. 195° (calcium salt). A small quantity of δ -ethyl- Δ^8 -hexen- δ -ol, b. p. 150—154°, was also isolated from the products of the original reaction.

G. M. BENNETT.

Reversibility of triazan formation. K. E. COOPER and E. H. INGOLD (J.C.S., 1926, 1894—1896).—The reversible formation of ethyl 1-phenyl-triazan-2:3-dicarboxylate from aniline and ethyl azodicarboxylate is studied quantitatively. The preparation of *azodicarboxymethylamide*, m. p. 170° (decomp.), from methylamine and ethyl azodicarboxylate, of *hydrazinedicarboxymethylamide*, m. p. 247°, by reducing the azo-methylamide with aniline or hydrogen sulphide, and of *hydrazinedicarboxamide*, m. p. 243—244°, by reducing azodicarboxamide with aniline, is described. J. S. H. DAVIES.

Germanium. XVI. Germanium tetramethyl. Analysis by combustion of a liquid containing carbon and hydrogen. L. M. DENNIS and F. E. HANCE (J. Physical Chem., 1926, 30, 1055—1059).—*Germanium tetramethyl*, prepared by the Grignard reaction, has m. p. approximately -88°, b. p. 43.4°, d_4^{20} 1.003—1.009, n_D^{25} 1.3868. L. S. THEOBALD.

Tin alkyl compounds. I. Some stannethanes. II. Trimethylbenzylstannane. C. A. KRAUS and R. H. BULLARD (J. Amer. Chem. Soc., 1926, 48, 2131—2136).—*Trimethyltriethyl-distannane*, liquid, obtained by condensation of sodium trimethylstannide with tin triethyl bromide, or of sodium triethylstannide with tin trimethyl bromide, is decomposed in boiling benzene, with formation of hexamethyl- and hexaethyl-distannanes. *Trimethyltriphenyl-distannane*, m. p. 106°, is obtained quantitatively by condensation of sodium triphenylstannide with tin trimethyl bromide in liquid ammonia, but similar condensation of sodium trimethylstannide with tin triphenyl bromide affords also hexamethyl- and hexaphenyl-distannanes. *Trimethylbenzylstannane*, liquid, decomp. 215°, obtained from benzyl chloride and sodium trimethylstannide, affords benzyl bromide and tin trimethyl bromide when brominated in ethereal solution (cf. Grüttner and Krause, A., 1916, i, 684; 1917, i, 256; 1918, i, 158).

F. G. WILLSON.

Modification of Baeyer's strain theory. I. W. F. SHORT (Chem. News, 1926, 133, 145—150).—The energy contents of the cyclopropane and cyclobutane rings are in agreement with the Baeyer strain angles when the thermal values obtained are divided by the number of carbon atoms in the ring (cf. Ingold, J.C.S., 1921, 119, 305). The expression used by Ingold in calculating the angle between the carbon-to-carbon valencies is criticised and a new expression is given, based on the assumption that the angular space between the domains of each pair of attached carbon atoms subtended at the centre of the central atom is the same. This expression gives results in agreement with the relative ease of formation of the cyclopropane and cyclobutane rings, but not with their relative stabilities. It is concluded that the main factors controlling the relative ease of formation of carbon rings are (a) the "activities" of the atoms eliminated in ring formation as influenced by general and alternating polar effects produced by polar atoms, and (b) the spatial proximity of the polar atoms eliminated in ring formation. The second factor is most satisfactorily measured by the

"approach values" calculated from the "normal" angle deduced by the tangent method. Ruzicka's assertion that a double linking is more easily formed than any other ring system (this vol., 727) is not valid in all cases (cf. Ingold, *loc. cit.*). The stability of a carbon ring system is measured approximately by the angle of strain, and, except in extreme cases when strongly polar groups are present, polar conditions in the ring will not exert a powerful influence on the relative ease of ring fission.

R. BRIGHTMAN.

Oxidation in the benzene series by gaseous oxygen. I. Oxidation of methylbenzenes. H. N. STEPHENS (J. Amer. Chem. Soc., 1926, 48, 1824—1826).—Methylbenzenes are oxidised by dry oxygen in diffused daylight at 100° in two stages, the first and main product being the aldehyde, which is subsequently partly oxidised to the acid. The rate of oxidation increases with accumulation of methyl groups in the molecule, but in no case was there indication of the oxidation of more than one methyl group. The presence of water retards the oxidation and in the case of *m*-xylene and mesitylene almost entirely inhibits the reaction. Appreciable amounts of reddish-brown gum or solid resin are formed in all cases, and in the case of cymene the cumaldehyde and cumic acid are also accompanied by some *p*-tolyl methyl ketone.

R. BRIGHTMAN.

Dimagnesium derivatives of benzene compounds. G. BRUHAT and V. THOMAS (Compt. rend., 1926, 183, 297—299; cf. A., 1925, i, 1055).—The dimagnesium derivatives of *o*-, *m*-, and *p*-di-iodobenzene react with water, giving benzene; the *m*- and *p*-compounds react with carbon dioxide, giving isophthalic and terephthalic acids, respectively, whilst the *o*-compound does not react in this way, benzoic acid being obtained. Benzonitrile reacts with the *o*-compound, giving *o*-dibenzoylbenzene and a small amount of benzophenone, with the *m*-compound, giving isophthalophenone, and with the *p*-compound, giving terephthalophenone (oxime, m. p. 256—258°), and a compound, m. p. 160°. The dimagnesium derivatives react with aldehydes, and the products so obtained are decomposed by water, giving resinous products containing glycols which are not easily isolated; the *o*- and *p*-compounds react with benzophenone and the complexes obtained are decomposed by water, yielding tertiary glycols, whilst *m*-di-iodobenzene under these conditions yields a compound, m. p. about 213°. L. F. HEWITT.

2:3:4-Trinitrotoluene. F. H. GORNALL and R. ROBINSON (J.C.S., 1926, 1981—1984).—2:3:4-Trinitrotoluene, obtained from crude trinitrotoluene residues, was converted by the action of aqueous sodium sulphite into sodium 2:4-dinitrotoluene-3-sulphonate, which on reduction gave sodium 2:4-diaminotoluene-3-sulphonate; this compound, as well as its *monoacetyl* derivative, has been used as a component for the preparation of a number of azo-dyes; a *monobenzoyl* derivative is also described. Oxidation of sodium 2:4-dinitrotoluene-3-sulphonate with alkaline permanganate yields sodium 2:4-dinitro-3-sulphobenzoate. 2:3:4-Triaminotoluene, m. p. 106°,

is produced by reduction of the 2:4-dinitro-*m*-toluidine obtained by heating 2:3:4-trinitrotoluene with alcoholic ammonia. 2:4-Dinitro-3-methoxytoluene, m. p. 86°, is obtained by the action of methylalcoholic potassium hydroxide on 2:3:4-trinitrotoluene, and also by methylation of 2:4-dinitro-*m*-cresol. 2:4-Dinitro-3-benzylaminotoluene, by condensation of 2:3:4-trinitrotoluene with benzylamine, has m. p. 115–116°, and the corresponding dibenzylamine derivative, m. p. 87–88°; other condensation products with amines are: 2:4-dinitro-*m*-tolylpiperidine, m. p. 101°, and 2:4-dinitro-*m*-tolyl- α -naphthylamine, m. p. 169–170° (decomp.). C. J. STILL.

Orientation effects in the diphenyl series.

III. Mononitro-4:4'-dihalogenodiphenyls and allied compounds. R. J. W. LE FÈVRE and E. E. TURNER (J.C.S., 1926, 2041–2049).—The 4:4'-dibromo-2-nitrodiphenyl obtained by Lellmann (A., 1883, 343) has now been prepared by the regulated nitration of 4:4'-dibromodiphenyl, and by a similar process 4:4'-dichloro-2-nitrodiphenyl, m. p. 102°, is produced. 4:4'-Dibromo-3-nitrodiphenyl, m. p. 101–102°, when nitrated, yields a mixture of 4:4'-dibromo-2:3'-dinitrodiphenyl and 4:4'-dibromo-3:3'-dinitrodiphenyl, whereas 4:4'-dibromo-2-nitrodiphenyl gives a quantitative yield of 4:4'-dibromo-2:3'-dinitrodiphenyl. Nitration of 4-bromo-2'-nitrodiphenyl and of 4-bromo-4'-nitrodiphenyl gives rise to the same product, 4-bromo-2':3:4'-trinitrodiphenyl, m. p. 176–177°, and this, on treatment with piperidine, yields 2':3:4'-trinitro-4-piperidinodiphenyl, m. p. 144–145°. The product obtained from 2-nitrobenzidine by the perbromide method of Griess and Saunders is believed to be 3':4:4'-tribromo-2-nitrodiphenyl, and has m. p. 195–196°.

The preparation of 3-nitrobenzidine by the method of Koller (A., 1904, i, 778) was unsuccessful, as considerable quantities of 2-nitrobenzidine are produced instead.

Anilino-, methylanilino-, piperazino-, and some other derivatives of 4:4'-dichloro- and 4:4'-dibromo-2:3'-dinitrodiphenyls are described. 4-Bromo-2:3'-dinitro-4'-anilinodiphenyl, m. p. 151°, 4-chloro-2:3'-dinitro-4'-anilinodiphenyl, m. p. 129–130°, 4-bromo-2:3'-dinitro-4'-methylanilinodiphenyl, m. p. 142–143°, 4-chloro-2:3'-dinitro-4'-methylanilinodiphenyl, m. p. 134°, 4-bromo-2:3'-dinitro-4'-phenoxydiphenyl, m. p. 124–125°, 4-chloro-2:3'-dinitro-4'-phenoxydiphenyl, m. p. 113°, 4-bromo-2:3'-dinitro-4'-piperazinodiphenyl, m. p. 250°, 4-chloro-2:3'-dinitro-4'-piperazinodiphenyl, m. p. 250°, 4-chloro-2:3'-dinitro-4'-aminodiphenyl, m. p. 218–219°, 4-bromo-2:3'-dinitro-4'-aminodiphenyl, m. p. 219°. Products were also obtained from 4:4'-dibromo-3:3'-dinitrodiphenyl: 3:3'-dinitro-4:4'-dianilinodiphenyl, m. p. 240°, 3:3'-dinitro-4:4'-dimethylanilinodiphenyl, m. p. 250°, 3:3'-dinitro-4:4'-diphenoxydiphenyl, m. p. 139–140°. C. J. STILL.

β -Xenylhydroxylamine and its rearrangement.

H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1926, 48, 2190–2193).—Reduction of *p*-nitrodiphenyl with zinc dust and ammonium chloride in 95% alcohol affords *p*-hydroxylaminodiphenyl (β -xenyl-

hydroxylamine), m. p. 158° (decomp.) after softening. This is stable only in presence of dilute acetic acid, in absence of which it oxidises rapidly to 4:4'-azoxybisdiphenyl, m. p. 207.5° (cf. Zimmermann, A., 1881, 175). It does not rearrange to 4-amino-4'-hydroxydiphenyl. Condensation with benzaldehyde affords the compound, $\text{CHPh}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}$, m. p. 174–175° (cf. Gattermann, A., 1897, i, 189).

F. G. WILLSON.

Nitro- and gem-dinitro-ethylenes. P. LIPP [with W. LÜDICKE, N. KALINOV, and A. P. PETKOV] (Annalen, 1926, 449, 15–29).—Nitrous gases from nitrite and sulphuric acid react with α -diphenylethylene in light petroleum at low temperatures to give a blue, oily nitrosite, which on keeping at 0° evolves gas and forms β -nitro- α -diphenylethyl alcohol, m. p. 106–107°, and β -nitro- α -diphenylethylene, m. p. 86°, the latter being most readily obtained by heating the blue oil with acetyl chloride. Nitrodiphenylethylene is decomposed by boiling alcoholic potassium hydroxide into benzophenone and probably nitroacetic acid. $\beta\beta$ -Dinitro- α -diphenylethylene (Anschütz and Romig, A., 1886, 1033) reacts with boiling methylalcoholic potassium hydroxide to give $\beta\beta$ -dinitro- α -diphenylethyl alcohol [from the potassium salt, $\text{CPh}_2(\text{OH})\cdot\text{C}(\text{NO}_2)_2\text{NO}_2\text{K}$, by the action of water], which quickly decomposes into benzophenone and dinitromethane.

β -Nitro- α -diphenylethylene is reduced by aluminium amalgam in ether to α -diphenylethylamine (cf. Konovalov and Jatzewitsch, A., 1905, i, 763, who obtained a "syrupy base" and a hydrochloride, m. p. 170–173°), m. p. about 35–40°, b. p. 149°/4 mm. (corr.) (hydrochloride, m. p. 263–265°; phenylcarbamide, m. p. 191–192°; phenylthiocarbamide, m. p. 172–173°). The neutral products of the reduction are *bis*(diphenylvinyl)amine, m. p. 142–146°, and diphenylacetaldoxime, m. p. 110–115°, b. p. 156–158°/0.3 mm. (corr.). The secondary amine is hydrolysed by cold hydrochloric-acetic acid to diphenylacetaldehyde, b. p. about 170°/12 mm. (semicarbazone, m. p. 161–163°).

$\beta\beta$ -Dinitro- α -diphenylethylene is similarly reduced to diphenylacetamidoxime, m. p. 138–139° (hydrochloride, decomp. about 190°), which is also prepared from diphenylacetonitrile and hydroxylamine together with (probably) diphenylacetamide, m. p. 171–172°. Diphenylacetonitrile, m. p. 73–74°, b. p. 134°/0.6 mm., is amongst the neutral products of reduction.

C. HOLLINS.

Action of sunlight on tetranitrostilbene. A. PLISSOV (Ukraine Chem. J., 1925, 1, 643).—A solution of tetranitrostilbene in pyridine is coloured bright green in sunlight. The constitution of the substance formed, m. p. 219°, is not known.

S. BOTCHARSKY.

Replaceability of the halogen atom in 2-chloro- and 2-bromo-1:6:8-trinitronaphthalene. E. J. VAN DER KAM (Rec. trav. chim., 1926, 45, 564–581).—Trinitration of 2-chloro-, 2-bromo-, 2-methoxy-, and 2-ethoxy-naphthalene furnishes the corresponding 1:6:8-trinitro-derivatives, m. p. 194°, 205°, 215°, and 186°, respectively, together with lower nitration

products. The substituents in position 2 are replaced by the amino- or methylamino-group on treatment with the requisite reagents in alcoholic solution at 100° under pressure, yielding 1:6:8-trinitro- β -naphthylamine, m. p. 300° (decomp.), and 1:6:8-trinitro- β -naphthylmethylamine, m. p. 257° (decomp.), respectively. The former yields 4:6-dinitrophthalic acid with alkaline permanganate. Reaction velocity determinations show that the replacement of the halogen atoms by ethoxyl is more rapid than by methoxyl, that the chlorine atom is more readily replaced by alkyloxy-groups than is the bromine atom, and that, from the point of view of replacement by methoxyl, the chloro-compound is twice or three times as reactive as the bromo-compound, and is intermediate between chloro-2:4-dinitro- and chloro-2:4:6-trinitro-benzene.

J. S. H. DAVIS.

Alkylanthracenes and "transannular tautomerism." E. DE B. BARNETT and M. A. MATTHEWS (Ber., 1926, 59, [B], 1429—1438).—Evidence is adduced in favour of the view that alkylidene-9:10-dihydroanthracenes are immediately formed during reactions of alkylanthracenes. Since the migration of a hydrogen atom across the central ring is involved, the term "transannular tautomerism" is suggested.

9-Methylanthracene is converted by the calculated quantity of bromine in carbon disulphide into 10-bromo-9-methylanthracene, m. p. 173°, and by the halogen (2 mols.) into 10-bromo-9-bromomethylanthracene, m. p. 200° [corresponding pyridinium salt, m. p. 232° (decomp.)], [giving 10-bromo-9-acetoxymethylanthracene, m. p. 167°, and 10-bromo-9-hydroxymethylanthracene, m. p. 229° (decomp.) after darkening at 200°]. 9-Methylanthracene and bromine (4 mols.) afford 10-bromo-9-bromomethylanthracene tetrabromide, m. p. 140° (decomp.), oxidised by chromic acid to 2:3-dibromoanthraquinone. 9-Ethylanthracene yields successively 10-bromo-9-ethylanthracene, m. p. 104°, and 10-bromo-9-ethylanthracene tetrabromide, m. p. 177° (decomp.); the latter substance is converted by potassium hydroxide into 2:3:10-tribromo-9-ethylanthracene, m. p. 169°, oxidised to 2:3-dibromoanthraquinone. 9-isoPropylanthracene, m. p. 76°, prepared from anthrone and magnesium isopropyl bromide, gives 10-bromo-9-iso-propylanthracene, m. p. 97°, 10-bromo-9-iso-propylanthracene tetrabromide, m. p. 163° (decomp.), and 2:3:10-tribromo-9-iso-propylanthracene, m. p. 210°, oxidised to 2:3-dibromoanthraquinone. 10-Bromo-9-isoamylanthracene tetrabromide, m. p. 162° (decomp.), and 2:3:10-tribromo-9-isoamylanthracene, m. p. 121°, are described. 9:10-Dimethylanthracene, m. p. 181° [picrate, m. p. 175—176° (decomp.)], prepared from 9-methylanthrone and magnesium methyl iodide, is identical with the substance described as 9:10-dimethyl-9:10-dihydroanthracene; with bromine it affords 9:10-dibromomethylanthracene, darkening at 315° [dipyridinium salt; picrate, m. p. 247° (decomp.)]. 10-Phenyl-9-methylanthracene, m. p. 112°, prepared from 9-methylanthrone and magnesium phenyl bromide or phenylanthrone and magnesium methyl iodide yields 10-phenyl-9-bromomethylanthracene, m. p. 177°, whereas 9:10-diphenylanthracene, m. p. 241—

243°, affords 9:10-diphenylanthracene tetrabromide, m. p. 160° (decomp.). H. WREN.

Mechanism of substitution reactions in the aromatic nucleus. VII. E. DE B. BARNETT, M. A. MATTHEWS, and J. L. WILTSHIRE Rec. trav. chim., 1926, 45, 558—563).—1:4-Dichloroanthracene, m. p. 180°, forms a stable dibromide, m. p. 169° (decomp.), which has the *cis*-configuration, and on boiling with toluene reverts to the parent compound. With aniline, methylaniline, dimethylaniline, and piperidine, the dibromide forms 1:4-dichloro-9:10-dianilino-, dimethyldianilino-, tetramethyldiaminodiphenyl-, and dipiperidino-9:10-dihydroanthracene, m. p. 141°, 214°, 297°, 198°, respectively, without re-establishment of the "bridge" linking. With pyridine, 1:4-dichloro-9:10-dihydroanthraquinyl-9:10-dipyridinium dibromide is formed, which, in common with most salts of this type, loses 1 mol. of pyridine bromide on boiling in aqueous solution, and forms 1:4-dichloroanthranilpyridinium bromide, m. p. 315° (decomp.), with re-establishment of the bridge. Unlike 1:5-dichloroanthracene dibromide, the 1:4-dichloro-isomeride, on hydrolysis with aqueous acetone in presence of calcium carbonate, yields only a single dihydroxy-derivative, m. p. 204° (decomp.), together with 1:4-dichloroanthracene. 2:3-Dichloroanthracene, m. p. 261°, does not form a dibromide, but instead 2:3-dichloro-9:10-dibromoanthracene, m. p. 244°. With nitric and acetic acids, it gives 2:3-dichloro-9-nitroanthracene, m. p. 232°, or a mixture of this with 2:3-dichloro-9-nitro-9:10-dihydroanthranil acetate, m. p. 181° (decomp.), according to the conditions. 2:3-Dichloroanthrone, m. p. 202°, obtained by reducing 2:3-dichloroanthraquinone with tin and hydrochloric-acetic acid, or, better, with sulphuric acid and aluminium powder, appears to yield a pinacol condensation product, m. p. 210°, with zinc dust and acetic-hydrochloric acid, and when heated with pyridine and acetic anhydride yields 2:3-dichloroanthranil acetate, m. p. 168°. Poor yields of 1:4-dichloroanthraquinone were obtained by the chromic acid oxidation of 1:4-dichloroanthraquinone tetrachloride, m. p. 255—257° (decomp.), prepared by the action of phosphorus pentachloride on quinizarin suspended in nitrobenzene, whilst synthesis from phthalic anhydride, *p*-dichlorobenzene, and aluminium chloride was unsuccessful. J. S. H. DAVIES.

M. p. of 4-chloro-2:6-dibromoaniline. E. C. GILBERT (J. Amer. Chem. Soc., 1926, 48, 2242).—4-Chloro-2:6-dibromoaniline has m. p. 92.9° (lit. 95° and 97°). F. G. WILLSON.

Preparation and properties of *o*-toluidine. H. G. TANNER and P. A. LASSELLE (J. Amer. Chem. Soc., 1926, 48, 2163—2166).—*o*-Toluidine, prepared synthetically from phthalimide, gives, when treated with potassium dichromate by Schoen's method (A., 1890, 839), a greenish-black precipitate, the filtrate from which is practically identical with that given by *p*-toluidine; the presence of traces of the *p*-compound in *o*-toluidine cannot therefore be recognised by this test. *o*-Toluidine has b. p. 200.6°/754.6 mm., d_{20}^{20} 1.0053, n_D^{20} 1.5688. F. G. WILLSON.

Substituted amides. I. Preparation of substituted acetamides and the corresponding primary amines. H. O. NICHOLAS and J. E. L. ERICKSON (J. Amer. Chem. Soc., 1926, 48, 2174—2176).—The yield of benzylacetamide obtained by heating acetamide with benzyl chloride is very small, owing to the production of a large proportion of ammonium chloride (cf. Rudolph, A., 1879, 921). Treatment of anhydrous acetamide with hydrogen bromide at 200—220° affords ammonium bromide and diacetamide. The following substituted acetamides were obtained by heating together 1.6 mols. of acetamide and 0.4 mol. of the appropriate alkyl bromide at 200—220°, the yields being quoted in brackets: benzyl-, m. p. 61°, b. p. 157°/2 mm. (80%); β -phenylethyl-, m. p. 45°, b. p. 154°/2 mm. (40%); ethyl-, b. p. 206° (66%); *n*-propyl-, b. p. 225° (70%); *n*-butyl-, b. p. 229° (66%); and *iso*amyl-acetamide, b. p. 232° (42%). Hydrolysis of the above acetamides affords the corresponding amines in 80—90% yields.

F. G. WILLSON.

Autoxidation and antioxygenic action. Catalytic action of various nitrogen compounds. C. MOUREU, C. DUFRASSE, and M. BADOCHÉ (Compt. rend., 1926, 183, 408—412; cf. A., 1923, ii, 308; 1924, i, 635, ii, 602, 841).—Of 83 nitrogen compounds examined, secondary amines, diamines, and aminophenols possess the strongest antioxygenic properties. Thus diphenylamine, monomethylaniline, *o*-, *m*-, and *p*-aminophenol, *p*-phenylenediamine, *p*-anisidine, and *p*-phenetidine at concentrations of 1 in 10,000 inhibit the autoxidation of acetaldehyde, whilst with aniline, triphenylamine, and dimethylaniline a concentration of 1 in 1000 is necessary. *N*-Methyl derivatives of diamines or aminophenols are equally active, and derivatives such as tetramethyldiaminodiphenylmethane and Michler's ketone also possess antioxygenic properties, although in a lesser degree. Substitution of both amino- and phenolic groups, as in *p*-acetophenetidine, leads to inactivity, although *N*-acyl derivatives such as *o*-acetamidophenol are active. $\alpha\alpha$ - and $\beta\beta$ -Dinaphthylamines are good stabilisers for acetaldehyde, but cyclic compounds are much less active antioxidants, and pyridine and quinoline do not affect the autoxidation of benzaldehyde, although they are slightly active with furfuraldehyde. Amino-acids and amides generally have little or no antioxygenic properties. The following substances were used as autoxidants: acetaldehyde, benzaldehyde, furfuraldehyde, heptaldehyde, propionaldehyde, styrene, turpentine, linseed oil, and sodium sulphite (10% aqueous solution).

R. BRIGHTMAN.

Dependence of rotatory power on chemical constitution. XXIX. Resolution of sulphoxides into their optically active forms. P. W. B. HARRISON, J. KENYON, and H. PHILLIPS (J.C.S., 1926, 2079—2090).—It is shown that mixed sulphoxides exist in enantiomorphous forms, and the formula $\bar{O}-\overset{+}{S}<\overset{R}{\overset{R'}{}}$ is proposed (cf. Phillips, this vol., 159). *dl*-*p*-Aminophenyl *p*-tolyl sulphoxide, m. p. 169—170° (acetyl derivative, m. p. 183—184°) (prepared, together with *di*-*p*-tolyl disulphoxide, by

heating aniline and *p*-toluenesulphonic acid at 110—115°), is resolved, by use of *d*- and *l*-camphorsulphonic acids, into *d*-*p*-aminophenyl *p*-tolyl sulphoxide, m. p. 151°, $[\alpha]_{D}^{25} +123^\circ$ in ethyl alcohol (*d*-camphorsulphonate, m. p. 133—134°, $[\alpha]_{D}^{25} +17.2^\circ$ in ethyl alcohol; acetyl derivative, $[\alpha]_{D}^{25} +66.4^\circ$ in ethyl alcohol); and *l*-*p*-aminophenyl *p*-tolyl sulphoxide, m. p. 151°, $[\alpha]_{D}^{25} -122^\circ$ in ethyl alcohol (*l*-camphorsulphonate, m. p. 133—134°, $[\alpha]_{D}^{25} -18.1^\circ$ in ethyl alcohol; acetyl derivative, m. p. 173—174°, $[\alpha]_{D}^{25} -66.2^\circ$). *dl*-*m*-Carboxyphenyl methyl sulphoxide, m. p. 170—172° (prepared by oxidation of an aqueous solution of *m*-methylthiolbenzoic acid by hydrogen peroxide in presence of potassium carbonate) is resolved, by means of brucine and *l*-menthylamine, into *d*-*m*-carboxyphenyl methyl sulphoxide, m. p. 134°, $[\alpha]_{D}^{25} +137.6^\circ$ in methyl alcohol (brucine salt, m. p. 136—137°; *l*-menthylamine salt, m. p. 171°, $[\alpha]_{D}^{25} +68.9^\circ$) and *l*-*m*-carboxyphenyl methyl sulphoxide, m. p. 133°, $[\alpha]_{D}^{25} -133.5^\circ$. Optically inactive *p*-acetamidophenyl-*p*-tolylsulphone, m. p. 192—194°, is obtained by oxidation of *d*-*p*-acetamidophenyl *p*-tolyl sulphoxide, and also from *dl*-*p*-aminophenyl *p*-tolyl sulphoxide; *d*-*m*-carboxyphenyl methyl sulphoxide is oxidised to optically inactive *m*-carboxyphenylmethylsulphone. *l*-*p*-Aminophenyl *p*-tolyl sulphoxide, its acetyl derivative, and *d*-*m*-carboxyphenyl methyl sulphoxide exhibit complex rotatory dispersion. The sign of rotation of *l*-*p*-aminophenyl *p*-tolyl sulphoxide is reversed in hydrochloric acid solution; its rotatory power and that of *d*-*m*-carboxyphenyl methyl sulphoxide are tabulated for various wave-lengths and in different solvents.

F. M. HAMER.

Preparation of *N*-aralkylated aromatic amines [by hydrogenation of Schiff's bases]. J. D. RIEDEL A.-G.—See B., 1926, 771.

Preparation of *s*-diaminodiarylcarbamides. I. G. FARBERIND. A.-G. See B., 1926, 769.

Manufacture of diarylguanidines. BRIT. DYE-STUFFS CORP., C. J. T. CRONSHAW, and W. J. S. NAUNTON.—See B., 1926, 769.

Optically active dyes. III. Physical properties, dyeing reactions, and mechanism of dyeing. IV. Asymmetric dyes from *m*-aminomandelic acid. W. R. BRODE and R. ADAMS (J. Amer. Chem. Soc., 1926, 48, 2193—2201, 2202—2206; cf. A., 1924, i, 1242).—III. The active isomerides of the optically active dyes previously prepared by coupling β -naphthol and dimethylaniline with *d*-, *l*-, and *dl*-*p*-diazobenzamidophenylacetic acid have the same physical properties, including adsorption by active and inert materials, colour, and fastness to light. Their rotatory dispersion curves, as well as those of the intermediates used, are normal. Whilst the racemic dyes appear to be adsorbed to a greater extent than the active substances by both active and inactive adsorbing agents, no apparent difference in adsorption of the two active forms could be detected, and it is considered that Morgan and Skinner's results (A., 1925, i, 1191) are probably due to experimental error.

Condensation of 5-benzeneazosalicylaldehyde with

α -2-hydroxy-1-naphthylbenzylamine affords 5-benzene-azosalicylidene- α -2-hydroxy-1-naphthylbenzylamine, yellow-orange, m. p. 210—212°, of which the active modifications, m. p. 220—225°, were prepared. These are too insoluble in water for dyeing experiments.

IV. Repetition of the experiments of Porter and Hirst (A., 1919, i, 558) and of Porter and Ihrig (A., 1923, i, 1027) have failed to confirm the observation of these authors that one of the optically active isomerides of these dyes is selectively adsorbed, and the data so far obtained indicate that dyeing is not a chemical process. The absorption spectra of the azo-dyes obtained by coupling diazotised *m*-aminomandelic acid with phenol and β -naphthol, respectively, are described with curves. F. G. WILLSON.

Halogen and nitro-derivatives of benzene- and toluene-azonaphthylamine, their solid diazonium salts, and conversion of the latter into the corresponding hydrazinesulphonic acids. J. TRÖGER and R. SCHAEFER (J. pr. Chem., 1926, [ii], 113, 268—292).—The following compounds were prepared by addition of aqueous solutions of diazonium salts to alcoholic α -naphthylamine solution in presence of sodium acetate, at 35—50°: *o*-chlorobenzeneazo- α -naphthylamine, red-brown, m. p. 129°; *m*-chlorobenzene-, similar, m. p. 116° (hydrochloride, reddish-violet); *o*-bromobenzene-, red-brown, m. p. 117°; *m*-bromobenzene-, reddish-yellow, m. p. 103°; *o*-nitrobenzene-, dark red-brown, with green reflex, m. p. 170—171°; *m*-nitrobenzene-, light red, m. p. 179—180°; *p*-nitrobenzene-, blue-violet, m. p. 248°; 4-nitro-6-methylbenzene-, dark red, m. p. 198° (hydrochloride, violet-black); 3-nitro-2-methylbenzene-, light red, m. p. 202°; 5-nitro-2-methylbenzene-, red-brown, m. p. 186°; and 6-nitro-2-methylbenzene-azo- α -naphthylamine, deep red-brown, with green reflex, m. p. 162°. Diazotisation is effected by addition of powdered nitrite to suspensions of the above bases in hydrochloric acid, with subsequent agitation at temperatures up to 45°, the diazonium salts then crystallising from the warm solutions. *o*-Chlorobenzeneazo- α -naphthalenediazonium chloride, brown-yellow, loses nitrogen when kept. *m*-Chlorobenzeneazo- α -naphthalene-azoresorcinol, brown, amorphous, and azo- β -naphthol, violet-brown, were prepared from *m*-chlorobenzeneazo- α -naphthalenediazonium chloride, brown-yellow. The following compounds, prepared analogously, are described: *o*-bromobenzeneazo- α -naphthalenediazonium chloride, yellowish-brown; *m*-bromobenzeneazo- α -naphthalenediazonium chloride, red-brown, decomp. when kept a few hrs.; *p*-bromobenzeneazo- α -naphthalenediazonium chloride, cherry-red; *p*-bromobenzeneazo- α -naphthaleneazoresorcinol, dark red; *p*-bromobenzeneazo- α -naphthaleneazo- β -naphthol, dark violet; *o*-nitrobenzeneazo- α -naphthalenediazonium chloride, light brown; *m*-nitrobenzeneazo- α -naphthalenediazonium chloride, reddish-brown; *p*-nitrobenzeneazo- α -naphthalenediazonium chloride, similar; 3-nitro-2-methylbenzeneazo- α -naphthalenediazonium chloride, loam-coloured; 4-nitro-2-methylbenzeneazo- α -naphthalenediazonium chloride, yellow-brown; 4-nitro-2-methylbenzeneazo- α -naphthaleneazoresorcinol, dark violet; 4-nitro-2-methylbenzeneazo- α -naphthalene- β -naphthol, similar; 5-nitro-2-methylbenzeneazo- α -naphthalenediazonium chloride, yellow-

brown; and 6-nitro-2-methylbenzeneazo- α -naphthalenediazonium chloride, similar. In the above chloro-, bromo-, and nitro-benzene derivatives, the *ortho*-, *meta*-, and *ortho*-compounds, respectively, are the most stable, whilst in the toluene group the 5-nitro-derivatives are the most stable. Treatment of the above diazonium salts with aqueous alkaline hydrogen sulphite affords the corresponding diazosulphonates, which are converted, on reduction with ammonium sulphide or stannous chloride, into the corresponding hydrazinesulphonic acids (cf. Tröger and Piotrowski, A., 1917, i, 669). The following are described: sodium *m*-chlorobenzeneazo- α -naphthalenediazosulphonate, blood-red (labile) or golden-yellow; *m*-chlorobenzeneazo- α -naphthylhydrazinesulphonic acid, deep red (salicylaldehyde condensation product, yellowish-red, m. p. 155—157°); sodium *o*-bromobenzeneazo- α -naphthalenediazosulphonate, golden-yellow; sodium *m*-bromobenzeneazo- α -naphthalenediazosulphonate, similar; sodium *p*-bromobenzeneazo- α -naphthalenediazosulphonate, similar; *p*-bromobenzeneazo- α -naphthylhydrazinesulphonic acid, blue-black with green reflex (salicylaldehyde condensation product, wine-red, m. p. 198°); and sodium *p*-nitrobenzeneazo- α -naphthalenediazosulphonate, golden-yellow. 4-Nitro-2-methylbenzeneazo- α -naphthylhydrazinesulphonic acid, deep violet, is obtained by saturating a solution of the above corresponding diazonium chloride with sulphur dioxide, a similar reaction being also occasionally observed with *m*-chloro- and *p*-bromo-benzeneazo- α -naphthalenediazonium chlorides. Sodium 5-nitro-2-methylbenzeneazo- α -naphthalenediazosulphonate, reddish-yellow, yields the corresponding acid, brownish-black, on treatment with hydrochloric acid, and, on reduction with stannous chloride, 5-nitro-2-methylbenzeneazo- α -naphthylhydrazinesulphonic acid, reddish-violet (salicylaldehyde condensation product, magenta-red, m. p. 165°). F. G. WILLSON.

Chromium compounds of azo dyes. Soc. CHEM. IND. IN BASLE.—See B., 1926, 702.

Esterification of cyclohexanol and some of its homologues. I. Viscosity, surface tension, and thermochemistry. (MLLE.) G. CAUQUIL.—See this vol., 914.

Alcohols of the hydroaromatic and terpene series. V. Geometrical and optical isomerism of the methylcyclohexanols. G. A. C. GOUGH, H. HUNTER, and J. KENYON (J.C.S., 1926, 2052—2071).—Two geometrically isomeric forms of 2-methylcyclohexanol, two of 3-methylcyclohexanol (all resolvable into optical antipodes), and two of 4-methylcyclohexanol are described. After hydrogenation of *o*-cresol, the methylcyclohexanols obtained by fractional distillation are converted into dl- α -2-methylcyclohexyl hydrogen phthalate, m. p. 124—125° (β -eucaine salt, m. p. 173—174°), which is hydrolysed to dl- α -2-methylcyclohexanol, b. p. 78—79°/20 mm., d_4^{25} 0.9228, n_D^{25} 1.4596, η^{25} 0.336 (acetate, b. p. 79—80°/20 mm., d_4^{25} 0.9430, n_D^{25} 1.4389, η 0.0233; phenylcarbamate, m. p. 105—106°; *p*-nitrobenzoate, m. p. 65°; hydrogen succinate, m. p. 44—46°; *p*-toluenesulphonate, m. p. 27—28°), and dl- β -2-methylcyclohexyl hydrogen phthalate, m. p. 89—90° (β -eucaine

salt, m. p. 154°), or *dl*- β -2-methylcyclohexyl *p*-nitrobenzoate, m. p. 35–36°, may be prepared, either being hydrolysable to *dl*- β -2-methylcyclohexanol, b. p. 77–78°/20 mm., d_4^{25} 0.9228, $n_{D,5893}^{25}$ 1.4616, η^{25} 0.155 (acetate, b. p. 79–80°/20 mm., d_4^{25} 0.9434, $n_{D,5893}^{25}$ 1.4376, η^{25} 0.0211; phenylcarbamate, m. p. 78–80°; hydrogen succinate, m. p. 30–31°). Similarly are obtained from *p*-cresol α -4-methylcyclohexyl hydrogen phthalate, m. p. 119–120° (β -eucaine salt, m. p. 170–171°), yielding α -4-methylcyclohexanol, b. p. 78–79°/20 mm., d_4^{25} 0.9080, $n_{D,5893}^{25}$ 1.4544, η^{25} 0.385 (acetate, b. p. 78–80°/20 mm., d_4^{25} 0.9380, $n_{D,5893}^{25}$ 1.4373, η^{25} 0.0217; phenylcarbamate, m. p. 124–125°; *p*-nitrobenzoate, m. p. 67°; *p*-toluenesulphonate, m. p. 71–72°), and β -4-methylcyclohexyl hydrogen phthalate, m. p. 72–73° (β -eucaine salt, m. p. 170–171°), yielding β -4-methylcyclohexanol, b. p. 78–79°/20 mm., d_4^{25} 0.9180, $n_{D,5893}^{25}$ 1.4584, η^{25} 0.247 (acetate, b. p. 78–79°/20 mm., d_4^{25} 0.9337, $n_{D,5893}^{25}$ 1.4365, η^{25} 0.0196; phenylcarbamate, m. p. 124°; *p*-nitrobenzoate, m. p. 94°). From hydrogenated *m*-cresol are prepared *dl*- α -3-methylcyclohexyl *p*-nitrobenzoate, m. p. 58°, hydrolysable to *dl*- α -3-methylcyclohexanol, b. p. 77–79°/20 mm., d_4^{25} 0.9104, $n_{D,5893}^{25}$ 1.4530, η^{25} 0.251 [acetate, b. p. 81–82°/20 mm., d_4^{25} 0.9454, $n_{D,5893}^{25}$ 1.4313, η^{25} 0.0174; hydrogen phthalate, m. p. 93–94° (β -eucaine salt, m. p. 149–150°); phenylcarbamate, m. p. 92–93°; *p*-toluenesulphonate, m. p. 39–40°], and *dl*- β -3-methylcyclohexyl *p*-nitrobenzoate, m. p. 65°, hydrolysable to *dl*- β -3-methylcyclohexanol, b. p. 77–78°/20 mm., d_4^{25} 0.9091, $n_{D,5893}^{25}$ 1.4554, η^{25} 0.197 [acetate, b. p. 78–79°/20 mm., d_4^{25} 0.9430, $n_{D,5893}^{25}$ 1.4369, η^{25} 0.0195; hydrogen phthalate, m. p. 82–83° (β -eucaine salt, m. p. 171–172°); phenylcarbamate, m. p. 101–103°; *p*-toluenesulphonate, m. p. 46–47°]. With the methylcyclohexanols the convention is adopted of naming the more viscous isomeride the α - and the less viscous the β -; their viscosities, and those of their acetates, are studied, and the relationship between chemical constitution and viscosity is discussed (cf. Thole, J.C.S., 1912, 101, 552); it appears that the α -isomerides are probably the *trans*- and the β - the *cis*-methylcyclohexanols. The proportions of α - and β -2-methylcyclohexanols, produced by various methods of preparation, have been investigated by means of a viscosity-composition diagram.

Crystallisation of the strychnine salt, m. p. 190°, of *dl*- α -2-methylcyclohexyl hydrogen phthalate gives rise to the *d*- and *l*- α -2-methylcyclohexyl hydrogen phthalates, $[\alpha]_{5893}^{25} \pm 63^\circ$ in benzene, whence are obtained the *d*- and *l*- α -2-methylcyclohexanols, $[\alpha]_{5708}^{25} \pm 13^\circ$ (*l*- α -2-methylcyclohexyl acetate, d_4^{20} 0.9458, $\alpha_{5708}^{25} -19.27^\circ$). By use of *l*- α -phenylethylamine and strychnine, *dl*- β -2-methylcyclohexyl hydrogen phthalate was resolved with difficulty into the α - and *l*- β -2-methylcyclohexyl hydrogen phthalates, $[\alpha]_{5461}^{25} +46^\circ$ in benzene, whence are obtained *d*- β -2-methylcyclohexanol and *l*- β -2-methylcyclohexanol, d_4^{20} 0.9272, $\alpha_{5708}^{20} -4.62^\circ$ (acetate, d_4^{20} 0.9454, $\alpha_{5708}^{20} -9.11^\circ$). *l*- α -2-Methylcyclohexanol is oxidised to *l*-2-methylcyclohexanone, b. p. 59–60°/20 mm., $[\alpha]_{4359}^{25} -43.0^\circ$, d_4^{25} 0.9230, and *l*- β -2-methylcyclohexanol to *d*-2-methylcyclohexanone, $[\alpha]_{5893}^{18} +14.21^\circ$, d_4^{18} 0.9262. Crystallisation of the *p*-nitrobenzoic esters of the 3-methylcyclohexanols, obtained by reduction of *d*-3-methyl-

cyclohexanone (from pulegone), yields *l*- α -3-methylcyclohexyl *p*-nitrobenzoate, $[\alpha]_{5461}^{25} -3.8^\circ$ in methyl alcohol, m. p. 45.5–46.5°, which is hydrolysed to *l*- α -3-methylcyclohexanol, $[\alpha]_{5461}^{25.5} -4.22^\circ$, $d_4^{25.5}$ 0.9131, η^{25} 0.251 (hydrogen phthalate, m. p. 94–95°, $[\alpha]_{5461}^{19} -17.39^\circ$ in benzene; acetate, d_4^{19} 0.9511, $\alpha_{5708}^{19} -8.13^\circ$), oxidisable to *d*-3-methylcyclohexanone, b. p. 66–67°/25 mm., $\alpha_{5893}^{23} +11.54^\circ$ (also obtained by oxidation of *l*- β -3-methylcyclohexanol).

dl- α -2-Methylcyclohexyl *p*-toluenesulphonate is converted by potassium acetate into a methylcyclohexyl acetate, which on hydrolysis yields *dl*- β -2-methylcyclohexanol (cf. Phillips, J.C.S., 1923, 123, 43). Similarly, *dl*- α -3- and α -4-methylcyclohexyl *p*-toluenesulphonates give *dl*- β -3- and β -4-methylcyclohexanols, respectively. *l*- α -3-Methylcyclohexyl *p*-toluenesulphonate, m. p. 36–37°, $[\alpha]_{5461}^{19} -26.3^\circ$ in benzene, is similarly converted into *l*- β -3-methylcyclohexanol, $d_4^{16.5}$ 0.9245, $\alpha_{5708}^{16.5} -2.53^\circ$, η^{25} 0.196 (acetate, d_4^{20} 0.9448, $\alpha_{5708}^{20} -3.40^\circ$; hydrogen phthalate, m. p. 70–71°, $[\alpha]_{5461}^{19} -32.7^\circ$ in benzene), and *dl*- β -3-methylcyclohexyl *p*-toluenesulphonate into *dl*- α -3-methylcyclohexanol. The density at different temperatures and rotatory power for different wavelengths for some of the optically active methylcyclohexanols and their acetates are tabulated.

F. M. HAMER.

cis-trans Isomerism and steric hindrance.

III. 2-cyclohexylcyclohexanols. G. VAVON, ANZIANI, and HERYNK (Bull. Soc. chim., 1926, [iv], 39, 1138–1147).—When 2-cyclohexylcyclohexanone is reduced using hydrogen and platinum-black it yields mainly *cis*-2-cyclohexylcyclohexanol, b. p. 130–131°/10 mm., m. p. 60° (phenylurethane, m. p. 148°; hydrogen succinate, m. p. 114–114.5°; hydrogen phthalate in two interconvertible forms, m. p. 112–113° and 126–127°). If sodium and alcohol are used as the reducing agent *trans*-2-cyclohexylcyclohexanol, m. p. 53–54° (phenylurethane, m. p. 132°; hydrogen succinate, m. p. 131°; hydrogen phthalate, m. p. 123–124°), is obtained. Steric considerations of cyclohexyl derivatives suggest that the reactions of *cis*-forms should be much slower than those of the *trans*-isomerides (cf. Vavon, this vol., 837). Experiments on the esterification of *cis*- and *trans*-2-cyclohexylcyclohexanols show that the esterification rates of *cis*- and *trans*- are in the ratio 1 : 1.8, using acetic acid, and 1 : 4.5, using acetic acid containing 2% of sulphuric acid. Hydrolysis experiments also support this steric theory, the *trans*-hydrogen succinate hydrolysing thirty times as fast as the *cis*-isomeride and the *trans*-hydrogen phthalate thirteen to fourteen times as fast as the *cis*-form.

R. W. WEST.

Colour reactions of phenols with sodium nitroprusside. L. EKKERT and L. W. WINKLER (Pharm. Zentr., 1926, 67, 566–568).—Characteristic colour reactions are obtained by pouring concentrated sulphuric acid to form a layer beneath an aqueous (or alcoholic) solution of a phenol, dusting sodium nitroprusside on to the surface, and shaking gently until the surface of contact becomes coloured. Thus with phenol the upper layer is red and the surface of contact dark green. On mixing the two layers, the liquid is first violet and then green. Addition

of a small quantity of water gives a bluish colour, excess of water a red, and ammonia to alkalinity a bluish-green. Distinctive colorations are similarly described for thymol, pyrocatechol, resorcinol, quinol, orcinol, pyrogallol, phloroglucinol, crude cresol, Fagi creosote, and α - and β -naphthol. R. BRIGHTMAN.

Use of leucotrope [phenylbenzyl dimethylammonium chloride] as benzylating agent. H. BAW (J. Indian Chem. Soc., 1926, 3, 101—104).—The benzylation of phenols by means of leucotrope and of the corresponding *m*- and *p*-nitrobenzyl compounds is described. *o*-, *m*- and *p*-Chlorophenyl benzyl ethers have been prepared, having b. p. 296°, m. p. 59°, and m. p. 71°, respectively, the last being identical with that obtained by Sintenis (Annalen, 1872, 161, 345). 2:4-Dichlorophenyl benzyl ether has m. p. 60°. G. M. BENNETT.

Nitrosation of phenols. III. Nitrosation of 4-halogeno-*o*- and -*m*-cresols and oximation of the 4-halogeno-2:5-toluquinones. H. H. HODGSON and F. H. MOORE (J.C.S., 1926, 2036—2040; cf. *ibid.*, 1923, 123, 2499; A., 1925, i, 1408).—Nitrosation of 4-chloro-*o*-cresol, 4-bromo-*o*-cresol, m. p. 78°, and 4-iodo-*o*-cresol, m. p. 65°, obtained from the 4-halogeno-*o*-nitrotoluenes by reduction and diazotisation, yields 4-chloro-5-nitroso-*o*-cresol, m. p. 197° (decomp.), 4-bromo-5-nitroso-*o*-cresol, m. p. 197° (decomp.), and 4-iodo-5-nitroso-*o*-cresol, m. p. 200° (decomp.), respectively. Reduction gives 4-chloro-5-amino-*o*-cresol, 4-bromo-5-amino-*o*-cresol, m. p. 189° (lit. m. p. 180°), and 4-iodo-5-amino-*o*-cresol, m. p. 170°. The three nitroso-*o*-cresols exist in only one modification, and the high m. p. of the chloro- and bromo-compounds compared with those of 4-nitroso-3-chlorophenol, m. p. 135°, and 5-nitroso-*o*-cresol, m. p. 134.5°, are accepted as evidence for their quinoneoxime structure. Support for this view is obtained from the behaviour of 4-chloro-*m*-cresol, m. p. 45°, and 4-bromo-*m*-cresol, m. p. 38°, which yield, on nitrosation, 4-chloro-6-nitroso-*m*-cresol, m. p. 191° (decomp.), and 4-bromo-6-nitroso-*m*-cresol, m. p. 190° (decomp.), which are also obtained by the action of hydroxylamine hydrochloride on 4-chloro- and 4-bromo-2:5-toluquinones. 4-Iodo-*m*-cresol gives 4-iodo-6-nitroso-*m*-cresol, m. p. 170° (decomp.), whereas the product of oximation of 4-iodo-2:5-toluquinone, m. p. 92°, decomposes at 181°. The difference is ascribed to impurity and not to isomerism. Reduction of the nitroso-*m*-cresols gives 4-chloro-6-amino-*m*-cresol, m. p. 227° (slight decomp.) (cf. Kehrman, A., 1916, i, 657); 4-bromo-6-amino-*m*-cresol, m. p. 222° (slight decomp.) (cf. Kehrman, A., 1899, i, 129, m. p. 205—208°). 4-Iodo-6-amino-*m*-cresol, prepared from the quinoneoxime, has m. p. 208°. 4-Chlorotoluquinone-5-monoxime has m. p. 190°, 4-bromotoluquinone-5-monoxime, m. p. 190°, and 4-iodotoluquinone-5-monoxime, m. p. 181° (decomp.). No isomerism could be detected (cf. Kehrman, *loc. cit.*). M. CLARK.

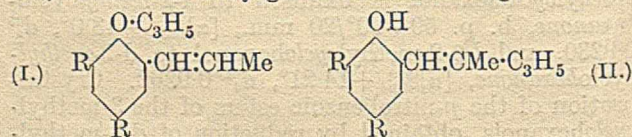
3:5-Dihalogenophenols. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1926, 2077—2079).—The 3-halogeno-5-nitroanisoles are prepared from 5-nitro-*m*-anisidine, m. p. 120°, and from them the 3-halogeno-5-nitrophenols. The 5-halogeno-*m*-anisidines are pre-

pared from the corresponding nitro-compounds, and are converted into the 3:5-dihalogenoanisoles. The 3:5-dihalogenophenols are obtained by hydrolysing the 5-halogeno-*m*-anisidines, diazotising, and applying the Sandmeyer process. The following compounds are described: 3-iodo-5-nitroanisole, m. p. 84°; 3-chloro-5-nitrophenyl benzoate, m. p. 78°, acetate, m. p. 84°; 3-bromo-5-nitrophenyl acetate, m. p. 99°; 3-iodo-5-nitrophenol, m. p. 136°, benzoate, m. p. 100.5°, acetate, m. p. 110°; 2:4:6-tribromo-3-iodo-5-nitrophenol, m. p. 176°; 5-chloro-*m*-anisidine, m. p. 33°; 5-bromo-*m*-anisidine, m. p. 52°; 5-iodo-*m*-anisidine, m. p. 86.5°; 3-chloro-5-iodoanisole, b. p. 267—268°; 3:5-di-iodoanisole, m. p. 85°; 3-chloro-5-bromoanisole, m. p. 33°; 3-bromo-5-iodoanisole, m. p. 54°; 3:5-dichlorophenyl benzoate, m. p. 55°, acetate, m. p. 38°; 3:5-dibromophenyl benzoate, m. p. 77°, acetate, m. p. 53°; 3:5-di-iodophenyl benzoate, m. p. 93°; 2:4:6-tribromo-3:5-di-iodophenol, m. p. 226—228°; 3-chloro-5-bromophenol, m. p. 70°, benzoate, m. p. 62°, acetate, m. p. 45°; 3-chloro-2:4:5:6-tetrabromophenol, m. p. 205°; 3-chloro-5-iodophenol, m. p. 60°, benzoate, m. p. 54°, acetate, m. p. 47°; 3-chloro-2:4:6-tribromo-5-iodophenol, m. p. 195°; 3-bromo-5-iodophenol, m. p. 82.5°, benzoate, m. p. 76°, acetate, m. p. 46°; 2:3:4:6-tetrabromo-5-iodophenol, m. p. 220—221°. F. M. HAMER.

Action of sodium methoxide on some derivatives of *o*-dichlorobenzene. G. M. KRAAY (Diss., Amsterdam, 1926, 1—68).—*o*-Dichlorobenzene, substituted in the *p*-position by fluorine, chlorine, bromine, iodine, nitro-, sulphonic, methyl, carboxyl, amino-, hydroxyl, nitroso-, cyano-, formyl, or benzoyl atoms or groups, was treated with methyl-alcoholic sodium methoxide at 180°. A halogen atom is first replaced by a methoxyl group, the anisole then reacting further with sodium methoxide, giving the sodium derivative of a phenol and dimethyl ether. The following substances are described: 3:4-dichloro-fluorobenzene, b. p. 171°; 3:4-dichloriodobenzene, m. p. 30.5°; 3:4-dichlorobenzonitrile, m. p. 72.1°; 3:4-dichloronitrosobenzene, m. p. 88°; 3:4-dichlorophenylhydroxylamine, m. p. 75° (decomp.); 3:3':4:4'-tetrachloroazoxybenzene, m. p. 139—139.5°; 3:4-dichlorobenzyl alcohol, m. p. 38°; 4-chloro-*m*-cresol, m. p. 46°; 2-chloro-5-bromophenol, m. p. 57°; 2-chloro-5-iodophenol, m. p. 56.5°; 2-chloro-5-iodonitrobenzene, m. p. 74.5°; 2-chloro-5-iodoaniline, m. p. 61.5°. Selective replacements of the halogens are discussed from the point of view of polarity.

CHEMICAL ABSTRACTS.

Migration of allyl in phenyl allyl ethers from oxygen to an unsaturated *ortho* side-chain. L. CLAISEN and E. TIETZE (Annalen, 1926, 449, 81—101).—The *O*-allyl group in phenyl allyl ethers of the type (I) is shown to migrate to the β -position in the side-chain, giving (II), the transformation being analogous to migration to a *para* carbon atom, i.e., across two conjugated double linkings.



When *m*-4-xylyl allyl ether, b. p. 105.5°/15 mm., is heated under reflux, the temperature of the liquid rises from 224° to 238° in about 20 min. and is then constant, the ether having been converted into 5-allyl-*m*-4-xylene, b. p. 245—245.5°/757 mm., 116—117°/11 mm. (phenylurethane, m. p. 109°; methyl ether, b. p. 230—233°). This, heated with a little pyridine hydrochloride, yields 2:5:7-trimethylcoumaran, b. p. 230—230.5°, or is reduced by the Paal-Skita method to 5-*n*-propyl-*m*-4-xylene, m. p. 31—32°, b. p. 243.5—245°, 125—126°/17 mm. (phenylurethane, m. p. 112—112.5°). Allylxylene is isomerised by hot methyl-alcoholic potassium hydroxide to 5-propenyl-*m*-4-xylene, m. p. 73.5—74°, b. p. 134—136°/17 mm. (phenylurethane, m. p. 135.5—136°; methyl ether, b. p. 244—244.5°). 5-Propenyl-*m*-4-xylyl allyl ether (I, R = Me), b. p. 141.5—143°/17 mm., is converted by heating under reduced pressure into α -(2-hydroxy-3:5-dimethylphenyl)- β -methyl- $\Delta^{\alpha\beta}$ -pentadiene (II, R = Me), b. p. 149—152°/16 mm. (methyl ether, b. p. 269° or 142°/14 mm.), from which may be obtained the $\Delta^{\alpha\gamma}$ -isomeric, b. p. 158—161°/14 mm. (methyl ether, b. p. 155—158°/14 mm.), by the action of alcoholic alkali, and by the Paal-Skita reduction method α -(2-hydroxy-3:5-dimethylphenyl)- β -methylpentane, b. p. 144—146°/16.5 mm. No migration to either of the meta-positions occurs, for when the allyl ether of 5-allyl- or 5-propyl-*m*-4-xylene is heated, the *O*-allyl group is eliminated in the form of diallyl (and, to a smaller extent, allene), leaving the free allyl- or propyl-xylene.

Dihydroeugenol (2-methoxy-4-*n*-propylphenol), b. p. 249—250°/752 mm., 128°/15 mm. (phenylurethane, m. p. 117.5—118°), forms an allyl ether, b. p. 159°/16 mm., which is converted by heating in hydrogen at 190—200° into 2-methoxy-4-*n*-propyl-6-allylphenol, b. p. 282—283° or 157—158°/14.5 mm. (phenylurethane, m. p. 103.5°). The isomeric 2-methoxy-4-*n*-propyl-6-*n*-propenylphenol, m. p. 59.5—60°, b. p. 165—167°/15 mm. (phenylurethane, m. p. 98—99°), obtained by the action of methyl-alcoholic potassium hydroxide on the 6-allyl compound, gives an allyl ether, b. p. 174—176°/15 mm., which is converted by heating under reduced pressure into α -(2-hydroxy-3-methoxy-5-*n*-propylphenyl)- β -methyl- $\Delta^{\alpha\beta}$ -pentadiene, b. p. 180°/12 mm. (phenylurethane syrupy, methyl ether, b. p. 166—169°/12 mm.).

Similarly, from 2:4-dichlorophenol are obtained 2:4-dichloro-6-allylphenol (phenylurethane, m. p. 120°), 2:4-dichloro-6-*n*-propenylphenol, m. p. 47—48°, b. p. 146—147°/15 mm. (prepared also from salicylaldehyde and ethyl magnesium bromide), its allyl ether, b. p. 156—157°/15 mm., and α -(2-hydroxy-3:5-dichlorophenyl)- β -methyl- $\Delta^{\alpha\beta}$ -pentadiene, b. p. 169—172°/16 mm.

C. HOLLINS.

Derivatives of homocatechol. I. F. R. GRAESSER-THOMAS, J. M. GULLAND, and R. ROBINSON (J.C.S., 1926, 1971—1976; cf. Oberlin, this vol., 283).—Treatment of isocresol (4-methoxy-*m*-cresol; acetyl derivative, m. p. 56—57°; benzoyl derivative, m. p. 80—81°) in ethereal solution with nitrous acid yields 2:6-dinitroisocresol, m. p. 152—153° (decomp.) [sodium salt; phenylhydrazine salt, +2H₂O, m. p. 109° (decomp.); hydroxylamine salt, pasty at 166°,

m. p. 208°; acetyl derivative, m. p. 106°]. Nitration of acetylresol in acetic anhydride yields 6-nitroacetylresol together with 2:6-dinitrohomocatechol, m. p. 92°. Further nitration gives 2:6-dinitroacetylresol, m. p. 103° (cf. Oberlin, *loc. cit.*, m. p. 101—102°), hydrolysed to 2:6-dinitroresol, which yields a quinoline salt, m. p. 110° (decomp.) after treatment with cold fuming nitric acid. The quinoline salt of 3:5:6-trinitroguaiacol has m. p. 185° (decomp.). Methylation of 2:6-dinitroisocresol or of 2:6-dinitroresol gives 2:6-dinitrohomoveratrole, m. p. 92° (Oberlin, m. p. 90—91°), which reacts with cotarnine in methyl alcohol to give anhydrocotarnine-2:6-dinitrohomoveratrole, m. p. 141°. M. CLARK.

Derivatives of homocatechol. II. J. M. GULLAND and R. ROBINSON (J.C.S., 1926, 1976—1981).—Homoveratrole-6-sulphonyl chloride, m. p. 75°, yields the amide, m. p. 193—194° (cf. Robinson, *ibid.*, 1917, 111, 955, oily chloride yielding amide, m. p. 191°). Nitration of the chloride yields 5-nitrohomoveratrole-6-sulphonyl chloride, m. p. 140—141°. Nitration of isocresol in ethereal solution gives a compound, m. p. 166—167°, and, under certain conditions, 2:6-dinitroisocresol. Nitration of acetylresol yields a compound, C₉H₉O₅N, m. p. 104—105° (probably 5-nitro-3-acetoxy-*p*-cresol, since treatment with alcoholic potassium hydroxide yields 5-nitrohomocatechol), and a compound, C₁₀H₁₁O₅N, m. p. 60—61° (probably 5-nitro-3-acetoxy-*p*-tolyl methyl ether). Reduction of 2:6-dinitroisocresol with sodium sulphide yields 2-nitro-6-aminoisocresol, m. p. 168—169° (decomp.) [N-acetyl derivative +H₂O, m. p. 183° (sodium salt, yellow needles)]. Reduction of 2:6-dinitrohomoveratrole with sodium sulphide gives a mixture of bases, m. p. 90—100°, from which 2-nitro-6-aminohomoveratrole, m. p. 90—92° (cf. Oberlin, *loc. cit.*, m. p. 92—93° or 104—105°), is obtained through the hydrochloride, m. p. about 210°, or through the piperonylidene derivative, m. p. 130—132°. By the Sandmeyer reaction, the nitroamine gives 6-bromo-2-nitrohomoveratrole, m. p. 102°, and a by-product, m. p. 241°. The action of sulphurous acid and copper powder on the diazo-sulphate gives a neutral compound, C₁₈H₁₉O₉N₅S, m. p. 142°, and a little nitrohomoveratrolesulphinic acid, which yields, on oxidation and hydrolysis, a nitrophenol, m. p. 62°, probably 2-nitro-3-hydroxy-*p*-tolyl methyl ether. Reduction of nitrohomoveratrodiazonium chloride with stannous chloride gives a nitrohydrazinohomoveratrole, in two physical modifications, m. p. 147—149° and 163—164° (piperonylidene derivative, m. p. 172—173°), converted by oxidation with copper sulphate in dilute acetic acid solution followed by permanganate oxidation into a mixture of 2- and 6-nitroveratric acids.

M. CLARK.

Derivatives of guaiacol and veratrole substituted in the 3- and 6-positions. A. E. OXFORD (J.C.S., 1926, 2004—2011).—The action of acetyl nitrate at -15° on *o*-anisyl acetate yields equal proportions of 3-nitroguaiacol, m. p. 68.5—69.5° (sodium salt; acetyl derivative, b. p. 168—169°/12—13 mm.; benzoyl derivative, m. p. 88—89°, identical with Meldola's benzoyl-*o*-nitroguaiacol,

Proc. C.S., 1896, 11, 127), and 5-nitroguaiacol. The constitution of the 3-nitro-compound follows from formation of 3-nitroveratrole on methylation. Reduction of 6-nitroguaiacol with sodium hyposulphite yields 6-aminoguaiacol, m. p. 83.5° (triacetyl derivative, m. p. 122—124°). Further nitration of 3-nitroguaiacol in acetic acid solution yields 3:4-dinitroguaiacol, m. p. 109.5—110° (sodium salt; acetyl derivative, m. p. 99—100.5°; benzoyl derivative, m. p. 132—133°), and 3:6-dinitroguaiacol, m. p. 69—70° (sodium salt; acetyl derivative, m. p. 56°). Methylation of the last-named compound gives 3:6-dinitroveratrole, m. p. 56°, reduced to 3:6-diaminoveratrole, m. p. 82° (triacetyl derivative, m. p. 96—97°). 3:4-Dinitroguaiacol and 3:4-dinitroveratrole yield, on reduction, diamines condensing with the sodium hydrogen sulphite compound of phenanthraquinone to give the corresponding ethers of 1:2-dihydroxyphenanthraquinone. Direct nitration of 3-nitroguaiacol by concentrated nitric acid or further nitration of 3:6-dinitroguaiacol gives 3:4:6-trinitroguaiacol, existing in two modifications, m. p. 108—109° and 113.5° [sodium salt; quinoline salt, softening at 185°, decomp. 190°; pyridine salt, softening at 146°, m. p. 150—153° (decomp.); benzoyl derivative, m. p. 146—147°]. 4:5:6-Trinitroguaiacol, m. p. 144—147° (decomp.) [quinoline salt, m. p. 207—209° (decomp.)], is obtained by direct nitration of 5-nitroguaiacol [cf. Kohn, A., 1925, i, 1265, m. p. 143—149° (decomp.), quinoline salt, m. p. 201° (decomp.)]. M. CLARK.

Hydrogenated dihydroxydiphenylmethane compounds. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING) and H. JORDAN.—See B., 1926, 720.

Co-ordination valency of two hydroxyl groups in the ortho position. II. Complexes of hydroxyquinol, 1:2-dihydroxynaphthalene, and protocatechualdehyde with acids of the molybdenum group. L. FERNANDES (Gazzetta, 1926, 56, 416—424; cf. A., 1925, i, 912).—Hydroxyquinol and 1:2-dihydroxynaphthalene form with molybdates and tungstates coloured complexes which can be detected as maxima on a concentration-absorption curve obtained from absorption spectra. In this way, the six complexes $\text{MoO}_3 \cdot m\text{C}_6\text{H}_3(\text{OH})_2 \cdot (\text{NH}_4)_2\text{O} \cdot n\text{H}_2\text{O}$; $\text{MoO}_3 \cdot m\text{C}_{10}\text{H}_6(\text{OH})_2 \cdot (\text{NH}_4)_2\text{O} \cdot n\text{H}_2\text{O}$, and $\text{WO}_3 \cdot m\text{C}_6\text{H}_3\text{O}_3 \cdot (\text{NH}_4)_2\text{O} \cdot n\text{H}_2\text{O}$, where $m = 1$ and 2 , are detected.

The following complexes are isolated in microcrystalline form by precipitation: *pyridinium hydroxyquinol-aquouranate*, $[\text{UO}_3 \cdot \text{C}_6\text{H}_3\text{O}_3 \cdot \text{H}_2\text{O}] (\text{C}_5\text{H}_5\text{N})\text{H}$, maroon; *pyridinium 1:2-dihydroxynaphthalene-aquouranate*, $[\text{UO}_3 \cdot \text{C}_{10}\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}] (\text{C}_5\text{H}_5\text{N})\text{H}$, red; *ammonium mono- and di-protocatechualdehyde-aquomolybdates*, $[\text{MoO}_3 \cdot (\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}] (\text{NH}_4)\text{H}$, orange, $[\text{MoO}_2 \cdot (\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2)_2] (\text{NH}_4)\text{H}$, maroon; *diguanydinium di-protocatechualdehyde-molybdate*, $[\text{MoO}_2 \cdot (\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2)_2] \text{CNH}_2(\text{NH}_2)_2$, brick-red; *thallium protocatechualdehyde-aquomolybdate*, $[\text{MoO}_3 \cdot (\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}] \text{TiH}$, red; *diammonium mono- and di-protocatechualdehyde-aquotungstates*, $[\text{WO}_3 \cdot \text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}] (\text{NH}_4)_2$ and $[\text{WO}_2 \cdot (\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_2)_2] (\text{NH}_4)_2$, maroon.

E. W. WIGNALL.

Typical reactions for phenols. K. BRAUER [with RUTHSATZ] (Chem.-Ztg., 1926, 74, 553—554).—The reaction recently described (B., 1926, 595) of resins or varnishes with phosphomolybdic acid and ammonia is characteristic of phenolic hydroxyl groups and can be used to differentiate *o*-, *m*-, and *p*-substitution in the polyhydric phenols. The green coloration given by *o*-dihydroxyphenols, such as pyrocatechol and pyrogallol, and phosphomolybdic acid is turned to blue on addition of ammonia, whilst the blue coloration obtained with *p*-dihydric phenols is unchanged by ammonia, and *m*-dihydric phenols, e.g., resorcinol, phloroglucinol, give a (blue) coloration only after addition of ammonia. Hydroxyquinol gives the reaction for a *p*-dihydric phenol. The reaction is very sensitive and can be applied in either ethereal or aqueous solution or suspension. Introduction of carboxyl groups weakens the reaction, and salol, for instance, gives a much weaker coloration than phenol. R. BRIGHTMAN.

Apiole of anethum and its propenyl isomeride. M. DELÉPINE and A. LONGUET (Bull. Soc. chim., 1926, [iv], 39, 1019—1024).—When treated in ethereal solution with iodine and mercuric oxide, apiole (5:6-dimethoxy-3:4-methylenedioxyallylbenzene, cf. A., 1909, i, 642) yields the *ethylene oxide*, $\text{C}_9\text{H}_9\text{O}_4 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, b. p. 195—200°/15 mm., which

could not be transformed into the isomeric aldehyde.

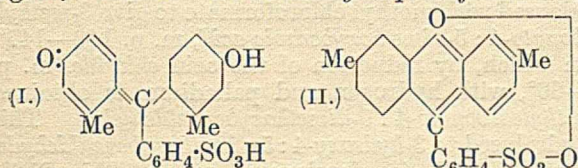
The addition of bromine to *isoapiole* (5:6-dimethoxy-3:4-methylenedioxypropenylbenzene) in ethereal solution yields a *dibromide*, $\text{C}_{12}\text{H}_{14}\text{O}_4\text{Br}_2$, m. p. 105°, which reacts with dilute acetone to give a *glycol bromohydrin*, probably $\text{C}_9\text{H}_9\text{O}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CHBrMe}$. This alcohol is converted by potassium hydroxide into the *oxide*, b. p. 185—192°/15 mm., which isomerises on distillation to a *ketone*, probably either $\text{C}_9\text{H}_9\text{O}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Me}$ or $\text{C}_9\text{H}_9\text{O}_4 \cdot \text{CH}_2 \cdot \text{COMe}$, b. p. 260° (*semicarbazone*, m. p. 159—160°). Potassium acetate reacts with the dibromide, yielding the *glycol diacetate*, m. p. 124°.

When treated with sodium iodide, *bromoisoapiole* dibromide yields 2-bromo-5:6-dimethoxy-3:4-methylenedioxypropenylbenzene (*bromoisoapiole*), m. p. 66° (*picrate*, m. p. 72°), whilst boiling with alcohols yields alkoxy-derivatives, $\text{C}_9\text{H}_8\text{O}_4\text{Br} \cdot \text{CH}(\text{OR}) \cdot \text{CHBrMe}$ (*methoxy*-, m. p. 59°; *ethoxy*-, m. p. 82—83°; *propoxy*-, m. p. 64°), and a *substance*, $\text{C}_{11}\text{H}_9\text{O}_4\text{Br}$, m. p. 108° (*bromo-derivative*, m. p. 151—152°), possibly 3-bromo-6-methoxy-4:5-methylenedioxyethylbenzofuran. The following reactions of *bromoisoapiole* dibromide are described: dilute acetone yields the *glycol bromohydrin*, $\text{C}_9\text{H}_8\text{O}_4\text{Br} \cdot \text{CH}(\text{OH}) \cdot \text{CHBrMe}$, m. p. 125° (*benzoate*, m. p. 132°); alcoholic potassium hydroxide yields the *oxide*, $\text{C}_{12}\text{H}_{13}\text{O}_5\text{Br}$, m. p. 99—100°, which yields the *glycol monoacetate*, $\text{C}_{14}\text{H}_{17}\text{O}_7\text{Br}$, m. p. 121—123°; potassium acetate in acetic acid solution yields the *glycol diacetate*, $\text{C}_9\text{H}_8\text{O}_4\text{Br} \cdot [\text{CH} \cdot \text{OAc}]_2 \cdot \text{Me}$, m. p. 88—90°.

R. W. WEST.

***m*-Cresolsulphonaphthalein, 3:6-dimethylsulphonfluoran, and some of their derivatives.** W. R. ORNDORFF and A. C. PURDY (J. Amer. Chem. Soc., 1926, 48, 2212—2221).—Condensation of *o*-sulphobenzoic anhydride or chloride with *m*-cresol

in presence of zinc chloride at 105–110° affords *m*-cresolsulphonaphthalein, (I), deep red with green reflex, decomp. 250–300° after darkening and shrinking. The air-dried material contains about 1% of water, and is therefore to be considered as a solid solution of the inner carbonium or oxonium salt and the quinonoid hydrate (cf. Cohen, U.S. Pub. Health Reports, 1923, 38, 199; Orndorff and Cornwell, this vol., 610). The triammonium salt, deep red, mono-ammonium salt, light red, barium salt (+2EtOH), dark red, diacetate, m. p. 172–173°, and dibenzoate, m. p. 208–209°, were prepared. When boiled with methyl alcohol, *m*-cresolsulphonaphthalein affords a dark red monomethyl ether, m. p. 176–178°, and a colourless dimethyl ether, m. p. 164–165° after turning red, which is converted into a deep red isomeride (ammonium salt, red) when heated at 170° in carbon dioxide. Bromination in cold glacial acetic acid affords tetrabromo-*m*-cresolsulphonaphthalein, colourless, m. p. 218–219° (heptahydrate, brick-red, amorphous, m. p. 218–219° after becoming orange at 90° and colourless at 190°; ammonium salt; diacetate, m. p. 235–236°; dibenzoate, m. p. 205–206°). Condensation of *m*-cresol with *o*-sulphobenzoic anhydride at 125–145°, in absence of condensing agent, affords 3:6-dimethylsulphonfluoran (II),



orange, charring at 280–290° (hydrochloride, red), bromination of which in glacial acetic acid affords dibromo-3:6-dimethylsulphonfluoran, orange, darkening at 200°, m. p. not below 300° (triammonium salt), whilst reduction with zinc dust and boiling water yields the zinc salt of “dimethylhydrosulphofluoran acid” (3:6-dimethyl-9-phenylxanthen-*o*-sulphonic acid). F. G. WILLSON.

Action of benzoyl peroxide on benzene at low temperatures in presence of anhydrous metal chlorides. J. BÖESEKEN and A. F. A. REYNHART (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 598–602; cf. Gelissen and Hermans, A., 1925, 1, 379, 545).—Benzoyl peroxide acts on an excess of benzene at 0° in presence of aluminium chloride (1 mol.) to yield almost quantitatively benzoic acid (1 mol.) and phenyl benzoate (1 mol.), the production of carbon dioxide being negligible. Since carbon dioxide and diphenyl result in the absence of the aluminium chloride, the latter functions by activating the linking between the central oxygen atoms of the peroxide. In a similar reaction in presence of ferric chloride, no phenyl benzoate is isolated, but more than 1 mol. of benzoic acid together with dark-coloured compounds containing iron. Diphenyl and carbon dioxide are also produced, and the proportion of these increases as the temperature of reaction is raised to 35°. If the proportion of ferric chloride is much less (0.1 mol.), both phenyl benzoate and diphenyl are produced. The two reactions evidently proceed side by side. Zinc chloride has no catalytic action; stannic chloride has a slow effect similar to that of

aluminium chloride. Antimony pentachloride causes a violent reaction at 0°, some benzophenone being formed. G. M. BENNETT.

Preparation of nitriles by the diazo reaction. A. KORCZYNSKI and B. FANDRICH (Compt. rend., 1926, 183, 421–423).—The following nitriles have been obtained in greater purity and higher yields by the use of nickel cyanide instead of cuprous cyanide in the diazo-reaction (cf. A., 1920, i, 643): *o*- and *p*-toluonitrile, *o*- and *p*-anisonitrile, *o*-chlorobenzonitrile, m. p. 43–44°, *m*-chlorobenzonitrile, m. p. 40.5°, *o*-bromobenzonitrile, m. p. 53°, and *p*-bromobenzonitrile. The cyanides of iron, chromium, manganese, zinc, molybdenum, cadmium, tin, or thorium cannot be used. R. BRIGHTMAN.

Derivatives of anæsthesin [ethyl *p*-amino-benzoate]. G. GORI (Gazzetta, 1926, 56, 430–434).—Ethyl *p*-aminobenzoate has been condensed to give: with succinic acid, ethyl *p*-succinimidobenzoate, m. p. 150°; with phthalic anhydride, ethyl *p*-phthalimidobenzoate, m. p. 150–151°; with tetrachlorophthalic anhydride, ethyl *p*-tetrachlorophthalimidobenzoate, pale yellow, m. p. 255°; with piperonal, ethyl *p*-piperonylideneaminobenzoate, m. p. 109–110°; with 1-chloro-2:4-dinitrobenzene in the presence of sodium acetate, ethyl 2:4-dinitrodiphenylamine-4'-carboxylate, orange, m. p. 112–113°; with carbon disulphide in alcoholic solution, ethyl *s*-diphenylthiocarbamide-4:4'-dicarboxylate, yellow, m. p. 153°. In all these derivatives the anæsthetic property is lost (cf. Thoms and Ritsert, A., 1921, i, 343). E. W. WIGNALL.

Relationship between hydrogen-ion concentration and chemical constitution in certain local anæsthetics. E. B. VLIET and R. ADAMS (J. Amer. Chem. Soc., 1926, 48, 2158–2162).—The basicities of a series of compounds of the type $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot [\text{CH}_2]_x \cdot \text{NRR}'$ have been measured. The basicity decreases with increase in size of the groups R and R', except that dimethylamino-derivatives are slightly less basic than the corresponding diethylamino-compounds. Diisopropylamino-derivatives are slightly more basic than di-*n*-propylamino-derivatives, diiso- and di-*n*-amylamino-compounds have the same basicity, but that of the diisobutylamino-compounds is less than that of the *n*- and *sec*-butyl isomerides. Increase in the value of *x* causes increase in basicity, but branching of this chain reduces it. When the $[\text{CH}_2]_x$ group is replaced by the cyclohexyl group, the compounds behave as if the nitrogen and oxygen atoms were connected by two straight chains of carbon atoms, the basicity being determined by the length of the shorter chain. The two geometrical isomerides of *o*-dimethylamino-hexahydrophenyl *p*-aminobenzoate have the same basicity, although differing greatly in physical properties and anæsthetic effect. Borates of γ -di-*n*-butylaminopropyl and β -*n*-butylallylaminoethyl *p*-aminobenzoates are completely hydrolysed by water. F. G. WILLSON.

Isomeric phenylserines. M. O. FORSTER and K. A. N. RAO (J.C.S., 1926, 1943–1951).—Erlenmeyer's condensation of glycine with benzaldehyde

yields *trans*-phenylserine, m. p. 202° (decomp.) (A., 1899, i, 759). Reduction of α -triazol- β -hydroxy- β -phenylpropionic acid with ammonium sulphide yields *cis*-phenylserine, m. p. 230—232° (decomp.), hydrated form, m. p. 213° [ethyl ester picrate, m. p. 170°; *N*-benzoyl derivative, m. p. 197°; *O*-methyl derivative, m. p. 227—232° (decomp.), +2H₂O, m. p. 215—216°, with ethyl ester picrate, m. p. 155°; *O*-methyl-*N*-benzoyl derivative, m. p. 208°; amide, m. p. 199—200°]. Evidence for the *cis*-configuration of the new acid is found in the formation of a benzoyl derivative without dehydration, whereas benzoylation of *trans*-phenylserine gives Erlenmeyer's benzamidocinnamic acid lactimide and a compound, m. p. 160°. Further support is derived from its synthesis by the action of ammonia on cinnamic acid chlorohydrin or sodium oxidophenylacrylate. Erlenmeyer erroneously described the product of these two reactions as phenylisoserine. Attempts to convert the phenylserines into the parent compound of picrorocellin were unsuccessful, but Abderhalden and Komm's colour test (A., 1925, i, 175) showed that a diketopiperazine was formed when the phenylserines were heated at their decomposition temperature. M. CLARK.

Reactions of nitroso-derivatives with unsaturated compounds. IV. Dinitrones corresponding with α -diketonic acids. L. ALESSANDRI (Gazzetta, 1926, 56, 398—416).—The dinitrone from ethyl phenylpropionate and *p*-nitrosodimethylaniline, m. p. 168—169° (decomp.) (cf. this vol., 287), hydrolyses to the latter, ethyl benzoylglyoxylate, and *p*-aminodimethylaniline. In ethyl alcohol, the additive product previously described is obtained, orange-red with metallic reflex, m. p. 138—139° (slight decomp.), from which the dinitrone can be regenerated; and in methyl alcohol, the product, C₂₇H₃₀O₄N₄.MeOH, reddish-purple with metallic reflex, m. p. 143—144° (slight decomp.).

From ethyl phenylpropionate and *p*-nitrosomethylaniline, proceeding as before, there is obtained the dinitrone, C₂₅H₂₆O₄N₄, red, m. p. 189—190° (decomp.), which hydrolyses to *p*-nitrosomethylaniline and ethyl benzoylglyoxylate. E. W. WIGNALL.

2:3-Aminonaphthoic acid. SOC. CHEM. IND. IN BASLE.—See B., 1926, 736.

1:4- and 1:5-Naphthylaminesulphonic acids. E. F. EHRHARDT and R. M. HERWARD.—See B., 1926, 736.

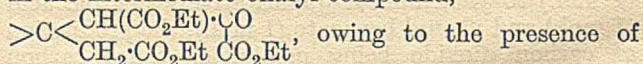
Optical activity and the polarity of substituent groups. IV. *sec*.- β -Octyl esters of *o*-, *m*-, and *p*-methoxy- and nitro-benzoic acids. H. G. RULE and (Miss) A. H. NUMBERS (J.C.S., 1926, 2116—2123).—In an examination of the influence of nuclear substitution on the optical rotatory power of β -octyl benzoate, the following were prepared, by condensation of *sec*.- β -octyl alcohol, $[\alpha]_D^{20} \pm 8.14^\circ$, with the required acid chloride in presence of pyridine: *l*- β -octyl *o*-methoxybenzoate, b. p. 187.5°/13 mm., $d_4^{20.3}$ 1.0004, $[\alpha]_D^{20} -12.59^\circ$; *m*-methoxybenzoate, b. p. 187.5°/12 mm., $d_4^{20.4}$ 0.9939, $[\alpha]_D^{20} -35.48^\circ$; *anisate*, b. p. 189°/13 mm., d_4^{20} 0.9968, $[\alpha]_D^{20} -42.88^\circ$; *o*-nitrobenzoate, b. p. 204°/15 mm., d_4^{20} 1.0735, $[\alpha]_D^{20} -43.56^\circ$;

m-nitrobenzoate, b. p. 212°/18 mm.; *p*-nitrobenzoate, m. p. 29.5—30°. Densities, rotatory powers, and specific rotations of *l*- β -octyl *o*-, *m*-, and *p*-methoxybenzoate, of *l*- β -octyl *o*-nitrobenzoate, and of *d*- β -octyl *m*- and *p*-nitrobenzoate, for various temperatures and wave-lengths, are tabulated, and also the molecular rotations and dispersion ratios of *d*- β -octyl *o*-, *m*-, and *p*-methoxybenzoates and *o*-, *m*-, and *p*-nitrobenzoates. The *o*-, *p*-directive methoxy-group causes a depression and the *m*-directive nitro-group an exaltation of rotatory power. The nitro-groups affect both rotation and acidic strength in the order *o*-NO₂ > *p*-NO₂ > *m*-NO₂ > H; the weaker methoxy-groups give the sequence, for rotatory powers, *p*-OMe > *m*-OMe > H > *o*-OMe, and for acidic strength *o*-OMe > H > *p*-OMe. Except in the case of octyl *o*-methoxybenzoate, the rotation of each ester falls with rise of temperature. F. M. HAMER.

Synthesis of iridic acid. F. MAUTHNER (Annalen, 1926, 449, 102—108).—3-Hydroxy-4:5-dimethoxybenzoic acid, m. p. 193—194°, is easily prepared by methylation of methyl gallate with methyl sulphate, followed by hydrolysis with alkali (cf. Herzog and Pollak, A., 1903, i, 89; Fischer and Freudenberg, *ibid.*, 1912, i, 471, 887). The acid is condensed with methyl chloroformate to give 3-methylcarbonato-4:5-dimethoxybenzoic acid, m. p. 146—147°, from which, by reduction of the acid chloride, m. p. 65—66°, with hydrogen and palladium, is obtained 3-methylcarbonato-4:5-dimethoxybenzaldehyde. This is hydrolysed to 3-hydroxy-4:5-dimethoxybenzaldehyde, m. p. 60—61° (semicarbazone, m. p. 211—212°; *p*-nitrophenylhydrazone, m. p. 212—213°), which is converted, by way of the azlactone (condensation product with hippuric acid), m. p. 140—141°, into iridic acid (3-hydroxy-4:5-dimethoxyphenylacetic acid), m. p. 118°, identical with the natural product (de Laire and Tiemann, A., 1894, i, 47).

C. HOLLINS.

Formation and stability of spiro-compounds. XIII. spiro-Compounds from substituted lævulic acids. E. ROTHSTEIN and J. F. THORPE (J.C.S., 1926, 2011—2017).—The failure of diethylglutaric acid and cyclohexanediacyetic acid to give cyclic pentadiones when condensed with ethyl oxalate was ascribed to overlapping of the end reacting groups in the intermediate oxalyl compound,



owing to the presence of the α - and α' -carbethoxy-groups, as the tetrahedral angle between the groups CH₂·CO₂Et became increasingly diminished by substitution (Dickens, Kon, and Thorpe, *ibid.*, 1922, 121, 1496). A four-membered ring is formed in the case of the diethyl compound, whereas with the cyclohexane derivative, where further overlapping occurs, no ring formation takes place. There is no possibility here of the three-membered ring formation which might be expected on the analogy of the production of cyclohexanespirocyclopropan-2-ol-2:3-dicarboxylic acid from α -ketocyclohexanediacyetic acid on boiling with concentrated potassium hydroxide solution. The correctness of these explanations is confirmed by preparation of

cyclopentane compounds from ethyl 1-acetylcyclohexane-1-acetate and ethyl $\beta\beta$ -dimethyl-lævulate by direct ring closure under the influence of dry sodium ethoxide. The distance between the two reacting groups is sufficiently increased by the substitution of the carbethoxy-groups by hydrogen atoms to make possible the formation of the five-membered ring, and the cyclohexane compound now gives a higher yield of cyclic dione than the $\beta\beta$ -dimethyl ester.

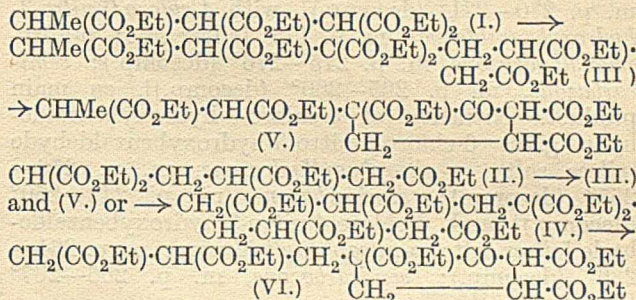
1-Carboxycyclohexane-1-acetic acid, m. p. 134° (cf. Lapworth, *ibid.*, 1922, 121, 2754, m. p. 132°), yields the anhydride, m. p. 55°, and the ethyl ester, b. p. 175–180°/11 mm. The latter is converted through the acid chloride, by the action of zinc methyl iodide, into ethyl 1-acetylcyclohexane-1-acetate, b. p. 155°/14 mm. The free acid has m. p. 82° (semicarbazone, m. p. 212°). The ethyl ester does not give a spirocyclopropane ring when boiled with concentrated potassium hydroxide solution, but yields, with sodium ethoxide, cyclohexanespirocyclopentane-2:4-dione, m. p. 180°. The constitution of the last-named compound is shown by oxidation with alkaline sodium hypochlorite to 1-carboxycyclohexane-1-acetic acid. cycloHexanespiro-3-bromo- Δ^2 -cyclopenten-2-ol-4-one has m. p. 238°. Ethyl $\beta\beta$ -dimethyl-lævulate yields 1:1-dimethylcyclopentane-2:4-dione, whence 3-bromo-1:1-dimethyl- Δ^2 -cyclopenten-2-ol-4-one, m. p. 203°, is obtained. M. CLARK.

Glutaconic acids. XX. Tetrahydroisophthalic acid. E. H. FARMER and H. L. RICHARDSON (J.C.S., 1926, 2172–2178).— Δ^2 -Tetrahydroisophthalic acid, prepared by reduction of isophthalic acid as described by Perkin and Pickles (*ibid.*, 1905, 87, 293), does not yield a hydroxy-anhydride by the methods applicable to glutaconic acids, whilst its ester cannot be methylated. When its anhydride is heated with ethyl alcohol, two forms of ethyl hydrogen Δ^2 -tetrahydroisophthalate are obtained, m. p. 44–45° and 40–41°. The anhydride with methyl alcohol yields one methyl hydrogen ester, m. p. 59°, which on addition of bromine followed by treatment with diethylamine gives bromotetrahydroisophthalic acid ester, reducible to a substance, m. p. 41–43°, the original acid ester, and the isomeric methyl hydrogen ester, b. p. 172–174°/1 mm. The action of methyl iodide on the silver salt of the acid forms methyl Δ^2 -tetrahydroisophthalate, b. p. 134–135°/7 mm.; amide, m. p. 239°. After an attempt to methylate the Δ^2 -ester by means of methyl iodide in the presence of sodium methoxide, the ester recovered was methyl Δ^3 -tetrahydroisophthalate. Oxidation of the original acid with ozone gives tricarballic acid, which cannot arise from the true Δ^2 -form. The behaviour of the Δ^2 -acid is unusual for a glutaconic acid and it is suggested that it is actually the *cis*- Δ^4 -compound.

F. M. HAMER.

Constitution of the yellow sodium compounds from ethyl citraconate (or itaconate) and ethyl sodiomalonate. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1926, 1912–1917; cf. Ingold, Shoppee, and Thorpe, *this vol.*, 939).—The yellow sodium compound formed as a by-product when ethyl malonate acts on ethyl citraconate (or itaconate) in the presence

of excess of sodium ethoxide is a mixture of two closely similar isomerides, which yield, on acidification, the corresponding ketonic esters. The mixture is produced by reaction of the primary condensation products, (I) and (II), with a second molecule of citraconic or itaconic ester, followed by elimination of alcohol to give the products (V) and (VI):



The results show that, under the experimental conditions used, ethyl citraconate and ethyl itaconate are interconvertible, their primary additive products with ethyl malonate being (I) and (II), respectively.

The constitution of both keto-esters follows from the fact that (I) condensed with either citraconic or itaconic ester gives only a liquid ester, ethyl α -1:3:4-tricarbethoxy-2-ketocyclopentyl- β -methylsuccinate (V), whilst (II) condensed in the same way gives a mixture of (V) with ethyl ω -1:3:4-tricarbethoxy-2-ketocyclopentylmethylsuccinate (VI), m. p. 83°. Hydrolysis of (V) gives α -4-carboxy-2-ketocyclopentyl- β -methylsuccinic acid, m. p. 148–149°. Hydrolysis of (VI) gives ω -4-carboxy-2-ketocyclopentylmethylsuccinic acid, m. p. 173° [ethyl ester, b. p. 247°/18 mm. (semicarbazone, m. p. 105°)], oxidised by permanganate to $\beta\delta$ -dicarboxysuberic acid, m. p. 206–207°. Butane- $\alpha\beta\gamma$ -tetracarboxamide, m. p. 267°, is obtained from (I) by the action of ammonia. M. CLARK.

Isomerism of the oximes. XXV. Dissociation constants of some isomeric aldoximes. O. L. BRADY and R. F. GOLDSTEIN (J.C.S., 1926, 1918–1924).—Measurement of the dissociation constants of four pairs of isomeric aldoximes, α - and β -benzaloxime, α - and β -o- and *m*-nitrobenzaloxime, and α - and β -cinnamaloxime, shows that, in each case, the α - is a stronger acid than the β -isomeride. One other β - and eight other α -aldoximes were investigated to determine whether the acidity of the α -isomeride bore any relation to the ease of formation of the β -compound, but without positive result. The evidence regarding the configuration of the aldoximes afforded by their physical properties is at variance with the deductions drawn from their chemical reactions. M. CLARK.

Nitration of chlorinated 3-hydroxybenzaldehydes and some consequences of adjacent substitution. H. H. HODGSON and H. G. BEARD (J.C.S., 1926, 2030–2036).—Nitration of 2-chloro-3-hydroxybenzaldehyde yields 2-chloro-4-nitro-3-hydroxybenzaldehyde, m. p. 166° [silver salt; *p*-nitrophenylhydrazone, m. p. 294–295° (decomp.); semicarbazone, m. p. 271–272° (decomp.); oxime, m. p. 170°; methyl ether, m. p. 107°], and 2-chloro-6-nitro-

3-hydroxybenzaldehyde, m. p. 153° [silver salt; p-nitrophenylhydrazone, m. p. 232—233°; semicarbazone, m. p. 234° (decomp.); oxime, m. p. 175°; methyl ether, m. p. 134°]. Nitration of 4-chloro-3-hydroxybenzaldehyde gives a little 4-chloro-2-nitro-3-hydroxybenzaldehyde, m. p. 161° [silver salt; p-nitrophenylhydrazone, m. p. 281—282° (decomp.); semicarbazone, m. p. 270—271° (decomp.)], with 4-chloro-6-nitro-3-hydroxybenzaldehyde, m. p. 175° [silver salt; p-nitrophenylhydrazone, m. p. 275—276° (decomp.); semicarbazone, m. p. 265—266° (decomp.)], as main product. Nitration of 6-chloro-3-hydroxybenzaldehyde gives 6-chloro-2-nitro-3-hydroxybenzaldehyde [silver salt; p-nitrophenylhydrazone, m. p. 256—257° (decomp.); semicarbazone, m. p. 249—250° (decomp.)] and 6-chloro-4-nitro-3-hydroxybenzaldehyde [silver salt; p-nitrophenylhydrazone, m. p. 284—286° (decomp.); semicarbazone, m. p. 266—267° (decomp.)].

Mononitration of 2:4- and 2:6-dichloro-3-hydroxybenzaldehydes gives 2:4-dichloro-6-nitro-3-hydroxybenzaldehyde, m. p. 107° (silver salt; p-nitrophenylhydrazone, m. p. 279—280°; semicarbazone, +H₂O, softening at 140—150°), and 2:6-dichloro-4-nitro-3-hydroxybenzaldehyde, m. p. 80° [silver salt; p-nitrophenylhydrazone, m. p. 279—280° (decomp.); semicarbazone, m. p. 255—256°; oxime, m. p. 195°]. Dinitration of 2-, 4-, and 6-chloro-3-hydroxybenzaldehydes gives 2-chloro-4:6-dinitro-3-hydroxybenzaldehyde, m. p. 110° [ammonium and silver salts; p-nitrophenylhydrazone, m. p. 277—279° (explosive decomp.); semicarbazone, m. p. 240—242° (decomp.); oxime, m. p. 142°]; 4-chloro-2:6-dinitro-3-hydroxybenzaldehyde, m. p. 118—119° (silver salt; p-nitrophenylhydrazone, exploding 235—236°; semicarbazone, exploding at about 200°); and 6-chloro-2:4-dinitro-3-hydroxybenzaldehyde, m. p. 121.5° [silver salt; p-nitrophenylhydrazone, m. p. 285—286° (decomp.); semicarbazone, m. p. 267—269° (decomp.)].

The potent influence on adjacent groups of chlorine substitution in position 2 is illustrated by reference to the volatility in steam of the 2-chloro-3-methoxyderivatives (where the methoxy-group is shown to function in this connexion as a phenolic hydroxyl) and to the anomalous colour reaction of 2-chloro-4:6-dinitro-3-hydroxybenzaldehyde-p-nitrophenylhydrazone in aqueous sodium hydroxide. Chlorinated 4-nitro-3-hydroxybenzaldehydes are, in general, sparingly soluble in water but readily soluble in non-hydroxylic solvents. The reverse holds for the 6-nitro-isomerides. The last-named compounds induce sneezing.

M. CLARK.

Three-carbon system. VI. Systems containing the benzoyl group. M. D. FARROW and G. A. R. KON (J.C.S., 1926, 2128—2138).— α - Δ^1 -cyclohexenylacetophenone, b. p. 172—178°/14 mm., d_4^{25} 1.04157, n_D^{25} 1.55630 [oxime, m. p. 101—102°; methyl derivative, b. p. 168—170°/15 mm., d_4^{18} 0.99896, n_D^{18} 1.54314, semicarbazone, m. p. 191—192°; ethyl derivative (prepared by ethylation; it could not be prepared by the action of magnesium phenyl bromide on α -cyclohexylidenebutynitrile, d_4^{25} 0.92283, n_D^{25} 1.48917, obtained by ethylating ethyl α -cyano-cyclohexylideneacetate and treating the product with

sodium ethoxide), b. p. 184—185°/19 mm., d_4^{25} 1.01155, n_D^{25} 1.54077, semicarbazone, m. p. 212°], is prepared by condensation of cyclohexanone and acetophenone in the presence of sodium ethoxide and also, together with diphenyl, by the action of magnesium phenyl bromide, or, better, its zinc chloride double compound, on α - Δ^1 -cyclohexenylacetyl chloride or cyclohexylideneacetyl chloride. The semicarbazone from either source has m. p. 94—115°, 120—121°, and the ketone is oxidised by ozone to an aldehydic oil, hydrolysable to benzoic acid, but the existence of the $\alpha\beta$ -phase of the ketone is indicated in that with ethyl sodioacetoacetate it gives a compound, C₁₇H₂₀O, b. p. 210—220°/20 mm., m. p. 69—70° (semicarbazone, m. p. 219°), which is regarded as

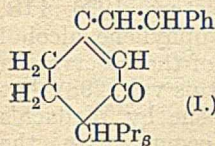
$\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CPh} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{CH}$. With sodium ethoxide, the ketone yields a substance, C₂₈H₃₂O₂, m. p. 201° (considered to be produced by condensation of the $\alpha\beta$ -phase with the sodio-derivative of the $\beta\gamma$ -phase), which with acetic acid gives a compound, C₂₈H₃₀O, m. p. 106°. From α - Δ^1 -cyclopentenylacetyl chloride or cyclopentylideneacetyl chloride is prepared α - Δ^1 -cyclopentenylacetophenone, b. p. 163—165°/16 mm., d_4^{25} 1.04982, n_D^{25} 1.56437 (semicarbazone, m. p. 157°; ethyl derivative, b. p. 162°/11 mm., d_4^{18} 1.01725, n_D^{18} 1.54191, semicarbazone, m. p. 196.5°); the product of its condensation with ethyl sodioacetoacetate gives a semicarbazone, m. p. 193°.

Condensation of acetophenone with $\beta\beta$ -diethylacryl chloride yields α -phenyl- γ -ethyl- $\Delta\beta$ -penten- α -one, b. p. 138°/8 mm., d_4^{18} 0.98638, n_D^{18} 1.54353 (semicarbazone, m. p. 90°; hydroxylamine yields the oximino-oxime, m. p. 158°, and a compound, m. p. 101—102°). Use of the chloride of γ -ethyl- $\Delta\gamma$ -pentenoic acid yields α -phenyl- γ -ethyl- $\Delta\gamma$ -penten- α -one, b. p. 146°/17 mm., d_4^{18} 0.98513, n_D^{18} 1.53372. These two ketones form an equilibrium mixture in the presence of sodium ethoxide. With ethyl sodioacetoacetate both give the same product (semicarbazone, m. p. 178—179°). All the four ketones are hydrolysed on boiling with acids and alkalis, yielding, respectively, cyclohexanone, cyclopentanone, and diethyl ketone, together with acetophenone; cyclohexenylacetone undergoes a similar fission. All the ketones show exaltation of the molecular refraction, and resemble closely the corresponding methyl ketones.

F. M. HAMER.

Piperitone. VIII. Condensation of piperitone with aldehydes. J. C. EARL and J. READ (J.C.S., 1926, 2072—2076; cf. *ibid.*, 1921, 119, 784).—Piperitone condenses with anisaldehyde in alcoholic solution, in presence of sodium ethoxide, giving anisylidene-dl-piperitone, m. p. 98°, rhombic crystals, $a:b:c=0.91900:1:0.82044$. Piperonylidene-dl-piperitone, m. p. 128°, and opianylidene-dl-piperitone, m. p. 157° (calcium salt described), are similarly prepared. Salicylidene-dl-piperitone, m. p. 177°, obtained by use of aqueous sodium hydroxide, is reduced by zinc dust and alkali to two isomeric dihydro-derivatives, C₁₇H₂₂O₂. The aldehyde condensations also take place, to a small extent, in presence of hydrochloric acid. Since benzylidene-piperitone is oxidised by potassium permanganate

to α -isopropylglutaric acid, it is concluded that condensation of piperitone with benzaldehyde occurs in the 7-position; the products previously described (A., 1924, i, 301) are regarded as 7-benzylidene-*dl*-piperitone (I), 7-benzyl-*dl*-isomenthone, 7-benzyl-*dl*-isomenthol, and 2-benzylidene-7-benzyl-*dl*-isomenthone. F. M. HAMER.



***p*'-Methylchalkone [*p*-tolyl styryl ketone].** Isomerism of the *cis*-cinnamic acids. C. WEYGAND and A. MATTHES (Annalen, 1926, 449, 29—62; cf. Weygand, A., 1924, i, 521).—The m. p. previously given for α - and β -forms of *p*-tolyl styryl ketone are now corrected to 74—75.4° (α) and 55—56° (β). A third (γ) isomeride, m. p. 45°, is obtained when either is heated for a short time at 200° and rapidly cooled. This passes spontaneously into the β - or α -form, and is extraordinarily sensitive to traces of the isomerides.

The α -form under all conditions gives only a monopicate, m. p. 99—100°; β gives the same monopicate, but only after about 30 min. (conversion into α). When the orange-yellow solution of α or β in sulphuric acid is diluted with water, the β -form (not α - as previously reported) is precipitated, the conversion of α into β taking place by way of the halochromic compound $>CO \dots HX$. The α -form exhibits behaviour which varies according to the previous history—age, heat treatment, vacuum distillation, crystallisation, etc.—and may give, after melting, a stable β -form, or β quickly changing to α , or the very labile γ -form. This supports the suggestion (cf. Schaum, Schaeling, and Klausung, A., 1916, i, 405) that solid solutions of two kinds of molecules are normally obtained. It is concluded that polymorphism is a special case in the relations of a pseudo-ternary system.

Phenyl styryl ketone gives under all conditions a dipicrate, m. p. 97—98°. Phenyl *p*-methylstyryl ketone, m. p. 96.5°, and *p*-tolyl *p*-methylstyryl ketone, m. p. 127.5—129° (from *p*-methylacetophenone and *p*-tolualdehyde), are α -compounds and also yield only dipicrates, m. p. 92—94° and 101—102.5°, respectively. *p*-Ethylphenyl styryl ketone, m. p. 61—61.5°, b. p. 218—221°/11 mm. (from *p*-ethylacetophenone, b. p. 116°/14 mm., and benzaldehyde), is a β -compound, whilst *p*-*n*-propylphenyl styryl ketone, m. p. 46—47.1° (from *p*-propylacetophenone, b. p. 140—142°/26 mm.), is a γ -compound; neither forms a picrate.

A review of the accumulated data on the isomeric *cis*-triads in the cases of cinnamic acid, *p*-tolyl styryl ketone, and phenyl β -bromo- α -ethoxystyryl ketone leads to the conclusion that isomerism may result from the intermolecular saturation of residual valencies (e.g., between the carbonyl group and a benzene nucleus) in different ways. C. HOLLINS.

Benzylbenzoin [benzoylphenylbenzylcarbinol]. J. PASCUAL (VILA) and J. CEREZO (Anal. Fís. Quím., 1926, 24, 395—399; cf. A., 1925, i, 557).—Experimental details relating to a previous communication are given. Benzylbenzoin acetate has m. p. 128—129°. G. W. ROBINSON.

Catalytic hydrogenation of the carbonyl group in aromatic compounds under pressure in presence of copper. I. B. KUBOTA and T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res., 1926, 5, 1—6; cf. this vol., 727).—Aromatic ketones undergo reduction to alcohols when treated with hydrogen under pressure in presence of copper. Benzil at 100° and 76—92 atm. when so treated gives benzoin, hydrobenzoin, and isohydrobenzoin; benzoylacetone at 83° gives β -hydroxy- β -phenylethyl methyl ketone, b. p. 134—136°/10 mm., phenylhydrazone, m. p. 120—122° (partial decomp.), and a small quantity of phenyl β -hydroxy-*n*-propyl ketone, whilst at 105° it gives α -phenyl-*n*-butane- α -diol. Phthalic anhydride at 120° yields “hydrophthalyl-lactonic acid” (benzylphthalide-*o*-carboxylic acid) and dihydroxyphthalan, $C_6H_4 \begin{smallmatrix} <CH(OH) \\ <CH(OH) \end{smallmatrix} >O$, a colourless liquid giving a dibenzoate. B. W. ANDERSON.

Hexoylresorcinol [2 : 4-dihydroxyphenyl *n*-amyl ketone] and some of its derivatives. D. TWISS (J. Amer. Chem. Soc., 1926, 48, 2206—2212).—Hexoylresorcinol, m. p. 56—57°, b. p. 217—218°/14 mm., or b. p. 343—345° (decomp.) at atmospheric pressure (cf. Dohme, Cox, and Miller, this vol., 838), is obtained by boiling ethyl hexoate with resorcinol and zinc chloride. The following derivatives are described: monomethyl ether, b. p. 189—192°/12—13 mm.; (?) dimethyl ether, m. p. 35—36°; oxime, m. p. 190—191° (decomp.); *p*-nitrobenzoate, m. p. 89—91°; monoacetate, b. p. 213—215°/14 mm.; diacetate, b. p. 229—232°/13 mm. (decomp.); mononitro-derivative, m. p. 73—74°; and dibromo-derivative, m. p. 102—103°. Hexylresorcinol (2 : 4-dihydroxy-*n*-hexylbenzene), m. p. 67—68°, b. p. 198—200°/13—14 mm., or b. p. 333—335° (decomp.) at atmospheric pressure, is obtained by reducing hexoylresorcinol with amalgamated zinc and hydrochloric acid. The dimethyl ether, b. p. 164—165°/12 mm., and diacetate, b. p. 198—199°/15 mm., are described. The influence of the keto-group in hexoylresorcinol is shown by the fact that this compound when methylated with methyl iodide or sulphate gives only a monomethyl ether, whilst hexylresorcinol readily gives the dimethyl ether. The monomethyl ether is probably 2-hydroxy-4-methoxyphenyl *n*-amyl ketone. Condensation of hexylresorcinol with ethyl acetoacetate in presence of 82% sulphuric acid affords 7-hydroxy-4-methyl-6-hexylcoumarin, m. p. 165°.

F. G. WILLSON.

Action of thionyl chloride on hydroxyanthraquinones. III. A. GREEN (J.C.S., 1926, 2198—2204; cf. A., 1924, i, 1080).—By boiling purpurin with thionyl chloride, it is converted into 1 : 2-thionylpurpurin, m. p. 211—213°, which is rapidly reconverted into purpurin by the action of moisture, and with boiling acetic acid yields 2-acetylpurpurin. Anthrapurpurin and thionyl chloride give 1 : 2-thionyl-7-chlorothionylantrapurpurin, m. p. 179° (decomp.), converted by boiling acetic acid into 2-acetylantrapurpurin, m. p. 296—298° (decomp.), by benzoic acid at 170° into 2-benzoylantrapurpurin, m. p. 203—205°, and by boiling acetic anhydride into triacetylantrapurpurin, m. p. 225—227°. Thionylhystazarin,

m. p. 200°, when boiled with acetic acid, reverts to hystazarin, and with boiling acetic anhydride slowly yields diacetylhystazarin, m. p. 211—213°. 2:3-Thionylantragallol with acetic acid gives anthragallol, m. p. 313—314°, and 3-acetylanthagallol, m. p. 210—212°, and by its regulated interaction with acetic anhydride gives 2:3-diacetylanthagallol, m. p. 223—224°, which indicates that the thionyl group is not linked to the 1-position of the anthragallol nucleus. Anthraquinone, 5-chloro-1-hydroxyanthraquinone, m. p. 223—224° (prepared from 5-chloro-1-aminoanthraquinone) (acetyl derivative, m. p. 205°), 1-hydroxy-, 4-chloro-1-hydroxy-, 1:8-dihydroxy-, and 2-hydroxy-anthraquinone do not react with boiling thionyl chloride. M. p. of hydroxyanthraquinones and their acetyl derivatives are tabulated.

F. M. HAMER.

Benzanthrone derivatives [from α -naphthaleneazobenzene-*m*-carboxylic acids]. G. KALTSCHER, R. MÜLLER, and F. FRISTER.—See B., 1926, 735.

Catalytic hydrogenation of carone. S. N. IYER and J. L. SIMONSEN (J.C.S., 1926, 2049—2052).—When carone is reduced using platinum chloride and hydrogen, it behaves like an $\alpha\beta$ -unsaturated ketone. After the absorption of 1 mol. of hydrogen, the product consists mainly of *p*-menthan-2-one, whilst on complete reduction (2 mols. of hydrogen) *p*-menthane (in small quantity), *p*-menthan-2-ol [phenylurethane, (carbamate), m. p. 107—108°], and *l*-*p*-menthane-2:8-diol are obtained.

R. W. WEST.

Identity of uncineol with eudesmol. A. R. PENFOLD (J. Proc. Roy. Soc. N.S. Wales, 59, 124—127).—The stearoptene, uncineol, isolated from the essential oil of *Melaleuca uncinata*, has been shown to be identical with eudesmol contained in eucalyptus oils. The pure substance has m. p. 80.5—81°, and after fusion m. p. 82°, b. p. 155—156°/10 mm., $[\alpha]_D^{20} +33.45^\circ$ in chloroform; the hydrochloride has m. p. 75—76°.

C. J. STILL.

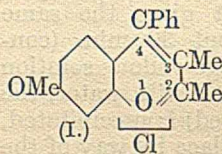
Steric hindrance and *cis-trans*-isomerism. II. Borneol, isoborneol, and their esters. G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1926, [iv], 39, 924—942).—Camphor is hydrogenated with difficulty in acetic acid using platinum-black, yielding 90% of isoborneol. This is then further dehydrated and reduced to isocamphane. Comparative measurements show that bornyl esters are more readily formed and also more readily hydrolysed than those of isoborneol. Moreover, borneol reacts more readily with magnesium ethyl bromide than does isoborneol. The lesser reactivity of the latter must be due to steric hindrance, and this fact, together with its direct formation from camphor, indicate that isoborneol has the *cis*-configuration, i.e., the hydroxyl group and the bridge are on the same side of the cyclohexane ring. *d*-Bornyl isovalerate, b. p. 151—152°/26 mm., $[\alpha]_{578} +36.7^\circ$, d_4^{18} 0.9486, n_D^{18} 1.4605; *l*-isobornyl isovalerate, b. p. 142—144°/18 mm., $[\alpha]_{578} -56^\circ$, d_4^{18} 0.9523, n_D^{18} 1.462, and *l*-isobornyl benzoate, b. p. 185°/11 mm. (corr.), $[\alpha]_{578} -78^\circ$, d_4^{18} 1.057, n_D^{18} 1.529, are described.

H. E. F. NOTTON.

Caryophyllene alcohols and their occurrence in nature. J. M. ROBERTSON (Nature, 1926, 118, 156).—The non-occurrence of caryophyllene alcohol in nature is not surprising in view of the observation (Henderson, Robertson, and Kerr, this vol., 298) that in its preparation from caryophyllene by Wallach's hydration method ring-closure occurs with the irreversible production of a tricyclic structure. Dicyclic caryophyllol (*loc. cit.*), however, should occur in nature, and this substance may, in fact, be identical with the dicyclic sesquiterpene alcohol obtained from clove stems by Semmler (A., 1912, i, 479).

A. A. ELDRIDGE.

Styrylbenzopyrylium salts. VII. Conversion of 7-methoxy-2:3-dimethylchromone into styrylpyrylium salts. I. M. HEILBRON and A. ZAKI (J.C.S., 1926, 1902—1906).—When 7-methoxy-2:3-dimethylchromone is treated in benzene solution with 2 mols. of magnesium phenyl bromide, it yields 7-methoxy-4-phenyl-2:3-dimethylbenzopyrylium chloride (I) (ferrichloride, m. p. 114°; perchlorate, m. p. 206°), which readily condenses with aromatic aldehydes in alcoholic solution to yield 2-styrylbenzopyrylium salts (cf. Buck and Heilbron, *ibid.*, 1923, 123, 2521). The



substitution of auxochromic groups in the phenyl group in position 4 has a decided influence on the colour of the salts. The following compounds are obtained by condensing (I) with aldehydes: 7-methoxy-4-phenyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium chloride, m. p. 275° (decomp.) (perchlorate described); 2-*p*-methoxystyryl compound (ferrichloride described); 2-*p*-hydroxy-*m*-methoxystyryl compound (ferrichloride described); 2-*p*-dimethylaminostyryl compound (ferrichloride, diperchlorate, and monopерchlorate described). When 7-methoxy-2:3-dimethylchromone is treated with magnesium *p*-anisyl bromide, it yields 7-methoxy-4-*p*-anisyl-2:3-dimethylbenzopyrylium chloride, m. p. 160° (ferrichloride described), whilst with magnesium *p*-dimethylaminophenyl iodide it yields 7-methoxy-4-*p*-dimethylaminophenyl-2:3-dimethylbenzopyrylium chloride (perchlorate described). The 4-*p*-anisyl chloride condenses with aldehydes in manner similar to that of the 4-phenyl analogue, and thus affords: 7-methoxy-4-*p*-anisyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium chloride (ferrichloride described); 2-*p*-methoxystyryl compound (ferrichloride described); and 2-*p*-dimethylaminostyryl compound (ferrichloride, m. p. 125°).

R. W. WEST.

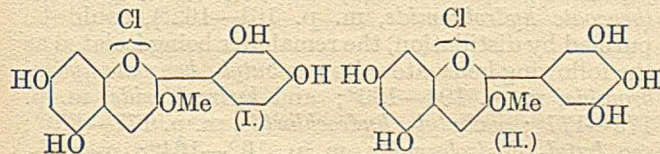
Synthesis of pyrylium salts of anthocyanidin type. IX. Hydroxyflavylium salts. A. ROBERTSON and R. ROBINSON (J.C.S., 1926, 1951—1959).—Condensation of salicylaldehyde with acetoveratrone yields 3:4-dimethoxyphenyl-2-hydroxystyryl ketone, m. p. 150—151°, which is readily converted into 3':4'-dimethoxyflavylium chloride (ferrichloride, m. p. 196—196.5°). This on demethylation yields 3':4'-dihydroxyflavylium chloride, which gives an intense ferric chloride reaction. β -Resorcyraldehyde condenses with acetoveratrone to yield 7-hydroxy-3':4'-dimethoxyflavylium chloride (ferrichloride, m. p. 182—183°), which on demethylation yields 7:3':4'-tri-

hydroxyflavylium chloride (butinidin chloride), of which the alkali reactions resemble those of meco-cyanin. By condensations and demethylation of the products, the following compounds are obtained: from salicylaldehyde and ω -methoxyacetoveratrone, 3:3':4'-trimethoxyflavylium ferrichloride, m. p. 173°, and 3:3':4'-trihydroxyflavylium chloride; from oreyl-aldehyde and ω -methoxyacetoveratrone, 7-hydroxy-3:3':4'-trimethoxy-5-methylflavylium ferrichloride, m. p. 182—183°, and 3:7:3':4'-tetrahydroxy-5-methylflavylium chloride, the ferric chloride and alkali reactions of which resemble those of cyanidin; from 6:4'-dimethoxyflavylium chloride by demethylation, 6:4'-dihydroxyflavylium chloride; from 2-hydroxy-5-methoxybenzaldehyde and acetoveratrone, 6:3':4'-trimethoxyflavylium ferrichloride, m. p. 186°, and 6:3':4'-trihydroxyflavylium chloride; from 2-hydroxy-5-methoxybenzaldehyde and ω -methoxyacetoveratrone, 3:6:3':4'-tetramethoxyflavylium ferrichloride, m. p. 198—199°, and 3:6:3':4'-tetrahydroxyflavylium chloride; from *o*-vanillin and acetoveratrone, 8:3':4'-trimethoxyflavylium ferrichloride, m. p. 193—194°, from *o*-vanillin and ω -methoxyacetoveratrone, 3:8:3':4'-tetramethoxyflavylium ferrichloride, m. p. 162—163°, and 3:8:3':4'-tetrahydroxyflavylium chloride.

In the alkali reaction, hydroxyl in position 6 tends to increase the intensity and stability of the colour, whilst hydroxyl in position 8 tends towards a reverse effect.

R. W. WEST.

Synthesis of pyrylium salts of anthocyanidin type. X. Delphinidin chloride 3-methyl ether. E. S. GATEWOOD and R. ROBINSON (J.C.S., 1926, 1959—1967).—2:4-Diacetoxy- ω -methoxyacetophenone condenses with 2:4:6-triacetoxybenzaldehyde in a formic acid solution of hydrogen chloride yielding a product which on hydrolysis gives *morinidin chloride 3-methyl ether* (I). Sodium hydroxide causes con-



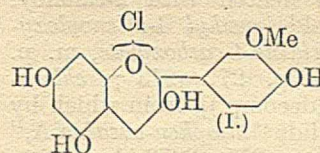
densation of 2-hydroxy-4:6-dimethoxybenzaldehyde with 3:4:5-trimethoxyacetophenone, m. p. 76—77°, yielding 3:4:5-trimethoxyphenyl 2-hydroxy-4:6-dimethoxystyryl ketone, m. p. 151—152°, which is readily converted by hydrochloric acid into 5:7:3':4':5'-pentamethoxyflavylium chloride, m. p. 150° (ferrichloride, m. p. 199—201°, perchlorate, and mercurichloride described). Demethylation of the chloride using phenol and hydriodic acid ultimately yields 7(or 5):3':4':5'-tetrahydroxy-5(or 7)-methoxyflavylium chloride.

When 3:4:5-triacetoxybenzoyl chloride reacts in ether solution with methyl sodio- α -dimethoxyacetate, the products after hydrolysis with aqueous-alcoholic potassium hydroxide may be separated by extraction first with ether and then with butyl alcohol. The ether-soluble product after acetylation is probably 3:4:5-triacetoxy- ω -methoxyacetophenone, m. p. 132—133°, but it will not condense with triacetoxybenzaldehyde to give a flavylium salt

analogous to (I). The product which is soluble in butyl alcohol probably contains the group $(OH)_3C_6H_2 \cdot CO \cdot CH(OMe) \cdot CO \cdot R$, since on acetylation it yields an oil which condenses with 2:4:6-triacetoxybenzaldehyde, the group $\cdot CO \cdot R$ being expelled, to give a product which hydrolyses to 5:7:3':4':5'-pentahydroxy-3-methoxyflavylium chloride (II). This delphinidin 3-methyl ether (II) is not identical with either myrtillidin chloride or petunidin chloride, and one of the possible formulæ for these compounds is thus eliminated.

R. W. WEST.

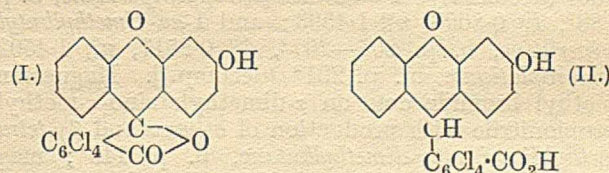
Synthesis of pyrylium salts of anthocyanidin type. XI. Synthesis of peonidin chloride. T. J. NOLAN, D. D. PRATT, and R. ROBINSON (J.C.S., 1926, 1968—1971).—When ω -chloro-4-acetoxyacetophenone is boiled with alcoholic potassium acetate, it yields 4-hydroxy- ω -acetoxyacetophenone, m. p. 127°, which on acetylation yields ω :4-diacetoxyacetophenone, m. p. 98°. Hydrogen chloride in formic acid solution causes condensation of ω :4-diacetoxyacetophenone with 2:4:6-triacetoxybenzaldehyde, and the product after hydrolysis gives a poor yield of pelargonidin chloride, $(OH)_2C_6H_2 \cdot C_3HO(OH) \cdot C_6H_4 \cdot OH \cdot Cl$. 4-Hydroxy- ω -acetoxy-3-methoxyacetophenone, m. p. 110°, is obtained from ω -chloroacetovanillone by the action of alcoholic potassium acetate, and on acetylation yields ω :4-



diacetoxy-3-methoxyacetophenone, m. p. 73°. Both these acetoxy-derivatives condense with 2:4:6-triacetoxybenzaldehyde, yielding products which give peonidin chloride (I) after hydrolysis.

R. W. WEST.

3-Hydroxytetrachlorofluoran and 3:4-dihydroxytetrachlorofluoran and some of their derivatives. W. R. ORNDORFF and C. H. JOHNSON (J. Amer. Chem. Soc., 1926, 48, 2221—2230).—Condensation of resorcinol with *o*-hydroxybenzoyltetrachlorobenzoic acid (cf. this vol., 290) in tetrachloroethane in presence of stannic chloride at 120—125° affords tetrachloro-3-hydroxyfluoran (I), m. p. not below 300° [monoammonium salt, red-brown, m. p. 277—280° (decomp.); monosodium salt, orange-red; m. p. not below 300°; barium salt (3H₂O), orange-red, decomp. above 300° (anhydrous); monoacetate, m. p. 198—200°; monobenzoate, m. p. 248—249°]. Bromination in glacial acetic acid affords tetrachloro-2:4-dibromo-3-hydroxyfluoran, m. p. not below 300° [mono-



acetate, (+1C₆H₆), m. p. 290—292°, whilst reduction with zinc and acetic acid yields tetrachloro-3-hydroxyhydrofluoran acid, (II), m. p. 257—258° (cf. Meyer and Hoffmeyer, A., 1892, 1228) (monoacetate, m. p. 187—188°). Substitution of pyrogallol for resorcinol

in the above condensation affords *tetrachloro-3:4-dihydroxyfluoran*, m. p. not below 300° [*monosodium* and *disodium* salts, m. p. not below 300°; *monobenzoate*, m. p. 238—240°; *dibenzoate*, m. p. 140° (+0.5C₆H₆), m. p. 220°]. Bromination in acetic acid yields *tetrachloro-2-bromo-3:4-dihydroxyfluoran*, m. p. not below 300° [*diacetate* (+0.5C₆H₆), m. p. 268—270° (decomp.)]. Whilst *tetrachlorohydroxyfluoran* does not absorb dry ammonia, its dibromo-derivative absorbs 1 mol., *tetrachlorodihydroxyfluoran* absorbs 1.22 mols., and its bromo-derivative absorbs 2.74 mols., the salts being orange-yellow, dark brown, and bluish-black, respectively. F. G. WILLSON.

Thiophen series. XIX. Thiophen-eucaine-A and some other thiophen derivatives. W. STEINKOPF and W. OHSE (*Annalen*, 1926, 448, 205—210).—Analogues of eucaine-A, stovaine, and benzoylquinine are prepared by the usual methods with the substitution of 2-thienoyl (thiophen-2-carboxyl) chloride for benzoyl chloride.

4-Hydroxy-2:2:6:6-tetramethylpiperidine-4-carboxylic acid (D.R.-P. 91121, 91122) has m. p. 340—343°, not 285° as given in the patents. The methyl ester hydrochloride, when heated with 2-thienoyl chloride at 145—155°, yields *methyl 4-thienoyloxy-2:2:6:6-tetramethylpiperidine-4-carboxylate*, m. p. 91—92° [*hydrochloride*, m. p. 272—273°; *chloroplatinate*, m. p. 234—235° (decomp.)], from which by methylation with methyl iodide "*thiophen-eucaine-A*," m. p. 123° [*hydrochloride*, m. p. 219—220° (decomp.)]; *chloroplatinate*, m. p. 239° (decomp.)], was obtained. By thienoylation of α -dimethylamino- β -methylbutan- β -ol, "*thiophen-stovaine*," C₄H₉S·CO₂·CMeEt·CH₂·NMe₂ (*hydrochloride*, m. p. 188°; *chloroplatinate*, m. p. 153°; *picrate*, m. p. 122°), is obtained. 2-Thienoylquinine (cf. benzoylquinine, D.R.-P. 178172, 178173), m. p. 133°, [α]_D²⁰ —11.4° (*chloroplatinate*, decomp. 240°), and 2-thienoyl-*p*-phenetidine, m. p. 172°, are also described.

C. HOLLINS.

Action of organo-magnesium compounds on nitriles. α -Aminonitriles. M. VELGHE (*Bull. Soc. chim. Belg.*, 1926, 35, 229—234; cf. A., 1925, i, 23).—Tertiary α -amino-nitriles react with organo-magnesium compounds by exchanging the nitrile group for the radical of the magnesium compound. Thus magnesium methyl, ethyl, and propyl bromides act on α -piperidino- α -methylpropionitrile to produce, respectively: 1- α -dimethylethylpiperidine, CMe₃·NC₅H₁₀, b. p. 166°, d_4^{20} 0.8465, n_D^{20} 1.4532 [*chloroplatinate*, m. p. 235° (decomp.)]; 1- α -dimethylpropylpiperidine, b. p. 188°, d_4^{20} 0.8608, n_D^{20} 1.4593; and 1- α -dimethylbutylpiperidine, b. p. 205—207°, d_4^{20} 0.8517, n_D^{20} 1.4592, [*chloroplatinate*, m. p. 221° (decomp.)]. Magnesium methyl bromide acts on α -dimethylamino- α -methylpropionitrile with production of ethane and β - γ -tetramethyldiamino- β - γ -dimethylbutane, b. p. 149°; magnesium ethyl bromide yields the same substance, and when the reaction is conducted at a low temperature and with high dilution, a little β -dimethylamino- β -methylbutane, b. p. 117—118°, is formed; whilst with magnesium propyl bromide the corresponding β -dimethylamino- β -methylpentane, b. p. 138—139°, d_4^{20}

0.7950 [*chloroplatinate*, m. p. 230° (decomp.)], is the main product of reaction. G. M. BENNETT.

Piperidine derivatives. II. 3-Carbethoxy-1-alkyl-4-piperidyl benzoates. III. 3-Carbethoxy-1-alkyl-4-piperidyl *p*-aminobenzoates. S. M. McELVAIN (*J. Amer. Chem. Soc.*, 1926, 48, 2179—2185, 2239—2242; cf. A., 1924, i, 985).—The following alkyl- β '-dicarbethoxydiethylamines, R·N(CH₂·CH₂·CO₂Et)₂, were prepared by condensation of the appropriate primary amines with ethyl β -bromopropionate and silver oxide in alcoholic solution (yields 65—75%): *ethyl*-, b. p. 126—128°/2 mm., d_{20}^{20} 1.0058, n_D^{20} 1.4385; *n-propyl*-, b. p. 132—134°/2 mm., d_{20}^{20} 0.9951, n_D^{20} 1.4393; *isopropyl*-, b. p. 128—130°/2 mm., d_{20}^{20} 0.9960, n_D^{20} 1.4388; *n-butyl*-, b. p. 154—156°/2 mm., d_{20}^{20} 0.9804, n_D^{20} 1.4400; *isobutyl*-, b. p. 153—156°/2 mm., d_{20}^{20} 0.9766, n_D^{20} 1.4384; *sec-butyl*-, b. p. 145—148°/2 mm., d_{20}^{20} 0.9861, n_D^{20} 1.4415; *n-amyl*-, b. p. 164—168°/2 mm., d_{20}^{20} 0.9669, n_D^{20} 1.4375; and *isoamyl*- β '-dicarbethoxydiethylamine, b. p. 160—164°/2 mm., d_{20}^{20} 0.9689, n_D^{20} 1.4370. Treatment of the above tertiary amines with sodium in boiling xylene affords the corresponding 3-carbethoxy-1-alkyl-4-piperidones, which were isolated as the following hydrochlorides: *ethyl*-, m. p. 143—145°, *n-propyl*-, m. p. 138—140°; *isopropyl*-, m. p. 144—146°; *n-butyl*-, m. p. 127—129°; *isobutyl*-, m. p. 124—126°; *sec-butyl*-, non-crystalline; *n-amyl*-, m. p. 141—143°; and 3-carbethoxyisoamyl-4-piperidone *hydrochloride*, m. p. 153—155°. When reduced with hydrogen in presence of platinum oxide, the above hydrochlorides yield the corresponding 4-hydroxy-3-carbethoxy-1-alkylpiperidines, of which only the *ethyl*-, b. p. 130—132°/2 mm., d_{20}^{20} 1.0754, n_D^{20} 1.4712 (*benzoate hydrochloride*, m. p. 214—216°), *n-propyl*-, b. p. 132—133°/2 mm., d_{20}^{20} 1.0502, n_D^{20} 1.4680 (*benzoate hydrochloride*, m. p. 208—210°), and 4-hydroxy-3-carbethoxyisopropylpiperidine, b. p. 128—130°/2 mm., d_{20}^{20} 1.0522, n_D^{20} 1.4695 (*benzoate hydrobromide*, m. p. 161—162°), could be purified by distillation, the remainder being isolated as the following benzoate salts: *n-butyl*-, *benzoate hydrobromide*, m. p. 194—196°; and *hydrochloride*, m. p. 175—177°; *isobutyl*-, *hydrochloride*, m. p. 177—179°; *sec-butyl*-, *hydrobromide*, m. p. 162—164°; *n-amyl*-, *hydrochloride*, m. p. 164—166°; and 4-benzoxo-3-carbethoxyisoamylpiperidine *hydrochloride*, m. p. 179—181°. These salts have marked local anaesthetic action, the effect of which increases, whilst the toxicity decreases, with increase in size of the alkyl radical attached to the nitrogen atom. The amyl derivatives possess greater anaesthetic power than cocaine, and show only about one thirtieth of its toxicity. Aqueous solutions of the salts are acid, and cause irritation and hyperæmia.

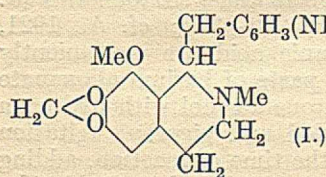
III. The following 3-carbethoxy-1-alkyl-4-piperidyl *p*-nitrobenzoate hydrochlorides were prepared as described for the corresponding benzoates: *methyl*-, m. p. 193—195°; *ethyl*-, m. p. 214—216°; *n-propyl*-, m. p. 206—208°; *isopropyl*-, m. p. 203—205°; *n-butyl*-, m. p. 192—194°; *isobutyl*-, m. p. 204—206°; and 3-carbethoxyisoamyl-4-piperidyl *p*-nitrobenzoate *hydrochloride*, m. p. 167—169°. On reduction with hydrogen in alcohol in presence of platinum oxide catalyst, these are converted into the corresponding

3-carbethoxy-1-alkyl-4-piperidyl *p*-aminobenzoates, which were isolated as the *dihydrochlorides*: methyl-, m. p. 190—192°; ethyl-, m. p. 204—206°; n-propyl-, m. p. 221—223°; isopropyl-, m. p. 196—198°; n-butyl-, m. p. 228—230°; isobutyl-, m. p. 230—232°; and 3-carbethoxyisoamyl-4-piperidyl *p*-aminobenzoate *dihydrochloride*, m. p. 213—215°. Whilst the effect of the size of the alkyl group on the anæsthetic power and toxicity in this series is the same as that observed among the corresponding benzoates, the toxicities of the *p*-aminobenzoates are markedly higher than those of the benzoates. Solutions of the *monohydrochlorides*, however, in which form the *p*-aminobenzoates were administered, are neutral, and do not cause irritation and hyperæmia. The isoamyl derivative has about $2\frac{1}{2}$ times the anæsthetic power, and one fourth the toxicity, of cocaine.

F. G. WILLSON.

Derivatives of 1-benzyltetrahydroisoquinoline.

R. ROBINSON and H. WEST (J.C.S., 1926, 1985—1987).—By gradually adding anhydrocotarnine-2:4-dinitrotoluene to a cold mixture of stannous chloride,



tin, acetic acid, and hydrochloric acid, reduction is effected, yielding *anhydrocotarnine-2:4-diaminotoluene* (I), m. p. 119° (*diacetyl* derivative, m. p. 211°; a monoacetyl derivative could not be obtained). When 2:3:4-trinitrotoluene is treated with a solution of sodium methoxide in methyl alcohol, it yields 2:4-dinitro-3-methoxytoluene, m. p. 86°, which condenses with cotarnine, yielding *anhydrocotarnine-2:4-dinitro-3-methoxytoluene*, m. p. 136° (*hydrochloride* described). Hydrastinine condenses readily with 2:4:6-trinitrotoluene, yielding *anhydrohydrastinine-2:4:6-trinitrotoluene*, m. p. 143° (*hydrochloride* described).

R. W. WEST.

Manufacture of derivatives [saturated or unsaturated dialkylamides] of pyridine-3-carboxylic acid. SOC. OF CHEM. IND. IN BASLE.—See B., 1926, 720.

Tryptophan-aldehyde reaction. III. Reaction of tryptophan with formaldehyde and with *p*-dimethylaminobenzaldehyde. E. KOMM (Z. physiol. Chem., 1926, 156, 35—60; cf. A., 1923, ii, 194; 1925, ii, 164; this vol., 959).—Optimum conditions for detection and determination of tryptophan by means of formaldehyde and *p*-dimethylaminobenzaldehyde are investigated. To 5 c.c. of the tryptophan solution are added 5 c.c. of 10% hydrochloric acid containing 0.1065 mg. of formaldehyde; 10 c.c. of concentrated sulphuric acid are run in below the mixture, and on cautiously mixing the two layers, a bluish to reddish-violet coloration results, reaching a maximum intensity after 5 days or on adding a trace of an oxidant. Reduction or further oxidation destroys the colour, which is also very sensitive to variations in the proportion of formaldehyde. More stable is the deep blue coloration given by *p*-dimethylaminobenzaldehyde (2 c.c. of trypto-

phan solution; 2 c.c. of 0.25% *p*-dimethylaminobenzaldehyde in 10% hydrochloric acid; 6 c.c. of 10% hydrochloric acid; 10 c.c. of concentrated sulphuric acid), which is equally specific for tryptophan, though less sensitive (detecting 1 in 125,000). The single tone of the coloration is an advantage. The colour is destroyed by reduction or further oxidation. Certain proline derivatives accelerate the development of the colour in both cases.

C. HOLLINS.

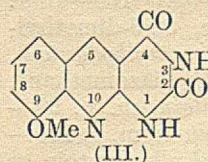
[Quinoline derivatives from] 2-amino-3-methoxybenzaldehyde. J. TRÖGER and S. GERO (J. pr. Chem., 1926, [ii], 113, 293—308; cf. this vol., 68).

—When treated with excess of acetone in alcoholic solution in presence of a trace of alkali, 2-amino-3-methoxybenzaldehyde affords 8-methoxy-2-methylquinoline (cf. Doebner and Miller, A., 1884, 1373) [*chloraurate*, brown, m. p. 153° (decomp.)]. Acetophenone affords similarly 8-methoxy-2-phenylquinoline [*chloroplatinate* (+2H₂O), decomp. 195—197°], which, on reduction with tin and hydrochloric acid, yields 8-methoxy-2-phenyl-1:2:3:4-tetrahydroquinoline, m. p. 58° (*benzoyl* derivative, m. p. 104°). 2-Amino-3-methoxybenzaldehyde and phenylacetone nitrile afford analogously 2-amino-8-methoxy-3-phenylquinoline, m. p. 222° (I) [*hydrochloride*, m. p. 238° (decomp.)]; *mercuric chloride* double salt, decomp. when heated; *chloraurate*, cherry-red], which, on reduction, yields 8-methoxy-3-phenyl-1:2:3:4-tetrahydroquinoline, (II), m. p. 61° (*benzoyl* derivative, m. p. 100°) (cf. Tröger and Ungar, this vol., 524). Condensation of (I) with benzyl chloride in presence of alcoholic sodium ethoxide affords 2-dibenzylamino-8-methoxy-3-phenylquinoline, m. p. 183°, which also yields (II) on reduction, together with dibenzylamine. Treatment of (I) with nitrous acid affords 2-hydroxy-8-methoxy-3-phenylquinoline, m. p. 191°. 2-Amino-3-methoxybenzaldehyde condenses with ethyl cyanoacetate in presence of pyridine, with formation of 3-cyano-2-hydroxy-8-methoxyquinoline, m. p. 252—253° (decomp.). The latter appears to be reduced without the cyano-group being affected, but a reduction product could not be identified. Hydrolysis of the cyano-derivative with alkali affords 2-hydroxy-8-methoxyquinoline-3-carboxylic acid, m. p. not below 295° (*disilver* salt). Condensation of 2-amino-3-methoxybenzaldehyde with barbituric acid in aqueous alcoholic solution affords 9-methoxy-2:4-diketo-1:2:3:4-tetrahydro-1:3:10-naphthtriazine [2:4-dihydroxy-9-methoxy-1:3:10-naphthtriazine] (III), m. p. 273—276°, which yields *mono-* and *monosilver* salts, and a *monobenzoyl* derivative, m. p. 242—243°. When heated with aqueous sodium hydroxide at 200°, (III) yields the above 2-hydroxy-8-methoxyquinoline-3-carboxylic acid.

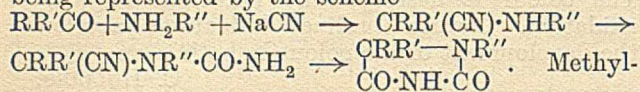
Condensation of 2-amino-3-methoxybenzaldehyde with malonic acid (more rapidly in presence of pyridine) also yields this carboxylic acid.

F. G. WILLSON.

Preparation of hydantoins. H. BILTZ and K. SLOTTA (J. pr. Chem., 1926, [ii], 113, 233—267).—Hydantoin, and its 1- and 5-derivatives, can be



conveniently prepared by the action of potassium cyanate on aminoacetonitriles (hydrochlorides or sulphates) (cf. Zelinsky and Stadnikov, A., 1908, i, 607) with subsequent ring closure from the resulting hydantoic acid nitrile by hydrolysis with concentrated hydrochloric acid, the complete synthesis being represented by the scheme



eneaminoacetonitrile is converted by alcohol and sulphuric acid into aminoacetonitrile sulphate. The latter, when treated with aqueous potassium cyanate after half-neutralising with aqueous sodium carbonate, strong illumination being avoided, with subsequent hydrolysis with hydrochloric acid, affords 175 g. of hydantoin (m. p. 207—210°) per kg. of formalin. 3-Alkylhydantoins can be readily prepared by direct alkylation. Syntheses of a number of typical hydantoins are described, in the course of which the following compounds were prepared: α -aminoisobutyronitrile, b. p. 55—60°/20 mm. (hydrochloride, decomp. 175°) (cf. Gulewitsch and Wasmus, A., 1906, i, 409); α -aminoisobutyric acid hydrochloride, decomp. 236—237° (cf. Tiemann and Friedländer, A., 1882, 56); α -cyanoisopropylcarbamide, m. p. 157°; α -aminomethylethylacetoneitrile, b. p. 68°/14 mm., 72°/20 mm., d 0.9 (hydrochloride, decomp. 110—115°); ureidomethylethylacetoneitrile, m. p. 142—143°; 5-methyl-5-ethylhydantoin, m. p. 149° (cf. Einhorn, D.R.-P. 289248); α -aminodiethylacetoneitrile, b. p. 78°/12 mm., 81°/15 mm. (hydrochloride, decomp. 155° after sintering at 140°); ureidodiethylacetoneitrile, m. p. 255° (decomp.); α -methylaminoacetonitrile hydrochloride, m. p. 104° (cf. Heimrod, A., 1914, i, 327); N- α -cyanomethyl-N-methylcarbamide, decomp. 212° after becoming brown at 180°; α -methylaminoisobutyronitrile, b. p. 59°/20 mm. (hydrochloride, decomp. 196°); N- α -cyanoisopropyl-N-methylcarbamide, decomp. 305°; 1:5:5-trimethylhydantoin; 1:3:5:5-tetramethylhydantoin, m. p. 85°; α -ethylaminoacetonitrile hydrochloride, decomp. 150—160° after sintering at 125° (cf. Knoevenagel and Mercklin, A., 1904, i, 981); N-cyanomethyl-N-ethylcarbamide, decomp. 208° after darkening from 175°; 1-ethylhydantoin, m. p. 103—104° (cf. Biltz, Marwitzky, and Heyn, A., 1921, i, 607); 3-methyl-1-ethylhydantoin, m. p. 93°, b. p. 278°; α -ethylaminoisobutyronitrile, b. p. 70—80°/20 mm. (hydrochloride, decomp. 110°); N- α -cyanoisopropyl-N-ethylcarbamide, decomp. 295—297°; and 5:5-dimethyl-1-ethylhydantoin, m. p. 138—139°. When boiled with acetic anhydride, 5:5-dimethylhydantoin affords 1-acetyl-5:5-dimethylhydantoin, m. p. 192°, which, on treatment with diazomethane, yields 1-acetyl-3:5:5-trimethylhydantoin, m. p. 99—100°. 1-Nitro-3:5:5-trimethylhydantoin, m. p. 115—116°, is obtained by nitrating trimethylhydantoin or methylation of 1-nitro-5:5-dimethylhydantoin (cf. Franchimont and Klobbie, A., 1889, 125). Chlorination of 5:5-dimethylhydantoin in aqueous solution affords 1:3-dichloro-5:5-dimethylhydantoin, m. p. 132°, which loses chlorine on treatment with alcohol or aqueous potassium iodide. 3-Phenylhydantoins are obtained by treating nitriles of α -amino-acids with phenylcarbimide in anhydrous benzene, with

subsequent hydrolysis of the resulting N'-phenyl-N-cyanoalkylcarbamides. N'-Phenyl-N-methyl-N- α -cyanoisopropylcarbamide, m. p. 118—120°, and 3-phenyl-1:5:5-trimethylhydantoin, m. p. 98—100°, are described. 1-Arylhydantoins are obtained by treating arylaminoacetic acids (cf. Hausdörfer, A., 1889, 1013) with potassium cyanate, and subsequent ring closure with hydrochloric acid. 1-Phenylhydantoin (potassium salt, decomp. 370—378°) (cf. Schwebel, A., 1878, 301) affords, on treatment with diazomethane and acetic anhydride, respectively, 1-phenyl-3-methylhydantoin, m. p. 185°, and 1-phenyl-3-acetylhydantoin, m. p. 145—146°. 1-Anisylhydantoin, m. p. 201° (cf. Frerichs and Breustedt, A., 1903, i, 16), 1-anisyl-3-acetylhydantoin, m. p. 172°, and 1-anisyl-3-methylhydantoin, m. p. 194°, are described. Treatment of aminoacetonitrile sulphate with phenylcarbimide affords phenylhydantoic acid, which, on treatment with hydrochloric acid, yields 3-phenylhydantoin, m. p. 168° (cf. Mouneyrat, A., 1900, i, 644).

F. G. WILLSON.

Alloxanic acid. H. BILTZ and F. LACHMANN (J. pr. Chem., 1926, [ii], 113, 309—332; cf. A., 1921, i, 617).—Esters of alloxanic acid are conveniently prepared by saturating a paste of barium alloxanate in the appropriate anhydrous alcohol with hydrogen chloride, air being excluded and vigorous agitation applied. By prolonging the time of reaction, adding fresh alcohol and re-saturating with hydrogen chloride, and finally raising the temperature to 30—40°, ether-esters can be obtained. Ethyl 5-ethoxyhydantoin-5-carboxylate has m. p. 84—86°. Alloxanic amides are readily obtained by treatment of ethyl alloxanate with amines at low temperatures. 5-Hydroxyhydantoinmethylamide is stable only as the monohydrate, decomp. 145—146°, or the monohydrate, decomp. 162—163°. The corresponding ethylamide, decomp. 136°, and anilide, m. p. 99—105°, are described. Treatment of methyl alloxanate with ethereal diazomethane affords methyl 5-methoxy-1:3-dimethylhydantoin-5-carboxylate, m. p. 72° (cf. Biltz and Bülow, A., 1921, i, 609). Amides of 5-ethoxyhydantoic acid are obtained from the esters as above. 5-Ethoxyhydantoinmethylamide, m. p. 111°, and -ethylamide, decomp. 136—137°, are described. When boiled with water, ethyl 5-ethoxyhydantoin-5-carboxylate yields 5-ethoxyhydantoin-5-carboxylic acid, stable only as the dihydrate, m. p. 54°, or monohydrate, m. p. 90—91°. 5-Methoxyhydantoinanilide has m. p. 134°. Treatment of ethyl 4-methylimino-5-ethoxy-1-methylhydantoincarbamate (cf. Biltz and Damm, A., 1914, i, 1095) with hot aqueous methylamine affords 4-methylimino-5-ethoxy-1-methylhydantoinmethylamide, m. p. 257—258° (acetyl derivative, m. p. 168°). The corresponding ethylamide, m. p. 224—225° (acetyl derivative, m. p. 163—164°), is described. Treatment of ethyl 5-ethoxy-1-methylhydantoincarbamate with aqueous ethylamine or methylamine affords 5-ethoxy-1-methylhydantoincarboxylamide (cf. Biltz and Damm, loc. cit.), whilst alcoholic hydrogen chloride yields similarly ethyl 5-ethoxy-1-methylhydantoincarboxylate, m. p. 82—83°. Methyl alcohol and hydrogen chloride yield similarly methyl 5-methoxy-1-methylhydantoin-

carboxylate. 5-Ethoxy-1-methylhydantoyl-amide, m. p. 206—207° (3-acetyl derivative, m. p. 136—137°), -methanamide (cf. Biltz, A., 1910, i, 523) (3-acetyl derivative, m. p. 111—112°), and -ethylamide, m. p. 131—132° (+1H₂O), or m. p. 101—102° (anhydrous), were prepared from the corresponding ethyl ester.

F. G. WILLSON.

Salts of alloxanic acid. Systematic study of hydrates. H. BILTZ and F. LACHMANN (J. pr. Chem., 1926, [ii], 113, 333—347).—Barium alloxanate crystallises from aqueous solution at below 35° as the *pentahydrate* (cf. Liebig and Wöhler, Annalen, 1838, 26, 296). Under reduced pressure, this rapidly loses water at 80°, with formation of a *hemihydrate*, which is then dehydrated more slowly. A *tetrahydrate* is obtained by drying the pentahydrate over calcium chloride. Strontium alloxanate forms a *pentahydrate*, and also a *sesquihydrate*, whilst normal calcium alloxanate forms a *pentahydrate* (cf. Schlieper, *ibid.*, 1845, 55, 275) and a *hemihydrate*. Calcium hydrogen alloxanate forms a *hexahydrate* (cf. Staedeler, *ibid.*, 1856, 97, 120) and a *monohydrate*. Normal potassium alloxanate crystallises only with 2·5H₂O, whilst potassium hydrogen alloxanate is anhydrous. It is pointed out that dehydration of the most highly hydrated salt in a vacuum, and subsequent plotting of a time-dehydration curve, will not necessarily give evidence of the existence of intermediate hydrates, for the identification of which exhaustive equilibrium measurements in salt-hydrate-water-vapour systems are required.

F. G. WILLSON.

Compounds of amino-acids with piperazines. E. ABDERHALDEN and KOHL-EGGER (Z. physiol. Chem., 1926, 156, 128—143).—2:5-Dimethylpiperazine is obtained from its tartrate (Bayer's "Lycetol") by shaking with chloroform and alkali. Peptides are prepared from it by condensation with suitable halogenated acid halides, followed by treatment with alcoholic ammonia etc.

1:4-Di-dl- α -bromoisocapro-nyl-2:5-dimethylpiperazine (1:4-di-dl- α -bromo- γ -methylvalero-nyl-2:5-dimethylpiperazine), m. p. 186°; 1:4-di-dl-leucyl-2:5-dimethylpiperazine, m. p. 134—135° [hydrobromide, m. p. 298—299° (decomp.)]; 1:4-di(chloroacetyl)-dileucyl-2:5-dimethylpiperazine, m. p. 243—244° (decomp.); 1:4-diglycyldileucyl-2:5-dimethylpiperazine, m. p. 205° [hydrochloride, m. p. 235—237° (decomp.)]; 1:4-di-(α -bromopropionyl)dileucyl-2:5-dimethylpiperazine, m. p. 260° (decomp.); 1:4-di-alanyldileucyl-2:5-dimethylpiperazine, m. p. 215—216° (hydrobromide, m. p. 255—256°).

1:4-Di(chloroacetyl)-2:5-dimethylpiperazine, m. p. 148°; 1:4-diglycyl-2:5-dimethylpiperazine, oily [hydrochloride, m. p. 282° (decomp.)]; 1:4-di-(α -bromopropionyl)diglycyl-2:5-dimethylpiperazine, m. p. 180—182° (decomp.); 1:4-dialanyldiglycyl-2:5-dimethylpiperazine, oily [hydrobromide, m. p. 265—269° (decomp.)].

1:4-Di-diglycyldileucyl-2:5-dimethylpiperazine is not fermented by macerated yeast-extract, whilst dl-leucylglycine is easily attacked under the same conditions.

C. HOLLINS.

Reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid leading to the preparation of phthalazine, phthalazone, and phthalimidine derivatives. F. M. ROWE, (Miss) E. LEVIN, A. C. BURNS, J. S. H. DAVIES, and W. TEPPER (J. Soc. Dyers Col., 1926, 42, 242—248).—See this vol., 625.

Indigo dye. S. N. GUPTA.—See B., 1926, 736.

Benzisooxazole [indoxazen]. H. LINDEMANN and H. THIELE (Annalen, 1926, 449, 63—81; cf. Lindemann and Mühlhaus, this vol., 80).—2-Chloro-5-nitrobenzaldoxime is converted by boiling alcoholic alkali into 5-nitro-2-hydroxybenzonitrile, m. p. 190°, which is also prepared by nitration of *o*-hydroxybenzonitrile, or by the action of alcoholic alkali on 4-nitrobenzisooxazole; intermediate formation of the nitrobenzisooxazole from chloronitrobenzaldoxime could not be demonstrated.

5-Nitro-2-hydroxybenzonitrile, heated at its m. p., yields 2:4:6-tri-(5'-nitro-2'-hydroxyphenyl)-1:3:5-triazine, m. p. above 340°. 2:4:6-Tri-(3':5'-dibromo-2'-hydroxyphenyl)-1:3:5-triazine, m. p. above 300°, is similarly obtained from 3:5-dibromo-2-hydroxybenzonitrile.

3:5-Dibromosalicylaldoxime, m. p. 218—220° (diacetyl derivative, m. p. 150°), could not be anhydri-ised to dibromobenzisooxazole, but when heated with acetic anhydride gave 3:5-dibromo-2-acetoxybenzonitrile, m. p. 85—87°, the corresponding hydroxy-compound being formed by heating the *monoacetyl* derivative, m. p. 146°, above its m. p. In the case of *salicylaldoxime monoacetate*, m. p. 75°, however, benzisooxazole itself, b. p. 82—83°/14 mm., d_4^{20} 1·172, is readily obtained by distillation in a vacuum at 120—130° (oil-bath temperature). With less precaution, the isomeric *o*-hydroxybenzonitrile results. The properties of benzisooxazole are in agreement with those of Conduché's product (A., 1908, i, 154). 4-Nitrobenzisooxazole, m. p. 126°, obtained by direct nitration, is converted above its m. p. into 5-nitro-2-hydroxybenzonitrile. 2-Methylbenzisooxazole, b. p. 92·5°/11 mm., d_4^{20} 1·1247, prepared by heating 2-hydroxyacetophenoneoxime *monoacetate*, m. p. 146°, gives on nitration 4-nitro-2-methylbenzisooxazole, m. p. 128°, and an isomeric *nitro*-compound, m. p. 250°. 4-Amino-2-methylbenzisooxazole, m. p. 105° (hydrochloride, sulphate, and acetyl derivative, m. p. 156°, described), obtained by reduction with stannous chloride, diazotised and coupled with β -naphthol, gives a *dye*. From the *monoacetate*, m. p. 114°, of 2-hydroxy-5-methylacetophenoneoxime, m. p. 145°, there is obtained 2:4-dimethylbenzisooxazole, b. p. 116°/13 mm., d_4^{20} 1·0949, which gives on nitration 6-nitro-2:4-dimethylbenzisooxazole, m. p. 72°.

C. HOLLINS.

Manufacturing thiazoles. L. B. SEBRELL and C. W. BEDFORD.—See B., 1926, 771.

Quinone vat dye. R. HERZ.—See B., 1926, 735.

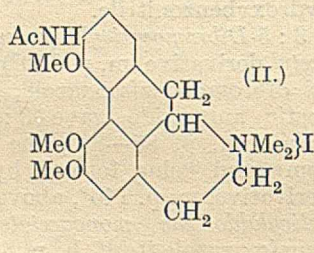
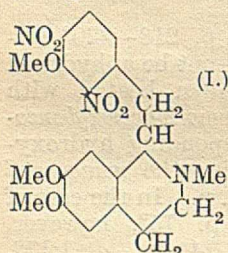
Benzoylecgonine ester. E. POULSON.—See B., 1926, 771.

Conessine. D. D. KANGA, P. R. AYYAR, and J. L. SIMONSEN (J.C.S., 1926, 2123—2127).—When an aqueous solution of conessine dimethiodide is treated

with silver oxide and the solution evaporated first on the water-bath and then under diminished pressure at 200°, an oil is obtained from which apoconessine, $C_{22}H_{33}N$, m. p. 68.5° (hydrochloride, hydrobromide, hydrogen sulphate, m. p. 107—108°, picrate, m. p. 110—111°, methiodide, m. p. 283—285°), may be isolated. Conessine, m. p. 125°, reacts vigorously with methyl sulphate, yielding a dimethosulphate, m. p. 240—242°, and an oil which on treatment with aqueous potassium hydroxide yielded a substance, m. p. 253—254° [picrate, m. p. 256° (decomp.)]. When heated with aqueous potassium hydroxide, conessine dimethosulphate yields a hygroscopic base, $C_{26}H_{44}N_2$ [dipicrate, m. p. 258—259° (decomp.)], and dimethiodide described]. Conessine reacts with mercuric acetate in acetic acid solution to give a base (needles).

R. W. WEST.

Synthetical experiments in the phenanthrene group of alkaloids. I. R. ROBINSON and J. SHINODA (J.C.S., 1926, 1987—1995).—The authors give the name "laudaline" to 1-hydroxy-6:7-dimethoxy-2-methyl-1:2:3:4-tetrahydroisoquinoline (cf. Pyman, *ibid.*, 1909, 95, 1266).



Laudalinium chloride condenses with 2:4-dinitro-3-methoxytoluene in the presence of sodium methoxide, yielding anhydrolaudaline-2:4-dinitro-3-methoxytoluene (I), m. p. 111—112° (hydrochloride described), which can be reduced to either anhydrolaudaline-2:4-diamino-3-methoxytoluene (dihydrochloride, m. p. 236—237°) or anhydrolaudaline-2-nitro-4-amino-3-methoxytoluene, m. p. 145°. Acetic anhydride converts the nitro-amine into the acetyl derivative, m. p. 151°, and a substance, $C_{26}H_{33}O_9N_3$, m. p. 194°. The acetyl derivative is reduced by hydrogen and palladium chloride to anhydrolaudaline-2-amino-4-acetamido-3-methoxytoluene, m. p. 110° (picrate, m. p. 168—169°), which after diazotisation and treatment with copper powder yields dehydroanhydrolaudaline-4-acetamido-3-methoxytoluene methiodide (II), m. p. 210° (decomp.).

The structure of the nitro-amine (see above) is brought out by its conversion into (II) and further by analogy from the following experiments: Anhydrocotarnine-2:4-dinitro-3-methoxytoluene is reduced by stannous chloride, yielding anhydrocotarnine-2-nitro-4-amino-3-methoxytoluene, m. p. 184° (acetyl derivative, m. p. 134°), which is oxidised by potassium permanganate to 2-nitro-4-acetamido-3-methoxybenzoic acid, m. p. 228—229°. This acid is also obtained by the oxidation of 2-nitro-3-methoxy-p-acetotoluidide, m. p. 108—109°, prepared from 2-nitro-3-methoxy-p-toluidine (hydrochloride, m. p. 205°), which is obtained by the action of hydrogen sulphide on 2:4-dinitro-3-methoxytoluene and yields 2-nitro-m-tolyl methyl ether on deamination.

isoapoMorphine dimethyl ether (cf. Robinson and Robinson, *ibid.*, 1914, 105, 1456) combines readily with methyl sulphate to give isoapomorphine dimethyl ether methosulphate, m. p. 246°, which is converted by boiling aqueous sodium hydroxide into 6:7-dimethoxy-1-(β-dimethylaminoethyl)phenanthrene, $C_{14}H_7(OMe)_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, m. p. 111° (hydrochloride and methiodide described). R. W. WEST.

Ferricyanide reaction of potassium morphine. R. A. BERETEVIDE (Rev. Fac. Cien. Quím., 1925, 3, 89—123).—In the oxidation of morphine by potassium ferricyanide in the presence of potassium hydroxide, time of contact has only a slight effect. The amount of potassium ferricyanide reduced is, however, increased by heating, and also by increasing the proportion of potassium ferricyanide to morphine. Reduction is greater in alkaline than in neutral solution. The reaction does not appear to take place in definite molecular proportions.

G. W. ROBINSON.

Reactions of certain nitroso-derivatives with alkaloids. E. NAVARRO (Anal. Fís. Quím., 1926, 24, 413—419).—The author has studied the reactions of the principal alkaloids with nitrosoresorcinol, nitrosophloroglucinol, nitrosopyrogallol, and sodium dihydroxynaphthalenedisulphonate. The colorations and precipitates obtained are not sufficiently distinctive for these reactions to be used for the characterisation of alkaloids. G. W. ROBINSON.

Manufacture of salts of cinchona alkaloids.—See B., 1926, 769.

Preparation of derivatives of aromatic arseno-compounds and their complex metal compounds. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 769.

Derivatives of ethyl β-aceto-α-methylsuccinate; constitution of hæmatoporphyrin. W. KÜSTER, H. MAURER, and A. PALM.—See this vol., 1024.

Coproporphyrin synthesis by means of yeast. O. SCHUMM (Z. physiol. Chem., 1926, 156, 159—160).—Polemical against Fischer and Hilger (this vol., 189, 324, 544). C. HOLLINS.

Occurrence and detection of copratin and copratoporphyrin. IV. O. SCHUMM and E. MERTENS (Z. physiol. Chem., 1926, 156, 61—67; cf. this vol., 87, 538, 751).—The non-identity of coproporphyrin, copratoporphyrin, and hæmateric acid (α-hæmatoporphyrin) is established by spectroscopic examination in dilute ether-acetic acid solution, in 25% hydrochloric acid, in 98% sulphuric acid, and in the presence of bromine, by the hydrochloric acid number, and by spectra of the methyl esters, and of complex iron and copper compounds. During flesh-free dieting, copratin predominates over hæmatin. C. HOLLINS.

Decomposition of soya-bean protein. I. Decomposition by hydrochloric acid. II. Decomposition by sulphuric acid. M. MASHINO (J. Soc. Chem. Ind. Japan, 1926, 29, 179—186, 187—190).—I. Soya beans from four different sources were treated with light petroleum and the resulting proteins decomposed by hydrochloric acid. With 38.5% acid at 100°

9.1–9.7% of ammoniacal nitrogen (calculated on total nitrogen) was obtained after 30 min. treatment and 67.4–68.9% of amino-nitrogen after 12 hrs.; 20% acid yielded at 100° about 10% of ammoniacal nitrogen after 30 min. and about 62% of amino-nitrogen after 12 hrs., and at 40° 9.4% of ammoniacal nitrogen after 38–48 hrs. and 9.7% of amino-nitrogen after 48 hrs. About 1% of ammoniacal nitrogen and 4.3% of amino-nitrogen were formed by 0.4% acid at 40° after 48 hrs.

II. Sulphuric acid (20%) yielded 8–9% of ammoniacal nitrogen after $\frac{1}{2}$ –1 hr. and 9–10% after 2–12 hrs., and 52–54% of amino-nitrogen.

K. KASHIMA.

Heat coagulation of egg-albumin. H. MASTIN and H. G. REES (Biochem. J., 1926, 20, 759–762).—Wu and Wu's observation (A., 1925, i, 1110) that tyrosine is eliminated when albumin is coagulated by heat is not confirmed. A reducing substance, probably containing a thiol group, is liberated in the filtrate when an albumin is precipitated by sodium tungstate or colloidal ferric hydroxide.

S. S. ZILVA.

Isolation of some hitherto undescribed products of hydrolysis of proteins. III. S. B. SCHRYVER and H. W. BUSTON (Proc. Roy. Soc., 1926, B, 100, 360–367).—A re-examination of the basic fraction obtained by the hydrolysis of the proteins of the castor bean and of oats, using the technique previously described (cf. A., 1925, i, 794), showed that the cold-water-soluble carbamates on decomposition yield a solution which contains a fraction precipitable with phosphotungstic acid. This fraction on purification yields a base, $C_8H_5O_3N_3$, which has been named "protocetine" ("C₈-base"). It chars at 220°, is very soluble in water (*M* found, 192), readily soluble in alcohol (wherein it differs from all other known basic hydrolysis products), and insoluble in ether. It is precipitated from solution by mercuric chloride and barium hydroxide, but not by silver nitrate and alkali. Its solutions decolorise acid permanganate and give a series of colour reactions with diazobenzenesulphonic acid differing rather in degree than in kind from those obtainable with histidine. With bromine water, a flocculent yellow precipitate is obtained, which is destroyed on warming, the solution becoming colourless. The *hydrochloride*; *nitrate* (amorphous); *chloroaurate*, golden-brown needles; *chloroplatinate*, yellow needles; *picrate*, decomp. 205–210°; *dibenzoyl* derivative, *m. p.* 109°; *phenylcarbimide* derivative, $C_{15}H_{20}O_4N_4$, *m. p.* 130°; and the phenylhydantoin, *m. p.* 148°, are described. Beyond the fact that the molecule contains one amino-, one carboxyl, and one hydroxyl group, its constitution is unknown. It is suggested, however, that the other two nitrogen atoms are in the form of some basic functioning group similar to the glyoxaline ring.

W. ROBSON.

Enzymic proteolysis. I. Structure of clupein. E. WALDSCHMIDT-LEITZ, A. SCHÄFFNER, and W. GRASSMANN (Z. physiol. Chem., 1926, 156, 68–98).—An improved method for the separation of the pancreatic proteases has yielded erepsin, trypsin, and "trypsin-kinase" (i.e., trypsin activated by the

presence of enterokinase). These individual enzymes, and also papain in the form of its hydrogen cyanide compound, are employed for the fractional hydrolysis of clupein, the progress being followed by determinations of carboxyl and amino-groups. Throughout the hydrolysis sensibly equivalent amounts of carboxyl and amino-groups are liberated; hence the process consists essentially in the fission of amide (peptide) linkings. It follows further that in clupein the NH group of proline (not determinable by the method adopted) is not set free during this fission, and that the guanidine group of arginine is not concerned in the peptide linkings. C. HOLLINS.

Enzymic proteolysis. II. Enzymic hydrolysis of casein. E. WALDSCHMIDT-LEITZ and E. SIMONS (Z. physiol. Chem., 1926, 156, 99–113; cf. preceding abstract).—The products of peptic hydrolysis of casein are further hydrolysed by trypsin-kinase, and these again by intestinal erepsin. Trypsin alone is only half as effective, and further hydrolysis is produced on addition of enterokinase or of yeast-erepsin. The pepsin-peptone from casein, unlike that from egg-albumin, is hydrolysed to some extent by erepsin. The product of exhaustive hydrolysis of casein by trypsin-kinase is still not completely hydrolysed after successive treatment with pepsin, trypsin-kinase, and erepsin, or with erepsin and pepsin. The method used in following these hydrolyses is determination of carboxylic acidity by titration in alcoholic solution with 0.2*N*-potassium hydroxide.

C. HOLLINS.

Potentiometric determination of aromatic nitroso- and nitro-compounds by means of titanous chloride. E. DACHSELT (Z. anal. Chem., 1926, 68, 404–410).—The determination is carried out by direct titration at 50–80°, compounds insoluble in water being dissolved in alcohol. The break in the curve is satisfactory, but is much more pronounced in presence of sodium potassium tartrate, which also renders the colour change sharp.

S. I. LEVY.

Use of acetic anhydride in Zeisel's method for the determination of methoxyl groups. M. NIERENSTEIN (Analyst, 1926, 51, 456).—The use of acetic anhydride in connexion with Zeisel's method is again deprecated, since besides formation of some acetyl iodide which distils into the silver nitrate solution, acetic anhydride and hydriodic acid by themselves yield weighable quantities of silver iodide (confirmed by their nearly quantitative conversion on keeping for 10–11 years).

D. G. HEWER.

Gasometric determination of primary aromatic amines. P. GRIGORJEV (Z. anal. Chem., 1926, 69, 47–50).—The aqueous solution of the amine sulphate containing 0.1–0.2 g. of amine is mixed with a slight excess of dilute sulphuric acid, cooled in ice-water, and treated with a solution of sodium nitrite added slowly from a burette until the solution turns iodide-starch paper blue. The liquid is transferred to a nitrometer and a solution of ferrous sulphate in sulphuric acid is added, whereby the diazo-compound is decomposed with evolution of

nitrogen. After 2—3 min., the contents of the tube are agitated to complete the reaction and to absorb the greater part of the nitric oxide, formed simultaneously, in the ferrous sulphate solution. The gas is measured after cooling and finally transferred to a gas burette filled with sodium sulphite solution, whereby the last traces of nitric oxide are removed. The volume of the nitrogen remaining, after correction, indicates the amount of amine present.

A. R. POWELL.

Gravimetric determination of benzidine and its analogues and new complex salts of these bases. W. HERZOG (Chem.-Ztg., 1926, 50, 642—643).—Benzidine mercurichloride (cf. Spacu, Bul. Soc. Stiinte Cluj, 2, 137 etc.) is so insoluble in water or dilute acetic acid that benzidine can be gravimetrically determined by precipitation with mercuric chloride. The solution must contain no free mineral acid. The precipitate is dried to constant weight without heat. *Benzidine mercuribromide*, $C_{12}H_{12}N_2 \cdot HgBr_2$, the *iodide*, and *o-tolidine mercurichloride*, *bromide*, and *iodide* are described. Mercury is quantitatively precipitated by excess of benzidine acetate.

W. A. SILVESTER.

Colorimetric determination of tyrosine, tryptophan, and cystine in proteins. II. J. M. LOONEY (J. Biol. Chem., 1926, 69, 519—538).—A reply is made to the criticisms of Fürth (A., 1924, ii, 575) and Kraus (*ibid.*, 1925, ii, 448) of the method of Folin and Looney (*ibid.*, 1922, ii, 539) for the deter-

mination of the above amino-acids, and further results are brought forward in support of the latter method; it is pointed out that the results obtained by this method are in good agreement with the mol. wts. of the proteins concerned, as estimated by Cohn (*ibid.*, 1925, ii, 641). The recent method of Hanke (this vol., 633) for the determination of tyrosine is criticised on the ground that this author has neglected the simultaneous precipitation of tryptophan and cystine under the conditions he employs.

C. R. HARINGTON.

Marquis' reagent and hydroxydimorphine. A. LEULIER and R. DUBREUIL (Compt. rend. Soc. Biol., 1925, 93, 1313—1314; from Chem. Zentr., 1926, I, 1865).—Addition of 1 drop of Marquis' reagent (1 c.c. of concentrated sulphuric acid+1 drop of formaldehyde) to a small quantity of hydroxydimorphine previously moistened with hydrogen peroxide produces a green colour. In the absence of hydrogen peroxide, barium dioxide, etc., a dirty reddish-brown colour is obtained. Excess of hydrogen peroxide must be avoided. The reaction is specific.

J. S. CARTER.

Crystallisation by inoculation in micro-chemistry. N. SCHOORL (Mikrochem., 1926, 4, 103—108).—When the precipitant contains traces of the crystalline alkaloid, the precipitation of quinidine by sodium hydrogen carbonate and of atropine by sodium carbonate always leads to crystalline deposits.

J. S. CARTER.

Biochemistry.

Transport of oxygen and carbon dioxide by bloods containing hæmocyannin. A. C. REDFIELD, T. COOLIDGE, and A. L. HURD (J. Biol. Chem., 1926, 69, 475—509).—Investigation of a number of different species shows that, whilst each hæmocyannin has its own individual properties, the general physico-chemical behaviour of all the blood pigments, in the transport of oxygen and carbon dioxide, is the same, and is similar to that of hæmoglobin. In the case of certain hæmocyannins, the pigment differs from hæmoglobin in having its greatest affinity for oxygen at high tensions of carbon dioxide.

C. R. HARINGTON.

So-called oxygen content of methæmoglobin. J. B. CONANT and N. D. SCOTT (J. Biol. Chem., 1926, 69, 575—587).—Whilst the experimental observations of Nicloux (this vol., 191) regarding the oxygen content of methæmoglobin are confirmed, his deductions are criticised on the ground that (1) in the titration with sodium hyposulphite he neglected the difference between the titration of oxyhæmoglobin, where, owing to the presence of free oxygen, formation of hydrogen peroxide can take place, and that of methæmoglobin, where this is not the case; (2) that under the conditions employed by him for the oxidation of carboxyhæmoglobin the reaction was incomplete; (3) that in his experiments on the oxidation

of oxyhæmoglobin he used twice the amount of ferricyanide necessary to liberate the oxygen, hence obtaining a fictitious ratio. The present authors' interpretation of the results leads to the conclusion that methæmoglobin contains one fourth of the oxygen of oxyhæmoglobin.

C. R. HARINGTON.

Comparison of the sensitivities of methæmoglobin and of oxyhæmoglobin to a reducing agent. M. NICLOUX and J. ROCHE (Compt. rend. Soc. Biol., 1925, 93, 1659—1662; from Chem. Zentr., 1926, I, 2109).—In mixtures of methæmoglobin and oxyhæmoglobin in the ratios 1:3, 1:1, and 3:1, the latter substance is preferentially and sometimes exclusively reduced by sodium hyposulphite.

J. PRYDE.

Detection of variation in acid content of blood. K. GOLLWITZER-MEIER (Deut. Archiv klin. Med., 1925, 149, 151—156; from Chem. Zentr., 1926, I, 1678).—The determination of the ability to take up carbon dioxide furnishes no information in cases of disease regarding the quantity of abnormal acids in blood. A true estimate is obtained only when the sum of the inorganic anions and cations is determined. The excess of cations over the normal content is equivalent to the quantity of abnormal organic acids.

J. S. CARTER.

Presence of combined sugar in the blood. M. BUFANO (Arch. Farm. speriment., 1925, 40, 235—240, 241—250; from Chem. Zentr., 1926, I, 2213).—Evidence is adduced of the presence of combined sugar in the blood. W. O. KERMACK.

Irritability and blood-sugar. E. M. GREISHEIMER (Amer. J. Physiol., 1925, 72, 213).—In experiments with decerebrate dogs, the nerve irritability increased when the blood-sugar decreased, and *vice versa*. A. A. ELDRIDGE.

Glycolysis. VI. Distribution of phosphorus in the blood. P. RONA and K. IWASAKI (Biochem. Z., 1926, 174, 293—307).—The amount of phosphate precipitated by molybdate increases when blood is kept at 37°. This increase is due neither to glycolysis, since it is unaffected by the addition of sodium fluoride or the maintenance of a p_H unfavourable to glycolysis, nor to autolysis, since the total phosphorus of the blood-filtrate after precipitation of the proteins is unchanged. It is probably due to the liberation of phosphoric acid by the action of enzymes from compounds of the ester type. The optimum reaction of the phosphatase is in the neighbourhood of p_H 6. The esters are of two types, easily and difficultly hydrolysable by acids. E. C. SMITH.

Influence of various factors on the course of blood glycolysis. Carbohydrate metabolism. XI. S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, 93, 1681—1683; from Chem. Zentr., 1926, I, 2113—2114).—Glycolysis does not occur in plasma, but is confined to the corpuscles. Addition of fluoride prevents glycolysis, oxalate retards it, whilst citrate and hirudin are without influence. Glycolysis is more rapid at 37° than at 20°. Slight increases in the alkalinity of the blood and variations in the initial concentration of the blood-sugar are without effect on the rate of glycolysis. J. PRYDE.

Rate of glycolysis in normal and diabetic blood. Carbohydrate metabolism. XII. S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, 93, 1684—1686; from Chem. Zentr., 1926, I, 2114).—The rate of glycolysis is independent of the concentration of dextrose in both diabetic and normal blood. During the first 2 hrs. after collection glycolysis proceeds more rapidly in normal than in diabetic blood, but this difference disappears later. This is ascribed to the presence of less "neo-glucose" in diabetic than in normal blood. J. PRYDE.

Effect of zinc ions on glycolysis in blood. L. J. VIVIANI (Rev. Fac. Cien. Quím., 1926, 4, 31—72).—Defibrinated blood from well-nourished dogs maintained at 39° shows a loss of dextrose in 1 hr. amounting to 20—40%. The addition of zinc as sulphate in concentrations varying from 10^{-9} to 10^{-4} g. per c.c. does not affect glycolysis. With a concentration of 0.002 g. of zinc per c.c., glycolysis is completely inhibited. The effect is attributed entirely to the zinc ions. G. W. ROBINSON.

Volume of the proteins of serum. A. NITSCHKE (Arch. exp. Path. Pharm., 1926, 115, 134—138).—From the distribution of chlorides across a membrane separating serum and physiological saline at the isoelectric point of the serum proteins, the volume

occupied by the proteins has been calculated. The mean for a serum containing 7% of protein gave a protein volume of 7.5%. Similarly, from the distribution of dextrose there was derived a protein volume of 7.1%, which was independent of temperature, dilution of the serum, and hydrogen-ion concentration. The existence of a water envelope about the protein particle is improbable. R. K. CANNAN.

Condition of calcium in serum. A. NITSCHKE and H. J. FREYSCHMIDT (Biochem. Z., 1926, 174, 287—292).—By application of the Donnan theory to the dialysis of serum maintained at constant p_H against physiological saline containing sodium hydrogen carbonate and phosphate, it is deduced that in serum at p_H 7.4 and 20° containing 0.010% of calcium and 0.0035% of phosphate the ionised calcium in the form of a saturated solution of calcium mono- and di-hydrogen phosphate represents 80% of the total, the remainder being present in the un-ionised, non-dialysable form, half as calcium proteinate and half as an unrecognised calcium phosphate complex. The solubility of the calcium phosphate is less than half that of the hydrogen carbonate under the same conditions. The equation $[Ca^{++}][HPO_4^{--}] = K$ holds, where $K(20^\circ) = 1.8$. Addition of calcium or phosphate or decrease of p_H must lead to the separation of molecular calcium phosphate. E. C. SMITH.

Vaso-constrictor substances of blood-serum. H. BORGERT and K. KEITEL (Biochem. Z., 1926, 175, 1—7).—The vaso-constrictor substance of blood-serum arises from the disintegration of blood-platelets. Its formation does not depend on the presence of light, heat, oxygen, or bacteria, but after 24 hrs. it wholly or partly disappears and the preparation then has a vaso-dilator action. The vaso-constrictor substance is dialysable, not extracted with ether or acetone, and cannot be distilled.

P. W. CLUTTERBUCK.

Lipolytic activity of serum and the precipitin reaction of Sachs-Georgi. D. LAPPONI (Ann. d'Igiene, 1925, 35, 865—871; from Chem. Zentr., 1926, I, 1592).—The precipitin reaction depends on the presence of certain lipins. It comprises a number of conditions which affect the colloidal system of antigen or serum in different ways according to the precipitation intensity of the serum. The lysis of the lipins which surround the colloidal micelles of cholesterinised antigen, does not occur with sera which precipitate the colloidal suspensions of the same extract, although these sera show lipolytic activity towards lipins of other colloidal lipo-protein systems. C. RIMINGTON.

Effect of certain substances on the precipitin reaction. C. M. DOWNS and K. GOODNER (J. Infect. Dis., 1926, 38, 240—245).—Heterologous proteins do not interfere with the precipitin reaction or intensify the prozone, but cause dissociation of the formed precipitate. Concentrated solutions of dextrose or sucrose inhibit the formation of a precipitate; the former causes true, and the latter slight, dissociation of the formed precipitate. Other carbohydrates, in less concentrated solutions, interfered little with the reaction and acted as weak dissociating agents.

CHEMICAL ABSTRACTS.

Ultrafiltration through collodion membranes. A. GROLLMAN (J. Gen. Physiol., 1926, 9, 813—826).—The author has attempted to determine how far such factors as the mode of filtration, the pressure applied, the nature of the filter, and the solution being filtered affect the validity of the deductions made from ultrafiltration experiments. He concludes that such factors as these render data obtained by ultrafiltration open to criticism, unless they are checked by other methods and certain precautions taken. Considering all the factors which might modify the effective pore size, he regards the view that ultrafiltration has a sieve-like action as adequate, and argues that it is unsound to make any deductions about living tissues from the demonstration of changes produced in the behaviour of collodion membranes. W. ROBSON.

Behaviour of the vitally important amino-acids during the incubation of the hen's egg. Y. SENDJU (J. Biochem. [Japan], 1925, 5, 391—415).—Both free and bound tryptophan are significant in the synthesis of blood and bile pigments. Possibly tyrosine is a building material for inner secretions or for substances essential for the normal progress of cellular metabolism. The free and combined purine-nitrogen increase during incubation and growth of the embryo. The amount of nitrogen which is not precipitated by phosphotungstic acid remains practically constant during the development of the egg. CHEMICAL ABSTRACTS.

Chicken embryos: p_{H} , chloride, carbonic acid, and protein concentration in the tissues as functions of age. H. A. MURRAY (J. Gen. Physiol., 1926, 9, 789—803).—The p_{H} and the chloride concentration of the tissues decrease with age, the former from 7.00 to 6.64 (8 days), the latter from 4.82 to 1.00% of dry tissue (13 days), the fall being most rapid between the 10th and the 13th day of incubation. The carbon dioxide and protein concentrations increase with age, the latter especially between the 12th and the 16th days. W. ROBSON.

Iodine storage in individual organs. T. VON FELLEBERG (Biochem. Z., 1926, 174, 355—363).—Iodine is present in all organs of the body, the thyroid gland being usually the richest. Administration of iodine as potassium iodide increases the iodine content of most organs. In the lung, 3 hrs. after administration a considerable accumulation occurs, which disappears after 48 hrs. In skin, hair, and, especially, muscle, a more permanent increase is observed, and it is in these tissues that the iodine reserve of the body is maintained. The organs in a case of malaria treated with iodotrypaflavine were found to contain large quantities of iodine. The thyroid gland of a newly-born child contained only a very small amount of iodine. E. C. SMITH.

Carotin-like compound as eye pigment of copepod. Origin and development during ontogeny. A. Lvov (Compt. rend. Soc. Biol., 1925, 93, 1602—1604; from Chem. Zentr., 1926, I, 2212).—An orange-yellow pigment has been isolated from the eye of *Idya furcata*. W. O. KERMACK.

Human fat. O. WAGNER (Biochem. Z., 1926, 174, 412—419).—The mean iodine value of the liquid fatty acids of human depot fat at 0° is 100. Arachidonic acid (isolated as the bromo-derivative) is present to the extent of 0.3%, linoleic acid (isolated as the hydroxy-derivative) to the extent of 0.54% of the total fat. Saticic acid, m. p. 162°, was isolated from the products of oxidation of the fat with potassium permanganate. E. C. SMITH.

Mineral composition of the skeletons of some invertebrates from Barents and Kara seas. Y. V. SAMOILOV and K. F. TERENCEVA (Trans. Inst. Econ. Min. Petr., Pamphlet, 1925, 12, 3—32).—In the magnesium-calcareous group (*Strongylocentrotus drobachiensis*, *Ophiopleura borealis*, and *Asteria linckii robusta*) the percentage of magnesium carbonate depends on the temperature of the water in which the organism lives; the calcium carbonate is present as calcite. In *Leda pernula*, *Tellina calcarea*, and *Natica clausa* it is present as aragonite; in *Astarte borealis*, *Pecten islandicus*, and *Neptunea despecta* the outer portion is calcite and the inner aragonite. CHEMICAL ABSTRACTS.

Iodine content of the thyroid. E. HERGLOZ (Biochem. Z., 1926, 175, 175—180).—The iodine of the thyroid gland was determined in a number of animals by Winkler's method. The central part of the gland contains more iodine than the peripheral part. P. W. CLUTTERBUCK.

Lactic acid content of cerebrospinal fluid. J. GLASER (J. Biol. Chem., 1926, 69, 539—547).—Normal cerebrospinal fluid contains 0.011—0.027% of lactic acid, the figures amounting to 60—100% of those for the corresponding blood. The lactic acid content of the cerebrospinal fluid tends to be diminished in cerebrospinal syphilis and to be increased in meningitis and in cases of brain tumour when the sample is taken from the part of the spinal cord which is in contact with the tumour. C. R. HARRINGTON.

Relation of blood- to cerebrospinal fluid-sugar and the diagnostic value of sugar determinations in cerebrospinal fluid. F. G. DIETEL (Z. ges. Neurol. Psychiat., 1925, 95, 563—587; from Chem. Zentr., 1926, I, 1593).—Normal cerebrospinal fluid contains about 44.2 mg. of sugar %, and the ratio of blood-sugar to this is 2 : 1. There is a rise in the sugar of cerebrospinal fluid after dextrose injection which follows that of the blood-sugar. C. RIMINGTON.

Gastric juice of the pregnant woman. T. NAKAI (J. Biochem. [Japan], 1925, 5, 465—477).—The following minimum, maximum, and average values were obtained: total acidity 2.0, 14.4, 6.4 c.c.; pepsin action (by Mett's tube) 0.2, 2, 0.97; lactic acid 0; free hydrochloric acid present in 2 of 14 cases. CHEMICAL ABSTRACTS.

Sputum. H. REINWEIN (Z. physiol. Chem., 1926, 156, 144—152).—Four litres of sputum were collected from a bronchitic patient. After removal of mucus, the total nitrogen (11 g.) was distributed as follows: purine bases, 0.102 g. (no uric acid);

histidine fraction, 6.104 g. (histidine picrolonate, m. p. 220°, isolated); arginine fraction, 0.142 g.; lysine fraction, 2.9 g., divided into α -fraction, 2.04 g. of nitrogen, in which neosine is identified by its chloraurate, m. p. 207°, and β -fraction, consisting of putrescine (chloraurate, m. p. 210°). Histamine was probably present.
C. HOLLINS.

Basal urea excretion. C. RICHET, jun., and MINET (Compt. rend. Soc. Biol., 1925, 93, 1270—1271; from Chem. Zentr., 1926, 1, 1594—1595).—The results are expressed in terms of urea excretion per square metre per day. The surface is calculated from the formula $10.7\sqrt[3]{p^2}$. For dogs, the mean value is 7.5, but individual variations were great. The diet supplied consisted of ample nitrogen-free food.
C. RIMINGTON.

Excretion of uric acid by the kidney. H. GREMELS and R. BODO (Proc. Roy. Soc., 1926, B, 100, 336—359).—The behaviour of the isolated perfused kidney towards uric acid has been studied in relation to the various theories of kidney excretion. The technique employed involved Starling's heart-lung-kidney preparation using dogs, with, in some cases, the introduction of the liver into the circuit. The toxic effect on the kidney observed with defibrinated blood was avoided by the use of hirudinised blood. Lithium urate was injected in a solution made isotonic by the addition of dextrose. Using the above preparation, all the uric acid disappearing from the blood was recoverable from the urine, whilst the rate of fall of the blood uric acid depended on the rate of urinary flow. The urinary percentage is at least two or three times as great as that of blood. The suppression, by the use of cyanide, of the glomerular and tubular functions of the kidney leads to the secretion of uric acid into the glomerular filtrate by the tubular cells. Only when the liver is included in the heart-lung-kidney preparation is there a marked and rapid oxidation of the blood uric acid, confirming the conclusions of Mann and Magath (cf. *Ergeb. Physiol.*, 1924, 23, 1, 250). No evidence was found for Folin's statement that the kidney removes uric acid from the blood only to return it there for oxidation. Its initial rapid disappearance is due, not to its destruction, but to the establishment of an equilibrium between its concentration in the blood and in the tissues.
W. ROBSON.

Site of ammonia formation and rôle of vomiting in ammonia formation. S. R. BENEDICT and T. P. NASH, jun. (*J. Biol. Chem.*, 1926, 69, 381—396).—The conclusions of Bliss (this vol., 428) are criticised in detail and further arguments are brought forward in support of the theory previously advanced by the present authors (A., 1922, i, 191).
C. R. HARRINGTON.

Origin of urinary ammonia. III. I. M. RABINOWITCH (*J. Biol. Chem.*, 1926, 69, 283—288).—In cases of severe diabetes the urinary excretion of ammonia is much greater than the total amount of ammonia which can be brought to the kidneys by the blood-stream; this fact supports the theory of

Nash and Benedict (A., 1922, i, 191) that the greater part of the urinary ammonia is formed in the kidneys.
C. R. HARRINGTON.

Excretion of chlorine by the kidneys after exposure to X-rays. A. ENGELHARD and H. SIELMANN (Deut. Archiv klin. Med., 1925, 149, 168—176; from Chem. Zentr., 1926, I, 1671).—Persons who are in sodium chloride equilibrium show a retention of chlorine for some days after exposure of any part of the body to X-rays. There is no increase of chlorine in the blood. Irradiation of single cells (goose-blood corpuscles) in serum causes no uptake of chlorine by the cells.
H. I. COOMBS.

Composition of glomerular urine. J. T. WEARN and A. N. RICHARDS (*Amer. J. Physiol.*, 1924—1925, 71, 209—227).—The glomerular fluid of the frog is free from protein when the blood flow through the glomerular capillaries is rapid. Sugar was absent from the blood of starving frogs in winter. Glomerular urine contains sugar (when the blood-sugar concentration, obtained by subcutaneous injection of dextrose, is less than 0.05%) and chlorides; bladder urine contains neither. Preliminary investigations of the urea content and reaction of the glomerular urine were made.
A. A. ELDRIDGE.

Excreta of *Tineola crinella*. A. C. HOLLANDE and H. CORDEBARD (*Bull. Soc. Chim. biol.*, 1926, 8, 631—635).—The excreta of the caterpillar of *Tineola crinella* are strongly acid, contain soluble urates, ammonium salts, and a very small quantity of urea; alkali and alkaline-earth chlorides, phosphates, and sulphates are present. Intraperitoneal and subcutaneous injections of solutions into rabbits and guinea-pigs had no harmful effects.
H. J. CHANNON.

Catalase activity of the oral mucous membrane. T. SOLLMANN and R. L. HOWARD (*J. Lab. Clin. Med.*, 1925, 11, 130—139).—The median value (c.c. of 0.1N-hydrogen peroxide decomposed per min.) is 3.3 for the first and 2.3 for the second determination, the value varying from day to day. Very bad clinical conditions were associated with values of 6.0 and 5.0, respectively.

CHEMICAL ABSTRACTS.

Potassium and calcium content and ratio in blood-serum in physiological and pathological conditions. X. The adrenaline reaction. E. KYLIN (Deut. Archiv klin. Med., 1925, 149, 354—365; from Chem. Zentr., 1926, I, 1670).—The ratio K:Ca in serum, which is normally 1.7—2.15, is changed in diseases. When the quotient is high, adrenaline produces a vagotonic effect and lower blood pressure; when low, it produces a sympatheticotonic effect and higher blood pressure. The relation between this phenomenon and the causes of the diseases with the changed K:Ca ratio is discussed.
H. I. COOMBS.

Effect of excretion of acids and bases on development of acidosis in experimental diabetes. B. M. HENDRIX, M. FAY, D. B. CALVIN, and M. BODANSKY (*J. Biol. Chem.*, 1926, 69, 449—473).—In depancreatized dogs, acidosis developed only when there was marked diuresis. The total

organic acids of the urine were greater in amount than the ketonic acids. The acidosis was not necessarily accompanied by diminution in the total base of the blood. C. R. HARRINGTON.

Influence of dihydroxyacetone on the blood-sugar and glycosuria. E. H. MASON (Canad. Med. Assoc. J., 1926, 16, 367—374).—Ingestion of dihydroxyacetone in 25—50 g. doses by persons with normal carbohydrate tolerance causes a slight transitory rise in the blood-sugar; with small interrupted doses there is a progressive fall. Diabetics who have a fair carbohydrate tolerance show very little rise in blood-sugar following a 25 g. intravenous dose. It appears that in certain cases the ingested dihydroxyacetone is not converted quantitatively into dextrose. CHEMICAL ABSTRACTS.

Insulin content of pancreas of diabetics. L. POLLAK (Arch. exp. Path. Pharm., 1926, 116, 15—34).—The pancreas of human diabetics contains insulin, but much less than the pancreas of normal individuals. W. O. KERMACK.

Appearance of phenol in the blood during kidney inefficiency. E. BECHER and S. LITZNER (Klin. Woch., 1926, 5, 147; from Chem. Zentr., 1926, I, 2015).—Free phenol may appear in the blood in moderate as well as in extreme cases of kidney inefficiency, and is separated by distillation with sodium hydrogen carbonate or dilute acetic acid. Its appearance may be transitory and dependent on the diet, and the amount is small in comparison with the large increase of bound phenol in the blood. W. O. KERMACK.

Amino-acid content of blood in melano-dermatitis. M. LOEPER, J. OLLIVIER, and A. LESURE (Compt. rend. Soc. Biol., 1925, 93, 1290—1291; from Chem. Zentr., 1926, I, 1591).—The increase in total sulphur which accompanies melano-dermatitis bears no constant relation to the amino-acid content of the blood. C. RIMINGTON.

Significance of cholesterol in bile and serum. III. **The equilibrium between cholesterol and its esters in disordered liver function.** R. STERN and G. SUCHANTKE (Arch. exp. Path. Pharm., 1926, 115, 221—231).—Although disorders of liver function and experimental poisoning of the liver are accompanied by changes in the concentration of cholesterol in the blood, the ratio of free cholesterol to its esters is not consistently modified. It is not considered that the liver function is the sole factor in the control of these substances in the blood. R. K. CANNAN.

Blood in leprosy. I. Non-protein nitrogenous substances, sugar, and chlorine. E. M. PARAS (Philippine J. Sci., 1926, 30, 219—234).—In cases of leprosy, the non-protein nitrogenous substances, sugar, and chlorine of the blood are essentially normal. In cases of leprosy with nephritis, the findings are typical of nephritis. In cases with lepra reaction, the total non-protein nitrogen and urea is high, but the chlorides remain normal. C. P. STEWART.

Blood in pneumonia. I. Method of constructing an alinement diagram to represent changes in gaseous composition of blood and in electrolyte concentration of plasma. T. E. BUCKMAN, F. D. ADAMS, M. SMITH, and H. T. EDWARDS (Boston Med. Surg. J., 1925, 193, 997—1020).—A nomogram shows quantitatively the association of changes in the carbon dioxide and oxygen percentage saturation with oxygen tension, hydrogen carbonate content of whole blood and plasma, hydrogen-ion concentration, and sodium chloride content of plasma. Two methods are described for the construction of diagrams in which the following factors are alined: carbon dioxide tension and hydrogen carbonate content of whole blood and plasma, oxygen tension and oxygen percentage saturation of the whole blood, sodium chloride content of the plasma, and hydrogen-ion concentration of the whole blood and plasma. CHEMICAL ABSTRACTS.

Post mortem blood chemical determinations. J. R. PAUL (Bull. Ayer Clin. Lab. Pennsylvania Hosp., 1925, 9, 51—62).—During the first 24 hrs. after death, the dextrose fell to insignificant values; the total non-protein nitrogen increased, urea-nitrogen and creatinine were unchanged, whilst the chlorides and uric acid changed irregularly. In blood taken within 24 hrs. after death, the average values of urea-nitrogen (mg. per 100 c.c.) were: lobar pneumonia, 88; advanced renal lesions, 197; cardio-vascular-renal cases, 22; heterogeneous cases, 27. A marked terminal increase apparently occurred in the blood urea-nitrogen. CHEMICAL ABSTRACTS.

Detection of guanidine substances in the blood in parathyroid tetany and their simultaneous appearance in the urine. J. KÜHNAU (Arch. exp. Path. Pharm., 1926, 115, 75—87).—A gravimetric method, requiring only 20 c.c. of blood, is described for the determination of guanidine bases in the blood. The method takes advantage of the solubility of the phosphotungstates of the guanidine bases in methyl alcohol. In cases of post-operative and idiopathic tetany and in parathyroidectomised dogs, the concentration of guanidine substances in the blood and urine was several times as great as normal. The view that parathyroid tetany is a condition of guanidine poisoning is supported. R. K. CANNAN.

Guanidine hypoglycæmia. E. FRANK, M. NOTHMANN, and A. WAGNER (Arch. exp. Path. Pharm., 1926, 115, 55—63).—Hypoglycæmia accompanies the tetany which follows the administration of toxic doses of guanidine to rabbits. Rabbits which had been fed survived longer than starved animals. Both dextrose and adrenaline delayed convulsions and prolonged life. Moreover, simultaneous administration of guanidine and adrenaline resulted in less hyperglycæmia than that produced by adrenaline alone, and the effect of guanidine was, like that of insulin, shown to be peripheral in origin. Nevertheless, the contention of Collip that insulin is a guanidine-like body does not find support in some important differences between the behaviour of the two substances and also of the methylated guanidines. R. K. CANNAN.

Determination of protein in cerebrospinal fluid. Increase of protein in typhus fever. S. M. LING (J. Biol. Chem., 1926, 69, 397—401).—By simultaneous determinations of total nitrogen and of tyrosine in the precipitate obtained by treating cerebrospinal fluid with tungstic acid, the relation between the amount of tyrosine and that of protein was established. The concentration of protein could then be determined rapidly by the use of the colorimetric method of Folin and Looney for the determination of tyrosine (A., 1922, ii, 539). In most cases of typhus fever the proteins of the cerebrospinal fluid are much increased. C. R. HARRINGTON.

Animal calorimetry. XXXIV. Influence of glycylglycine on respiratory metabolism of the dog. N. H. PLUMMER, H. J. DEUEL, jun., and G. LUSK (J. Biol. Chem., 1926, 69, 339—348).—The increase in the basal heat-production of dogs following administration of glycylglycine is exactly the same as that following administration of equivalent amounts of glycine itself. C. R. HARRINGTON.

Oxidation potential of the cell and oxidation-reduction phenomena. R. WURMSER (Compt. rend. Soc. Biol., 1925, 93, 1478—1479; from Chem. Zentr., 1926, I, 2109).—A consideration of the energetics of the intracellular oxidation and reduction of dextrose. J. PRYDE.

Decomposition of sugar in the central nervous system of man. J. WOHLGEMUTH and Y. NAKAMURA (Biochem. Z., 1926, 175, 233—240).—Brain attacks dextrose, glycogen, lactose, and galactose yielding aldehyde, the substances being placed in the order of their ease of oxidation. Lævulose, lactic acid, and amino-acids, however, are not attacked. Grey matter is much less active than white matter. In contrast with the liver, insulin does not increase, but often reduces aldehyde formation.

P. W. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XVI. Glycolysis and glycometamorphosis with special reference to insulin. XVII. Myophosphate. XVIII. Hydrolysis of zymohexosediphosphoric acid by muscle and its product of fission, monohexosephosphoric acid. XIX. Mechanism of insulin action. XX. p_H of whole blood after injection of insulin into rabbits. T. BRUGSCH and H. HORSTERS (Biochem. Z., 1926, 175, 90—114, 115—119, 120—126, 127—129, 130—134).—XVI. "Glycolysis" is limited to mean the decomposition of dextrose to lactic acid, "glycometamorphosis," the esterification of dextrose with phosphoric acid. Glycolysis occurs only in presence of phosphate, the optimum conditions being: dextrose, 0.3—0.4%, phosphate, 3%, p_H , 6.3—6.4. $\alpha\beta$ -, α -, and β -Glucose are subject alike to glycolysis. Higher concentrations than 0.3% of potassium chloride and 0.4% of calcium chloride inhibit glycolysis, and sodium fluoride does not appear to be more powerfully inhibiting. Glycometamorphosis is favoured by higher concentrations of sugar, and the concentration of phosphate must be above 3%. Glycometamorphosis involves the conversion of $\alpha\beta$ -glucose by an isomerase into an active γ -glucose which

becomes stabilised by esterification with phosphoric acid. This hexosephosphoric acid arising in the muscle is called myophosphate, to distinguish it from zymophosphate, with which it is not identical. The esterification process depends on a phosphatase which is active in presence of sugar, phosphoric acid, and a co-enzyme which is contained in the muscle, and can be replaced by insulin. Glycometamorphosis takes place independently of glycolysis, not only in muscle, but also in liver and in kidney. In the liver, myophosphate is then built up into the hexosan complex, glycogen (cf. A., 1925, i, 208, 483; this vol., 197, 198).

XVII. Using the neutral brucine salt for identification and purification, the authors show that lactacidogen is identical with the fermentation hexosediphosphoric acid $[\alpha]_D +3.2$. Myophosphate, however, is strongly laevorotatory, is a hexosediphosphoric acid, and gives rise on treatment with acid or alkali to a monophosphoric ester, probably identical with Robison's zymohexosemonophosphoric acid, $[\alpha]_D +25^\circ$.

XVIII. [With M. CAHEN.]—Zymophosphate, zymodiphosphate, or yeast hexosediphosphoric acid is hydrolysed by a phosphatase of the liver and muscle of warm-blooded animals, first into hexosemonophosphoric acid and phosphoric acid and then into lævulose and phosphoric acid. The hexosemonophosphoric acid is identical with Robison's acid $[\alpha]_D +25^\circ$. The optima for the action of phosphatase, zymodiphosphatase, and zymomonophosphatase are identical. Zymophosphate is not identical with myophosphate.

XIX. A discussion of Virtanen's results (see A., 1925, i, 753, 866; this vol., 95, 435, 760).

XX. After intravenous injection of fairly large doses of insulin into starving rabbits, the acidity of the blood is usually increased, but in well-fed animals the glycogen supply appears to ensure the maintenance of p_H almost unchanged.

P. W. CLUTTERBUCK.

Production of sugar in the perfused liver from non-protein sources. J. H. BURN and H. P. MARKS (J. Physiol., 1926, 61, 497—517).—When the liver taken from a cat or dog fed on a fat diet is perfused with blood from the same species, there is a production of reducing sugar at a rate of from 2 to 4 mg. per g. of liver per hr. A small formation of glycogen is demonstrable. The sugar production is not obviously influenced by insulin, adrenaline, or pituitrin. The sugar does not come from lactic acid or from any diffusible constituent of the liver and, from the concurrent formation of urea and ammonia, only a small fraction can come from protein. R. K. CANNAN.

Assimilation of lævulose, galactose, and dextrose in fasting and on a protein-fat diet. S. NAGASAYE (J. Biochem. [Japan], 1925, 5, 449—463).—The rise in blood-sugar following the ingestion of lævulose is less, and after that of galactose much greater, than that after administration of dextrose. Except with lævulose, the blood-sugar level rises much higher in fasting or on a protein-fat diet than on a normal mixed diet. The ingestion of either

dextrose or galactose in the fasting condition causes only a slight increase in the liver glycogen, whilst lævulose contributes considerably to raising the glycogen content of the liver both in fasting and on a protein-fat diet.

CHEMICAL ABSTRACTS.

Content of lactic acid and development of tension in cardiac muscle. A. C. REDFIELD and D. N. MEDEARIS (Amer. J. Physiol., 1926, 77, 662—668).—From measurements of the tension developed in strips of the ventricle of the turtle and the lactic acid content, it is suggested that the stress developed at any beat varies with the difference between the lactic acid concentration of complete fatigue and the concentration at the time of the beat.

R. K. CANNAN.

Mineral metabolism of horses fed solely on bran. O. BANG (Kong. Vet.- og Landsbehejskole Aarskrift, 1925, 383—404; from Chem. Zentr., 1926, I, 2016).—Analysis of the urine and fæces of a horse fed on white or red bran which contains an excess of acid over basic constituents shows that there is a negative calcium balance due to the excretion of calcium phosphate. Addition of calcium carbonate to the diet restores the calcium balance.

W. O. KERMAK.

Disturbance of the mineral metabolism and its effect on the action of white phosphorus. H. BERNHARDT and C. R. H. RABL (Z. klin. Med., 1925, 102, 147—173; from Chem. Zentr., 1926, I, 1595).—Addition of 2% of ammonium chloride to a diet rich in vitamins, but as low as possible in phosphorus and calcium without being rachitic, interferes with calcification. The action of white phosphorus is dependent upon the mineral content of the diet. Fall in calcium content of the bones and appearance of rachitic symptoms do not run parallel. Many other organs were also investigated.

C. RIMINGTON.

Effect of white phosphorus on calcium metabolism. H. BERNHARDT (Z. klin. Med., 1925, 102, 174—181; from Chem. Zentr., 1926, I, 1595).—In dogs fed on a diet poor in calcium, white phosphorus causes a retention of calcium and phosphorus. In three adults taking ammonium chloride, white phosphorus improved the calcium balance, but its effect on young animals is in many respects different. The action is very prompt and disappears again when the phosphorus is withdrawn from the diet.

C. RIMINGTON.

Effect of ovariectomy on calcium and phosphorus metabolism. J. DALSACE and C. O. GUILLAUMIN (Compt. rend. Soc. Biol., 1925, 93, 1209—1210; from Chem. Zentr., 1926, I, 1595).—In the majority of cases a fall in blood calcium was observed and also in phosphorus where a previous hyperphosphatæmia existed.

C. RIMINGTON.

Iodine metabolism. II. T. VON FELLEBERG (Biochem. Z., 1926, 174, 341—354).—The urinary iodine excretion is greater in the inhabitants of non-goiterous than in those of goiterous districts. In adults, the excretion is constant, in children less at night, and increased by psychic stimuli. Administration of potassium iodide results in the retention of

about half the amount administered. The iodine excreted is mainly in organic form. Feeding with thyroid gland hinders resorption. The iodine of plants is only partly present in assimilable form. The inorganic iodine of hay is largely removed by watering.

E. C. SMITH.

β -d-Glycuronic acid monobenzoate (benzoyl-glycuronic acid). A. J. QUICK (J. Biol. Chem., 1926, 69, 549—563).—Urine obtained from dogs after oral administration of large amounts of benzoic acid was cleared by addition of lead acetate; the filtrate, after neutralisation, was treated with basic lead acetate and the precipitate decomposed with hydrogen sulphide at a low temperature; the filtrate from the lead sulphide was concentrated in a vacuum until most of the hippuric acid crystallised out, and the filtrate from the latter, on keeping in the cold, deposited d-glycuronic acid monobenzoate contaminated with some hippuric acid which could be removed by extraction with ether; the pure substance had m. p. 170—172° (decomp.), k 1.4×10^{-3} , $[\alpha]_D^{20}$ -25.2° in water or dilute acid. In alkaline solution, it exhibited mutarotation, the equilibrium value being $[\alpha]_D^{20}$ $+50.0^\circ$; the methyl ester had m. p. 178—180°, $[\alpha]_D^{20}$ -25.0° , after mutarotation $[\alpha]_D^{20}$ $+35-37^\circ$; the lactone had $[\alpha]_D^{20}$ $+48^\circ$. The compound reacted with hydrogen cyanide and reduced Fehling's solution readily; it must therefore be regarded as a benzoic ester of glycuronic acid and not as a glucoside (cf. Magnus-Levy, A., 1907, ii, 979).

C. R. HARINGTON.

Metabolism of sulphur. XI. Can taurine replace cystine in the diet of the young rat? G. T. LEWIS and H. B. LEWIS (J. Biol. Chem., 1926, 69, 589—598).—Neither taurine nor cysteine acid, when added to a basal diet lacking cystine, could produce normal growth in young white rats.

C. R. HARINGTON.

Availability of taurine as a supplementing agent in diets deficient in cystine. W. C. ROSE and B. T. HUDDLESTON (J. Biol. Chem., 1926, 69, 599—605).—Deficiency of cystine in the diet of young rats cannot be made good by addition of taurine (cf. preceding abstract).

C. R. HARINGTON.

Catabolism of uric acid in vertebrates. I and II. S. J. PRZYLECKI (Arch. int. Physiol., 1924, 24, 238—263, 317—355).—On subcutaneous injection of various purines in frogs, or incubation with extracts of frog tissues, the uric acid was catabolised by means of enzymes by way of allantoin and other intermediate products to ammonia, oxalic acid, and urea. Since amphibia and fish catabolise uric acid through allantoin and are probably unable to synthesise it except from purine bases, whilst birds synthesise it (not through allantoin) and cannot destroy it, these processes are presumably irreversible in the vertebrates.

CHEMICAL ABSTRACTS.

Behaviour and action of bile acids in the organism. E. NEUBAUER (Deut. med. Woch., 1925, 51, 2150; from Chem. Zentr., 1926, I, 2017).—After intravenous injection of sodium dehydrocholate, the amount of bilirubin in the bile of rabbits, dogs,

and men was decreased, but an increase in the bile pigments was observed after the injection of more poisonous bile acids, such as cholic acid or deoxycholic acid.

W. O. KERMACK.

Behaviour and action of bile acids. A. ADLER (Deut. med. Woch., 1925, 51, 2150—2151; from Chem. Zentr., 1926, I, 2017).—A reply to Neubauer (cf. preceding abstract).

W. O. KERMACK.

Comparative physiological action of guanidine derivatives. G. A. ALLES (J. Pharm. Exp. Ther., 1926, 28, 251—276).—The effects of guanidine and its alkyl, acetyl, and amino-derivatives on blood pressure and respiration have been studied; these substances have no hypoglycæmic properties; minimum lethal doses are given.

H. J. CHANNON.

Reaction between acetylcholine and muscle cells. A. J. CLARK (J. Physiol., 1926, 61, 530—546).—Acetylcholine produces a graded action on the ventricle and the Rectus abdominis of the frog over a 100,000-fold range of concentration. The relation between the concentration of the drug and the action produced may be expressed by $K \cdot x = y/(100 - y)$, where x is the concentration of drug, y the action produced as a percentage of the maximum possible action, and K is a constant. This suggests a reversible unimolecular reaction between the drug and some substance in the cell or on its surface. The quantity of drug fixed by the cell is very small and sufficient to cover only a small fraction of the surface. There is no direct relation between the amount of drug entering the cells and the action produced.

R. K. CANNAN.

Pentamethylenetetrazole (cardiazol). I. F. HILDEBRANDT (Arch. exp. Path. Pharm., 1926, 116, 100—109).—The pharmacological action of pentamethylenetetrazole on the central nervous system and the heart is described. It does not act on plain muscle.

W. O. KERMACK.

Pentamethylenetetrazole (cardiazol). II. O. EICHLER and F. HILDEBRANDT (Arch. exp. Path. Pharm., 1926, 116, 110—116).—The pharmacological action of pentamethylenetetrazole on the circulation and blood pressure is described. Pentamethylenetetrazole counteracts the harmful effects of chloroform and chloral hydrate on the circulation.

W. O. KERMACK.

Action of quinine and its derivatives on metabolism and heat regulation. B. ROSENTHAL and W. LIPSCHITZ (Arch. exp. Path. Pharm., 1926, 116, 39—66).—Quinine, hydroquinine, optoquin, eucupin, and vuzin have been investigated as to their effect on the autolysis of macerated guinea-pig or dog liver, and on nitrogen metabolism, and as to their pyretic or antipyretic action. Eucupin and vuzin are peculiar in increasing the excretion of nitrogen and in causing a marked rise in body temperature.

W. O. KERMACK.

Influence of administration of active and inactive iron oxide on the C : N urinary quotient in rabbits. H. WADA (Biochem. Z., 1926, 175, 62—67).—Whereas administration of "active" (magnetic) iron oxide caused the urinary C : N ratio to

increase considerably, inactive oxide had only a slight delayed effect.

P. W. CLUTTERBUCK.

Composition of blood-serum and its significance in the action of poisons. I. Introduction. H. HANDOVSKY. II. Characterisation of the protein fractions of normal serum by viscosity. P. BOSSE and H. HANDOVSKY. III. Action of ether on serum. P. BOSSE. IV. Determination of cholesterol in blood-serum. H. HANDOVSKY and K. LOHMANN. V. State of cholesterol in blood-serum. H. HANDOVSKY, K. LOHMANN, and P. BOSSE (Pflüger's Archiv, 1925, 35—49, 50—55, 56—58, 59—62, 63—69; from Chem. Zentr., 1926, I, 1669—1670).—I. Normal ox-serum contains on the average 6.68% of protein and 0.123% of cholesterol. The average distribution of the protein is 59% of albumin, 23% of pseudoglobulin, and 18% of euglobulin. The author assigns to the cholesterol—as a constituent of the cell walls—a share in the action of poisons on the cell.

II. For the determination of the different protein fractions in normal ox-serum, the refractometric method of Robertson was found to be satisfactory. In viscosimetric and refractometric determinations it was found that the viscosity of normal serum is an additive property of the protein fractions, and this can serve for their characterisation. One % of euglobulin raises the viscosity of water by 0.21, 1% of pseudoglobulin by 0.12, 1% of albumin by 0.08%. Sera of tuberculous humans and oxen always show a viscosity higher than normal.

III. Ether, as alcohol and chloroform, precipitates globulins first. It also denatures the albumin.

IV. For the determination of total cholesterol in serum 1 c.c. of serum is boiled with 1 c.c. of saturated sodium hydroxide on the water-bath; the neutralised—preferably slightly alkaline—liquid is shaken three times with ether and the cholesterol determined colorimetrically in the extract by the method of Liebermann and Burchardt. The cholesterol which can be shaken out directly from serum is determined colorimetrically in the extract made by shaking 2—10 c.c. of the serum with twice the amount of ether for 6 hrs. The extract contains cholesterol in the free and ester form in about the ratio 1 : 1.

V. In experiments on the precipitation of the protein fractions and determination of the phosphorus and cholesterol of serum, it was found that after the proteins were precipitated by acetic acid or ammonium sulphate the phosphatides and the greater part of the cholesterol remain in the aqueous solution. Only 22—25% of the cholesterol was found in the protein precipitate, and this exclusively with the globulin. To determine the intensity of the cholesterol linking, the serum was shaken with ether. On the average, 16—50% of the total cholesterol was extracted. The amount thus extracted does not depend on the cholesterol content of the serum. It is raised by increased albumin content. From sera poor in euglobulin large amounts, from sera rich in euglobulin small amounts of cholesterol can be extracted. It is further influenced by the salt and water content of the serum; small additions (0.1%) of potassium, sodium, and calcium chlorides and

dextrose raise the amount which can be extracted, but two or three times this quantity lowers it; dilution with Ringer or Tyrode solution does not change it; on the other hand, dilution with water lowers it and concentration strongly raises it.

H. I. COOMBS.

Effect of carbon tetrachloride and of alcohol on acid-base balance of the blood. P. D. LAMSON and R. WING (J. Biol. Chem., 1926, 69, 349—355).—No significant changes in the acid-base balance of the dog's blood were observed after oral administration of carbon tetrachloride and alcohol, separately or together, or after inhalation for 30 min. of carbon tetrachloride in sufficient concentration to produce deep anaesthesia.

C. R. HARRINGTON.

Action of ethyl alcohol on the sensitivity of proteins towards electrolytes. P. WELS (Arch. exp. Path. Pharm., 1926, 116, 67—99).—0.25% Ethyl alcohol increases the sensitiveness of proteins towards electrolytes, whilst 0.5% decreases it. The bearing of these results on the physico-chemical condition of cells, more particularly in relation to the effects of alcoholic poisoning, is discussed.

W. O. KERMACK.

Ethylene narcosis. I. Behaviour of the narcotic in blood. II. Distribution of ethylene between blood corpuscles and plasma *in vitro* and during narcosis. M. NICLOUX and A. YOVANOVITCH (Comp. rend. Soc. Biol., 1925, 93, 1653—1656, 1657—1658; from Chem. Zentr., 1926, I, 2217).—The concentration of ethylene in the blood of a dog is dependent on its concentration in the inhaled gas and amounts to 8—10 c.c. per 100 c.c. of blood, when there is 66—77.5% in the gas. *In vitro* as *in vivo*, 70—80% of the ethylene in the blood is in the corpuscles and 20—30% in the plasma.

W. O. KERMACK.

Determination of ethylene in blood. M. NICLOUX (Compt. rend. Soc. Biol., 1925, 93, 1650—1653; from Chem. Zentr., 1926, I, 2217).—The blood is extracted in an apparatus previously described by the author for the determination of carbon monoxide and analysed eudiometrically (cf. "L'oxyde de carbone et l'intoxication oxycarbonique," 1925, Paris).

W. O. KERMACK.

Influence of experimental poisoning by acids and of excision of the suprarenals on the inorganic cation content of blood-serum. K. KEITEL (Biochem. Z., 1926, 175, 86—89).—The inorganic cation (especially sodium ion) content of dog's serum falls after intravenous injection of hydrogen chloride, but rises after extirpation of the suprarenals.

P. W. CLUTTERBUCK.

Toxicity of arsinetri-*N*-piperidinium chloride. C. S. LEONARD (J. Pharm. Exp. Ther., 1926, 28, 233—239).—The effects of the drug injected into rabbits and dogs were those characteristic, not of organic arsenic compounds, but of substituted ammonium salts.

H. J. CHANNON.

Toxic action of copper on *Nitella*. S. F. COOK (J. Gen. Physiol., 1926, 9, 735—754).—Using the loss of turgidity of the cells as a criterion, it is found that the toxicity curve of copper chloride with

Nitella is sigmoid. When the concentration of the copper chloride is varied, the toxic effect varies as a constant, fractional power of the concentration. This relation holds when the concentration is plotted against either (1) the time necessary to reach a given point on the ordinate of the survivor curve, (2) the maximum speed of toxic action as shown by the tangent to the survivor curve, or (3) the first derivative of the equation which fits the survivor curve. When the temperature is varied, and the logarithm of the reciprocal of the time necessary to reach a given point on the survivor curves is plotted against the reciprocal of the absolute temperature, the resulting figure consists of curves intersecting at 16°, 27°, and 32°.

W. ROBSON.

Toxicological considerations on the production of hydrocyanic and thiocyanic acids in the putrefying animal organism. I and II. G. SENSI and M. REVELLO (Annali Chim. Appl., 1926, 16, 268—275, 275—280; cf. A., 1925, ii, 607).—I. Hydrocyanic acid disappears rapidly from the body after poisoning. It is transformed into thiocyanic acid, but this conversion is not quantitative and varies according to conditions. In the putrefaction of animal tissues thiocyanic acid is sometimes formed, and this can lead to wrong deductions as to hydrocyanic acid poisoning.

II. A description of a case of fatal poisoning by hydrocyanic acid in which the dose was small and the acid could not be detected in the body with certainty.

S. B. TALLANTYRE.

Purification of enzymes by electrodialysis and electro-osmosis. R. FRICKE, F. A. FISCHER, and H. BORCHERS (Kolloid-Z., 1926, 39, 371—372).—Addenda to a previous paper (this vol., 791).

N. H. HARTSHORNE.

Biochemistry of electrolytes. L. HUGOUNENQ and J. LOISELEUR (Bull. Soc. Chim. biol., 1926, 8, 610—620).—Enzyme activity is considered to be due to catalytically active ions adsorbed on protein, and will in consequence be a function of the selective adsorption by the protein and the p_H . The existence within the cells of proteins with different isoelectric points and the selective adsorption of ions allows control of wide variations in enzyme activity by small changes in the hydrogen-ion concentration. It is suggested that the nucleoproteins may be the colloidal support for more than one catalytically active ion.

H. J. CHANNON.

Hydrogen cyanide in the metallic poisoning of enzymes. M. JACOBY (Biochem. Z., 1926, 175, 79—85).—Papain is inactivated by zinc only when the metal, in presence of excess of potassium cyanide, is brought into contact with the enzyme. The inactivation is similar to that of pepsin, but different from that of urease.

P. W. CLUTTERBUCK.

Effect of potassium thiocyanate on diastatic action. A. BITTORF and VON FALKENHAUSEN (Arch. exp. Path. Pharm., 1926, 115, 9—17).—The amylolytic activity of saliva is notably increased by addition of potassium thiocyanate. The optimum concentration of the latter increases with the dilution of the enzyme. Experiments with dialysed saliva

show that the effect is not merely that of neutral salts activating the amylase, since the presence of sodium chloride is also necessary for the full effect to be observed. The diastase of the submaxillary gland, the pancreas, and the liver are similarly activated by thiocyanate. R. K. CANNAN.

Supposed hydrolysis of starch by salts and protein degradation products. K. TAKANE (Biochem. Z., 1926, 175, 241—252).—The view that starch can be hydrolysed by solutions of salts, amino-acids, and peptones, advocated by Iljin (A., 1923, i, 172), Biedermann (*ibid.*, 655), Haehn (*ibid.*, 443), and by Haehn and Berentzen (Chem. Zelle Gewebe, 1925, 12, 286) is shown to be erroneous. When starch was carefully purified and when the solutions both of starch and of salts etc. were boiled sufficiently and the apparatus was carefully sterilised, no evidence of hydrolysis could be obtained.

P. W. CLUTTERBUCK.

[Alleged] artificial glycolytic enzyme. H. KÖCHLING (Chem. Zelle Gewebe, 1925, 247—285; from Chem. Zentr., 1926, I, 1587).—So far, all attempts to prepare an agent capable of degrading dextrose under aseptic conditions have failed. The activity of the peptone-dextrose-hydrogen carbonate system of Schlatter, as also of the oleate-fibrin-dextrose-buffer system of Warden, was due to bacteria, whilst the fibrin-containing preparations of Schroeders and of Sieber are not active if cell-free plasma is used. C. RIMINGTON.

Retardation of invertase action by dextrose and lævulose. J. M. NELSON and R. S. ANDERSON (J. Biol. Chem., 1926, 69, 443—448).—Curves obtained by plotting the retarding effect on inversion of sucrose exerted by β -glucose, α -fructose, and β -fructose against the concentration of sucrose are all of the same shape; with α -glucose curves of another type were obtained, the retardation due to this substance being greater at 2% and less at 20% sucrose concentration than that of the other hexoses mentioned above. C. R. HARRINGTON.

Effect of esterifying carbocyclic acids on their action in preventing the development of micro-organisms. T. SABALITSCHKA, K. R. DIETRICH, and E. BÖHM (Pharm. Ztg., 1926, 53, 834—836).—*Penicillium glaucum* was added to a suitable nutrient medium to different portions of which the substance under investigation had been added in varying amounts. Phenol was used as a standard for comparison. Of the free acids used, benzoic acid was found the most active, its activity being one-third that of phenol. Then came in descending order of activity, anisic, salicylic, and cinnamic acids, whilst *m*- and *p*-hydroxybenzoic acids were the least active. Benzoic and salicylic acids show a stronger activity than their methyl esters, a behaviour, however, which is reversed in the case of the other acids and esters. Esterification leads to similar results, whilst the introduction of chlorine further increases the activity, so that methyl *m*-chloro-*p*-hydroxybenzoate has an activity comparable with that of phenol. The action of this ester (a commercial preservative) was tested, in comparison with the commoner pre-

servatives, against various fungi and bacteria and was found to be superior to them. The conclusion is reached that whilst the salts of the acids act only in an acid medium, the free acids only in acid or non-acid-binding medium, the activities of the esters remain unchanged whether the medium is acid, neutral, or alkaline. W. ROBSON.

Formation of lactic acid from methylglyoxal by ketone-aldehyde mutase of animal and vegetable origin. G. GORR and G. PERLMANN (Biochem. Z., 1926, 174, 433—439).—Methylglyoxal is converted into lactic acid by aqueous extracts of muscle to the extent of 77—90%, of liver to the extent of 64% in 15 hrs. at 37°, and by *Bacterium pasteurianum*, under anaerobic conditions, to the extent of 90% in 26 hrs. E. C. SMITH.

Conversion of phenylglyoxal into mandelic acid by the ketone-aldehyde mutase of green plants. G. BINDER-KOTRBA (Biochem. Z., 1926, 174, 443—447).—Phenylglyoxal is converted into *l*-mandelic acid by the action of pea-meal, aqueous extract of peas, the alcohol-ether precipitate from the latter, and the acetone-dried pea-meal preparation. The presence of the ketone-aldehyde mutase inhibits the spontaneous formation of *dl*-mandelic acid, the product after 6 days' action of bean-meal being 90% *l*-mandelic acid. E. C. SMITH.

Determination of lipase in germinating pine-seeds. H. W. NICOLAI (Biochem. Z., 1926, 174, 373—383).—Lipase is determined by a modification of the method of Rona and Lasnitski (A., 1925, i, 471). The lipase content of pine seeds increases up to the fifth day of germination. The amount of fat hydrolysed during the first 7 days, calculated from the lipase action, corresponds with that determined by analysis. The seeds contain maltase, but no glycolytic enzymes. E. C. SMITH.

Behaviour of lipase during autolysis of the liver. H. KOSTERLITZ and H. PETOW (Biochem. Z., 1926, 175, 31—45).—Solutions obtained by extraction at 2° of liver pulp after autolysis have much greater lipolytic power than extracts made before autolysis. The lipolytic power of extracts obtained by combining autolysis with dialysis is at first still greater and then falls away. P. W. CLUTTERBUCK.

Specificity of luciferin and luciferinase. E. N. HARVEY (Amer. J. Physiol., 1926, 77, 548—554).—Among 41 different genera of luminous animals, only *Pholas dactylus*, ostracods, fire-flies, and *Odontosyllis* give the luciferin-luciferinase reaction. *Cypridina* luciferin (or luciferinase) will react with the luciferinase (or luciferin) of two other genera of ostracods with luminescence, but with none of the other luminous animals. The oxy-luciferin of *Cypridina* and *Pholas*, but not of *Pelagia* or *Chaetopterus*, can be reduced again with hydrogen and platinised asbestos. It is suggested that the absence of the luciferin-luciferinase reaction is in many cases due to the fact that just enough luciferinase is present to be completely used up by the luciferin during the attempted preparation of the former. R. K. CANNAN

Bioluminescence and fluorescence in the living world. E. N. HARVEY (Amer. J. Physiol., 1926, 77, 555—561).—A survey has been made of the fluorescence in near ultra-violet light of the tissues and photogenic material of luminescent animals. In general, the luminous organs show a marked fluorescence, the colour of which is the same as that of the luminescence, although there are exceptions to both of these statements. Dried fire-flies and some fish preserved in formalin show this fluorescence, which, in some cases, seems definitely to be associated with the oxidation product of the luminous material.

R. K. CANNAN.

Regeneration of enzymes made inactive by heating. A. N. BAKH and A. I. OPARIN (Trans. Karpov Inst. Chem., 1925, [4], 217—231).—The properties of peroxidase, inactivated by heating, are restored to a noticeable extent only in presence of atmospheric oxygen; the conditions are most favourable in slightly alkaline solutions. The absorption of oxygen by slightly alkaline solutions of vegetable extracts is due to the presence of "breathing chromogens" which unite with oxygen and thereby become coloured. If such chromogens and pigments are removed from vegetable extracts containing enzymes, regeneration of the activity of the latter does not take place. Isolated crystalline pigment (chlorogenic acid) regenerates enzymes in solutions which otherwise exhibit no regeneration. The process is therefore one of oxidation of the zymogen.

CHEMICAL ABSTRACTS.

Specificity of animal proteases. VI. Mode of action of pepsin. E. WALDSCHMIDT-LEITZ and E. SIMONS (Z. physiol. Chem., 1926, 156, 114—127).—The equivalence of carboxyl and amino-groups liberated by the hydrolysis of various proteins by pepsin suggests that the peptolysis consists in the fission of carboxylamides. Exceptions in which the ratio $\text{NH}_2 : \text{CO}_2\text{H}$ varies from unity are probably due to the presence of such compounds as glutamic and pyrrolidinecarboxylic acids in the products. The peptolysis of caseinogen, egg-albumin, globulin from ricinus seeds, gliadin, zein, and gelatin is described, and the $\text{NH}_2 : \text{CO}_2\text{H}$ ratios are determined.

C. HOLLINS.

Determination of pepsin using Congo-red. M. KAWAHARA and O. PECZENIK (Wien. med. Woch., 1926, 76, 129—130; from Chem. Zentr., 1926, I, 1865).—A modification of the Congo red-albumin method previously described (Pflüger's Archiv, 1924, 206, 360). Using the easily digestible and completely soluble caseinogen, 2—4 hrs. is a sufficient time for digestion.

J. S. CARTER.

Pancreatic protein digestion. R. WILLSTÄTTER (Deut. med. Woch., 1926, 52, 1—2; from Chem. Zentr., 1926, I, 1672).—The pancreatic enzyme mixture is separated into its components—lipase, trypsin, and amylase—by separating the lipase and trypsin from the amylase by adsorption on alumina and kaolin, respectively. The pure trypsin is not able to act on simple peptides, but is able to hydrolyse peptones (also thymus histone and clupein). The recent view of the predominantly disintegrating

action of trypsin and pepsin is not borne out by quantitative experiments. It appears more likely that the breakdown of protein compounds in the animal body is essentially by hydrolytic reactions which convert protein through peptones and peptides into amino-acids.

H. I. COOMBS.

Digestibility of deaminated proteins by proteolytic enzymes. R. NAKASHIMA (J. Biochem. [Japan], 1925, 5, 293—310).—Caseinogen, edestin, and zein (5—10 g.) were deaminated with a cold mixture of 50 c.c. of glacial acetic acid and 100 c.c. of 30% sodium nitrite solution, the yellow mass being collected after 4—6 hrs., and washed successively with cold urea solution, water, alcohol (unless the protein is soluble), and ether. The products, which were practically free from amino-nitrogen, were dried in a vacuum. The reactions given by the deaminated proteins are detailed. The optimum acidity for peptic and tryptic digestion differs from that for the natural protein, but (except for zein) at that optimum acidity there is no difference in digestibility between the natural and deaminated proteins.

CHEMICAL ABSTRACTS.

Enzymes of the skin. J. WOHLGEMUTH. V. **Respiration and glycolysis of the skin and the influence of hormones.** E. KLOPSTOCK. VI. **Behaviour of lipase and presence of phosphatase, sulphatase, and carboxylase in the skin.** Y. NAKAMURA (Biochem. Z., 1926, 175, 202—215, 216—232).—V. Respiration and glycolysis are determined by Warburg's method. The mean values for human skin are, for respiration $Q_{O_2} = -2.1$ and for anaerobic glycolysis $Q_{CO_2} = +6$. The corresponding values for the skin of a cadaver are $Q_{O_2} = -2.0$ and for $Q_{CO_2} = +3.4$. These values refer only to superficial layers of skin, the deeper layers giving lower values. Aerobic glycolysis of skin gave only very small values. Adrenaline causes a slight increase in respiration of the skin. The active principles of the thyroid, ovaries, and testis increase the respiration to 300, 220, and 170%, respectively, whilst insulin and hypophysis decrease respiration to 65 and 30% of the original value. Glycolysis is reduced by the active substances of the thyroid, testis, and hypophysis to 40, 60, 70%, but is slightly increased by that of the ovaries and is scarcely at all affected by insulin (cf. A., 1925, ii, 203, 472; this vol., 93, 864).

VI. Lipase of the skin has its optimum action at p_H 7.1—7.5, and is activated by the phosphate ion. The resistance of this lipase to quinine and atoxyl depends, not on any specific property of the enzyme, but on the presence of certain dialysable substances. In the skin and in the subcutaneous fat a phosphatase is present and in the skin a sulphatase. Since the skin can also break down pyruvic acid to aldehyde, a carboxylase is probably present.

P. W. CLUTTERBUCK.

Sulphatase. VIII. Difference between sulphatase and myrosinase. C. NEUBERG and J. WAGNER (Biochem. Z., 1926, 174, 457—463).—Sinigrin is resistant to plant sulphatase, whilst myrosinase from *Sinapis alba* is without action on the substrates normally used for determining sulphatase action.

E. C. SMITH.

Isolation and crystallisation of urease. J. B. SUMNER (J. Biol. Chem., 1926, 69, 435—441).—Jack-bean meal is extracted at the ordinary temperature with 5 parts of 31.6% acetone; on keeping the filtrate over-night at 2—2.5° a crystalline deposit is obtained, which is soluble in water and dilute alkalis, gives the reactions for protein, but no reactions for carbohydrate; 1 mg. will produce 100 mg. of ammonia nitrogen from urea in 5 min. at 20°. The substance is denatured on keeping in the dry state and on treatment with acid; it is regarded as a globulin and as being identical with urease.

C. R. HARRINGTON.

Fermentation. S. N. CAGAN (Z. angew. Chem., 1926, 39, 951—952).—Pyruvic acid, one of the intermediate products of the fermentation of sucrose with yeast, yields α -isobutyl- β -naphthocinchonic acid with an ethereal solution of isovaleraldehyde and β -naphthylamine, and this acid is readily purified by recrystallisation from ethyl acetate. An attempt to obtain a large yield of the pyruvic acid derivative by shaking a dilute sugar solution containing yeast with an ethereal solution of the above aldehyde and amine failed, however, only 0.85 g. of the cinchoninic acid being obtained from 90 g. of sucrose owing to the phytochemical reduction of the aldehyde to isoamyl alcohol. At the same time, it appeared that pyruvic acid must undergo fermentation at an extraordinarily rapid rate to account for such a poor yield.

A. R. POWELL.

Carbohydrate metabolism. XIV. Presence of "neo-glucose" in the course of fermentation of α -glucose. C. LUNDSGAARD and S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, 93, 1688—1690; from Chem. Zentr., 1926, I, 2114).—Aqueous and ethereal extracts of various yeasts are mixed with α -glucose and subjected to dialysis. Good correspondence between reduction and polarimetric values for glucose is found in the dialysates. It is concluded that "neo-glucose" is not formed during the fermentation of sugar by yeast.

J. PRYDE.

Action of oxygen on the alcoholic fermentation of sugar. G. GORR and G. PERLMANN (Biochem. Z., 1926, 174, 425—432).—The combined ethyl alcohol and acetaldehyde formation during the fermentation of sucrose by yeast is only very slightly less in the presence of air than under anaërobic conditions. The yield of butylene glycol is in each case minute, and acetylmethylcarbinol and diacetyl cannot be detected.

E. C. SMITH.

Action of ammonium salts on yeast fermentation. IV. H. ZELLER (Biochem. Z., 1926, 175, 135—161).—The fermenting power of pressed yeast is increased by 80—140% by addition of ammonium phosphate, carbonate, oxalate, citrate, tartrate, and formate and by 20—30% by ammonium chloride, sulphate, bromide, iodide, nitrate, benzoate, molybdate, thiocyanate, and ammonium magnesium sulphate. The fermenting power of brewers' yeast is also increased by these salts with the following exceptions: ammonium benzoate inhibits fermentation strongly, and ammonium citrate, which assists fermentation with pressed yeast only when in small concentration

and inhibits in more concentrated solution, increases fermentation with brewers' yeast both in concentrated and dilute solution. The permeability of ammonium salts is approximately proportional to the increase in fermenting power with the exception of ammonium phosphate. The increased fermentation is probably related to the formation of complex sugar-ammonium salt compounds. Ammonium salts do not increase the action of Lebedev's extract. Insulin, which cannot replace the enzyme, partly inhibits the action of ammonium salts.

P. W. CLUTTERBUCK.

Fermentation of hexosediphosphoric acid, dextrose, lævulose, sucrose, and invert-sugar by yeast juice and fresh yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, 174, 480—492).—At the commencement of the fermentation of sodium or magnesium hexosediphosphate in the presence of arsenate, fermentation is more rapid than is the case with the simple sugars. This supports the hypothesis that the breakdown of the ester results in the liberation of a more readily fermentable sugar, but later in the course of fermentation the breakdown of the simple sugars is the more rapid, and preliminary treatment of the hexosediphosphate with tissue phosphatase does not result in a more rapid fermentation than that of dextrose or lævulose. The fermentation of the hexosediphosphate is accelerated by the addition of toluene, bile salts, and other substances which affect the permeability of the cell.

E. C. SMITH.

Fermentation of phenylglyoxylic acid. G. BINDER-KOTRBA (Biochem. Z., 1926, 174, 440—442).—Phenylglyoxylic acid is converted by yeast in the presence of sodium hydrogen sulphite into benzaldehyde, which separates as the hydrogen sulphite compound.

E. C. SMITH.

Reaction between sugars and amino-acids. Fermentation of mixtures of amino-acids and sugars. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, 174, 464—479).—It is shown by means of the alteration of rotation of solutions of the sugars and amino-acids on admixture that reactions take place between the following: lævulose, dextrose, maltose, and magnesium hexosediphosphate with urea, asparagine, and glutamic acid; lævulose and dextrose with L-alanine, thiourea, acetamide, and arginine. The fact that amino-acids are fermented only in the presence of carbohydrate is considered to be explained by the necessity for this combination to occur.

E. C. SMITH.

Zymophosphate formation and biochemical transformation of sugar. H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1925, 37, 301—307; from Chem. Zentr., 1926, I, 2013).—The formation of zymophosphate by yeast is inhibited by phenol at approximately the same concentration at which it retards fermentation.

W. O. KERMAK.

Separation of the oxidoreductase from the zymase complex. I. A. LEBEDEV (Z. physiol. Chem., 1926, 156, 153—158).—The filtrate from macerated yeast-extract which has been coagulated at 60—65° does not ferment sucrose, but decolorises

methylene-blue. The oxidoreductase, precipitated from the filtrate by ammonium sulphate, has no action on methylene-blue, and the residual liquor, after boiling, is also without action. The latter, however, contains a co-enzyme, for a mixture of the boiled liquor and the precipitated oxidoreductase decolorises methylene-blue. C. HOLLINS.

Bacterial filters. S. P. KRAMER (J. Gen. Physiol., 1926, 9, 811—812).—Regarding a filter in action as a suspension of the material composing the filter in the fluid which is being filtered, it is found that colloids or micro-organisms which pass filters of silica (electronegative charge) will not pass filters of plaster of Paris or of pure calcium sulphate to which calcium carbonate has been added (electropositive charge) and *vice versa*. Filters of pure calcium sulphate (no electrical charge) have no action on the dyes or organisms used. W. ROBSON.

Dismutation of aldol by *Bacterium ascendens*. G. BINDER-KOTRBA (Biochem. Z., 1926, 174, 448—451).—Aldol is converted by *Bacterium ascendens* into *d*- β -butylene glycol, $[\alpha]_D +14.6^\circ$, and into β -hydroxybutyric acid of only very small dextrorotation, $[\alpha]_D +1.0^\circ$. E. C. SMITH.

Biochemistry of the asymmetry problem. P. MAYER (Biochem. Z., 1926, 174, 420—424).—Phenylglyoxal is quantitatively converted into *d*-mandelic acid by treatment with *Bacterium ascendens*, and into *l*-mandelic acid with lactic acid bacteria or an acetone-dried preparation of the latter. The two bacteria contain therefore a ketone-aldehyde mutase. E. C. SMITH.

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; from Chem. Zentr., 1926, I, 1666).—Cytosine can be hydrolytically deaminated to uracil by means of an enzyme found in yeast. *B. coli* can also convert cytosine into uracil. Uracil is not attacked by *B. coli*. H. I. COOMBS.

Bacterial metabolism. LXXVI. Soluble proteolytic enzyme of *Bacillus proteus*. A. I. KENDALL and H. R. KEITH. LXXVII. Intestinal flora of nurslings. LXXVIII. Intestinal bacteria of artificially fed infants. LXXIX. Intestinal flora of normal adults. LXXX. Intestinal flora of man containing abnormal numbers of gas bacilli. A. J. KENDALL, A. A. DAY, and A. W. WALKER (J. Infect. Dis., 1926, 38, 193—199, 200—204, 205—210, 211—216, 217—221).—The soluble proteolytic enzyme of *Bacillus proteus* effects a rapid change, tryptic rather than peptic, in the gelatin molecule. Bacteria from nurslings induce but small nitrogenous changes, but effect pronounced fermentation of dextrose and lactose, with formation of acid. Bacteria from artificially fed infants cause putrefaction in sugar-free media, and fermentation in similar media containing carbohydrates. Moderate proteolysis and some putrefaction, caused by bacteria from normal adults in media containing no utilisable carbohydrate, are suppressed when utilisable carbohydrates are present. Rapid degradation of protein and extensive deamin-

ation, caused by bacteria from subjects containing abnormal numbers of gas bacilli in solutions free from utilisable carbohydrate, are also suppressed in presence of carbohydrate. CHEMICAL ABSTRACTS.

Pyorubrin, a red, water-soluble pigment characteristic of *Bacillus pyocyaneus*. P. D. MEADER, G. H. ROBINSON, and V. LEONARD (Amer. J. Hyg., 1925, 5, 682—708).—Like the fluorescent pigment and pyocyanin, pyorubrin yields its specific leuco-base on reduction with zinc and hydrochloric acid, and is regenerated therefrom on oxidation; unlike the first two substances, it is not an indicator. CHEMICAL ABSTRACTS.

Carbamide [formed] by bacteria. N. N. IVANOV (Biochem. Z., 1926, 175, 181—184).—Cultures of *Bacillus megatherium* and *B. tumescens* form from peptone containing gelatin and from amino-acids containing arginine, considerable amounts of carbamide which is derived from the arginine (cf. A., 1925, i, 344, 746).

P. W. CLUTTERBUCK.

Dismutation of α -methylbutaldehyde. C. NEUBERG and E. SIMON (Biochem. Z., 1926, 174, 452—456).—*dl*- α -Methyl-*n*-butaldehyde is quantitatively converted by *Bacterium xylinum* into the corresponding *dl*-amyl alcohol and *dl*-valeric acid. Suspensions of horse-liver act very slowly and incompletely, the amyl alcohol obtained being inactive.

E. C. SMITH.

Attenuation and antigenic power of diphtheria toxin after treatment with various substances. P. NELIS (Ann. Inst. Pasteur, 1926, 40, 666—696). The removal of dialysable substances from diphtheria toxin (which itself dialyses slowly) causes it to lose rapidly much of its toxic power. The dialysed toxin is the more rapidly acted on by ozone. In the preparation of the anatoxin, most of the formaldehyde is taken up by the dialysable substances. Sodium oleate solution at 37° destroys the toxin completely. Quinine salts destroy it in part. The antigenic power of the toxins treated by these methods is given. H. J. CHANNON.

Peptone culture medium for *Bacillus tuberculosis*. L. BOEZ (Ann. Inst. Pasteur, 1926, 40, 746—754).—The use of a medium consisting of the product of pancreatic digestion of beef, together with glycerol, dextrose, and salts, is advocated. H. J. CHANNON.

Isolation of a crystalline protein with tuberculin activity. F. E. SEIBERT (Science, 1926, 63, 619—620).—The protein was completely precipitated from tuberculin by saturation with ammonium sulphate; the product consisted of a water-soluble, non-coagulable protein, a water-soluble, heat-coagulable protein, and a water-insoluble protein, the first two containing most of the tuberculin activity. When the water-soluble, non-coagulable dialysed fraction was treated by Hopkins' method for isolating crystalline ovalbumin, needles were obtained which gave the biuret, Millon, and Molisch reactions, together with a marked skin reaction in tuberculous guinea-pigs. A. A. ELDRIDGE.

Isolation of insulin. C. FUNK (Science, 1926, 63, 401—402).—Insulin, purified by way of its com-

pound with flavianic acid, yields analytical results corresponding with the formula $C_{69}H_{102}O_{22}N_{18}S$ or $C_{74}H_{114}O_{24}N_{20}S$. The structure may be that of a polypeptide composed of about 15 amino-acids.

A. A. ELDRIDGE.

Crystalline insulin. J. J. ABEL (Proc. Nat. Acad. Sci., 1926, 12, 132—136).—A purified preparation of insulin is dissolved in weak acetic acid. Contaminating substances are precipitated by addition of a solution of brucine in acetic acid and removed in the centrifuge. On adding *N*/6-pyridine to the clear solution, crystalline insulin together with some amorphous insulin separate from the liquid. This crystalline insulin has m. p. 233°, and gives biuret, Millon's, Pauly's, and the ninhydrin reactions.

H. W. DUDLEY.

Biuret-free insulin. R. S. ALLEN and J. R. MURLIN (Amer. J. Physiol., 1925, 75, 131—139).—Perfusion is followed by salting out with sodium chloride (35 g. per 100 c.c. of solution); the dry substance is then extracted with 70% alcohol, the residue after evaporation of the filtrate being extracted with 80% alcohol, and the process repeated several times. The product is insoluble in acid solutions and in water, but is readily soluble in dilute alkali. It is unstable, but gives none of the colour reactions for proteins.

A. A. ELDRIDGE.

Mechanism of the action of insulin. G. VIALE (Arch. ital. Biol., 1924, 74, 131—140; from Chem. Zentr., 1926, I, 2112).—The observations of Stosse (Compt. rend. Soc. Biol., 1924, 89, 98) and of Winter and Smith (J. Physiol., 1923, 57, 100) are not confirmed. An ultra-filtrate from blood concentrated in a stream of warm air gives the same reduction and polarimetric value for dextrose. A mixture of liver extract, insulin, and dextrose after keeping at 38° for 5 hrs., also shows, when deproteinised, identical reduction and polarimetric values. Insulin does not increase glycolysis in normal or diabetic blood, nor does it alter the blood reaction. Formic acid in the blood is increased after insulin and diminished by extirpation of the pancreas.

J. PRYDE.

Action of insulin on the disappearance of dextrose and oxidations in blood *in vitro*. O. KAUFFMANN-COSLA and J. ROCHE (Bull. Soc. Chim. biol., 1926, 8, 636—654).—Addition of insulin to defibrinated blood increases glycolysis and carbon dioxide production, but the latter is usually less than that which would account for all the dextrose disappearing. The increased carbon dioxide production is not affected by cyanide. Glycolysis and carbon dioxide production decrease in blood kept at 0°, but are restored by the addition of insulin. Insulin added to a suspension of washed corpuscles in dextrose-Ringer solution causes disappearance of sugar, but has no effect on carbon dioxide production.

H. J. CHANNON.

Action of insulin and pituitary extract on constituents of blood. A. GIGON (Biochem. Z., 1926, 174, 257—261).—The injection of insulin into rabbits causes a decrease in the total carbon and nitrogen of the blood and an increase in the water content. With pituitrin, the same changes occur,

but the blood-sugar increases slightly. When insulin and pituitrin are injected simultaneously, the effect is that of insulin alone, except that the effect on the blood-sugar is weakened, but insulin injected 48 hrs. after the injection of pituitrin causes a rise in the total carbon and nitrogen of the blood and a fall in the water content, with very little effect on the blood-sugar. In mild cases of diabetes, in which insulin has a similar action on the blood constituents, disturbance of the pituitary gland may be the primary cause. The action of adrenaline on animals in insulin hypoglycæmia is also reversed by previous treatment with pituitrin. The imbibition of frog's muscle in Ringer's solution is increased 50% by previous treatment of the animal with pituitrin.

E. C. SMITH.

Influence of insulin on liver glycogen. D. BINDI (Arch. ital. Biol., 1924, 74, 141—145; from Chem. Zentr., 1926, I, 2113).—The amount of glycogen in the fluid from a perfused liver is diminished when insulin is present. On perfusing one half of the liver with insulin, the other without, the former always shows a higher glycogen content.

J. PRYDE.

Supposed influence of insulin on sugar formation in the liver. I. L. CHAIKOFF (Trans. Roy. Soc. Canada, 1926, [iii], 20, [V], 27—31).—Repeating part of the work of Brugsch and his co-workers (cf. A., 1924, i, 1017), the author concludes that, contrary to their findings, insulin has no influence on the rate of appearance of dextrose or phosphoric acid in incubated suspensions of liver-tissue.

W. ROBSON.

Influence of glucosamine on insulin hypoglycæmia. Possible change of glucosamine into dextrose in the organism. A. MOSCHINI (Arch. ital. Biol., 1924, 74, 117—125; from Chem. Zentr., 1926, I, 2113).—Hypoglycæmic symptoms in rabbits are not relieved either by subcutaneous or oral administration of glucosamine hydrochloride. The symptoms are less marked and are later in appearing when 8—10 g. of glucosamine are given along with, or previous to, the insulin injection. It is concluded that glucosamine is transformed but slowly into dextrose *in vivo*.

J. PRYDE.

Action of mono- and di-saccharides administered orally on insulin hypoglycæmia. A. MOSCHINI (Arch. ital. Biol., 1924, 74, 126—130; from Chem. Zentr., 1926, I, 2113).—To relieve hypoglycæmic symptoms 10 g. of dextrose, administered *per os*, are necessary, or 5 g. if given simultaneously with the insulin injection. Lævulose must be administered half an hour before the insulin injection. Galactose is practically inactive. Sucrose behaves like dextrose, maltose is intermediate in its action between those of sucrose and lævulose, whilst lactose is inactive.

J. PRYDE.

Effect of glyceraldehyde and dihydroxyacetone on insulin hypoglycæmia. H. G. REEVES and J. A. HEWITT (J. Physiol., 1926, 61, Proc. xxxv).—Dihydroxyacetone proved as efficient as dextrose in allaying the symptoms of insulin hypoglycæmia in mice and rabbits. Glyceraldehyde had no beneficial action.

R. K. CANNAN.

Presence of an insulin complement in the muscles of warm and cold-blooded animals. Carbohydrate metabolism. XIII. C. LUNDSGAARD and S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, 93, 1687—1688; from Chem. Zentr., 1926, I, 2114).—As in the muscles of warm-blooded animals, so in those of cold-blooded animals, a substance is present which, with insulin, converts $\alpha\beta$ -glucose into "neo-glucose." Minced frog muscle is placed in an isotonic solution of $\alpha\beta$ -glucose containing insulin. On subjecting a sample taken after 2 hrs. to dialysis, differences between polarimetric and reduction values are found. Later samples show an increased polarimetric value, rising until the equilibrium value for dextrose is reached. This so-called "insulin complement" has a temperature optimum of 20° for cold-blooded animals and 37° for warm-blooded animals.

J. PRYDE.

Extraction of ovarian hormone and some chemical properties of the product. J. O. RALLS, C. N. JORDAN, and E. A. DOISY (J. Biol. Chem., 1926, 69, 357—380; cf. A., 1924, i, 1387).—Liquor folliculi is treated with alcohol to remove proteins and the filtrate evaporated to dryness in a vacuum; the aqueous solution of the residue is made alkaline to phenolphthalein and extracted with ether; the residue obtained on evaporation of the ether is dissolved in 70% alcohol and the solution repeatedly extracted with light petroleum; evaporation in a vacuum of the aqueous-alcoholic solution then yields a preparation, free from cholesterol, of which 0.03—0.04 mg. is 1 rat unit. The purest preparations so far obtained, by further fractionation with light petroleum, have 1 rat unit per 0.015 mg. Further purification cannot be effected by vacuum distillation, which always involves the loss of at least 50% of the active material. The product having 1 rat unit per 0.04 mg. had C 80.5, H 10.7, N 0.93%; *M* was, however, 418—458, so that the nitrogen may have been due to impurity. The activity of this product was lost on acylation in pyridine and on bromination, but was scarcely affected by hydrogenation, hydrolysis, or treatment with *p*-nitrophenylhydrazine; it is therefore suggested that the hormone may contain a hydroxyl group and a double linking, but no carbonyl group.

C. R. HARRINGTON.

Ovarian hormone. M. HARTMANN and H. ISLER (Biochem. Z., 1926, 175, 46—61).—Using a new method of purification and after preliminary treatment with acetic anhydride, the active substance of the ovaries and placenta may be readily distilled in a high vacuum. The active fraction consists of esters of higher unsaturated acids and is of approximately constant composition. On saponification, it yields an active substance, b. p. 145°/0.02 mm., of average composition, C 81.83, H 11.43%.

P. W. CLUTTERBUCK.

Effect of spaying, pregnancy, and administration of ovarian extracts on the urinary quotient C:N. H. WADA (Biochem. Z., 1926, 174, 400—411).—Spaying had no effect on the urinary quotient of two bitches, apart from an exaggeration of the daily variation. Subcutaneous and oral administration of oophorin had no effect on the spayed

animals, apart from a further increase in the daily variation in one case, but in a normal female rabbit the injection brought about a decrease in carbon and an increase in nitrogen, indicating increased oxidation in intermediate metabolism. No effect was observed on a male rabbit. Pregnancy and parturition had no effect on the quotient.

E. C. SMITH.

Effect of administration of thyroid and pituitary gland preparations on the urinary quotient C:N. H. WADA (Biochem. Z., 1926, 174, 392—399).—The urinary quotient C:N is lowered by feeding with thyroid gland owing to an increase in nitrogen excretion. Pituitary extract has the reverse effect. Considerable changes may occur in the urinary nitrogen without any corresponding effect on the dysoxidisable carbon.

E. C. SMITH.

Active substances of the posterior lobe of the hypophysis present in the cerebrospinal fluid. P. TREDELENBERG (Arch. exp. Path. Pharm., 1926, 114, 255—261).—Whilst an extract of the posterior lobes of the hypophysis has a strong action on the frog's melanophores, solutions of various alkaloidal salts produce no darkening in them; 0.01% solutions of quinine hydrochloride and curarine produced a slight darkening, but 0.001% solutions had no effect. Extracts from lung, liver, kidneys, spleen, heart, brain, suprarenal capsule, guinea-pig muscle, and blood were inactive. The conclusion is reached that the substance of the posterior lobe of the hypophysis which acts on the melanophores is also present in the cerebrospinal fluid.

W. ROBSON.

Distribution of the active substance of the hypophysis in its different parts. H. B. VAN DYKE (Arch. exp. Path. Pharm., 1926, 114, 262—274).—The *pars nervosa* is much richer than the *pars intermedia* in the substance which stimulates the uterus, raises the blood pressure, and acts as an antidiuretic. The stem and particularly the *tuber cinereum* are very poor in the uterus-stimulating substance. On the other hand, the substance responsible for expanding the melanophores is present particularly in the *pars intermedia*. After injecting extracts of *pars intermedia* and of *pars nervosa* into rabbits, the author was unable to detect the changes in fatty-acid content of the liver reported by Coope and Chamberlain (cf. J. Physiol., 1925, 60, 69).

W. ROBSON.

Isolation of secretin. J. MELLANBY (J. Physiol., 1926, 61, Proc. xxxvii).—The method depends on the extraction of the secretin from the mucous membrane by alcohol, its removal from aqueous solution by adsorption to a precipitate of bile acids induced in the solution, and its precipitation from alcoholic solution containing bile acids by means of acetone. Secretin is destroyed by pepsin, trypsin, and by boiling acid or alkali (0.1*N*). It is probably a polypeptide.

R. K. CANNAN.

Vitamin content of human milk. L. F. MEYER and E. NASSAU (Klin. Woch., 1925, 4, 2380—2383; from Chem. Zentr., 1926, I, 2117).—The failure of guinea-pigs to grow on oats and human milk is ascribed, not to vitamin deficiency, but to a deficiency

of protein. Guinea-pig milk and cow's milk contain about three times as much protein as human milk.

J. PRYDE.

Metabolism and vitamin-A. V. E. NELSON and C. M. McCAY (Proc. Iowa Acad. Sci., 1924, 31, 286).—With rats, lack of vitamin-A led to an unusually large percentage of the nitrogen being excreted as urea; uric acid, creatine, and creatinine were unchanged. Albumin is apparently a normal constituent of the urine of the rat.

CHEMICAL ABSTRACTS.

Spectroscopic observations on cod-liver oil.
II. Absorption bands of cholesterol. F. W. SCHLUTZ and M. R. ZIEGLER (J. Biol. Chem., 1926, 69, 415—419).—The spectrum of cholesterol (+1H₂O) shows two absorption bands; that of anhydrous cholesterol shows greater general absorption, but no bands; irradiation of an ethereal solution of cholesterol with ultra-violet light increases the general absorption to a greater extent in the case of hydrated than in that of anhydrous cholesterol.

C. R. HARRINGTON.

Vitamins. XIV. Influence of ultra-violet light on purified rations used in study of vitamin-A. R. A. DUTCHER and J. H. KRUGER (J. Biol. Chem., 1926, 69, 277—282).—A basal diet of caseinogen, agar, dextrin, and salts, such as is customarily employed in investigations of vitamin-A, has no antirachitic properties; after irradiation with ultra-violet light such a diet becomes antirachitic, owing, exclusively, to the activation of the dextrin; the degree of activation of the dextrin is, however, slight in comparison with that induced in maize oil or olive oil by similar treatment.

C. R. HARRINGTON.

Photo-activation of vitamin-A, cholesterol, fats, and other substances by ultra-violet rays. S. HAMANO (Proc. Imp. Acad. Japan, 1926, 2, 53—55, 56—57).—See this vol., 98, 546.

Water-soluble growth-promoting and antineuritic substances. S. M. HAUGE and C. W. CARRICK (J. Biol. Chem., 1926, 69, 403—413).—Addition of yeast to a basal diet, lacking water-soluble vitamins, permitted normal growth in chickens, but did not protect against polyneuritis, whereas addition of maize protected against polyneuritis, but did not yield good growth. It is therefore concluded that, in addition to the water-soluble antineuritic substance (vitamin-B), there exists a separate water-soluble growth-promoting vitamin.

C. R. HARRINGTON.

Preservation of vitamin-C in dried orange juice. G. J. HUMPHREY (J. Biol. Chem., 1926, 69, 511—512).—Orange juice, treated with 25% of sugar and dried in a vacuum, retained its antiscorbutic potency when kept for 5 years under reduced pressure.

C. R. HARRINGTON.

Chemical nature of the cell membrane. F. M. WOOD (Ann. Bot., 1926, 40, 547—570).—The liberation of iodine from potassium iodide after treatment of sections with chlorine followed by sodium hydrogen phosphate solution has been used for the detection of protein in cell-wall. Not more than 0.001% of protein

occurs in the cellulose cell-wall of any of the plants examined; tests for oxycellulose before and after chlorination were made. The tests have been applied to the leaves, petioles, aerial and underground stems and roots of a number of plants.

H. J. CHANNON.

Kinetics of carbon dioxide assimilation. J. HOLLUTA.—See this vol., 1011.

Reciprocal relationship between carbohydrates in foliage leaves and water content. W. AHRNS (Bot. Arch., 1924, 5, 234—259).—Only sucrose and hexoses take part in the production of sugar through starch hydrolysis in the wilting leaf. In the presence of starch, the sucrose content rises (independently of light) with falling, and falls with rising, water content. The hexose content rises in starch-containing leaves kept in the dark; the maltose content decreases during darkness. In *Tropaeolum* and *Helianthus*, the hexoses alone are transported.

CHEMICAL ABSTRACTS.

Chemical constituents of fruit spurs associated with blossom bud formation in the apple. H. R. KRAYBILL, G. F. POTTER, S. W. WENTWORTH, P. T. BLOOD, and J. T. SULLIVAN (New Hampshire Agric. Exp. Sta., Tech. Bull., 1925, 29, 1—40).—At various dates during the growing season, the carbohydrate, nitrogen, phosphorus, ash, and dry matter content of bearing and non-bearing spurs of Baldwin apple trees, growing in sod or in a highly nitrogen-fertilised plot, were determined. Significant differences were observed.

CHEMICAL ABSTRACTS.

Normal variation in the chemical composition of fruit spurs and the relation of composition to fruit-bud formation. C. P. HARLEY (Proc. Amer. Soc. Hort. Sci., 1925, 134—146).—The trustworthiness of results may largely depend on the uniformity of spurs selected for analysis. Indication is afforded of the importance of sugar and starch in relation to fruit-bud formation. A high percentage of nitrogen, especially of soluble nitrogen, is present in new growths of bearing spurs immediately following fruit setting.

CHEMICAL ABSTRACTS.

Ripening of tomatoes. J. T. ROSA (Proc. Amer. Soc. Hort. Sci., 1925, 315—322).—The hydrogen-ion concentration and total acidity are maximal at the turning stage and minimal in the ripe fruit. Sugars (chiefly dextrose) and nitrogen increase from the green-mature to the ripe condition; starch practically disappears in the earliest stages of ripening. The proportions of total soluble nitrogen and soluble solids increase, the insoluble solids decreasing. Ethylene acts as a stimulus to normal oxidative processes in the fruit.

CHEMICAL ABSTRACTS.

Influence of fertilising ingredients on the hydrogen-ion concentration of the juice of the rice plant. K. MIYAKE and M. ADACHI (J. Biochem. [Japan], 1925, 5, 321—326).—Nitrogen lowers the hydrogen-ion concentration of the juice of the rice plant, the effect being greater when applied in conjunction with phosphate and potassium. Phosphate increases the hydrogen-ion concentration, the effect being weakened by potassium or nitrogen. In the first period of plant growth, potassium decreases,

and in the second period increases, the hydrogen-ion concentration of the juice. The rise in the p_H value caused by lime is not influenced by the amount used, or by the application of phosphate, nitrogen, or potassium.

CHEMICAL ABSTRACTS.

Effect of soil reaction on germination of meadow grasses and clovers. L. MÜLLER (Fortschr. Landw., 1926, 1, 52—57; Chem. Zentr., 1926, I., 1698).—Meadow grasses and clovers prefer a slightly acid reaction for germination. Grasses tolerate an alkaline reaction better than clovers. The anions present, as well as the hydrogen-ion concentration of the soil solution, have an influence on germination.

C. T. GIMINGHAM.

Influence of potassium chlorate on germination of rye, wheat, barley, and oats. A. STROBEL and K. SCHARRER (Fortschr. Landw., 1926, 1, 62—63; Chem. Zentr., 1926, I, 1697—1698).—In small amounts, potassium chlorate does not injure germination of winter rye and wheat; higher doses produce a morbid light green colour in the seedlings. Barley is most sensitive; oats were not injured by the highest doses used.

C. T. GIMINGHAM.

Toxicity and antagonism in salt solutions as indicated by growth of wheat roots. S. F. TRELEASE and H. M. TRELEASE (Bull. Torrey Bot. Club, 1926, 53, 136—156).—A study of the rates of elongation of wheat roots in 0.0006—0.36*M*-potassium, calcium, or magnesium nitrate solutions, and in 0.06*M*-solutions of pairs of these salts in varied proportions. No stimulation was observed; magnesium was more toxic than potassium or calcium. Antagonistic effects were marked with potassium and calcium, less marked with calcium and magnesium, and only slight with potassium and magnesium.

CHEMICAL ABSTRACTS.

Action of sodium carbonate on germination and growth in plants. II. D. FEHÉR and S. VÁGI (Biochem. Z., 1926, 175, 172—174).—With increasing amounts of carbonate, the growth of plants is considerably inhibited, more especially in regard to the root development (cf. A., 1925, i, 1023).

P. W. CLUTTERBUCK.

Action of nitrites on the growth of plants. D. FEHÉR and S. VÁGI (Biochem. Z., 1926, 174, 262—270).—The lethal concentration of nitrites in the soil varies from 0.09 to 0.10% of N_2O_3 , whereas the concentration in the Hungarian alkaline soils is only 0.000027—0.000114%, which has no action on the growth of the plant. The lethal concentration for cultures in water is much higher, 0.125—0.372% of N_2O_3 . The percentage absorption of nitrites diminishes with the concentration. When the nitrites are present in sufficient concentration to cause injury, the effect is most apparent on the root.

E. C. SMITH.

Nitrogen and dry matter content of sweet clover tops and roots at various stages of growth. H. J. SNIDER and M. A. HEIN (J. Amer. Soc. Agron., 1926, 18, 273—280).—In the autumn and winter, the roots, and in the spring and summer the tops, contained the highest percentage of nitrogen.

CHEMICAL ABSTRACTS.

Latex. A. J. ULTEE (Pharm. Tijdschr. Nederl.-Indie, 1925, 2, 515—528; from Chem. Zentr., 1926, I, 2110).—The dry alcohol coagulum from the latex of *Ficus elastica* yielded 96.2% of caoutchouc; latex from *Castilleja elastica* yielded 84.9%; from *F. Vogelii* 72.9%; from *F. glomerata* 16.6%; from *F. procera* 12.1%; from *F. fulva* 1.1%; from *F. alba* a trace; from *Atrocarpus elastica* and *Broussonetia papyrifera* nil. Latex is classified in groups according to its richness in : (1) caoutchouc, (2) phytosterols (containing principally lupeol and α - and β -amyrol), (3) protein, (4) tannins, e.g., latex of *Jatropha curcas*, (5) salts, e.g., latex of *Plumiera acutifolia* yielded a coagulum containing 46.42% of salts, chiefly calcium plumierate, and 44.6% of sterols, (6) alkaloids.

J. PRYDE.

Oxidation and reducing properties of hermidin, the chromogen of *Mercurialis*. P. HAAS and T. G. HILL (Ann. Bot., 1926, 40, 709; cf. this vol., 99).—Chrysohermidin can be reduced to cyanohermidin by hermidin and by sodium hyposulphite only in freshly-prepared solutions.

H. J. CHANNON.

Lævulosans of the Gramineæ; graminin and tricitin. H. COLIN and A. DE CUGNAC (Bull. Soc. Chim. biol., 1926, 8, 621—630).—Preparations of graminin from *Arrhenatherum bulbosum*, Presl., and of tricitin from *Triticum repens*, L., have been made. Graminin has m. p. 199°, $[\alpha]_D -44^\circ$, $[\alpha]_{H_2O}^{green} -54^\circ$; tricitin m. p. 198°, $[\alpha]_D -47^\circ$, $[\alpha]_{H_2O}^{green} -57^\circ$; after inversion both substances have $[\alpha]_D^{15} -93^\circ$. Triticin is more soluble in water at 15° and in alcohol at 60° than is graminin. These substances are not precipitated from neutral or acid solutions by salts of heavy metals; they yield insoluble compounds with barium hydroxide, whilst the corresponding compounds with the hydroxides of calcium and strontium are soluble. They have no reducing action and on hydrolysis yield lævulose only. The plants from which they are prepared contain enzymes which hydrolyse them. Graminin is readily hydrolysed by top yeast and tricitin less readily.

H. J. CHANNON.

Proteins of the Adzuki bean (*Adzukia subtrilobata*). E. TAKAHASHI and T. ITAGAKI (J. Biochem. [Japan], 1925, 5, 311—319).—The bean contains about 25.7% of protein, of which 15% is albumin and globulin. Two globulins (β_1 and β_2), resembling the β -globulin of *Phaseolus angularis*, were isolated, the respective contents of lysine being 10.2 and 5.8%, and of amino-nitrogen, 55.2 and 61.2%. The arginine and histidine content is lower in β_2 than in β_1 ; the former is the principal protein in the Adzuki bean.

CHEMICAL ABSTRACTS.

Differences in the physico-chemical properties of the protein, oryzanin, as found in glutinous and in common rice. T. TADOKORO, Y. NAKAMURA, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1925, 14, 129—169).—The differences in the starches of glutinous and common rices are attributed on biochemical grounds to differences in the chief protein of rice, oryzanin. Preparations of oryzanin from the two varieties show that the protein from common rice, which is less soluble in alkali and has a higher acid-binding capacity, con-

tains a higher proportion of nitrogen and of ash; it contains relatively fewer carboxyl groups, and more free amino-, ammonia-, arginine-, and lysine-nitrogen, but less monoamino-, histidine-, and cystine-nitrogen. The acetyl derivative of common rice oryzanin contains more nitrogen, and its hydrolysis produces the more basic substances. The amount of tyrosine and tryptophan is the same in both proteins. Pancreatin decomposes glutinous rice oryzanin more rapidly than the compound from common rice, indicating a higher molecular complexity for the latter. The rotatory power of the alkali solution of common rice protein is the higher. Exposure of the alkali solutions of the oryzanins to ultra-violet light increases the free amino-nitrogen, the velocity of increase being greater for the compound from glutinous rice.

CHEMICAL ABSTRACTS.

Electrodialysis in biochemistry. C. DHÉRE (Bull. Soc. Chim. biol., 1926, 8, 604—610).—Extension of the review already published (cf. this vol., 762).

H. J. CHANNON.

Open gas analytical method for metabolic measurements. L. CAPPELLEN and A. K. NOYONS (Compt. rend. Soc. Biol., 1925, 93, 1530—1533; from Chem. Zentr., 1926, I, 1864).—An apparatus designed to avoid working in closed systems is described.

J. S. CARTER.

Apparatus for graphical registration of oxygen-consumption and carbon dioxide production. H. DETHLOFF (Klin. Woch., 1925, 4, 2440—2441; from Chem. Zentr., 1926, I, 2223).—An apparatus is described which allows the oxygen consumed and the carbon dioxide produced by a person under examination to be recorded graphically in a continuous manner. Air is circulated through the system; the oxygen consumed is given by the total diminution in volume of the system as recorded by a spirometer; the carbon dioxide formed is given by the difference between the readings of meters, placed one on each side of an absorption apparatus containing soda-lime.

J. S. CARTER.

Portable calorimeter for determination of oxygen and carbon dioxide. J. F. McCLENDON, G. J. HUMPHREY, and M. M. LOUCKS (J. Biol. Chem., 1926, 69, 513—517).—In a closed circuit respiration apparatus the expired air is passed through a chamber containing a known amount of barium hydroxide solution in rapid agitation and containing phenolphthalein. As soon as the latter is decolorised, the total volume of gas in the apparatus is measured; the difference between this and the initial volume gives the oxygen utilised, whilst the carbon dioxide produced can be calculated from the amount of barium hydroxide neutralised, a correction being applied for incomplete absorption.

C. R. HARRINGTON.

Determination of p_H of blood. New hydrogen electrode. G. ETIENNE, M. VERAÏN, and M. BOURGEAUD (Compt. rend. Soc. Biol., 1925, 93, 765—766; from Chem. Zentr., 1926, I, 1866—1867).—A modified Michaelis electrode is described.

J. S. CARTER.

Modification of Widmark's microchemical method for the determination of blood-alcohol. M. AOKI (J. Biochem. [Japan], 1925, 5, 327—331).—A weighed quantity of blood is distilled at 100° in a

Gréhaut micro-distillation apparatus, the receiver containing a solution of potassium dichromate and sulphuric acid. The contents are finally heated for 1—2 min. on the water-bath, washings from the apparatus being added, and the unreduced dichromate is titrated using thiosulphate. The average alcohol content of rabbit's blood is 0.0025%.

CHEMICAL ABSTRACTS.

Determination of sugar in blood. A. D. STAMMERS (S. Afric. Med. Record, 1925, 23, 426—427).—The blood-proteins are precipitated by heating with sodium hydrogen sulphate and treatment with "dialysed iron," an aliquot part of the filtrate being then boiled for 2.5 min. with 1 c.c. of 0.0075% methylene-blue in alkaline solution. Quantities of sugar between 0.075 and 0.3% are determined by means of a graph if the time taken for the blue colour to disappear is observed.

CHEMICAL ABSTRACTS.

Micro-determination of blood-sugar. S. L. WRIGHT, jun. (Bull. Ayer Clin. Lab. Pennsylvania Hosp., 1925, 9, 65).—A modification of the Folin-Wu method.

CHEMICAL ABSTRACTS.

Effect of potassium oxalate on blood-sugar determinations. H. J. JOHN (J. Lab. Clin. Med., 1925, 10, 1000—1004).—When 10 c.c. or less of blood are used, 15 mg. of potassium oxalate are sufficient to prevent clotting; low values are obtained if more than 30 mg. are employed.

CHEMICAL ABSTRACTS.

Determination of hydrogen carbonate in small amounts of serum. J. P. BOUCKAERT (Compt. rend. Soc. Biol., 1925, 93, 841—843; from Chem. Zentr., 1926, I, 1867).—0.5—1.0 C.c. of serum is dialysed, the dialysate decomposed with 0.01N-hydrochloric acid, and titrated back, using 0.01N-barium hydroxide, to p_H 7.4.

J. S. CARTER.

Mendel-Goldscheider method for the determination of lactic acid in blood. M. VAS and A. LÁNG (Biochem. Z., 1926, 172, 428—431).—The Mendel-Goldscheider method (this vol., 212) is adaptable to clinical requirements, being rapid and requiring not more than 1 c.c. of blood. The accuracy is within 5—10%.

C. RIMINGTON.

Micro-determination of the blood urea. A. BORVIN (Bull. Soc. Chim. biol., 1926, 8, 456—461).—After removal of protein, urea is precipitated by xanthhydrol and the nitrogen content of the precipitate is determined by the micro-Kjeldahl method. The results are claimed to be more exact than the higher values obtained by the urease or hypobromite methods.

C. P. STEWART.

Contributing cause of turbidity of nesslerised solutions in the determination of urea in the whole blood. F. B. COOPER (J. Lab. Clin. Med., 1925, 10, 1012).—A mixture of 1 c.c. of toluene and 0.02 c.c. of octyl alcohol, which prevents foaming for 45 min. and gives clear solutions for 1 hr., is used in the aëration tubes in the Gradwohl-Blaivas method.

CHEMICAL ABSTRACTS.

Micro-determination of phosphorus in blood. M. MACHEBOEUF (Bull. Soc. Chim. biol., 1926, 8, 464—468).—The blood (1 c.c.) is ashed with a mixture of sulphuric and nitric acids, and the phosphorus precipitated as phosphomolybdate. The precipitate is

separated by means of a Pregl micro-filter, washed, and dissolved in ammonia. Standard sodium hydroxide is added, the ammonia boiled off, excess of standard acid added, carbon dioxide boiled off, and the excess acid titrated with sodium hydroxide.

C. P. STEWART.

Determination of calcium, magnesium, phosphate, and carbonate in bone. B. KRAMER and J. HOWLAND (J. Biol. Chem., 1926, 68, 711—719).—The bone is dried and pulverised; in the resulting powder the carbonate is determined gasometrically by shaking with hydrochloric acid; the remaining acid solution is made up to known volume and aliquot portions are used for determinations of calcium, magnesium, and phosphorus by standard methods.

C. R. HARINGTON.

Nephelometric determination of phosphoric acid. H. KLEINMANN (Biochem. Z., 1926, 174, 43—52).—A modification of the author's original method (*ibid.*, 1919, 99, 134) capable of the determination of 0.001 mg. of phosphoric acid (as P_2O_5) with an error of $\pm 2\%$.

E. C. SMITH.

Detection of traces of fluorine in organic material. H. LÜHRIG (Pharm. Zentr., 1926, 67, 465—474).—0.2 Mg. of fluorine may be detected in solid organic material by mixing with milk of lime, drying the mixture, igniting at a fairly low temperature, carefully adding sulphuric acid, and observing the etching of a cooled glass surface by the hydrogen fluoride liberated. Fluorides may first be precipitated by lanthanum acetate. No fluorine could be detected in 100 c.c. of cow's milk or in hen's eggs, but a trace was found in 25 g. of milk powder. Normal urine and human liver did not contain fluorine except after administration of fluosilicates etc. No fluorine could be detected in the urine 4 days after oral administration of fluosilicates.

L. F. HEWITT.

Biochemistry of strontium. Determination of strontium in the presence of calcium. O. ARND and E. A. HAFNER (Biochem. Z., 1926, 174, 182—187).—The determination of strontium in the presence of calcium is most accurately carried out by precipitation and weighing together as oxalate, followed by titration of the oxalate (cf. Hodel, A., 1925, i, 1496). The titration of strontium oxalate in quantities greater than 0.1 mg. is accurate to 3.3%. The determination in serum can be carried out without ashing, and is accurate to 5%.

E. C. SMITH.

Micro-determination of potassium in pure solutions and in biological media. M. DELAVILLE and P. CARLIER (Bull. Soc. Chim. biol., 1926, 8, 481—488).—See this vol., 491. The application of the process to small volumes of serum, plasma, etc. is described.

Sampling and analysis of stomach gas. A. D. DUNN and F. L. DUNN (J. Lab. Clin. Med., 1925, 10, 769—776).—An apparatus is described. In air of known composition, introduced into the stomach

of a normal individual, the carbon dioxide and oxygen tend to reach equilibrium at relatively constant values.

CHEMICAL ABSTRACTS.

Determination of free hydrochloric acid in gastric contents. E. HALLANDER (J. Lab. Clin. Med., 1925, 10, 935—937).—Paper impregnated with dimethylaminoazobenzene (0.25% alcoholic solution) is treated with solutions containing, respectively, 10, 20, 30, 40, or 50 c.c. of 0.1N-hydrochloric acid per 100 c.c. of water, and with the gastric contents, the resulting colours being compared.

CHEMICAL ABSTRACTS.

Comparison of electrometric and colorimetric methods for determination of p_H of gastric contents. G. KAHN and J. STOKES, JUN. (J. Biol. Chem., 1926, 69, 75—84).—Good agreement between the results of electrometric and direct colorimetric determinations of the p_H of gastric content is obtained only at reactions more acid than p_H 2.1; on the alkaline side of this point, moderate agreement between the two methods can be obtained if the fluid be dialysed against physiological salt solution and the colorimetric method applied to the dialysate.

C. R. HARINGTON.

Metabolism of sulphur. X. Determination of cystine in urine. H. B. LEWIS and R. H. WILSON (J. Biol. Chem., 1926, 69, 125—131).—It has been shown that, when the concentration of cystine is low, the precipitation methods of Gaskell (A., 1908, ii, 75) and of Magnus Levy (A., 1925, i, 610) may involve losses of as much as 50% of the cystine present, although, owing to precipitation of impurities, the actual weight of the precipitate may be as great as, or greater than, that of the cystine; it is therefore concluded that the best available method for the determination of cystine in urine is the direct colorimetric method of Looney (A., 1923, ii, 195).

C. R. HARINGTON.

Solubility of some picrates and determination of guanidines in urine. I. GREENWALD (Biochem. J., 1926, 20, 665—667).—Sharpe's method (A., 1925, i, 722) for the detection and determination of guanidines in urine is criticised mainly on the basis that other picrates, such as creatinine picrate, might separate with guanidine picrate and especially with the picrates of methyl- and dimethyl-guanidine. There is also a possibility of ammonium salts dissolving in the alcoholic extract of the treated urine.

S. S. ZILVA.

Determination of total nitrogen in plants and plant solutions. E. R. RANKER (Ann. Mo. Bot. Garden, 1926, 12, 367—380).—Since 75% of the total nitrogen may fail to be recovered by means of the "salicylic-thiosulphate" method, a modification is proposed which is accurate for the determination of amino-, amido-, ammonia-, nitrate-nitrogen and of total plant nitrogen in the presence of nitrate-nitrogen. In the presence of water, methods dependent on the reduction of nitrates in an acid medium are inaccurate; much sugar causes a slight loss of nitrate-nitrogen.

CHEMICAL ABSTRACTS.