BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1933.

General, Physical, and Inorganic Chemistry.

Intensities of the spectra emitted by high-frequency discharges in helium. J. E. Keyston (Phil. Mag., 1933, [vii], 16, 625—639; cf. A., 1932, 1071).—Measurements on the line, band, and continuous spectra of He have been verified and extended spectrophotometrically. H. J. E.

Excitation probabilities of helium, argon, and neon at zero scattering angle. J. E. Taylor and R. Whiddington (Proc. Leeds Phil. Soc., 1933, 2, 417—419).—The probability curve for A is linear, but rises more steeply than the He curve; the smooth curve is in accord with the singlet transitions 3^1S-4^1P and $3^1S-4^1P_2$. In Ne the transitions likely to be involved are $2^1S-3^1P_1$ and $2^1S-3^3P_2$, the triplet transition giving rise to a hump in the curve at about 150 volts. Experimental data are compared with vals. computed from the theory of Massey and Mohr (this vol., 761). W. R. A.

Excited electronic states of Li_2. W. F. Furry (Physical Rev., 1932, [ii], 39, 1015—1017; cf. A., 1932, 319). L. S. T.

Zeeman effect of the third positive carbon bands. R. F. Schmid (Physical Rev., 1932, [ii], 39, 538—539). L. S. T.

Absorption lines of N v in stellar spectra. C. H. Payne (Astrophys. J., 1933, 77, 299).—These lines have been observed in several Wolf–Rayet stars. L. S. T.

Modification of the intensity in the band spectrum of nitrogen. J. Okubo and H. Hamada (Astrophys. J., 1933, 77, 130—140).—Modifications by changes of pressure, temp., and shape of the discharge tube are discussed. L. S. T.

Equivalent widths in the *A* and *B* bands of oxygen. W. H. J. Childs (Astrophys. J., 1933, 77, 212—220). L. S. T.

Series of alkaline atoms in an electric field. E. Amaldi and E. Segrè (Nature, 1933, 132, 444—445).—Details of the absorption spectra (I) of Na and K in an electric field are recorded. (I) polarised parallel and perpendicular to the field have been photographed simultaneously and separated by means of a spar crystal. L. S. T.

Width of the *D* lines in sodium vapour. S. A. Korff (Physical Rev., 1932, [ii], 39, 549—560). L. S. T.

Hyperfine structure and nuclear moment of krypton. H. Kopfermann and N. Wieth-Knudsen (Z. Physik, 1933, 85, 353—359).—The mechanical moment of Kr^{83} is 7/2. A. B. D. C.

Ratio of oscillator intensities for resonance lines of silver. A. Filippov and I. Islamov (Z. Physik, 1933, 85, 409—410).—The ratio of *f* for the doublet components is 2·03. A. B. D. C.

Band spectrum of ionised cadmium hydride. E. Svensson and F. Tyrén (Z. Physik, 1933, 85, 257—263).—Dissociation energy of the normal state of Cd^+H is 2·0 volts. A. B. D. C.

Heat of dissociation of the cadmium molecule from thermo-optical observations. A. Jabłoński (Z. Physik, 1933, 85, 268).—A disclaimer of a reference given by Kuhn and Arrhenius (this vol., 759). A. B. D. C.

Hyperfine structure in the spark spectrum of cadmium. E. G. Jones (Proc. Physical Soc., 1933, 45, 625—626).—The Cd II spectrum has been investigated in the region 4200—8500 Å., three new lines being observed and classified. Of the 13 lines examined only that at 8067 Å. ($6^2S_{1/2}-6^2P_{3/2}$) shows any fine structure. It is calc. that the $g(I)$ factor of the odd isotopes is $-1·25$ proton magnetons. J. W. S.

Nuclear spin and magnetic moment of tin. S. Tolansky (Nature, 1933, 132, 318).—Structures have been obtained in several lines of the spectrum of Sn II. The nuclear spin is ½. The $g(I)$ factor, calc. by Goudsmit's formula, is $-1·81$. L. S. T.

Fluorescence of diatomic molecules of antimony. J. Genard (Physical Rev., 1933, [ii], 44, 468—469).—Data for the four resonance series of Sb excited by the λλ 2967, 3022, 3126, and 3132 Hg arc lines are given, and lead to the val. 2·21 Å. for the equilibrium interat. separation, and 489×10^{-40} g.-cm.^{2} for the moment of inertia. N. M. B.

Extinction of fluorescence of tellurium vapour by magnetic fields. R. Smoluchowski (Z. Physik, 1933, 85, 191—200; cf. this vol., 759).—The extinction observed does not agree with a diminution of the no. of excited mols., and is explained with the Condon–Lenz theory of intensities. A. B. D. C.

Enhancement of the iodine absorption spectrum by the admixture of oxygen. F. W. Loomis and H. Q. Fuller (Physical Rev., 1932, [ii], 39, 180).—O_2 markedly enhances many of the I absorption bands, and in certain circumstances the I changes colour. L. S. T.

Spectra of halogen molecules. I. Iodine. W. E. Curtis and S. F. Evans (Proc. Roy. Soc., 1933, A, 141, 603—625).—The chief problem in the absorption spectrum of I_2 is the nature of the excited states connected with the various systems. Consideration of the potential energy curve for the upper level of Sponer and Watson's ultra-violet system leads to the conclusion that the dissociation products are not excited atoms, but probably ions. Some possible regularities are proposed in the far ultraviolet absorption bands, and new data derived from microphotometer records of the diffuse emission bands are presented. The fluorescence system of diffuse bands due to ultra-violet excitation is considered, and Kuhn's conclusions (A., 1930, 1089) are modified. It is shown that a secondary transition must intervene between those of excitation and fluorescence. L. L. B.

Nuclear moment of xenon. H. Kopfermann (Naturwiss., 1933, 21, 704).—The hyperfine structure of a series of Ne lines shows that the mechanical moment of Xe^{129} is 1/2, and of Xe^{131} 3/2. The even isotopes do not give appreciable splitting. The ratio of the magnetic moment (μ) of Xe^{129} to that of Xe^{131} is 1·1; μ_{129} is negative, and μ_{131} positive. A. J. M.

Pressure effects in the spectra Xe I and Xe II. J. F. Heard (Proc. Physical Soc., 1933, 45, 734—740).—At high pressures the lines of the Xe I spectrum show broadenings which correspond qualitatively with their respective Stark effects, indicating the existence of strong interionic electric fields within the discharge. Many pressure displacements are also found in the Xe II spectrum, and are attributed to interionic fields. J. W. S.

Displacement and asymmetric widening of absorption lines by foreign gases. C. Füchtbauer and F. Gössler (Naturwiss., 1933, 21, 675—676).—The changes occurring in the Cs absorption lines (4555 and 3786 Å.) by admixture with pure He, Ne, A, and N_2 at 4—5·5 atm., and at 125° (for 4555 Å.) and 180° (for 3786 Å.) were investigated. A. J. M.

Under-water spark spectrum of cerium. J. S. Badami (Indian J. Physics, 1933, 17, 19—24).—Wave-lengths and intensities of 128 lines in the region λ 3900—4580, identified with those of the arc spectrum, are tabulated. N. M. B.

Arc spectrum of cerium. P. Karlson (Z. Physik, 1933, 85, 482—503).—Some 3000 lines and 105 energy levels are tabulated. A. B. D. C.

Temperature classification of the spectrum of neodymium. A. S. King (Astrophys. J., 1933, 78, 9—45).—2863 Nd lines in the range 2963—7005 Å. are classified on the basis of their relative intensities at three temp. stages of the electric furnace. A comparison of lines apparently common to both Nd and Sm, which might belong to element 61, indicated only chance coincidences of true Nd and Sm lines. L. S. T.

Preliminary list of terms for the arc spectrum of tantalum. C. C. Kiess and H. K. Kiess (Bur. Stand. J. Res., 1933, 11, 277—278).—Terms for Ta I are tabulated. H. J. E.

Radiation of metal surfaces bombarded by positive alkali ions. H. Mayer (Phil. Mag., 1933, [vii], 16, 594—606).—Pt, Cu, and Al bombarded with alkali ions gave a surface luminosity, showing line spectra of the alkali atoms. H. J. E.

Weak lines in the *L*-spectra of 79 Au and 74 W. H. Claësson (Z. Physik, 1933, 85, 231—239). A. B. D. C.

Effect of heat on mercury bands. J. G. Winans (Physical Rev., 1932, [ii], 39, 745—746).—Heating destroys the 4850 band and reduces the intensities of the bands at 2345, 2476, and 2540 Å. and the continuous spectrum between 2536 and 3300 Å. Moderate heating enhances, whilst strong heating destroys, the 3300 band. Only four arc lines are weakened. The weakening of the bands must be due to the destruction of Hg mols. by heat. L. S. T.

Inversion of circular polarisation by thallium fluorescence. W. Hanle (Z. Physik, 1933, 85, 300—303).—Excitation of the λ 5350 Tl line by circularly polarised λ 3776 Tl light gives fluorescence radiation circularly polarised, but in the opposite direction. A. B. D. C.

Absorption spectrum of diatomic bismuth. G. M. Almy and F. M. Sparks (Physical Rev., 1933, [ii], 44, 365—375).—Data and analyses for four systems of bands are given: the visible system, 4500—7900 Å., consisting of > 300 bands; the ultra-violet, 2600—2900 Å., system of forty bands; the far ultra-violet system, below 2250 Å., and the violet system, appearing only above 1000°, consisting of fifteen sharp band heads, nine continuous bands, and a series of closely-spaced diffuse bands. There is also an extended continuum around 3100 Å. Potential energy curves for the mol. states are given. The estimated heat of dissociation of the lowest state is 1·71 volts. N. M. B.

Classification of certain lines of radium. W. Albertson (Physical Rev., 1932, [ii], 39, 385—386). L. S. T.

Remarkable optical properties of the alkali metals. R. W. Wood (Physical Rev., 1933, [ii], 44, 353—360).—Thin films of alkali metals opaque to visible light are highly transparent in the ultraviolet, the commencement of transparency moving towards shorter wave-lengths with decreasing at. no.: Cs 4400; Rb 3600; K 3150; Na 2100; Li 2050 Å. Transparency continues at least as far as 1860 Å., where plane polarisation by reflexion is observed. Reflecting powers of these metals for different wave-lengths have been measured. The refractive index of a K film varies from 0·90 at 2147 to 0·50 at 3100 Å. Total reflexion takes place, the crit. angle not being sharply defined. N. M. B.

Influence of a magnetic field on a glow discharge. T. Takamine, T. Suga, and A. Yanagihara (Nature, 1933, 132, 351—352).—With a He tube, a bright pink-coloured ring (II) suddenly appears around the anode spot (I) when a magnetic field is applied (cf. this vol., 547). (I) gives mainly the at. line spectrum of He, and (II) is rich in the mol. band spectrum. L. S. T.

Hydrocarbon bands in the solar spectrum. R. S. Richardson (Astrophys. J., 1933, 77, 195—211). L. S. T.

Hyperfine structure in intermediate coupling. G. Breit and L. A. Wills (Physical Rev., 1933, [ii], 44, 470—490).—Mathematical. N. M. B.

Absolute value of transition probabilities in band spectra. R. Ladenburg, S. Levy, and G. Wolfsohn (Physical Rev., 1932, [ii], 39, 180). L. S. T.

Optical properties of the alkali metals. R. de L. Kronig (Nature, 1933, 132, 601).—A discussion. Recent experimental results (this vol., 547, 1096) can be explained by the author's quantum theory of metallic dispersion (A., 1931, 1209). L. S. T.

Electromagnetic fields due to variable electric charges and the intensities of spectrum lines according to the quantum theory. V. Fock (Proc. Roy. Soc., 1933, **A**, 141, 550—553).—Polemical against Schott (this vol., 206). The usual methods of calculating the intensities of spectral lines are shown to be correct. L. L. B.

Fine structure in the *K* *X*-ray absorption spectrum of bromine. S. T. Stephenson (Physical Rev., 1933, [ii], 44, 349—352).—An extended Kronig type fine structure, more pronounced for partly polarised than for unpolarised *X*-rays, was found. N. M. B.

Extreme ultra-violet and the very soft *X*-ray region. M. Siegbahn (Proc. Physical Soc., 1933, 45, 689—698).—Using plane and concave ruled gratings at grazing incidence, the Hg arc and Al and Cu spark spectra have been photographed down to 50 Å. The C $K\alpha^{II}$ line has also been investigated and shown to have an extended structure, whilst a no. of new lines have been found in the *X*-ray series. Preliminary experiments on absorption spectra in the *X*-ray region are also reported. J. W. S.

Soft *X*-ray critical potentials of beryllium. R. J. Christensen (Physical Rev., 1932, [ii], 39, 549).—Soft *X*-ray crit. potentials up to 250 volts are recorded for fresh Be surfaces. L. S. T.

Peripheral *X*-ray levels of the heavy elements. J. A. Eldridge (Physical Rev., 1932, [ii], 39, 177). L. S. T.

***N*- and *O*-series [of tungsten] and *N*-absorption edge of *X*-spectra.** V. Dolejšek (Nature, 1933, 132, 443—444). L. S. T.

Ionisation of light gases by *X*-rays. I. Technique. II. Ionisation of hydrogen by recoil electrons. W. R. Harper (Proc. Roy. Soc., 1933, **A**, 141, 669—686, 686—696).—I. A technique is described for determining the ratio of the ionisation in a light gas (H_2 or He) to that in air when ionised by the same *X*-ray beam, homogeneous rays of medium wave-length and soft heterogeneous rays being available for the measurement. The method measures (*a*) the ionisation due to the secondary electrons ejected by the primary beam from the gas, and (*b*) that due to reabsorption by the gas of the fluorescence radiation excited by the primary beam in the gas.

II. The ionisation in H_2 produced by recoil electrons liberated by homogeneous *X*-rays is determined by means of the above technique. The experimental val. agrees with that calc. using Dirac's theory of recoil scattering as a basis. L. L. B.

Ionisation of mercury vapour by positive ions of mercury and potassium. R. M. Chaudhri (Proc. Roy. Soc., 1933, **A**, 141, 386—397).—A method, free from the defects existing in previous methods, is described for the investigation of the ionisation of Hg vapour by Hg^+ and K^+ ions of moderate energies. The Hg^+ ions ionise with greater efficiency than K^+ ions of the same energy. L. L. B.

Evidence on the ionisation potentials of O_2. E. W. Pike (Physical Rev., 1932, [ii], 39, 534—535).—The transformation of an oxide surface by means of an intermittent discharge in one of the rare gases may afford evidence in support of Mulliken's val. of 11·7 volts for the ionisation potential of O_2. L. S. T.

Visual observation of interference of slow cathode rays. W. Ehrenberg (Naturwiss., 1933, 21, 673—674). A. J. M.

Polarisation of electrons by reflexion. T. Förster (Z. Physik, 1933, 85, 514—529).—Polarisation cannot be obtained by means of a plane potential barrier. A. B. D. C.

Modified field equations with a finite radius of the electron. M. Born (Nature, 1933, 132, 282).—Theoretical. L. S. T.

Nomenclature of the electron. E. A. Wildman (Science, 1933, 78, 191). L. S. T.

Scattering of electrons by metal vapours. I. Cadmium. E. C. Childs and H. S. W. Massey (Proc. Roy. Soc., 1933, **A**, 141, 473—483).—The angular distributions of slow electrons scattered from Cd vapour have been examined over the angular range 25—130°. The scattering curves exhibit max. and min. closely resembling those appearing in corresponding curves for Hg vapour. L. L. B.

Anomalous reflexion of high-speed electrons at a single-crystal face. S. Kikuchi and S. Nakagawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 256—265).—Results obtained for the reflexion of 100—40-kv. electrons at a ZnS crystal surface are discussed. J. W. S.

Electron diffraction and structure of metallic films. J. A. Prins (Z. Krist., 1933, 86, 301—303; cf. A., 1932, 893).—Electron diffraction patterns obtained with fast electrons (30—60 kv.) of films ($< 0{\cdot}1\ \mu$) of metal supported on collodion show that the cubic metals (*e.g.*, Au, Ag, Al) give perfect powder diagrams indicating completely irregular arrangement of the crystallites. The hexagonal metals (*e.g.*, Sb, Cd, Zn, Bi) give with perpendicular incidence imperfect diagrams, and with oblique incidence fibre diagrams, indicating a tendency of the crystallites towards orientation, most marked in Bi, least in Sb (cf. A., 1930, 1354; this vol., 657). Where there has been allotropic or chemical change subsequent to first deposition the pattern shows traces of that of the first deposit. C. A. S.

Study of crystalline orientation by electron diffraction. J. J. Trillat (Trans. Faraday Soc., 1933, 29, 995—1002).—A review of published work. E. S. H.

Emission of electrons from tungsten and molybdenum under the action of soft X-rays from copper. J. Bell (Proc. Roy. Soc., 1933, A, 141, 641—651).—The photo-electric emission increases regularly with increase of X-ray exciting voltage throughout the range 1—20 kv. Heating may cause either an increase or a decrease in the emission, depending on the previous treatment of the metal, but relative vals. for Mo and W are only slightly affected by heat treatment. The emission from Mo is about 70% of that from W. L. L. B.

Electrostatic deflexion of positive electrons. J. Thibaud (Nature, 1933, 132, 480—481).—The positive electron has been deflected in an electrostatic field; its sp. charge is of the same order of magnitude as that of the negative electron. L. S. T.

Energy losses of slow electrons in nitrogen. G. W. Brindley (Proc. Leeds Phil. Soc., 1933, 2, 420—426).—By analysing the beam which results from the passage of electrons through N_2 using Whiddington's magnetic spectrum method the energy losses of the electrons are found to occur at 8·6, 12·2$_5$, 12·9, and 14·9 volts. These vals. agree with those of singlet levels calc. from spectroscopic data, but do not agree with Rudberg's vals. (A., 1931, 12) for N_2. W. R. A.

Atomic particles of small range from lithium and boron. F. Kirchner (Naturwiss., 1933, 21, 676).—By bombardment with H canal rays particles were obtained from Li with a range of 1—1·5 cm. A considerably weaker group of range 2 cm. was also found, identical with those noted by Cockcroft and Walton at higher potentials. With B, particles with a range of 6 mm. were produced. The proportion of particles with ranges $<$ 2 cm. is, however, much $<$ with Li. A. J. M.

Emission of metallic ions from oxide surfaces. I. Identification of the ions by mobility measurements. L. Brata. **II. Mechanism of the emission.** C. F. Powell and L. Brata (Proc. Roy. Soc., 1933, A, 141, 454—462, 463—472).—I. A method of producing sources of positive ions of Tl, In, and Ga is described. The ions are identified by determining their mobilities in N_2, this giving a measure of their mass. The mobilities of Tl and In ions have also been determined in He, Ne, and A.

II. A method by means of which a known no. of Tl, Ga, or In atoms can be deposited on an Fe oxide surface is described. On heating the oxide a large proportion of the deposited atoms is re-evaporated as ions. An explanation of the characteristics of the positive ion emission from Kunsman sources and of their catalytic action in the synthesis of NH_3 is thus suggested. L. L. B.

Difference in size of ions of zirconium and hafnium. A. Hoffmann (Naturwiss., 1933, 21, 676).—The lattice consts. (a) of $SrZrO_3$ and $SrHfO_3$ are 4·089±0·003 Å., and 4·069±0·003 Å., respectively. The radius of Hf^{++++} is 0·01 Å. $<$ that of Zr^{++++}. A. J. M.

High-speed protons. M. A. Tuve, L. R. Hafstad, and O. Dahl (Physical Rev., 1932, [ii], 39, 384—385).—The tracks produced in a Wilson cloud chamber by high-speed protons from a high-voltage tube used with a Tesla coil have been photographed, and preliminary measurements of the range in air of 1000-kv. protons have been made. The results indicate that the law governing the range of protons approximates to the v^3 law which holds for α-particle ranges. L. S. T.

Evaporation of atoms, ions, and electrons from cæsium films on tungsten. J. B. Taylor and I. Langmuir (Physical Rev., 1933, [ii], 44, 423—458).—Methods of measuring the no. of Cs atoms adsorbed on W, and θ (the fraction of the W surface covered with Cs), are described, giving data for the rates of atom, ion, and electron emission as functions of θ and T (the filament temp.). A limiting true monat. layer is found; theory and evidence for a second and polyat. layers are given. The heat of evaporation for Cs from W is 2·83 volts (65,140 g.-cal.). The procedure for obtaining electron and ion emission for zero field, and the large changes in the effect of external field with θ, are described. The calc. contact potential agrees with that calc. from neutral atom evaporation. The condensation coeff. for atoms striking a W filament is unity for θ=0—1. The effect of this and the observed surface migration or diffusion on the mechanism of evaporation and condensation in dil. and conc. films is discussed. A surface phase postulate is developed by which all the properties of the adsorbed film are uniquely determined by θ and T. N. M. B.

Nature of gas ions. O. Luhr (Physical Rev., 1933, [ii], 44, 459—462; cf. A., 1932, 4).—The mass of gas ions formed in a glow discharge and aged up to 10^5 impacts was determined by a Dempster type mass-spectrograph. In H_2 the primary ion H_2^+ changes within a few thousand collisions to H_3^+, with traces of H^+. The N_2 primary ions N^+ and N_2^+ attach to neutral mols. in about 10^5 impacts to form N_3^+ and N_4^+. In pure O_2 the ions are O_2^+ with traces of O^+. Air ions include all possible N_2 and O_2 ions, the aged air ions consisting mainly of N_3^+, N_4^+, and O_2^+, with oxides of N. Charges are transferred from O_2^+ to NO, NO_2, and N_2O. H_2O vapour readily acquires a charge by transfer. No heavier clusters than N_4^+ and no negative ions were observed. N. M. B.

Emission of positive ions from metals. H. B. Wahlin (Physical Rev., 1932, [ii], 39, 183).—W wire containing UO_2 emits U^+, W^+, and an ion of mass 254±2, probably UO^+, at approx. 1800°. Ions of Ag and Cu are emitted at temp. near their m.p. L. S. T.

Intensity measurements of molecular rays. L. Estermann and O. Stern (Z. Physik, 1933, 85, 135—143).—Intensity measurements, much more sensitive than those hitherto obtained, were made by observing the increase in electron current due to disturbance of the space charge around a glowing wire by the presence of mol. rays. A. B. D. C.

Test of the classical "momentum transfer" theory of accommodation coefficients of ions at

cathodes. K. T. Compton and E. S. Lamar (Physical Rev., 1933, [ii], 44, 338—344; cf. *ibid.*, 43, 169).—The transfer of momentum for A ions striking Mo and Al was measured by the deflexion of a delicate pendulum bob consisting of the metal cathode under investigation. Results support the prediction that the accommodation coeff. should be $<$ 1 only if the mass of the metal atom composing the cathode is $>$ that of the ion (cf. this vol., 109). N. M. B.

Method for determining the thermionic work functions of metals, and its application to nickel. G. W. Fox and R. M. Bowie (Physical Rev., 1933, [ii], **44**, 345—348).—Experimental. Vals. for Ni are: Φ 5·03±0·05 volts; A $1{\cdot}38\times10^3$ amp./cm.^{2} deg.^{2} N. M. B.

Collision cross-section of argon atoms for 300- to 2500-volt electrons. R. B. Brode (Physical Rev., 1932, [ii], 39, 547). L. S. T.

Molecular scattering in gases. I. Method of crossed molecular beams. R. G. J. Fraser and L. F. Broadway. **II. Collision of sodium and potassium atoms with mercury.** L. F. Broadway (Proc. Roy. Soc., 1933, **A**, **141**, 626—633, 634—641).—I. The angular distribution of the scattering of mol. beams of Na and K in a stream of *trans*-$C_2H_2I_2$ vapour over an angular range of 2—10° has been determined, using the method of crossed mol. beams.

II. The decay consts. of beams of Na and K in Hg vapour have been measured. The experimental decay curves can be extrapolated to zero angle, if use is made of the collision theory of Massey and Mohr, and thus decay consts. (or mean free paths) may be determined, independent of the geometry of the apparatus. L. L. B.

At. wt. of erbium. Analysis of erbium trichloride. O. Hönigschmid and W. Kapfenberger (Z. anorg. Chem., 1933, **214**, 97—103).—Er_2O_3, examined for purity by its *X*-ray spectrum, was converted into anhyd. $ErCl_3$. From the ratios $ErCl_3 : 3Ag$ and $ErCl_3 : 3AgCl$ the at. wt. 165·204 was found. The previous accepted val. was 167·64. H. J. E.

At. wt. of uranium lead. O. Hönigschmid, R. Sachtleben, and H. Baudrexler (Z. anorg. Chem., 1933, **214**, 104—110).—Nephelometric determinations of the ratio $PbCl_2 : 2Ag : 2AgCl$ for Pb from a U ore, curit, and Katanga pitchblende, gave vals. of 206·035, 206·032, and 206·022, respectively. These vals. are $>$ those of Baxter and Alter (this vol., 659). H. J. E.

At. wt. of lead from Katanga pitchblende. A. von Grosse (J. Amer. Chem. Soc., 1933, **55**, 3893; cf. Baxter and Alter, this vol., 659, 882).—The difference between the at. wts. of Pb from the yellow and the black portions of Katanga pitchblende is due to the greater difficulty with which Pb, as compared with U, is leached from pitchblende. Therefore, the data support the author's theory of the origin of the Ac series. J. G. A. G.

Isotopic constitution of zinc. K. T. Bainbridge (Physical Rev., 1932, [ii], 39, 847—848).—The mass nos. of the isotopes of Zn, determined by a new method, are 64, 66, 68, 67, and 70 in order of relative abundance. No evidence has been obtained for the existence of Zn^{65} or Zn^{69} (A., 1928, 1069; 1931, 280), and this new analysis indicates that the ions of mass nos. 65 and 69 measured by Aston are hydrides of Zn^{64} and Zn^{68}. The calc. val. for the at. wt. of Zn is 65·32(7)±0·02 on the chemical scale after deducting 2·2 parts in 10^4 to transfer from the physical mass scale. L. S. T.

[Isotopic] constitution of tellurium. K. T. Bainbridge (Physical Rev., 1932, [ii], 39, 1021).—Aston's analysis (A., 1931, 1208) has been confirmed and extended by the method previously described (preceding abstract). Additional isotopes 124, 123, and 122 with faint indications of 127 have been found. The relative abundances are 130 (33·1), 128 (32·8), 127 (?), 126 (19·0), 125 (4·5), 123 (1·6), 122 (2·9); the "isotopic moment" is 1·74 and the mean mass no. 127·67. Correcting for a packing fraction of −5·0 and changing to the chemical scale gives an at. wt. 127·58±0·15 (cf. Aston's val. 128·03). Te^{124} forms an isobaric triplet with the heaviest isotope of Sn and the lightest of Xe; the remaining isotopes of Te form isobaric pairs. L. S. T.

Relative abundance of the isotopes of lead in uranium-bearing minerals. J. L. Rose and L. P. Granath (Physical Rev., 1932, [ii], 39, 1017).—The ratio of the contents of the 207 to the 208 isotopes is greater in U-bearing minerals (Belgian Congo) than in ordinary Pb. The association of the Ac-decay product with that of the U series may be universal. Relative abundance of the isotopes can easily be determined by observations of hyperfine structure. L. S. T.

Experiments on isotopes of some of the noble gases and hydrogen by means of J. J. Thomson's mass spectrograph. P. Zeeman and J. de Gier (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 609—611).—Using a new apparatus, some evidence of possible hydrides was found for He, Ne, and A; a H isotope mixture gave evidence of the $(H^1H^2)^+$ and $(H^1H_2{}^2)^+$ ions. N. M. B.

Nuclear moment of tin. H. Schüler and H. Westmeyer (Naturwiss., 1933, 21, 660).—Sn^{117} and Sn^{119} have nuclear moment $I=-0{\cdot}5$. The at. nuclei can be arranged in two groups according as they have even (*a*) or odd (*b*) at. wt. Only those in (*b*) have magnetic moment. Group (*b*) can be further subdivided into those with even (b_1), and those with odd (b_2) nuclear charge no. Atoms in (b_1) have nuclear moment either positive or negative, whilst those in (b_2) have positive moment only. In (*a*), the sum of protons and neutrons is even, whilst in (*b*) it is odd, so that an unpaired neutron or proton is necessary for the development of magnetic moment. In (b_1) there is an unpaired neutron. A. J. M.

Radiation emitted on disintegration of lithium. A. Eckardt, R. Gebauer, and H. R. von Traubenberg (Naturwiss., 1933, 21, 694).—The chief component is a soft ray which is reduced to half by passage through 0·3 mm. Pb. The soft components differ slightly in energy from α-rays. When the radiation is passed into several cm. of Pb, an increase in the no. of particles in the counter tube is observed, perhaps due to neutrons. A. J. M.

β-Disintegration. A. Bramley (Physical Rev., 1932, [ii], **39**, 188).—An integral for the probability of a β-particle emission from the nucleus is derived. The reciprocal of the mean life should vary as the 4·5 power of the energy of the excited α-particle. L. S. T.

Energy relations in the β-ray type of radioactive disintegration. C. D. Ellis and N. F. Mott (Proc. Roy. Soc., 1933, **A**, **141**, 502—511).—Experimental evidence is given in support of the hypothesis that the upper limit of the continuous β-ray spectrum corresponds with the difference of binding energies of the initial and final nuclei. L. L. B.

Photo-electric absorption of γ-rays by heavy elements. J. McDougall and H. R. Hulme (Nature, 1933, **132**, 352—353). L. S. T.

Scattering of γ-rays in air and water. W. J. Rees and L. H. Clark (Phil. Mag., 1933, [vii], **16**, 691—703).—The wave-length shift on scattering exceeds the max. predicted by Compton's theory for a single encounter, suggesting that much of the radiation undergoes > one scattering process. H. J. E.

Nuclear excitation by hard γ-rays. T. Heiting (Naturwiss., 1933, **21**, 674).—Al, Fe, Cu, and Pb gave nuclear γ-radiation when excited by Th-*C''* γ-rays, of wave-length 4·7 X. The intensity of the nuclear γ-radiation was proportional to the square of at. no. Secondary radiation without change of wave-length was not observed. A. J. M.

Protons produced in the artificial disintegration of the nitrogen nucleus. E. C. Pollard (Proc. Roy. Soc., 1933, **A**, **141**, 375—385).—Experiment indicates that entry of the α-particle into the N_2 nucleus is in general over the top of the potential barrier, the height of which is fixed as $4{\cdot}1$—$4{\cdot}4\times10^6$ electron volts. Further study of the absorption curve of the protons confirms the work of Steudel (A., 1932, 980). L. L. B.

Transmutation of lithium by protons and by ions of the heavy isotope of hydrogen. M. L. E. Oliphant, B. B. Kinsey, and (Lord) Rutherford (Proc. Roy. Soc., 1933, **A**, **141**, 722—733).—The absorption curve for the disintegration particles produced from Li by protons consists of three parts: a long range of $8{\cdot}4\pm0{\cdot}2$ cm. and two short ranges of $1{\cdot}15\pm0{\cdot}2$ and $0{\cdot}65\pm0{\cdot}2$ cm., respectively. The protons ejected from Li by ions of the heavy isotope of H_2 fall into two groups: one of $13{\cdot}0\pm0{\cdot}2$ cm., corresponding with an energy of $11{\cdot}5\times10^6$ ev., and a shorter-range group which is complex and consists of particles with energies from 1·7 to $8{\cdot}3\times10^6$ ev. The rate of increase in the no. of particles with increase of bombarding energy is much > for protons. The particles are probably He nuclei, the 13·0-cm. group arising from the reaction ${}_3\mathrm{Li}^6+{}_1\mathrm{H}^2\longrightarrow{}_2\mathrm{He}^4+{}_2\mathrm{He}^4$, whilst the complex group is a result of the 3-body nuclear reaction ${}_3\mathrm{Li}^7+{}_1\mathrm{H}^2\longrightarrow2{}_2\mathrm{He}^4+{}_0n^1$. L. L. B.

Photographic investigation of the transmutation of lithium and boron by protons and of lithium by ions of the heavy isotope of hydrogen. P. I. Dee and E. T. S. Walton (Proc. Roy. Soc., 1933, **A**, **141**, 733—742).—Using an expansion chamber and double camera, the tracks emitted in the transmutations of Li and B by protons and of Li by ions of the heavy isotope of H_2 have been photographed. The apparatus used for the production of the high voltage and its application to the tubes used for accelerating the bombarding particles was that described by Cockcroft and Walton (A., 1932, 789), and potentials up to 400 kv. were used. The modes of disintegration ${}_3\mathrm{Li}^7+{}_1\mathrm{H}^1\longrightarrow{}_2\mathrm{He}^4+{}_2\mathrm{He}^4$ and ${}_3\mathrm{Li}^6+{}_2\mathrm{H}^2\longrightarrow{}_2\mathrm{He}^4+{}_2\mathrm{He}^4$ have been confirmed (cf. preceding abstract). L. L. B.

Collisions of neutrons with protons. F. N. D. Kurie (Physical Rev., 1933, [ii], **44**, 463—467).—Neutrons from Be containing a Po source eject protons from a surrounding layer of paraffin wax. The Wilson tracks due to the protons are photographed. The bearing on the structure of the neutron of the distribution given by the no. of tracks–angle of projection curve is discussed. N. M. B.

Neutrons and positive electrons. R. Fürth (Z. Physik, 1933, **85**, 294—299).—The hypothesis of elementary indeterminancy gives the mass and radius of the neutron in terms of universal consts., and predicts positive electrons and negative protons. A. B. D. C.

Neutrons and protons in atomic nuclei. H. S. Allen (Nature, 1933, **132**, 322).—A brief survey. L. S. T.

Atomic transmutation. Anon. (Nature, 1933, **132**, 432—433).—A brief summary of the British Association (Section A) discussion. L. S. T.

Absorption spectra and atmospheres of the major planets. R. Wildt (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1932, 87—96; Chem. Zentr., 1933, i, 2048).

Solar activity and cosmic rays. V. F. Hess and R. Steinmaurer (Nature, 1933, **132**, 601—602).—The results described support, in part, the corpuscular theory of cosmic radiation. L. S. T.

Cosmic-ray light on nuclear physics. R. A. Millikan (Science, 1933, **78**, 153—158).—A lecture. L. S. T.

Hardest cosmic rays and the electric charge of the earth. W. Kolhörster (Nature, 1933, **132**, 407). L. S. T.

Cosmic-ray positive and negative electrons. C. D. Anderson (Physical Rev., 1933, [ii], **44**, 406—416; cf. this vol., 441).—Sp. ionisation, as determined by a modified Wilson chamber method, indicates that positrons and electrons occur in nearly equal nos., and have similar energy distribution, curves for which are given. The absorption of Th-*C''* rays, in the light of these results, is discussed. N. M. B.

Atomic disintegration by cosmic rays. J. Barnóthy (Z. Physik, 1933, **85**, 201—209).—At. radii are approx. 2½ times less for cosmic rays than those required by artificial disintegration experiments. A. B. D. C.

[Atomic disintegration by cosmic rays.] E. G. Steinke (Z. Physik, 1933, **85**, 210—211).—The work noted in the preceding abstract is discussed in the light of more recent empirical data. A. B. D. C.

Absorption of penetrating radiation by water and analysis of the absorption function. W. Kramer (Z. Physik, 1933, 85, 411—434).—Absorption of penetrating radiation by H_2O of the Alpine lakes is described. An analysis of these together with Regener's results (A., 1932, 440) is possible only if scattered radiation is added to the primary radiation. A. B. D. C.

Penetrating power and absorption coefficient of cosmic rays. E. Lenz (Z. Physik, 1933, 85, 435—438).—Mean range is equal to 3·1 μ, where μ is the absorption coeff. A. B. D. C.

Variation with pressure of residual ionisation in cosmic-ray measurements. P. Pfundt (Z. Physik, 1933, 85, 439—441).—The dependence of residual ionisation on pressure was studied in a high-pressure ionisation chamber filled with CO_2. A. B. D. C.

Variation with pressure of residual ionisation. E. Körner (Z. Physik, 1933, 85, 442—447).—Cylindrical ionisation chambers with inner walls contaminated with radioactive substances gave ionisation–pressure curves similar to those observed by Pfundt (cf. preceding abstract). A. B. D. C.

Variation with pressure of residual ionisation. J. A. Priebsch (Z. Physik, 1933, 85, 448—450).—Dependence of residual ionisation on pressure was studied for air and A. A. B. D. C.

Neutrons and magnetic nuclear moments. B. Venkatesachar and T. S. Subbaraya (Z. Physik, 1933, 85, 264—267).—Assuming neutrons to have orbital moments in nuclei, the magnetic moment of a neutron is 1/2 that of a proton; this gives correctly the magnetic moments of 17 nuclei. A. B. D. C.

Magnetic moments of atomic nuclei. H. Schüler and H. Westmeyer (Naturwiss., 1933, 21, 674—675).—If the val. of the magnetic moment of the proton is taken as 2·5/1840 Bohr magneton, the μ/μ_0 vals. (μ_0 being the Bohr magneton) of various elements agree with experimental vals. or are twice these, for elements with odd at. wt. and odd nuclear charge no. For elements of odd at. wt. and even nuclear charge no. it is better to use the val. 1/1840 Bohr magneton for the magnetic moment of the proton. In comparison with the effect on the magnetic moment of the proton, or odd neutrons, that of the nuclear residue is small. No magnetic moment results from the motion and arrangement of charges and masses in the residue. A. J. M.

Nuclear moments and their dependence on atomic number and mass number. N. S. Grace (Physical Rev., 1933, [ii], 44, 361—364).—Nuclei are grouped into four classes depending on whether the at. no. Z and mass no. are even or odd. Similarities within classes are found, and differences between classes for mechanical and magnetic moments and nuclear g-factors. Results indicate that nearly all nuclei having large magnetic and mechanical moments lie in columns of the periodic table with Z odd, and those having small or zero moments lie in columns with Z even. N. M. B.

Uncertainty principle. H. T. Flint (Nature, 1933, 132, 282). L. S. T.

Kinetic electron energy and interatomic forces. H. Hellmann (Z. Physik, 1933, 85, 180—190).—A general relation between kinetic, potential, and total energy is deduced for a system of atoms at rest, and is applied to the interat. forces in crystals and to van der Waals forces of inert gas atoms. A. B. D. C.

Free paths and transport phenomena in gases, and the quantum theory of collisions. I. Rigid sphere model. H. S. W. Massey and C. B. O. Mohr (Proc. Roy. Soc., 1933, A, 141, 434—453).—Using the rigid-sphere model, the range of validity of the classical theory of free paths, viscosity, and diffusion is determined. The use of quantum mechanics improves the applicability of this model to the viscosity of He. L. L. B.

Scattering of light by excited atoms. V. Weisskopf (Z. Physik, 1933, 85, 451—482).—The Kramers–Heisenberg formula is extended to include excited at. states of appreciable life period. A. B. D. C.

Coefficients of absorption and opacity of a partly degenerate gas. (Miss) B. Swirles (Proc. Roy. Soc., 1933, A, 141, 554—566).—Mathematical. The absorption coeffs. due to both "bound–free" and "free–free" transitions, and the opacity for "free–free" transitions, are evaluated. The results are applied to the two-phase standard model of a star. L. L. B.

Magnetic deviation of oxygen molecules. R. Schnurmann (Z. Physik, 1933, 85, 212—230).—Results give O_2 a magnetic moment of 2 Bohr magnetons together with a coupling of this with rotation of the mol. A. B. D. C.

Calculations of atomic wave functions. I. Survey, and self-consistent fields for Cl^- and Cu^+. D. R. Hartree (Proc. Roy. Soc., 1933, A, 141, 282—301).—The results for Cu^+ are compared with those for the alkali metals, and characteristic differences noted. The relation between the interat. distance in metals and the wave function of the series electron is pointed out. L. L. B.

Intensity distribution in a band system of symmetrical triatomic molecules. Z. W. Ku (Physical Rev., 1933, [ii], 44, 383—390).—Mathematical. N. M. B.

Spectrum of hydrogen sulphide. I, II. N. O. Stein (Astrophys. J., 1933, 77, 270—273; 78, 159—160).—I. No characteristic emission spectrum of H_2S could be observed using a valve oscillator. H_2S gave the Balmer series, the H_2 secondary and continuous spectrum, and a group of diffuse bands, 2470—2860 Å., also given by CS_2, and therefore ascribed to S.

II. The bands, attributed to S, appear to be identical with those of CS. L. S. T.

Intensities of bands in the spectrum of boron monoxide. A. Elliott (Proc. Physical Soc., 1933, 45, 627—634).—The total intensities of the α-bands of BO have been measured. The harmonic wave-function theory shows fair agreement with experiment for the intensities of the β-bands of BO (A., 1931, 279), but a few bands show divergencies > experimental error. The intensity ratio of the $B^{11}O$ and $B^{10}O$ bands (3·5 : 1) is in good agreement with that determined from the β-bands (3·66 : 1). J. W. S.

Absorption spectrum of chlorine dioxide. Z. W. Ku (Physical Rev., 1933, [ii], 44, 376—382).—Measurements of band heads in the visible and ultra-violet, and a vibrational analysis, are given. Two fundamental bands and one combination band in the region 4—11 μ were recorded. Calc. mol. consts. are consistent with the observed isotope effect. N. M. B.

New band systems in the gadolinium oxide spectrum. G. Piccardi (Nature, 1933, 132, 481).—Formulæ representing two new systems originating at 4615·6 and 4892·1 Å. are given. L. S. T.

Vanadium oxide bands. C. Ghosh (Nature, 1933, 132, 318).—Measurements have been extended to 4500 Å.; band heads are double with a separation of approx. 2·8 ν between them, and the band system is due to a $^2\Sigma \longrightarrow {}^2\Sigma$ transition. L. S. T.

Far ultra-violet eigenfrequencies of the alkali halides. A. Smith (Physical Rev., 1932, [ii], 39, 1013—1014).—Preliminary results for NaCl are recorded. L. S. T.

Absorption spectra of salts with halogenoid complex ions. H. Fesefeldt (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1932, 353—355; Chem. Zentr., 1933, i, 1583—1584).—The absorption spectra of thin layers of cryst. KCN, KCNS, and PbCNS show bands at 169, 183, and 183 mμ, respectively. For KCN the Coulomb fraction of the lattice energy is calc. as 7·62 volts. TlCNS exhibits deformation. A. A. E.

Action of light on rubidium iodide vapour. M. S. Desai (Z. Physik, 1933, 85, 360—365).—Absorption was observed at 3700, 2900, 2548, and 2150 Å., and four corresponding dissociations of the mol. are given. A. B. D. C.

Excitation of the carbon dioxide emission spectrum in a Back box. R. F. Schmid (Physical Rev., 1932, [ii], 39, 539).—The entire CO_2 (or CO_2^+) band spectrum can be obtained from a Back box, with an arc current of approx. 0·5 amp. through streaming CO_2 gas. Most of the band groups appear to be those of a $^1\Sigma \longrightarrow {}^1\Sigma$ transition of a diat. mol. L. S. T.

Doubling and staggering in simple emission bands of the carbon dioxide spectrum. R. Schmid (Z. Physik, 1933, 85, 384—388).—High dispersion shows CO_2 bands near 3670 Å. to consist of doublets 0·3 cm.$^{-1}$ apart. A. B. D. C.

Absorption of amines in the near infra-red. U. Liddel and O. R. Wulf (J. Amer. Chem. Soc., 1933, 55, 3574—3583).—Mol. absorption coeffs., ε, of 34 compounds containing the :NH group have been determined in the neighbourhood of 1·5 μ using, in general, 0·033*M* solutions in CCl_4. Although ε remains of the same order of magnitude, there are definite differences between the vals. of ε for primary and *sec.* aliphatic and aromatic amines as well as variations in the position of the max. of absorption, *M*. The sp. vals. of ε and positions of *M* do not change as the primary and *sec.* aliphatic series are ascended beyond the Et derivatives. An extension of these results for the determination of mol. constitution in certain cases is suggested. J. G. A. G.

Infra-red absorption spectrum of nitrogen tetroxide and the structure of the molecule. G. B. B. M. Sutherland (Proc. Roy. Soc., 1933, A, 141, 342—362).—The absorption bands due to the N_2O_4 mol. have been distinguished from those due to NO_2, and the main bands due to the former have been examined. The data on the infra-red and Raman spectra are in favour of the formula $O_2N{\cdot}NO_2$. Certain relations between the fundamental frequencies are deduced, and 11 of the 12 frequencies are determined. The binding const. between the two NO_2 groups is calc. to be $1{\cdot}5\times10^5$ dynes per cm., in accord with the ease of dissociation of the mol. and the observed low heat of dissociation (13 kg.-cal. per mol.). L. L. B.

Far infra-red absorption spectra of ammonia and phosphine gases under high resolving power. N. Wright and H. M. Randall (Physical Rev., 1933, [ii], 44, 391—398).—The pure rotation absorption spectra of H_2O vapour, NH_3, and PH_3 were investigated. The NH_3 absorption lines, previously single, were shown as doublets, with separation 1·33 cm.$^{-1}$ The pure rotation lines of PH_3 showed no trace of doubling. Moments of inertia were determined. N. M. B.

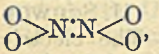
Raman effect in water vapour. H. L. Johnston and M. K. Walker (Physical Rev., 1932, [ii], 39, 535).—Raman lines corresponding with shifts of 3654 (±5), 1648 (±5), and 984 (±10) cm.$^{-1}$ have been observed in H_2O vapour at approx. 275° and 2—3 atm. excited by the total radiation of the Hg arc in the visible and near ultra-violet. These are interpreted as pure vibration frequencies and represent the three fundamentals to be expected for the H_2O mol. L. S. T.

Constitution of water in different states. I. R. Rao (Nature, 1933, 132, 480).—The proportions of H_2O, $(H_2O)_2$, and $(H_2O)_3$ mols. present in ice, and in water at 0°, 4°, 38°, and 98°, have been evaluated from Raman data on certain assumptions. The max. no. of the more compact $(H_2O)_2$ mols. found for H_2O at 4° may explain the max. density of H_2O at this temp. L. S. T.

Raman effect of sulphuric acid. L. Médard (Compt. rend., 1933, 197, 582—584).—The fluorescence usually observed in H_2SO_4 is removed by heating at 150° with $KMnO_4$. Pure H_2SO_4 does not show the line 1050 cm.$^{-1}$ appearing first in 98·5% acid; a new line is found at 975, and lines at 391 and 437 in place of that at 415 (cf. A., 1929, 1215; 1931, 997; this vol., 337). Changes on dilution are traced, and lines assigned as follows: 990 to SO_4^{--}, 1050 to HSO_4^-, 430 and a line at 565—600 to the heteropolar mol. $[SO_4][H_2]$, and 395, 975, 1150—1180, 1370, and perhaps 920 to the homopolar mol. $SO_2(OH)_2$. C. A. S.

Raman effect in silicic acid esters and silicic acid gels. J. Weiler (Helv. phys. Acta, 1932, 5, 302; Chem. Zentr., 1933, ii, 3839).—Raman spectra for silicic acid esters up to the decameride have been determined. Frequencies for amorphous and cryst. SiO_2 as well as different glasses are compared. The lines 1100 and 1200 cm.$^{-1}$ are independent of the degree of polymerisation, and 850 and 645 cm.$^{-1}$ appear with the monomeric ester, but higher esters show smaller vals. L. S. T.

Ions of the type $M(OH)_n^{x+}$ in the Raman effect. Z. Ollano (Nuovo Cim., 1932, [ii], **9**, 264—269; Chem. Zentr., 1933, i, 1585).—A discussion of the behaviour of $Bi(NO_3)_3$. A. A. E.

Raman effect at very low temperatures. G. B. B. M. Sutherland (Proc. Roy. Soc., 1933, A, **141**, 535—549).—A simple apparatus for the rapid examination of Raman spectra at very low temp. is described. The lines of the Raman spectrum of N_2O_4 are divided into two classes: those due to characteristic vibrations within a mol. of the form  $\genfrac{}{}{0pt}{}{O}{O}{>}N{:}N{<}\genfrac{}{}{0pt}{}{O}{O}$, and those due to oscillations of this mol. about an equilibrium position in the crystal. The failure to obtain any strong Raman spectrum from O_3 indicates that the O_3 mol. is triangular but not equilateral. The Raman spectra of CH_4, NH_4OH, CCl_4, ice, and liquid air have also been examined. The results for CCl_4 at the temp. of liquid air agree with those obtained at room temp., but the results for ice at the temp. of liquid air differ markedly from those obtained at 0°. This can be accounted for by the existence of strong intermol. fields in the crystal. Whilst there is strong evidence in favour of the presence of $(H_2O)_2$ mols. in H_2O and in ice, all the observed phenomena can be better explained without assuming the existence of higher aggregates. L. L. B.

Infra-red and Raman spectra of carbon disulphide. S. Bhagavantam (Physical Rev., 1932, [ii], **39**, 1020).—A discussion. L. S. T.

Influence of ultra-violet absorption on the relative intensities of Stokes and anti-Stokes lines in the Raman spectrum. S. C. Sirkar (Indian J. Physics, 1933, **17**, 67—75; cf. A., 1932, 108).—The intensity ratio for the 655 line of CS_2 excited by the 4358 Å. line has been determined, and indicates the influence of the absorption frequency. N. M. B.

Photo-active emanations from irradiated organic substances. C. Serono and A. Cruto (Bull. Soc. Chim. biol., 1933, **15**, 833—839).—The luminescence produced by lecithin and other lipins and resins when exposed to ultra-violet light is due to oxidation of the unsaturated parts of the mols. The irradiation of lecithin affords the same products as are obtained on treatment with H_2O_2. A. L.

Unidirectional layer photo-effect and Einstein's relation. F. von Kőrösy and P. Selényi (Physikal. Z., 1933, **34**, 716—718).—The effect of different coloured light on the emission of Se and Cu_2O cells is investigated. A. J. M.

Theory of photo-electric effect on metals. I. Tamm (Physical Rev., 1932, [ii], **39**, 170—172).—A reply to criticism (A., 1931, 1106). L. S. T.

Influence of adsorbed gas layer on photo-electric sensitivity. B. Abendroth (Z. Physik, 1933, **85**, 530—544).—Unimol. layers of H_2O, C_5H_5N, $EtCO_2H$, and C_6H_6 give max. sensitivity for Pt and CdI; zero layer gives zero sensitivity, and this diminishes as the layer increases in thickness beyond the unimol. form. The dipole moment is thus not of primary importance. A. B. D. C.

Photo-electric cells sensitive to red and infra-red light. W. Kluge (Z. wiss. Phot., 1933, **32**, 142—144).—Ag–Cs_2O–Cs cells show max. sensitivities about 400 and 700—800 mμ. J. L.

Conduction in poor electronic conductors. J. Frenkel (Nature, 1933, **132**, 312).—The mechanism of photo-electric conduction is discussed. L. S. T.

Electrical conductivity of inorganic substances with electron conductivity. W. Meyer (Z. Physik, 1933, **85**, 278—293).—Variation of the electrical conductivity with temp. is represented by an exponential formula with the index b/T; the variation of the consts. with the substance and metalloid content was investigated for WO_3, ZnO, and UO_2. A. B. D. C.

Dielectric losses of insulating oils at very high frequencies. H. Beck (Physikal. Z., 1933, **34**, 721—729).—The dielectric losses of oils at frequencies of 10^7 to 10^8 Hertz was determined by a calorimetric method. No connexion between the losses and the breakdown characteristics at low frequency could be found. Purification of the oil had no effect. The losses are to be ascribed almost entirely to mol. dipoles. A. J. M.

Dipole moment and solvent. H. Müller (Physikal. Z., 1933, **34**, 689—710).—An apparatus for the determination of dielectric consts. is described, and used for finding the dependence of mol. polarisation of solutes on the solvent. This is a function of the dielectric const. of the latter, and an empirical relationship can be derived to govern it. The effect can be explained by assuming a saturation effect in the electric field of the dipole, analogous to the theory of the dielectric const. of dil. solutions of electrolytes. A. J. M.

Investigations of the influence of a magnetic field on the dielectric constants of argon and oxygen by means of a new resonance method. H. Voss (Z. Physik, 1933, **85**, 172—179).—Changes of 10^{-8} in the dielectric const. could be measured, but no effect was observed for magnetic fields up to 1080 gauss. A. B. D. C.

Resultant electric moment of complex molecules. H. Eyring (Physical Rev., 1932, [ii], **39**, 746—748).—Theoretical. L. S. T.

Relation between apparent atomic volumes and centres of co-ordination of insoluble internal complexes. R. Gutzeit (Arch. Sci. phys. nat., 1933, [v], **138**, 173—176).—Theoretical. C. W. G.

Rotatory dispersion of certain classes of organic molecules. D. Biquard (Ann. Chim., 1933, [x], **20**, 153—199).—A detailed account of work previously summarised (A., 1932, 679), the vals. of $[\alpha]_{5780}$, $[\alpha]_{5461}$, and $[\alpha]_{4358}$ and the dispersions between

5780 and 4358 for *l*-benzyl-lactic acid (I) and its Me_2 ester (II) in various solvents, and for the pure ester at temp. between 21° and 174°, also being given. The existence of an equilibrium mixture of $>$ two forms (two of which are of opposite sign) is assumed with Me phenylsuccinate, *d*-phenyl-lactic acid, its Me_2 ester, (I), and (II). J. W. B.

Optical activity in triphenylmethane derivatives. I. I. Lifschitz (Z. wiss. Phot., 1933, 32, 131—141; cf. A., 1931, 349, 840).—Theoretical. Arguments in favour of the existence of optically active halochromic derivatives of CAr_3X are given. F. L. U.

Refractive index. IV. A. M. Taylor and A. King (J. Opt. Soc. Amer., 1933, 23, 308—312).—The surface layers of molten undecoic, lauric, and myristic acids suddenly become birefringent on cooling to within a few degrees of the m.p., indicating orientation of the mols. D. R. D.

Optical properties of the double salt $(NH_4)_2SO_4,CaSO_4,2H_2O$. A. R. Merz, J. O. Hardesty, and S. B. Hendricks (J. Amer. Chem. Soc., 1933, 55, 3571—3573).—The refractive indices of the crystals, *d* 2·07, are recorded. J. G. A. G.

Optical properties of liquid nitrobenzene near its transition point. M. Wolfke and S. Ziemecki (Acta phys. Polon., 1932, 1, 271—279; Chem. Zentr., 1932, ii, 3828).—The refractive index between 6·4° and 19° has been measured by three different methods; it changes continuously at the transition temp.; on the other hand at 9·5° the mol. refraction showed a discontinuity. The Raman spectrum shows no change at the transition temp. L. S. T.

Two different states of liquid nitrobenzene. M. Wolfke and J. Mazur (Acta phys. Polon., 1932, 1, 71—77; Chem. Zentr., 1932, ii, 3828). L. S. T.

Optical anisotropy of molecular crystals. I. S. B. Hendricks and M. E. Jefferson (J. Opt. Soc. Amer., 1933, 23, 299—307).—Densities and refractive indices are given (α, β, γ, from 4861 to 6676 Å.) of BzOH, $(CH_2Ph)_2$, C_6Et_6, $(CH_2)_6N_4$, C_6HMe_5, Ph_2, $C_{10}H_8$, $C_6H_4Br_2$, C_6Me_6, and *o*- and *m*-$C_6H_4(OH)_2$, in the liquid and solid states. Densities only are given for acenaphthene, *p*-$C_6H_4Me{\cdot}NH_2$, *o*-$C_6H_4Me{\cdot}CO_2H$, and C_6H_6. D. R. D.

Dispersion measurements for NaCl in the long-wave infra-red. C. H. Cartwright and M. Czerny (Z. Physik, 1933, 85, 269—277).—Refractive indices and extinction coeffs. were measured between 70 and 125 μ; subsidiary max. observed in the nearer infra-red were absent in this region, in agreement with Born and Blackman's theory (this vol., 661). A. B. D. C.

Dispersion of gases and vapours and its representation by the dispersion theory. V. Interferometer for dispersion measurements in the Schumann region. G. Wolfsohn (Z. Physik, 1933, 85, 366—372).—Preliminary measurements were made of anomalous dispersion due to the 1850 Å. Hg line. A. B. D. C.

Dispersion of the Kerr electro-optic effect in the short infra-red spectrum. L. R. Ingersoll and W. R. Winch (Physical Rev., 1933, [ii], 44, 399—405).—Measurements of the Kerr electro-optic effect were made on CS_2, $PhNO_2$, *o*-$C_6H_4Me{\cdot}NO_2$, PhCl, and "halowax" oil in the region 0·589—2 μ. Satisfactory agreement was found with the Havelock formula; the Born and Serber (cf. this vol., 763) formulæ were also satisfactory. N. M. B.

Electrical Kerr effect with gases and vapours at higher temperatures. H. A. Stuart and H. Volkmann (Ann. Physik, 1933, [v], 18, 121—149).—An apparatus for the abs. determination of the Kerr const. of vapours up to 230° is described. The dependence of Kerr const. on temp. for EtCl was determined between 15° and 177°. The results confirm the Langevin–Born theory. The Kerr consts. of a no. of org. vapours have been obtained, and for some, *e.g.*, $EtNO_2$ and the lower ketones, the polarisation ellipsoids were calc. and discussed. The const. for $COPr^{\beta}_2$ is negative. A. J. M.

Electric birefringence of camphor. M. Schwob (Compt. rend., 1933, 197, 615—617).—The electric birefringence of camphor has been determined at various temp. from 20° to 183°, in solution in CCl_4 and paraffin oil, and fused, showing that the dispersion is normal. The temp. variation in the oil is in accord with Langevin's law; the sp. birefringence varies with the solvent. These results support the hypothesis of mol. polymorphism in solution (cf. A., 1932, 900). C. A. S.

Cotton–Mouton constant of nitrobenzene at the transition point. H. König (Physikal. Z., 1933, 34, 731—734).—The Cotton–Mouton effect for $PhNO_2$, and the effect of temp. on it, have been investigated. The temp. curve shows no deviation at the supposed transition point of the two liquid forms (9·6°). The val. of the const. at 20° and 546 mμ is $25{\cdot}7\times10^{-13}\pm0{\cdot}4\%$. A. J. M.

Absence of inertia in the diamagnetic Faraday effect. W. Hanle (Z. Physik, 1933, 85, 304—309).—No inertia was observed for frequencies up to 10^8 Hertz. A. B. D. C.

Magnetic properties of iodine in different solvents. S. S. Bhatnagar and C. L. Lakra (Indian J. Physics, 1933, 17, 43—47).—Vals. of the magnetic susceptibility indicate slight ionisation of I in C_6H_6 and CS_2, but not in *cyclo*hexane. N. M. B.

Influence of temperature on the diamagnetism of certain liquids. M. A. Azim and S. S. Bhatnagar (Phil. Mag., 1933, [vii], 16, 580—593).—The susceptibility of *cyclo*hexane and CCl_4 was independent of temp.; for H_2O, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, and $Bu^{\beta}OH$ it increased with rise of temp. For a no. of aromatic compounds it decreased. For H_2O and alcohols the increase is connected with changing association. The vals. for the aromatic compounds are correlated with the dipole moment and magnetic birefringence. H. J. E.

Diamagnetic susceptibility of the rare gas atoms according to Slater's method. W. R. Angus (Physical Rev., 1932, [ii], 39, 844—845; cf. A., 1932, 795).—Biswas' results (this vol., 449) are incorrect. Vals. for the effective nuclear charge, diamagnetic increments, and at. diamagnetic susceptibilities calc. by Slater's method and by a modified method are compared with those calc. by Biswas for Kr, Xe, and Rn. Agreement is not good. L. S. T.

Magnetic properties of mesomorphic substances. Analogies with ferromagnetics. G. Föex (Trans. Faraday Soc., 1933, 29, 958—972).—Published data show a close correspondence between the magnetic properties of ferromagnetic and nematic substances, especially in those characteristics which depend on orientation. The changes of magnetic susceptibility with temp. for smectic substances are small and approx. linear while the mesomorphic state persists, becoming very strong and discontinuous on passing into the isotropic state. The effect of a magnetic field on crystallisation and the relation between diamagnetism and mol. structure are discussed. E. S. H.

Molecular configuration of N_2O. C. R. Bailey and A. B. D. Cassie (Physical Rev., 1932, [ii], 39, 534).—Plyler and Barker's data (A., 1932, 108) give a formula $N\vdots N:O$ and not $N:N\vdots O$. The vals. of the force consts. obtained by the authors for an asymmetrical rectilinear mol. (A., 1932, 444) give a formula $N:N:O$ or $:\ddot{N}::N::\ddot{O}:$. L. S. T.

Aminoformates of copper and zinc, relatively stable internal complexes involving four linkings. G. Gutzeit and R. Duckert (Arch. Sci. phys. nat., 1933, [v], 15, 168—173).—The formulæ $(NH_2\cdot CO\cdot O)M^{II}$ are established. C. W. G.

Surface tension of liquids near the critical temperature. C. A. Winkler and O. Maass (Canad. J. Res., 1933, 9, 65—79).—The surface tension–temp. curves for Me_2O and C_3H_6 have been determined by capillary rise to within 1—2° of the crit. temp. The curves do not appear to be asymptotic to the temp. axis, *i.e.*, the mol. surface energy does not fall to zero when the meniscus disappears. Sugden's equation is valid for the ranges studied, and Katayama's equation is more accurate than that of Ramsay and Shields. The Macleod relation between surface tension and *d* is valid for Me_2O, but for C_3H_6 the const. increases progressively with rise of temp. The calc. parachor of Me_2O agrees with the theoretical val., but for C_3H_6 it shows an increasing deviation as the crit. temp. is approached. The ring method, with certain modifications, should be applicable to determinations of surface tension in the neighbourhood of the crit. temp.; it yields results confirming that the angle of contact between Me_2O and glass is zero. H. F. G.

Molecular beams of salt vapours. W. H. Rodebush and W. F. Henry (Physical Rev., 1932, [ii], 39, 386).—No ions could be detected in mol. beams of the alkali halides, but when a beam is passed through an inhomogeneous magnetic field a considerable broadening, due to the magnetic moment of the rotating dipoles, is observed. L. S. T.

***X*-Ray examination of crystals with long-wave radiation.** G. Hägg (Z. Krist., 1933, 86, 246—252).—Apparatus for use with, *e.g.*, Ca-$K\alpha$ radiation is described. C. A. S.

Deviation from the Bragg equation for the powder method. G. Hägg and G. Phragmén (Z. Krist., 1933, 86, 306—308; cf. A., 1927, 298).—The effect of refraction of the radiation used on the correctness of the Bragg equation is discussed and shown to be negligible as a rule. It is least when θ is large. If it is necessary to take it into consideration this is best done by calibration, a method for which is outlined. C. A. S.

Heteropolar crystals. H. M. Evjen (Physical Rev., 1933, [ii], 44, 501—509; cf. this vol., 1109).—The failure of theories of the solid state to account for the stability of ideal crystals cannot be due to inadequacy of the force postulate. A possible type of departure from the ideal state is considered. The assumption that all crystals have a secondary structure leads to an explanation of the doublet nature of residual rays in cubic crystals and to an improved form of Lindemann's law. N. M. B.

Thermal motions of atoms in crystals. B. D. Holbrook (Physical Rev., 1932, [ii], 39, 177).—An expression, involving only measured quantities, is deduced for the distribution of the atom centres about their mean positions. Atoms possess more translational energy than is predicted by classical theory, indicating the presence of zero-point energy. L. S. T.

Focal conic structures. (Sir) W. Bragg (Trans. Faraday Soc., 1933, 29, 1056—1060).—Theoretical. E. S. H.

Theory of recrystallisation. U. Dehlinger (Metallwirt., 1933, 12, 48—50; Chem. Zentr., 1933, i, 1569).

Lattice distortion and fibre structure in metals. W. A. Wood (Nature, 1933, 132, 352).—As the temp. of a metal is raised, lattice distortion (I) produced by cold-working (A., 1932, 1193) is removed before that of the fibre structure (II), and this intermediate state, in which (II) exists to the exclusion of (I), persists as the metal is slowly cooled. L. S. T.

Relation between the separation processes of single and poly-crystals. P. Wiest (Metallwirt., 1933, 12, 47—48; Chem. Zentr., 1933, i, 1569).—Experiments concerning the structure and velocity of crystallisation of Cu+10% Ag are described. A. A. E.

Synthetic metal bodies. VII. Crystallisation between surfaces in structural equilibrium. F. Sauerwald and L. Holub (Z. Elektrochem., 1933, 39, 750—753; cf. B., 1932, 428).—Compression of powdered Fe or Cu above 400° at 3000—5000 kg. per sq. cm. produced blurring of the $K\alpha$ doublet, attributed to inner strain. Powdered Cu, prepared by reduction, showed growth from one crystal to another after heating to 900°, but not at 500°. A powder composed mainly of single crystals, prepared by fusing powdered Cu mixed with MgO and removing the MgO, gave much less growth between crystals at 900° and none at 500°. H. J. E.

Structure of technical zinc dust. G. Wassermann (Metallwirt., 1933, 12, 1—2; Chem. Zentr., 1933, i, 1993).—Debye–Scherrer lines indicate a mean crystal size of 10 μ; microscopical examination indicates considerable variation in particle size (2—20 μ), the diameter of most of the spherical particles being 5—7 μ. ZnO appears to be present as a film on the Zn particles. A. A. E.

Structure of magnesium, zinc, and aluminium films. G. I. Finch and A. G. Quarrell (Proc. Roy. Soc., 1933, A, **141**, 398—414).—Electron diffraction examination shows that (i) the structure of a thin Al film deposited on Pt is that of a face-centred tetragonal lattice; (ii) thin layers of Mg and Zn on Pt also show abnormal crystal structure; (iii) heating of the receiver causes the crystals in the films examined to orient themselves in certain preferred directions; (iv) the metal vapours do not diffract, but scatter the electrons. It is concluded that (i) the abnormal crystal structures are due to pseudomorphic strain effects; (ii) such strain effects are not evident at the surface of sufficiently thick films; (iii) in Al the pseudomorphic strain effects are confined to the two dimensions of the basal planes; (iv) Mg, Zn, and Al vapours are monat. L. L. B.

Crystal parameters of four metals when under reduced pressure. E. A. Owen and E. L. Yates (Phil. Mag., 1933, [vii], **16**, 606—610; cf. this vol., 341).—Measurements on Au, Pt, Pd, and Rh, made without admitting air, after heating to temp. up to 600°, gave the same vals. as after exposure to air. H. J. E.

Rapid method of determining the crystal axes of single-crystal wires of certain metals. R. Roscoe and P. J. Hutchings (Phil. Mag., 1933, [vii], **16**, 703—707).—A method is given for measuring the direction of the elliptical slip-bands for a stretched single-crystal wire of Cd, and deducing the orientation of the crystal axes. H. J. E.

Cadmium azide. L. Birckenbach (Z. anorg. Chem., 1933, **214**, 94—96).—99·5% pure $Cd(N_3)_2$ is as explosive as $Pb(N_3)_2$. It decomposes in vac. at 100—200° into Cd_3N_2 and N_2. No N_3 or $(N_3)_2$ could be detected in the decomp. products by its effect on a Na film. H. J. E.

Adsorption, oriented overgrowth, and mixed crystal formation. C. W. Bunn (Proc. Roy. Soc., 1933, A, **141**, 567—593).—Crystals usually considered as being built up by continual adsorption and inclusion of impurity during growth ("adsorption bodies") are to be regarded as unstable mixed crystals. The application of knowledge on mixed crystal formation to adsorption leads to the suggestion that the condition for strong adsorption is similarity of lattice structure and interat. distances on sp. planes only. This condition is identical with that necessary for oriented overgrowth of different crystals on each other. Evidence is adduced in support of these conceptions. Thus the 100 plane of NH_4Cl is similar to 001 of $CO(NH_2)_2$; reciprocal modification of habit occurs on these faces, and oriented overgrowths can be obtained with these faces in contact. A simple explanation of habit modification is suggested; on the affected faces a mixed crystal is formed, which, being unstable, tends to redissolve, thus reducing the rate of growth. L. L. B.

Pseudo-crystalline structure of water. R. H. Fowler and J. D. Bernal (Trans. Faraday Soc., 1933, **29**, 1049—1056).—Theoretical. E. S. H.

Lattice constants of ferric oxide. S. Katzoff and E. Ott (Z. Krist., 1933, **86**, 311—312; cf. A., 1932, 1079).—Fe_2O_3 prepared from $Fe(NO_3)_3$ has a 5·413$_5$, α 55° 17·$_5$′. C. A. S.

Thallous oxide. F. Halla, H. Tompa, and L. Zimmermann (Z. Krist., 1933, **86**, 303—305).—TlOH was obtained in white needles by evaporating its aq. solution in vac.; these turn yellow below 100°. Its powder diagram is incompatible with the cubic form, and so lends no support to the existence of Pb_2O (cf. A., 1927, 9). 6 days' heating in vac. failed to remove CO_2 from Tl_2CO_3; if melted in vac. in a SiO_2 vessel a bright yellow solid solution of Tl_2O in Tl silicate is obtained on the walls. Tl_2O is distinctly volatile in vac. at 300°. It is not obtained by heating Tl_2O_3. Decomp. of $Tl_2C_2O_4$ yields Tl. C. A. S.

Potassium and cuprous ferric sulphides. H. O'Daniel (Z. Krist., 1933, **86**, 192—202; cf. Pogg. Ann., 1869, **136**, 460).—$KFeS_2$ prepared by melting together $1Fe+6S+5K_2CO_3+1Na_2CO_3$ forms small flexible leaflets; if $6K_2CO_3$ replace $5K_2CO_3+1Na_2CO_3$ minute hexagonal crystals are obtained, d 2·66, $a : c =$ 1 : 0·3939. X-ray: a 13·041, c 5·403 Å., space-group D_{3d}, 8 mols. in hexagonal unit cell. When treated with CuCl–aq. HCl it is slowly and incompletely transformed into $CuFeS_2$ (chalcopyrite) (cf. A., 1932, 682), some $KFeS_2$ apparently remaining in mixed crystals. Probably each crystal of $KFeS_2$ is transformed into a mosaic of minute crystals of $CuFeS_2$. The mechanism of the change is discussed. $CuFeS_2$ is a good, $KFeS_2$ a non-conductor. C. A. S.

Structure of minerals of the stibnite group. W. Hofmann (Z. Krist., 1933, **86**, 225—245; cf. this vol., 214).—Stibnite has a 11·20, b 11·28, c 3·83 Å., with $4Sb_2S_3$ in the unit cell, space-group V_h^{16}. Sb and S atoms alternate in zigzag chains in the direction of the length of the crystals. Co-ordinates of atoms and detailed structure are given, and the connexion thereof with cleavage and twinning is elucidated (cf. A., 1928, 350). Bismuthite is isomorphous, with a 11·13, b 11·27, c 3·97 Å. C. A. S.

Complex chromium and iron carbides. A. Westgren (Nature, 1933, **132**, 480).—The formula of cubic Cr carbide is $Cr_{23}C_6$; space-group O_h^5. The formula of the Cr W carbide (approx. 7 at.-% W) of this type may be written $Cr_{21}W_2C_6$, whilst the Fe W and Fe Mo carbides (this vol., 896) may be regarded as $Fe_{21}W_2C_6$ and $Fe_{21}Mo_2C_6$, respectively, with W and Mo substituted to some extent by Fe. L. S. T.

Crystal structure of some compounds of the type K_2PtCl_6. G. Engel (Naturwiss., 1933, **21**, 704).—The cryst. structure of the salts $A^{I}_{2}B^{IV}Cl_6$, where A = Rb and Cs, and B = Sn, Te, Pt, Pb, has been investigated. All possess a face-centred cubic lattice. Lattice consts. are given. A. J. M.

Crystal structure of nitropentamminocobaltic perchlorate. L. W. Strock (Z. Krist., 1933, **86**, 186—191).—$[CoNO_2(NH_3)_5](ClO_4)_2$ (cf. A., 1923, i, 644), d^{22} 2·275, is orthorhombic hemimorphic, C_{2v},

$a : b : c = 1{\cdot}9135 : 1 : 2{\cdot}4668$. The corresponding nitrate, d^{22} 1·799, is monoclinic hemihedral, C_s, $a : b : c = 0{\cdot}9995 : 1 : 0{\cdot}9646$, β 90° 11′. Both show strong double diffraction. C. A. S.

Crystal structure of carbonatotetramminocobaltic perchlorate. L. W. Strock (Z. Krist., 1933, **86**, 270—279; cf. A., 1932, 1116).—$[CoCO_3(NH_3)_4]ClO_4$, d^{22} 1·8474, is orthorhombic hemimorphic, C_{2v}, $a : b : c = 2{\cdot}2136 : 1 : 0{\cdot}8548$. *X*-Ray: *a* 18·05, *b* 8·10, *c* 6·95 Å., 4 mols. in unit cell, space-group C_{2v}^{7}. C. A. S.

Crystal structure of magnesium platinocyanide heptahydrate. R. M. Bozorth and L. Pauling (Physical Rev., 1932, [ii], **39**, 537—538).—A modification of earlier conclusions (A., 1927, 297). The structural unit, $14{\cdot}6 \times 14{\cdot}6 \times 6{\cdot}28$ Å.^{3}, contains 4 mols. and has a simple tetragonal lattice. Each Pt is regarded as being surrounded by 4 CN at the corners of a square; the Mg are not between the Pt as previously supposed. L. S. T.

***X*-Ray structure of sodium fluorophosphate.** E. W. Neuman (Z. Krist., 1933, **86**, 298—300).—$2Na_3PO_4,NaF,19H_2O$, prepared by dissolving 400 g. Na_2HPO_4, 30 g. NaF, and 13 g. 85% HPO_3 in 450 g. hot H_2O, forms regular octahedra, *d* 2·2165. *X*-Ray: cubic, *a* 27·86 Å., 40 mols. in unit cell, space-group (probably) O_h^{3} (cf. J.C.S., 1885, **47**, 353). C. A. S.

Structure of the crystals of 12-phosphotungstic acid. J. F. Keggin (Nature, 1933, **132**, 351; cf. this vol., 215, 768).—The 12-phosphotungstic acid which crystallises from aq. solutions at room temp. probably contains 30 H_2O to 1 $H_3PW_{12}O_{16}$. The edge of the unit cubic, containing 8 mols. of acid, is $23{\cdot}281 \pm 0{\cdot}002$ Å.; the centres of the acid anions, $(PW_{12}O_{40})'''$ are arranged in positions corresponding with the diamond structure. L. S. T.

Structure of vitreous oxides. W. H. Zachariasen (Physical Rev., 1932, [ii], **39**, 185).—An hypothesis which accounts for the limited no. of oxides which have been prepared in a vitreous form is discussed. L. S. T.

Crystal structure of diaspore. M. Deflandre (Bull. Soc. franç. Min., 1932, **55**, 140—165; Chem. Zentr., 1933, i, 2075).—Diaspore has *a* 4·40, *b* 9·38, *c* 2·83 Å.; space-group D_{2h}^{16}. The unit cell contains $2(Al_2O_3,H_2O)$. A. A. E.

Crystal orientation in parallel-fibre aggregates. W. Jansen (Z. Krist., 1933, **86**, 171—185; cf. this vol., 666).—Laue and rotation photographs of twenty fibrous minerals show structures similar to those of spherulites, save only in fibrous celestite (pseudomorphous after fibrous gypsum) in which there is no orientation. In other cases orientation is accurate to within 1—2°, and usually (in eleven of eighteen cases) along the direction of least identity period. It is due to unidimensional lattice parallelism. C. A. S.

Structure of euclase. J. Biscoe and B. E. Warren (Z. Krist., 1933, **86**, 292—297; cf. A., 1930, 140).—Euclase, $BeHAlSi_2O_5$, is monoclinic, *a* 4·62, *b* 14·24, *c* 4·75 Å., β 79° 44′, 4 mols. in unit cell, space-group C_{2h}^{5}. Detailed structure and co-ordinates of all atoms are given. Each Al is surrounded octahedrally by 5 O and 1 OH, each Si tetrahedrally by 4 O, each Be tetrahedrally by 3 O and 1 OH. C. A. S.

Wöhlerite. B. Gossner and O. Kraus (Z. Krist., 1933, **86**, 308—310; cf. A., 1909, ii, 1028).—Wöhlerite is monoclinic, $a : b : c = 1{\cdot}0523 : 1 : 0{\cdot}7104$, β 109° 3′: *X*-Ray: *a* 10·80, *b* 10·26, *c* 7·26 Å., 2 mols. in unit cell. The formula $NaCa_2[(ZrF)(NbO)](SiO_4)_2$ is suggested, in which ZrF : NbO is approx. 3 : 2 (mol.). C. A. S.

Inclinations of molecules in some crystalline-fluid substances. K. Herrmann (Trans. Faraday Soc., 1933, **29**, 972—976).—*X*-Ray examination shows that in Tl stearate and oleate double mols. are arranged at an angle of inclination to the smectic planes, which is greater in the cryst.-fluid phase than in the cryst.-solid phase. E. S. H.

Rotating molecules and the liquid-crystalline state. *X*-Ray examination of long-chain esters. T. Malkin (Trans. Faraday Soc., 1933, **29**, 977—982).—A study of heating and cooling curves shows that Pr, Bu, and amyl margarates assume the α form more readily than do the corresponding palmitates and stearates. *X*-Ray examination shows that the α forms give only one side spacing of 4·2 Å., whilst the β forms give the two side spacings usually associated with long-chain compounds, thus behaving similarly to the paraffins. The evidence for mol. rotation is discussed, and it is suggested that in the liquid cryst. state the mols. rotate about their long axes, which are perpendicular to the planes formed by the terminal groups. E. S. H.

Arrangement of chain molecules in liquid *n*-paraffins. A. Müller (Trans. Faraday Soc., 1933, **29**, 990—993).—The strong diffraction ring observed appears to be produced by the assembly of the mols. in the liquid, having an average distance of 4·5—5 Å. at temp. near the m.p. E. S. H.

Crystalline phases of some substances studied as liquid crystals. J. D. Bernal and D. Crowfoot (Trans. Faraday Soc., 1933, **29**, 1032—1049).—*X*-Ray crystallographic data have been obtained for *p*-azoxyanisole (two forms), *p*-azoxyphenetole, anisylidene-1 : 5-diaminonaphthalene (two forms), cholesteryl chloride and bromide, dibenzylidinebenzidine, and Et *p*-anisylideneaminocinnamate. The results are correlated with optical observations, which were extended to include Et *p*-*p*′-phenylbenzylideneaminocinnamate and Et_2 *p*-*p*′-xylylidenebisaminocinnamate, and lead to the view that mesophases should be considered as definite stages in the progression from ideal liquid to ideal crystal, rather than as anomalies. E. S. H.

***X*-Ray investigation of the crystal structure of *p*-aminoazobenzene.** M. Prasad and M. R. Kapadia (Indian J. Physics, 1933, **17**, 77—81).—The unit cell has *a* 13·69, *b* 5·604, *c* 14·18 Å., β 81° 49′; space-group C_{2h}^{5}, 4 mols. per unit cell, *d* 1·174. N. M. B.

***X*-Ray investigation of crystals of stilbene and tolane.** M. Prasad (Phil. Mag., 1933, [vii], **16**, 639—640).—Both compounds show a pseudorhombic symmetry (*a* 12·20, *b* 5·72, *c* 29·0 Å., and *a* 12·80, *b* 5·68, *c* 28·4 Å., respectively). The crystals resemble those of azobenzene. The ·N:N· and ·C:C· linkings are equiv. in length, within the errors of experiment. The C:C linking is somewhat longer. H. J. E.

Crystal and optical properties of some aromatic fluorine compounds. W. Faber (Z. Krist., 1933, 86, 161—170).—The following data are given: *d*, crystal system, *a* : *b* : *c*, β (unless 90°), n_α, n_β, n_γ (Na light): 3-fluoro-4-nitrotoluene, 1·43$_8$, monoclinic, 0·994 : 1 : ?, 123° 25′, 1·42, < 1·73, > 1·74; 2 : 2′-difluorodiphenyl, 1·393$_5$, orthorhombic, 0·913 : 1 : 0·870, 1·623, 1·648, 1·713; 4 : 4′-difluoro-2-nitrodiphenyl, 1·488, orthorhombic, 0·703$_7$: 1 : 0·374$_6$, 1·5336, 1·5944, 1·7871; 4 : 4′-difluoro-3 : 3′-dimethyldiphenyl, 1·345, orthorhombic, 0·955$_6$: 1 : 0·604$_1$, 1·5070, 1·697$_9$, 1·816; 4 : 4′-dichloro-3 : 3′-dimethyldiphenyl (m.p. 58—58·5°), 1·330, monoclinic (?), ? : 1 : ?, 1·507, ?, 1·729 (cf. A., 1929, 1051; 1932, 729). C. A. S.

***X*-Ray analysis of the crystal structure of durene.** J. M. Robertson (Proc. Roy. Soc., 1933, A, 141, 594—602).—Durene has *a* 11·57±0·05, *b* 5·77 ±0·02, *c* 7·03±0·05 Å., β 113·3°, space-group C^5_{2h} ($P2_1/a$), 2 mols. per unit cell. The structure is thus similar to the $C_{10}H_8$–anthracene (I) type, but the cell dimensions give no clue to the orientation of the mols., which is deduced directly from the intensity measurements. The mols. are flat or disc-like, as in (I) and C_6Me_6, but the planes of mols. in neighbouring rows are almost perpendicular, instead of being parallel as in C_6Me_6. The closest distance of approach between atoms in adjacent mols. is 3·71 Å., the corresponding val. for (I) being 3·77 Å. L. L. B.

Direction of growth of the needle-like crystals of glucose penta-acetate and cellobiose octa-acetate. K. Hutino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 270—272).—*X*-Ray patterns are shown for the above crystals prepared by pptn. from $CHCl_3$ solution with MeOH. This form consists of parallel, needle-like unit crystals. J. W. S.

***X*-Ray interpretation of the molecular structure of gelatin.** W. T. Astbury and W. R. Atkin (Nature, 1933, 132, 348). L. S. T.

***X*-Ray investigations of natural and regenerated silks.** I. Sakurada and K. Hutino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 266—269).—The lattice structure of silk fibres remains unaltered after dispersion and regeneration. The structures of silks from different insects are compared and discussed. J. W. S.

Theory of liquid crystals. C. W. Oseen (Trans. Faraday Soc., 1933, 29, 883—899).—A mathematical review. E. S. H.

Systems with mixed dimensions. D. Vorländer (Trans. Faraday Soc., 1933, 29, 899—902).—The formation of liquid crystals is particularly favoured by mols. having mixed dimensions (*e.g.*, consisting of a plane with a straight line attached). E. S. H.

Supercrystallinity of *p*-azoxybenzoic acid. D. Vorländer (Trans. Faraday Soc., 1933, 29, 902—906).—*X*-Ray examination shows that powdered *p*-azoxybenzoic acid is not liquid-cryst., but solid-cryst. The prep. of p-*azoxybenzoyl chloride*, m.p. 155°, and *Et* p-*azoxybenzoate*, decomp. > 260°, is described. E. S. H.

Liquocrystalline resins and lacquers. D. Vorländer (Trans. Faraday Soc., 1933, 29, 907—910).—A review of published work. E. S. H.

Polymorphism of liquid crystals. A demonstration. D. Vorländer (Trans. Faraday Soc., 1933, 29, 913—914).—Examples of substances having three or four liquid-cryst. phases are given. E. S. H.

Forces causing the orientation of an anisotropic liquid. V. Fréedericksz and V. Zolina (Trans. Faraday Soc., 1933, 29, 919—930).—Mainly mathematical. Some observations on the behaviour of liquid crystals in electric and magnetic fields are made. E. S. H.

Swarm theory of liquid crystals. L. S. Ornstein and W. Kast (Trans. Faraday Soc., 1933, 29, 931—944).—Theoretical. E. S. H.

Effect of a magnetic field on the nematic state. H. Zocher [with W. Eisenschimmel] (Trans. Faraday Soc., 1933, 29, 945—957).—Mainly mathematical. Nematic conc. solutions of bromo- and chloro-phenanthrenesulphonic acid are exceptions to the rule that optic axes tend to set parallel to the lines of magnetic force. E. S. H.

Alterations in the nature of a fluid from a gaseous to liquid-crystalline conditions as shown by *X*-rays. G. W. Stewart (Trans. Faraday Soc., 1933, 29, 982—990).—*X*-Ray and optical tests agree in showing that the relatively large groups in the liquid crystal do not exist in the liquid, but *X*-ray examination demonstrates the persistence of cybotactic groups in both states. The liquid crystal is regarded as an orderly arrangement of cybotactic groups. E. S. H.

Anisotropic melts: change of state. F. I. G. Rawlins (Trans. Faraday Soc., 1933, 29, 993—994).—Theoretical. E. S. H.

Lyotropic mesomorphism. A. S. C. Lawrence (Trans. Faraday Soc., 1933, 39, 1008—1015).—Observations on both colloidal and crystalloidal solutions (especially of soaps) show that structures can be recognised in the liquids, although they may not be always apparent or highly organised. E. S. H.

Paracrystallinity. F. Rinne (Trans. Faraday Soc., 1933, 29, 1016—1032).—A review of published work on liquid crystals and a discussion of their significance in the study of biological systems. E. S. H.

Physical significance of certain apparent irregularities in the magneto-resistance curves of nickel. M. M. S. Gupta and M. S. Alam (Indian J. Physics, 1933, 17, 9—17).—The negative change in resistance of Ni wire (cf. Stierstadt, A., 1931, 898) depends on the max. field used in a cycle, and is not observed if the max. field applied in a resistance–hysteresis cycle exceeds a certain val. The intersections of parts of the hysteresis curves for demagnetisation appear to be due to a process of electrical conduction, no satisfactory theory being available. N. M. B.

Crystal structure and electrical properties. II. Crystal structure and conductivity of Bi single crystals in transverse magnetic fields. O. Stierstadt (Z. Physik, 1933, 85, 310—331; cf. this vol., 342).—Conductivity in the magnetic field shows the same symmetry as the crystal, and may be used to determine the elementary cell of the crystal system. A. B. D. C.

Magnetic interaction of metal electrons. H. Bethe and H. Fröhlich (Z. Physik, 1933, 85, 389—397).—Polemical, against Frenkel's theory of superconductivity (cf. this vol., 769). A. B. D. C.

Theory of the dependence on pressure of the electrical conductivity of metals. W. Kroll (Z. Physik, 1933, 85, 398—402). A. B. D. C.

Pleochroism and birefringence in crystals. K. S. Krishnan and B. Mukhopadhyay (Nature, 1933, 132, 411). L. S. T.

Pleochroism and the birefringence of the NO_3' ion in crystals. K. S. Krishnan and A. C. Das-Gupta (Indian J. Physics, 1933, 17, 49—66).—Data for the pleochroism, birefringence, and principal refractive indices of KNO_3 crystals in the visible and near ultra-violet are given. The 3000 Å. absorption band due to NO_3' is strongly polarised; it has no influence on the principal refractive indices of the ion. N. M. B.

Magneto-optical rotation of nickel. K. H. von Klitzing (Z. Physik, 1933, 85, 240—252).—Rotation dispersion curves were obtained for the Kerr and Faraday effects up to 3 μ. Zero rotation occurs at 1·5 μ for the Kerr and at 1 μ for the Faraday effect, and this is independent of temp. and field strength. A. B. D. C.

Complex indicatrices of weakly absorbing rhombic minerals. M. Berek and F. Strieder (Z. Krist., 1933, 86, 212—224; cf. A., 1931, 1113).—Using a modification of Berek's microphotometer (cf. A., 1931, 703) the extinction and absorption coeff. along the three principal axes for λλ 6320, 6010, and 5230 of andalusite, cordierite, anhydrite, brookite, and astrophyllite have been determined. From these the positions of the singular optic directions, and the polarisation and absorption axes are deduced for λ 6010. C. A. S.

Allotropism of beryllium. F. M. Jaeger and J. E. Zanstra (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 636—644; cf. this vol., 15).—*X*-Ray powder spectrograms of the α and β forms gave evidence of a new modification, probably a metastable form of ordinary α-Be. N. M. B.

Supposed allotropy of antimony. A. Schulze and L. Graf (Metallwirt., 1933, 12, 19—21; Chem. Zentr., 1933, i, 1563—1564).—Irregularities between 105° and 110° in the electrical resistance and expansion of polycryst. Sb disappear after tempering at 600°; hence they are due to mechanical deformation. *X*-Ray observations at room temp., 150°, and 210° show the same structure. A. A. E.

Correlation of thermo-electric and thermomagnetic data. L. F. Bates (Phil. Mag., 1933, [vii], 16, 657—672; cf. A., 1932, 324).—Mn_3As_2, unheated after its prep., is ferromagnetic up to approx. 45°. Each subsequent transition from the ferromagnetic to the paramagnetic state progressively increases the intrinsic magnetisation and lowers the Curie point until a steady val. is reached. This is correlated with changes in the thermo-electric power. The changes are due to interaction between the spin moment of one atom and the orbital moment of another. H. J. E.

Dependence of the m.p. of carbon tetrachloride on the previous thermal treatment. W. E. Nieuwenhuis (Z. Elektrochem., 1933, 39, 727—731).—The m.p., −22·3°, of purified CCl_4 was unaltered by maintaining the liquid at −20°, 17°, or 45° for a time before making the measurement, or by fractionation. The max. variation was 0·04°. Brüll's results (A., 1932, 1194) were not confirmed. H. J. E.

Specific heat of copper from −78° to 0°. S. M. Dockerty (Canad. J. Res., 1933, 9, 84—93).—The sp. heat of Cu between −78° and 500° (joules per g. per degree) may be calc. to within 0·05% of the observed vals. by means of the equation $C_p=0{\cdot}3889+5{\cdot}65\times10^{-5}T-2000(1-321^2/28T^2+321^4/910T^4)/T^2$, which contains four terms of the Debye expansion. The agreement between the theoretical and observed vals. of the consts. is discussed. H. F. G.

Isopycnals of liquid helium. W. H. Keesom and (Miss) A. P. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 612—615; cf. this vol., 894).—Data as previously reported are continued for the range 25—35 atm. Parts of the solidification curve were determined more accurately; the λ point is at 1·753° abs., and 29·91 atm. N. M. B.

Thermal expansion of niobium. P. Hidnert and H. S. Krider (Bur. Stand. J. Res., 1933, 11, 279—284).—Nb (0·93% Sn, 0·26% Fe), annealed at 400°, has a body-centred cubic lattice (a 3·293±0·002 Å.). The coeff. of expansion, measured between −135° and 305°, increases regularly with rise of temp. H. J. E.

Thermal expansion of electrolytic chromium. P. Hidnert (Physical Rev., 1932, [ii], 39, 186).—Average coeffs. of expansion per degree are recorded for various temp. intervals from 20° to 500°. L. S. T.

Analysis of Slater's compressibility data. H. M. Evjen (Physical Rev., 1933, [ii], 44, 491—500).—Slater's data for the alkali halides (cf. A., 1924, ii, 383) are translated into terms of interionic forces and considered in relation to the variation of interat. forces with interat. distances in crystals. N. M. B.

Viscosity of gases and vapours. R. Plank (Forsch. Ingenieurw., 1933, A, 4, 1—7; Chem. Zentr., 1933, i, 2037).—The dependence of viscosity on temp. and pressure is examined theoretically. A. A. E.

Anomalous viscosity in mesomorphic melts. Wo. Ostwald (Trans. Faraday Soc., 1933, 29, 1002—1005).—Mesomorphic melts of Et *p*-azoxybenzoate, cholesteryl acetate, butyrate, and propionate, in the ranges in which they are anisotropic, show marked structure viscosity, thus indicating a close relation to colloids. E. S. H.

Viscosity of liquid crystals. R. O. Herzog and H. Kudar (Trans. Faraday Soc., 1933, 29, 1006—1008).—Theoretical. E. S. H.

Effect of electrostatic fields on the viscosity of liquids. R. O. Herzog, H. Kudar, and E. Paersch (Naturwiss., 1933, 21, 662).—The effect of an electric field on the viscosity of 17 org. liquids has been investigated and the differences are discussed. A. J. M.

Diffusion coefficients of bromine–argon, bromine–methane, bromine–hydrogen chloride, and bromine–nitrous oxide. J. E. Mackensie and H. W. Melville (Proc. Roy. Soc. Edin., 1932—1933, 53, 255—259).—An extension of previous work (A., 1932, 1081). Visual observations have been checked by photo-electric measurements. H. S. P.

Formation of nuclei from condensed vapours in non-ionised dust-free air. II. System methyl alcohol–water. J. A. Froemke, C. R. Bloomquist, and E. X. Anderson (Z. physikal. Chem., 1933, 166, 305—315; cf. A., 1929, 1234).—The rain point and fog point for H_2O, MeOH, and mixtures of the two have been determined. Condensability is a max. for a mixture of 3 mols. of MeOH with 1 mol. of H_2O. The condensation curves are similar in form to the curves representing the mobility and vol. contraction as a function of the composition. The results support the coalescence theory of drop formation. R. C.

Densities and contraction of binary liquid mixtures. L. A. Alberti (Atti R. Ist. Veneto Sci. Lett., 1932—1933, 92, 1—7; Chem. Zentr., 1933, i, 2064).—Relations between *d*, vol. contraction, and composition are expressed graphically. A. A. E.

Volume contraction in mixtures of nitrobenzene with benzene and with chloroform. G. Bottecchia (Atti R. Ist. Veneto Sci. Lett., 1932—1933, 92, 9—17; Chem. Zentr., 1933, i, 2064).—With C_6H_6–$PhNO_2$ mixtures at 16—40°, max. contraction occurs at approx. 70 wt.-% $PhNO_2$; with $CHCl_3$–$PhNO_2$ mixtures it occurs at 50% (16°) or 65% (40°) $PhNO_2$. The mean coeff. of expansion between 16° and 40° has been calc.; it is min. in the neighbourhood of max. contraction. A. A. E.

Solvent action. VII. Rotatory power of diethyl tartrate in relation to solvent, concentration, degree of association, and temperature. H. G. Rule, (Miss) M. M. Barnett, and J. P. Cunningham (J.C.S., 1933, 1217—1223).—$M[\alpha]^{20}_{5461}$ has been determined in the pure state and in numerous org. solvents. $M[\alpha]$ increases with the polarity of the solvent, and, in the case of non-polar solvents, with the concn. CCl_4, CS_2, and C_6H_{14} give exceptionally high vals., owing to association of the ester. The $M[\alpha]$–T curves for polar and non-polar solvents converge at high temp., the ester itself giving a curve lying between the two extremes. D. R. D.

Diffusion of metals in mercury. F. Weischedel (Z. Physik, 1933, 85, 29—35).—Diffusion coeffs. have been determined for Zn and Cd from electrical conductivity measurements. A. B. D. C.

Diffusion of metals in solid lead. III. Diffusion in gold–lead and silver–lead alloys. W. Seith and A. Keil (Z. physikal. Chem., 1933, B, 22, 350—358; cf. this vol., 669).—Pb is able to form mixed crystals with small amounts of Ag and of Au; solubility data are recorded. Measurements of the rate of self-diffusion of Pb in such mixed crystals show that the rapidity of the diffusion of Au in Pb does not depend on exchange of places of Au atoms and Pb atoms. Self-diffusion is more rapid in mechanically worked than in recryst. Pb; recrystallisation may be delayed by adding 0·03 at.-% of Au or 0·08 at.-% of Ag. R. C.

Dependence of lattice constant on hydrogen concentration in the palladium–hydrogen system. G. Rosenhall (Ann. Physik, 1933, [v], 18, 150—154).—The Pd–H_2 system has been investigated by the *X*-ray method, and the lattice const. obtained for various Pd/H concns. The results indicate the existence of two phases up to 0·64H/Pd, the lattice const. of one phase remaining const. at 4·02 Å., the other at 3·88 Å. Above this limiting concn. the lattice const. increases with increasing concn. Results of other workers are discussed. A. J. M.

Elastic properties of the mixed crystal series Au–Cu and Au–Pd, and the alloys Cu_3Pt, Cu_3Pd, and CuPd. H. Röhl (Ann. Physik, 1933, [v], 18, 155—168).—Previous investigations on single crystals (A., 1931, 900; this vol., 561) have been continued with mixed crystal series in the polycryst. state. Progressive tempering at 203° produces an initial increase in the extension modulus of polycryst. Cu–Au, but this decreases later. The alloys Cu_3Pt and Cu_3Pd show the same superstructure as Cu_3Au. The resistance–concn. diagram for the Au–Pd system has been derived. Extension and torsion moduli in this system do not agree with the mixture rule. The effect of adsorption of H_2 by these alloys on the elastic consts. is considered. A. J. M.

Spectral analysis by sensitive lines within the range of the glass spectrograph. Spark spectra of high-beryllium– and -nickel–iron alloys. W. Kraemer (Physikal. Z., 1933, 34, 714—715).—Results are given for Be–Fe and Ni–Fe alloys, using the apparatus previously described (A., 1932, 35, 355). A. J. M.

Mixed crystal formation with single and polycrystalline materials. E. Schmid and G. Siebel (Z. Physik, 1933, 85, 36—55).—*X*-Ray data show the dependence of the grating const. on particle size for the α-cryst. alloys of Al–Mg, Zn–Mg, and Ag–Cu. The saturation limits of Al–Mg and Ag–Cu are also discussed. A. B. D. C.

***X*-Ray studies on the system (Zn,Cd)–Sb. II.** F. Halla, H. Nowotny, and H. Tompa (Z. anorg. Chem., 1933, 214, 196—200; cf. A., 1930, 147).—The unit cell of Cd_3Sb_2 (monoclinic) has *a* 7·20, *b* 13·51, *c* 6·16 Å., β 100° 14′; and that of ZnSb (rhombic) has *a* 6·17, *b* 8·27, *c* 3·94 Å. Each contains 4 mols. At room temp. crystals of Zn_3Sb_2 are decomposed to Zn and ZnSb. F. L. U.

Constitution of the silver-rich aluminium–silver alloys. N. Ageev and D. Shoyket (Inst. Metals, Sept., 1933. Advance copy, 8 pp.).—The Al–Ag system up to 10% Al has been examined by micrographic and *X*-ray methods. The boundary of the α-phase extends from 5·1% Al at 200° to 6·52% Al at 500° and 6% Al at about 620°, whilst that of the γ-phase extends from 10% Al at 0—200° to about 10·5% Al at 300° and 8·8% Al at 500—600°. Between these two homogeneous fields is a complex region in which α+β, β, and β+γ fields exist above 600°, an α+γ field at 400—600°, and at $<400°$ α+β′ (with $<7·8\%$ Al) and β′+γ (with $>7·8\%$ Al). The β′-phase is Ag_3Al, and above 400° this is converted into α+γ eutectoid. A. R. P.

Constitution of the aluminium-rich aluminium–copper alloys above 400°. D. Stockdale (Inst. Metals, Sept., 1933. Advance copy, 6 pp.).—The solidus at the Al end of the Cu–Al system is very slightly convex to the Al-rich solid solution (κ) and meets the eutectic horizontal at 5·72% Cu, 548° (*A*). The boundary of κ is a straight line from *A* passing through 3% Cu, 462°. No evidence of the existence of $CuAl_2$ could be obtained; an alloy of this composition always contains two phases at $>400°$. A narrow range of solid solutions (θ) exists around 53·5% Cu; this alloy is homogeneous up to 591° and probably melts sharply at this temp. The triple point (θ, θ+liquid, θ+κ) is at 52·47% Cu, 548°. A. R. P.

Solid solutions of lead and tin in bismuth. E. R. Jette and F. Foote (Physical Rev., 1932, [ii], **39**, 1018—1020).—The *X*-ray data recorded show that the Bi lattice changes slightly when saturated solutions of Pb or Sn in Bi are formed. L. S. T.

***X*-Ray investigation of system iron–selenium.** G. Hägg and A. L. Kindström (Z. physikal. Chem., 1933, **B**, **22**, 453—464).—At 50 at.-% Se two intermediate phases occur. One is stable up to some temp. between 300° and 600°, and has the *B* 10 structure and a simple tetragonal unit cell with *a* 3·765 and *c* 5·518 Å. This is not stable for Se contents >50 atoms-%. At higher temp. a phase with the *B* 8 structure exists. After dissolving Se, which results in a considerable lattice contraction, it is stable at lower temp. At about 53 atoms-% Se deformation begins and passes through a max. at 55—56 atoms-% of Se; the orthohexagonal unit cell of the *B* 8 structure becomes a monoclinic cell. At 57·5 atoms-% the upper limit of the homogeneity region is reached, and with larger amounts of Se stable intermediate phases seem not to exist. Solutions of Se in FeSe are of the subtractional type. R. C.

Equilibria in alloyed bronzes. I. Cu–Ni–Sn system. II. Lead–tin bronzes. J. Veszelka (Mitt. berg.-hüttenm. Abt. Hochschule Sopron, 1932, **4**, 162—203; Chem. Zentr., 1933, i, 1674—1675).—I. Alloys up to 15% Ni and 30% Sn have been studied.

II. The solidification and transformation temp. of bronzes are little affected by Pb. A. A. E.

System iron–carbon–silicon. A. Kříža and F. Pobořil (Chem. Obzor, 1932, **7**, 147—151, 165—171, 192—197; Chem. Zentr., 1933, i, 1342).—The eutectic concns. up to 6% Si have been determined microscopically. At 8% Si there is no homogeneous γ-phase. A. A. E.

Molecular compounds in liquid steel and their influence on deoxidation equilibria. P. Herasymenko and F. Pobořil (Coll. Czech. Chem. Comm., 1933, **5**, 331—338).—Thermodynamic considerations afford evidence for the equilibrium $Fe+Si \rightleftharpoons FeSi$. Only the free Si takes part in deoxidation processes. Addition of Mn lowers [Si] owing to the formation of Mn_xSi, where *x* is probably 2 or 3. D. R. D.

Graphical method for converting weight percentage compositions of ternary systems into atomic or molecular percentages. W. Hume-Rothery (Inst. Metals, Sept., 1933. Advance copy, 5 pp.). A. R. P.

Internal friction of liquid mixtures of limited miscibility. I. Ternary system benzene–alcohol–water. II. Binary systems of paraffin oils with water with addition of acids and alkali. M. Pestemer [with M. Birkmann] (Kolloid-Z., 1933, **65**, 25—31).—Viscosity data are given for the systems $EtOH–H_2O$, $EtOH–C_6H_6$, and $EtOH–C_6H_6–H_2O$. A ternary max. occurs at EtOH 10, C_6H_6 55, H_2O 35%. The viscosity max. in the miscibility gap of the $C_6H_6–H_2O$ system is relatively weak. No max. is observed in the system paraffin–H_2O. E. S. H.

Ternary azeotropic systems. III. The heteroazeotrope ethyl alcohol–water–carbon disulphide. W. Swientosławski and E. Wardziński (Rocz. Chem., 1933, **13**, 379—383).—The heteroazeotrope (I), b.p. 41·345°, contains CS_2 92·36, EtOH 6·55, and H_2O 1·09%. The ratio of the coeff. dp/dt for (I) to that for H_2O is 1·05 at $p=1$ atm. R. T.

Solubility of calcium iodate in water and in aqueous solutions of electrolytes. J. B. Chloupek, V. Z. Daneš, and B. A. Danešova (Coll. Czech. Chem. Comm., 1933, **5**, 339—342).—The solubility in H_2O at 25° is 0·303% and is increased by the addition of KNO_3, K_2SO_4, $MgSO_4$, or $MgCl_2$. The solid phase is $Ca(IO_3)_2,6H_2O$. D. R. D.

Solubility of lead chromate. Application to volumetric determination of lead. M. Huybrechts and C. Degard (Bull. Soc. chim. Belg., 1933, **42**, 331—346).—The solubility of $PbCrO_4$ in H_2O measured colorimetrically as PbS is 0·00017 g. per litre at 20°. It is greatly decreased by a slight excess of CrO_4''. The solubility in aq. AcOH and aq. NH_4OAc is $>$ in H_2O. H. S. P.

Active oxides. LXVIII. Solubility of active zinc oxide in ammonia. G. F. Hüttig and H. Schmeiser (Kolloid-Z., 1933, **65**, 77—87; cf. this vol., 774).—The solubility in aq. NH_3 and KOH at 20° of ZnO and its hydrates prepared in different ways has been determined. About 90 min. is generally required for the attainment of equilibrium, although cryst. $Zn(OH)_2$ requires about 1000 min. In general, the solubility is less the higher is the temp. at which the oxide has been heated, and increases with increasing amount of the solid phase to a max. val. ZnO behaves as a mixture of two components having different solubilities. The difference of free energy between these forms is calc. as 700 g.-cal. E. S. H.

Liquid ammonia as a solvent. III. Solubility of inorganic salts at 25°. H. Hunt and L.

Boncyk (J. Amer. Chem. Soc., 1933, 55, 3528—3530).—The data refer to 26 inorg. compounds. Salts with a common ion decrease, whilst those without a common ion increase, each other's solubility. Some correlations are indicated. J. G. A. G.

Optical properties, densities, and solubilities of the normal formates of some metals of group II of the periodic system. F. W. Ashton, D. F. Houston, and C. P. Saylor (Bur. Stand. J. Res., 1933, 11, 233—253).—Crystallographic data, densities, and solubilities from 0° to 100° are recorded for the formates of Ca, Sr, Ba, Mg, Zn, and Cd. The system H_2O–$(HCO_2)_2Mg,2H_2O$ has a eutectic at $-5·05\pm0·03°$ [14·0 g. $(HCO_2)_2Mg$ per 100 g. H_2O]. For the Sr and Cd salts the dihydrate$\longrightarrow$anhyd. salt transition occurs at 72·0—72·5° and 66·0—66·5°, respectively. H. J. E.

Kinetic proof of the law of Berthelot and Jungfleisch concerning the partition of a substance between two immiscible solvents. A. Sconzo (Gazzetta, 1933, 63, 525—526; cf. this vol., 760).—A correction. O. J. W.

Clean-up of hydrogen by magnesium. A. L. Reimann (Phil. Mag., 1933, [vii], 16, 673—686).—1 in every $1·5\times10^6$ mols. of H_2 striking a clean Mg surface at room temp. is adsorbed. The adsorbed gas diffuses slowly into the metal. The formation of at. H by the passage of an electric discharge greatly accelerates the adsorption of H_2 by a Mg film. The ratio of adsorbed H atoms to Mg atoms may be as high as 1 : 6. The adsorbed H exerts a v.p., which increases with concn. and rise of temp. The H is also liberated by bombardment with electrons with velocities as low as 4 volts, or by CO^+ ions. H. J. E.

Adsorption. V. Sorption of vapours by activated charcoal. L. J. Burrage (Trans. Faraday Soc., 1933, 29, 665—672; cf. this vol., 898).—The effect of the C_xO_y complex existing at the surface of C on the sorption of H_2O vapour has been studied. The H_2O isothermal at 25° and 23·76—8 mm. consists of a series of steps. When the pressures at which the breaks occur are plotted against their sequence a smooth curve is obtained, especially after flushing out the system (cf. B., 1929, 153). A similar course has been observed in the CCl_4 isothermal at pressures $<$ 4 mm. Little C_xO_y is removed by evacuating at 110°. Evacuation at 800° "cleans up" a large no. of pores, giving rise to an increased adsorptive area; the C_xO_y is then removed as CO, whilst it is removed as CO_2 when the system is flushed out at 100°. E. S. H.

Change in the form of [adsorption] isotherms in the progressive activation of charcoal. B. Bruns and O. Zarubina (Kolloid-Z., 1933, 46, 279—287).—When C is activated by heating at 850° in a current of CO_2, its adsorptive power for vapours of C_6H_6, Et_2O, and H_2O and for aq. solutions of BuOH, $PrCO_2H$, and PhOH increases progressively with the duration of activation for saturated systems. At lower pressures or concns. the adsorptive power reaches a max. when about 30—50% of C has been lost by combustion. The mechanism of activation is discussed. E. S. H.

Prolongation of life of β-chloro-β-phenylethylamine on charcoal. H. Freundlich and G. Salomon (Z. physikal. Chem., 1933, 166, 179—204).—The adsorption of $CHPhCl\cdot CH_2\cdot NH_2,HCl$ and of $CH_2Br\cdot CH_2\cdot NH_2,HBr$ from aq. solution on blood charcoal at 0° and 25° follows Freundlich's isotherm and with each the cation is adsorbed more than the anion. The conversion of $CHPhCl\cdot CH_2\cdot NH_2$ (I) into styreneimine hydrochloride (II) in NaOH solution is strongly retarded by C at 25°. The unimol. velocity coeff., *k*, decreases as reaction proceeds until the concn. of (I), *c*, falls to a certain val. which, for a given proportion (*m*) of C, is independent of the initial concn., *a*; *k* subsequently remains const. The initial fall in *k* is the more pronounced for a given *m* the higher is *a*. For a given *a* the retarding action of the C increases rapidly with *m*. The retardation is ascribed to the mols. in the unimol. film being oriented so that the reacting groups, Cl and NH_2, rarely come in contact; the only mols. which react are those which reach the interior of the liquid phase. Corresponding with this theory the retardation diminishes rapidly with rise of temp. In the first phase of the reaction, when *x* is larger, multimol. films are present, and to these and to the non-homogeneous character of the C surface are attributed the peculiarities of this part of the reaction. The formation of (I) from (II) in HCl solution is accelerated by C, and in neutral solution the equilibrium is displaced in favour of (I). The reaction of $CH_2Br\cdot CH_2\cdot NH_2$ (A., 1930, 551) occurs, not within the liquid phase, but on the C surface. R. C.

Adsorption of gases on palladium oxide. P. V. McKinney (J. Amer. Chem. Soc., 1933, 55, 3626—3632; cf. this vol., 134, 913).—Between −78° and 218°, O_2 is not adsorbed either by PdO or by PdO partly reduced by CO. CO_2 is adsorbed reversibly, but the adsorption decreases with increased reduction. Adsorption of CO on PdO is physical, but that on Pd is activated at −78°. Chemical adsorption of CO on PdO increases slowly from 0° to a max. at 110° and the gas evaporates only as CO_2, desorption being incomplete below 218°. The rates of adsorption indicate a complex process, and the adsorption of CO by Pd is so strong that reduction of adjacent PdO is not accelerated. J. G. A. G.

[Adsorption of] atomic hydrogen on glass and calcium fluoride. J. H. de Boer and J. J. Lehr (Z. physikal. Chem., 1933, B, 22, 423—430).—On glass about 3×10^{15} atoms are adsorbed per sq. cm., a monat. film being formed. A vac.-sublimed CaF_2 film takes up more H and retains it more tenaciously, and adsorption is more rapid. The H is released only on heating, presumably due to sintering which reduces the surface area of the CaF_2. R. C.

Relation between van der Waals and activated adsorption on chromium oxide gel. J. Howard (Nature, 1933, 132, 603).—Low-temp. van der Waals isotherms have been determined for Cr oxide gel on which a known amount of high-temp. adsorption of H_2 (I) had taken place. (I) markedly diminishes the van der Waals adsorption. Slow adsorption, often described as chemical, secondary, or activated, is thus a true surface phenomenon. L. S. T.

So-called negative adsorption and vapour-pressure isotherms with permutites and clays. P. SZIGETI (Kolloid-Beih., 1933, **38**, 99—176).—Negative adsorption is observed with permutites and clays only when the substances have been dried at 110°. In a series of chloride solutions the extent of negative adsorption increases with the hydration of the cation (alkali or alkaline earth) of the adsorbent. The phenomenon is also observed in solutions of sucrose or EtOH. In all cases the degree of adsorption increases with dilution. The cause of the phenomenon is attributed to incipient dehydration during drying, resulting in a subsequent transfer of H_2O from the aq. phase. The H_2O v.-p. isotherms show that at equal v.p. the H_2O content of the permutites and clays increases with the degree of hydration of the cation, and is always greater for the permutites; the exponent of the Freundlich isotherm is also greater for permutites. A hysteresis between hydration and dehydration is established only for H-permutite. The modes of binding of the H_2O are discussed.
E. S. H.

Sorption of water by asbestos fibre. L. M. PIDGEON and A. VAN WINSEN (Canad. J. Res., 1933, **9**, 153—158).—The relative humidity (R.H.)-% H_2O curve is sigmoid, but no hysteresis is observed between R.H. 30% and 79%; at 90% R.H. the sorption is 2·5%. Below 70% R.H. equilibrium is reached in a few min. and the vals. agree with the adsorption isotherm $x/m=kp^{1/n}$; above 70% R.H. equilibrium is reached more slowly, and sorption increases more rapidly owing to condensation of liquid in the capillaries.
A. G.

Sorption of organic vapours by resinous and cellulosic materials. C. H. WINNING and J. W. WILLIAMS (J. Amer. Chem. Soc., 1933, **55**, 3560—3569).—The adsorption of $CHCl_3$ vapour by glyptal, phenophthalein benzoate, benzylcellulose, and cellulose acetate and of Et_2O by natural resins is succeeded by condensation of sorbate in capillary spaces, the capillaries being opened up when the structural units have been completely covered with sorbate mols. Sorption and desorption are not reversible, and although the cellulose derivatives afford closed hysteresis curves, the reduction of the partial pressure of vapour to very low vals. over the resinous materials causes only partial, if any, desorption. Regular arrangement of mols. in the sorbent is believed to favour almost complete removal of sorbed vapours at low partial pressures, whilst random arrangement may lead to conditions resulting in retention. The heats of the several sorption processes have been calc.
J. G. A. G.

Behaviour of the barium sulphate micelle towards Congo-red. E. R. RIEGEL and J. RIDSON, jun. (Kolloid-Z., 1933, **64**, 304—307).—The micelle $(BaSO_4)_xBa^{\cdot\cdot}$ adsorbs the anion of Congo-red, forming a red ppt., whilst no adsorption occurs with the micelle $(BaSO_4)_xSO_4''$. The micelles may thus be separated. The system should be adjusted to p_H 3·3—3·5.
E. S. H.

Exchange of cations by sulphite-cellulose. C. DU RIETZ (Svensk Kem. Tidskr., 1933, **45**, 185—195).—Cellulose (I), although insol. in H_2O, is characterised by an acid group analogous to permutite. Sulphite-(I) has a very strong acidic group (HSO_3) capable of quantitatively accepting cations, a weakly acidic group (probably CO_2H), and a very weak acidic group (probably of a phenolic nature). In agreement with the Donnan membrane equilibrium the partition of equi-valent ions in (I)–H_2O systems is independent of changes in the concn. of the external phase; the absorption of these ions with the greatest valency is, however, favoured. Thus sulphite-(I) partly saturated with $Na^{\cdot}$ readily takes up $Cu^{\cdot\cdot}$ (cf. B., 1931, 670; 1932, 222) and the $Cu^{\cdot\cdot}$ ions are less easily removed by subsequent washing than the $Na^{\cdot}$ ions. The "total lignin acid" can be determined by rapid treatment with $Cu^{\cdot\cdot}$, washing with H_2O, pulping in aq. KCNS in presence of KI, and titrating with $0{\cdot}01N$-$Na_2S_2O_3$.
F. O. H.

Effect of glycerol on absorption of lactic acid by gels. L. J. WEBER and A. N. RAO (Biochem. Z., 1933, **262**, 119—130).—Absorption of H_2O by gelatin gels (I) is markedly inhibited by glycerol (II), but is increased by lactic acid (III), and the swelling of (I) by (III) in high concns. can be prevented by addition of (II). Diffusion of H_2O or (III) into (I) is inhibited by increasing concns. of (II) in (I), but the absorptive power of (I) for (III) is little affected by the (II) concn. of the solution. Gelatin sols behave like (II) and natural membranes like (I). W. McC.

Capillary systems. XVI (1). Passage of a jet of material particles through a framework. E. MANEGOLD and W. VON ENGELHARDT (Kolloid-Z., 1933, **64**, 307—316; cf. this vol., 774).—Mathematical.
E. S. H.

Theory of the phenomenon of liquid drops on the surface of the same liquid. L. D. MAHAJAN (Kolloid-Z., 1933, **65**, 20—23).—The conditions for the formation of a film of air or other medium between a drop and a flat surface of the same liquid are discussed.
E. S. H.

Surface solutions. Two-dimensional liquids and unimolecular layers. A. MARCELIN (Kolloid-Beih., 1933, **38**, 177—336).—A comprehensive survey of published work on surface films on H_2O, Hg, and solid surfaces.
E. S. H.

Oriented molecules at the solid–liquid interface and the non-specific nature of ordinary adsorption. W. D. HARKINS (Physical Rev., 1932, [ii], **39**, 190).—The heats of immersion (I) of different powdered solids in a series of liquids are approx. equal when no chemical reaction occurs, and the heat evolved may be considered as due, in general, to non-sp. or non-chemical forces. The large increase in (I) produced by addition of polar groups shows that the mols. at the interface are oriented with their polar groups towards the solid and their non-polar groups towards the liquid.
L. S. T.

Preparation and properties of thin films of lead sulphide, with special reference to their detector action. I. G. BRÜCKMANN (Kolloid-Z., 1933, **65**, 1—11).—Mirrors of PbS are formed by mixing solutions of 4% $Pb(OAc)_2$, 2% $CS(NH_2)_2$, and 2% NaOH. The reaction depends on the catalytic decomp. of a complex salt of $Pb(OAc)_2$ and $CS(NH_2)_2$;

the temp. coeff. is 2·3. Compounds of As, Sb, or Sn, which form sulphides sol. in NaOH, retard the process, whilst particles of dust or of ppt. accelerate it. The amount of PbS pptd. is proportional to the surface; the nature of the surface on which the mirror is deposited has no influence, except with Cu, brass, and bronze, when some Cu_2S is formed. The amount of ppt. is greater when nuclei are already present on the surface. The theory of mirror formation is discussed. E. S. H.

Wetting experiments on hydrophilic and hydrophobic powders in a system of two nonmiscible liquids. III. E. Berl and B. Schmitt (Kolloid-Z., 1933, 65, 93—100).—The condition for the separation of two powders by shaking with two immiscible liquids is a difference in wettability of the powders, but this property may be affected in either direction by the presence of a selectively adsorbable substance. A mixture of C and SiO_2 can be separated by shaking with C_6H_6–H_2O mixture, but not when crystal-violet is added; on the other hand, C and $CaCO_3$ can be separated by adding "Tuchrot-*C*." The separation of PbS and ZnS depends on the age of the powder mixture, as the relative wettability is thereby affected; separation of old mixtures may be effected by adding K Et xanthate. A mixture of ZnS and $CaCO_3$ can be separated by K Et xanthate after addition of $CuSO_4$. E. S. H.

Solid–liquid–air angles and their dependence on the surface condition of the solid. F. E. Bartell and A. D. Wooley (J. Amer. Chem. Soc., 1933, 55, 3518—3527).—Corresponding angles of contact are calc. from the heights of columns of 1-$C_{10}H_7Br$ and $C_2H_2Br_4$ advancing and receding in Pyrex and SiO_2 capillaries which have been subject to various pretreatments. Receding angles, *R*, are largely independent of pretreatment and are equilibrium vals. characteristic of the given solid–liquid pair, whereas advancing angles, *A*, are very sensitive criteria of the condition of a solid surface, since a particular pretreatment affords a sp. reproducible val. of *A* for a given liquid. *A* falls rapidly during 1 hr. to a const. val. which decreases, with rise in the temp. of the heat-treatment, to a val. equal to *R* for the particular solid–liquid pair. The contact angle formed by an advancing or a receding liquid is apparently characteristic of the system as it then exists, and thus the contact angle is a very sensitive criterion of the actual energy relations. J. G. A. G.

Surface tension and complex formation in non-aqueous solutions of salts. P. P. Kozakevitsch and N. S. Kozakevitsch (Z. physikal. Chem., 1933, 166, 113—135).—The surface tension, γ, of solutions of electrolytes and non-electrolytes in various org. solvents has been measured at room temp. For most solutions γ increases linearly with the concn., *c*, at the higher concns., and the departure from linearity in dil. solutions is the more marked the greater is the tendency of the salt to complex formation. Since γ is influenced by several factors, there is rarely any discernible connexion between γ and the surface tension of the pure solute. The degree of dissociation of a salt, so far as it increases the no. of dissolved particles, influences the negative surface activity, *A*, comparatively slightly. Particularly in conc. solutions, *A* runs parallel with the degree of solvation of the undissociated salt mols., *B*. Whilst the cations follow the normal lyotropic series, $Li > Na > K$, the anion series is reversed, $I > Br > Cl$, owing to the lyotropic effects being determined by *B*, which is itself decided by the principle of ionic competition (A., 1931, 1231). For solutions in homologous series of alcohols, *A* decreases with increase in the no. of C atoms. The higher alcohols and EtOH have a differentiating action on various salts in so far as *A* is concerned. The γ–c curve of C_5H_5N–HCO_2H mixtures has a max. corresponding with the compound $C_5H_5N,4HCO_2H$. R. C.

Osmosis in systems consisting of water and tartaric acid and containing three liquids, separated by two membranes. II. F. A. H. Schreinemakers and H. H. Schreinemachers (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 629—635; cf. this vol., 459).—The influence of the position of the cellophane and pig's bladder membranes, and the use of a compound membrane of the two, were investigated. N. M. B.

Osmotic pressure and viscosity of cellulose nitrate solutions. E. H. Buchner and H. E. Steutel (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 671—677).—The osmotic pressure is not proportional to the concn., even in dil. solutions, and is assumed to consist of two parts, one proportional to the mol. concn., and one representing the interaction with the solvent ($COMe_2$). The viscosity relations are normal. N. M. B.

Calcium oxalate rings. A peculiar case of periodic precipitate formation. H. Döring (Naturwiss., 1933, 21, 675).—Rings of CaC_2O_4 have been observed under the microscope when a scale leaf of onion (*Allium cepa*) is treated with $0{\cdot}1N$-$K_2C_2O_4$. This is an example of non-colloidal periodic pptn., and is a transition between periodic separation of crystals in capillaries and Liesegang rings. A. J. M.

Change of the refractive index of mixtures of ketones and alcohols by small amounts of acid. T. Tomonari (J. Soc. Chem. Ind. Japan, 1933, 36, 485—487b).—Amounts of mineral acids or of AcOH > about 0·0002% change the *n* of mixtures of MeOH with $COMe_2$ or *cyclo*hexanone, but not of the pure substances. This is the cause of the change produced by impure cellulose nitrate. A. G.

Properties of quinine dissolved in absolute alcohol. C. Lapp (Arch. phys. biol., 1932, 10, 42—66; Chem. Zentr., 1933, i, 2254).—Polarimetric and viscosity measurements are reported. The no. of EtOH mols. combined with 1 mol. of quinine increases from 8·1 in a 10·1% solution to 35·4 in a 0·31% solution. Forty EtOH mols. are supposed to form a unimol. layer on the surface of a quinine mol. A. A. E.

Terpenes, sesquiterpenes, and related compounds. III. Molecular depression of the f.p. of camphene. IV. Fusion diagrams of the systems camphene–naphthalene and camphene–diphenyl. S. Uchida and K. Shimoyama (J. Soc. Chem. Ind. Japan, 1933, 36, 525—527b, 528—529b).

—III. The difference between the limiting vals. for camphene in $C_{10}H_8$ and Ph_2 may be due to the formation of solid solutions.

IV. The diagrams are discussed. J. L. D.

Manganous sulphate. F. Hammel (Compt. rend., 1933, 197, 684—686).—Cryoscopic determinations with aq. $MnSO_4$ show no differences when different hydrates, or differently prepared sample of anhyd. $MnSO_4$ (cf. A., 1932, 32), are used. C. A. S.

Determination of the size of ultramicroscopic particles by the interference microscope. A. Klimmeck (Z. Physik, 1933, 85, 68—84). A. B. D. C.

Lower limit of particle size in disperse systems. Gogoberidze (Kolloid-Z., 1933, 65, 24—25).—The lower limit is expressed by $2\alpha\partial/(p'-p)(1033-\partial)$, where p' and p are respectively the v.p. over curved and plane surfaces, α is the surface tension, and ∂ the v.d. The limit rises with rising temp. E. S. H.

Application of the centrifuge to the classification of suspensoids according to their size. S. A. Kamenetzki (Gorno-Obogat. Delo, 1932, No. 2—3, 77—79). Ch. Abs.

Influence of convection on Brownian movement. III. M. Satô (Z. Physik, 1933, 85, 403—408).—The effect of convection becomes appreciable only in rarefied gases. A reply is given to Sitte (cf. this vol., 901). A. B. D. C.

Size of electrolytically generated gas bubbles. B. Kabanov and A. Frumkin (Z. physikal. Chem., 1933, 166, 316—317).—Wark's calculations of the size of gas bubbles (B., 1933, 631) agree with the authors' results (this vol., 1016). R. C.

Rate of settling of a suspension as a function of the concentration of the suspensoid. N. A. Held (Gorno-Obogat. Delo, 1932, No. 9, 3—10).—In suspensions containing $\not> 10^7$ particles per c.c. the rate of settling follows Stokes' law; in those containing 10^7 to 10^9 partial coagulation occurs, and the rate of settling has no definite val., whilst in those containing 10^9 to 10^{11} coagulation is complete and the rate of settling depends on the concn. In the second and third groups introduction of a stabiliser, *e.g.*, OH′, displaces the regions of partial and complete coagulation towards higher concns. In the first group the rate of settling is independent of the presence of sol. salts, coagulation being accomplished only by raising the temp. Ch. Abs.

Preparation and properties of silver sols by reduction of silver halides with formaldehyde. T. I. Taylor and W. H. Cone (J. Amer. Chem. Soc. 1933, 55, 3512—3515).—Stable reddish-yellow to ruby-red Ag sols are obtained by adding slowly, with vigorous stirring, 250 c.c. of 0·0004*N*-KBr (or KI) to 250 c.c. of 0·004*N*-$AgNO_3$, followed successively by 10 c.c. of 2% aq. CH_2O and 100 c.c. of 0·03*M*-NaOH. Cataphoretic velocities, conductances, and pptn. vals. are recorded. With the exception of Cl′, anions which normally form a Ag salt of solubility < 0·002 g. per 100 g. of H_2O stabilise the colloid. The adsorption of Cl′, Br′, and I′ by colloidal Ag is in the ratio 1 : 2 : 57·7; this is discussed with reference to the structure of the sol particles. J. G. A. G.

Colloidal sulphur solutions [prepared] by the action of iodine on sodium sulphide. A. Janek (Kolloid-Z., 1933, 65, 87).—S sols may be prepared by adding a 5% solution of I in EtOH to dil. aq. Na_2S, but are stable for only 24—36 hr. E. S. H.

Pupa oil emulsion. I. Properties of dispersed system obtained by boiling dried pupa with water. H. Kaneko and K. Yamamoto (Bull. Sericult., Japan, 1933, 6, 3—4). E. S. H.

Viscosity of emulsions. E. G. Richardson (Kolloid-Z., 1933, 65, 32—37).—The viscosity of various conc. C_6H_6-in-H_2O and H_2O-in-C_6H_6 emulsions has been determined by the Couette method. The former show marked structure viscosity. The variation with concn. is given by $\eta=\eta_0 e^{k\phi}$, where η_0 and η are the viscosities of the dispersion medium and emulsion, respectively, ϕ is the vol. of the disperse phase, and k varies with the particular system. E. S. H.

Viscosity of ferric phosphate sol at different pressures. S. N. Banerji and S. Ghosh (Kolloid-Z., 1933, 65, 37—44).—The variation of viscosity of $FePO_4$ sols with pressure is greater the purer is the sol. With progressive dialysis the sol becomes unstable and its viscosity increases. The increase of viscosity with increasing concn. is > a linear function, but becomes more linear at higher pressures. The true viscosity is not measured; the property is defined as the "structure-flow coeff." for a given pressure. The viscosity increases with time and with the presence of electrolytes. The "solid" properties of highly viscous lyophilic sols are attributed to orientation of the micelles. E. S. H.

Viscosimetric investigations on solutions of high-molecular natural substances. I. Rubber in toluene. M. Reiner and R. Schoenfeld-Reiner (Kolloid-Z., 1933, 65, 44—62).—Solutions of crêpe rubber in PhMe of concn. 0·08—1·77% exhibit structure viscosity and deviate from Poiseuille's law. Below the limit specified the solutions behave as Newtonian liquids. The results are shown to be independent of the viscosimeter and are unaffected by temp. The phenomena cannot be explained by streaming orientation, but there is probably a relatively strong cohesive force between the particles of rubber. E. S. H.

Viscosity and elasticity of sols. B. Rabinovitsch (Z. physikal. Chem., 1933, 166, 257—269).—Solutions of cellite in dioxan, MeOAc, and furfuraldehyde have been examined in capillary viscosimeters. Over a wide range of pressures and capillary radii and lengths the flow is laminary and stationary. The relation between deformation velocity and shearing stress, P, is $\partial v/\partial r=UP+VP^3$, where U and V are consts. of the material and are independent of the solvent (cf. A., 1930, 32). For low vals. of P this becomes Newton's law. From U and V the viscosity, the modulus of elasticity, and the period of relaxation can be calc. The most dil. sols seem to have the properties of a swollen solid rather than a dil. solution. R. C.

Viscosity of colloids in presence of electrolytes. S. Gopala and K. Murty (Kolloid-Z., 1933, 64, 319—320).—Theoretical. The change of vol. and rigidity of the particles of a sol under the influence of additions of electrolytes is held to explain the observed changes of viscosity. E. S. H.

Structure of emulsoid sol particles and their hydration film. N. H. Kolkmeijer and J. C. L. Favejee (Nature, 1933, **132**, 602—603).—The majority of the *X*-ray lines of powdered cellulose and starch are probably due to the crystal structure of the hydration film surrounding the particles and not to the substance itself. The H_2O film has the structure, more or less deformed, of ordinary ice. L. S. T.

Emulsions. I. J. B. Parke and H. Graham (J.C.S., 1933, 1214—1217).—The effect of the addition of H_2O on the viscosity of the following emulsions has been examined: C_6H_6–Na oleate (I)–H_2O; tetrahydronaphthalene (II)–(I)–H_2O; C_6H_6–sulphonated fish oil (III)–NaOH–H_2O; (II)–(III)–NaOH–H_2O. In the case of emulsions stabilised by (I) the η–% H_2O curves are smooth, but with (III) there is an abrupt change of η when about 25% of H_2O has been added and a smaller one at approx. 60% H_2O. These changes are correlated with the formation of multiple emulsions preceding a change in the type of emulsion. D. R. D.

Electrical properties of colloids. III. Discrepancies between activity and conductivity in colloid solutions. J. Mukherjee (Kolloid-Z., 1933, **65**, 72—77; cf. this vol., 460).—The Cl′ activity of $Al(OH)_3$ sols has been determined by means of the Ag–AgCl and Hg–Hg_2Cl_2 electrodes. Concordant vals. are obtained by these methods. Discrepancies between observed and calc. activities are shown by this system and also by SiO_2 sol containing NaCl. E. S. H.

Physico-chemical investigations on ferric oxide sols. I. Charge of ferric oxide sols on dilution. II. Charge in irregular series. A. Lottermoser and T. Y. Chang (Kolloid-Z., 1933, **64**, 268—279; **65**, 62—72).—I. Determinations of migration velocity, electrical conductivity, and [Cl′] of $Fe(OH)_3$ sols show that when the sols are diluted with the ultra-filtrate the ζ potential remains unchanged, whilst the dissociation of the colloidal electrolyte increases. When the sols are diluted with H_2O, Cl′ is transferred from the particles to the liquid medium, so that const. [Cl′] is maintained over a wide concn. range, and the ζ potential falls.

II. An electrophoretic investigation of the electrical properties of positively-charged $Fe(OH)_3$ sols shows that as KH_2PO_4 is gradually added the ζ potential is lowered, flocculation beginning at a crit. potential, whilst with excess of KH_2PO_4 peptisation occurs, forming a negatively-charged sol, the charge of which is reduced at still higher concns. of KH_2PO_4. $H^{\cdot}$ and OH′, introduced by the KH_2PO_4, do not influence the course of the phenomena. Up to the discharge point Cl′ is liberated from the particles progressively in exchange for PO_4''', but thereafter PO_4''' is adsorbed without exchange until the sol acquires its max. negative charge, after which the amount of adsorbed PO_4''' remains const. E. S. H.

Variation of the charge of copper ferrocyanide hydrosol in presence of electrolytes and non-electrolytes. S. G. Chaudhury (J. Indian Chem. Soc., 1933, **10**, 431—452).—The influence of the method of prep., of centrifuging, and of adding electrolytes, *e.g.*, KCl, with and without EtOH on the cataphoretic velocity of $Cu_2Fe(CN)_6$ sols has been investigated. The results may be qualitatively explained on the basis of Mukherjee's double layer theory. An increase of the velocity is possible without adsorption of similarly charged ions or increase of the dielectric const. Coagulation cannot be regarded as occurring at a crit. potential, and different electrolytes at concns. having the same coagulating effects do not necessarily depress the charge on the colloidal particles to the same extent. H. F. G.

Cataphoretic behaviour of gas-charged particles. A. Pilojan, N. Krivorutschko, and N. Bach (Kolloid-Z., 1933, **64**, 287—293).—Platinised and non-platinised C activated in air at high temp. give positively-charged particles in presence of air in H_2O, dil. HCl, or NaOH. In higher concns. of NaOH a reversal of charge may occur, probably by reason of the formation of a surface layer of acid oxide. After activating in air at 400° for 15 hr. C is negatively charged, but the charge is reversed by $La^{\cdot\cdot\cdot}$ or $Th^{\cdot\cdot\cdot\cdot}$. Platinised C which has been heated in H_2 is negatively charged in H_2O, dil. HCl, or NaOH, and is converted into a positive suspension by adding $Th^{\cdot\cdot\cdot\cdot}$. With sufficient Pt content, the charge of positively-charged particles may be reversed by admitting an atm. of H_2. E. S. H.

Isoelectric point of orange-seed globulin. D. C. Carpenter and F. E. Lovelace (J. Amer. Chem. Soc., 1933, **55**, 3738—3740).—The electrophoretic velocity of the globulin (prep. described) is measured in citrate and phosphate buffers at p_H 1·5—7·8, and the electrical charge on the particle calc. The isoelectric point is at p_H 5·23 or c_H $5{\cdot}9\times10^{-6}$. H. B.

Colloidal chemical analysis. II. J. Mukherjee, S. Roychoudhury, S. K. Das-Gupta, A. K. Sen, B. Mazumdar, and A. Chatterjee (J. Indian Chem. Soc., 1933, **10**, 405—430; cf. A., 1931, 1123).—The observed sp. conductivities of $Fe(OH)_3$ sols are much > the vals. calc. from the activity measurements, and it is improbable that the high vals. are entirely attributable to the (unknown) [$H^{\cdot}$], whilst with $Al(OH)_3$ sols the observed vals. are the lower and cannot be explained on the assumption that the current carried by the colloidal particles and associated mobile ions is determined by the cataphoretic speed and free charge. With SiO_2 sols approx. agreement between the two sets of vals. is obtained. In SiO_2 sols containing NaCl the activity of the $H^{\cdot}$ rises more rapidly than the sol concn. as the latter is increased, although the total electrolyte concn. corresponds with that of a dil. solution. The significance of these results is not yet apparent. H. F. G.

Magnetic properties of nickel colloids. C. G. Montgomery (Physical Rev., 1932, [ii], 39, 163—164).—Magnetic data for sols prepared by dissociating Ni carbonyl dissolved in C_6H_6, PhMe, and *p*-

cymene and by the Bredig method in H_2O and in $Pr^{\beta}OH$ are recorded for fields of 3760 and 3500 gauss, respectively. The uncombined Ni ranges from 0·75 to 14·2%. A possible explanation is advanced.
L. S. T.

Study of coagulation by the coagulograph. R. Procházka (Chim. et Ind., 1933, 29, Spec. no., 281—283).—The separation of O_2 has been examined by means of a dropping Hg electrode. C. W. G.

Nephelometric studies of coagulation processes caused by acceleration of hydrolysis by heating. T. Katsurai (Kolloid-Z., 1933, 64, 317—319).—The turbidity of aq. $AlCl_3$, $MnCl_2$, and $CoCl_2$ is increased by heating at $>$ 160° and cooling, whilst aq. $NiCl_2$, $CrCl_3$, and $Pb(NO_3)_2$ show no change. The turbidity of aq. $FeCl_3$ is reduced by adding NaCl, $BaCl_2$, or $AlCl_3$, the effect increasing in the order given. E. S. H.

Influence of hydrophilic colloids and adsorbent substances on the solubility of sparingly soluble substances. II. Influence of gum arabic. H. Brintzinger and H. G. Beier (Kolloid-Z., 1933, 64, 300—304; cf. this vol., 902).—Gum arabic increases the solubility in H_2O of BzOH, salicylic acid, cinnamic acid, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, hippuric acid, *o*- and *p*-$C_6H_4Br{\cdot}CO_2H$, camphoric acid, anisic acid, and strychnine, decreases that of anthranilic acid, and has no influence on the solubility of *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. E. S. H.

Continuity of phases during the sol–gel transformation. S. Prakash (Kolloid-Z., 1933, 64, 293—300).—The phase rule is applied to colloid systems, assuming an additional degree of freedom due to the electric charge. A two-component gel is in equilibrium at a quintuple point. Experiments on the dehydration, and variation of $[H^{\cdot}]$, viscosity, electrical conductivity, and opalescence during the sol–gel transformation of $Ce(OH)_3$, $Zr(OH)_4$, $Al(OH)_3$, Th arsenate, phosphate, and molybdate afford no evidence of discontinuity. E. S. H.

Changes of surface and structure of gels and minerals at high temperatures. J. Splichal (Chim. et Ind., 1933, 29, Spec. no., 757—781).—SiO_2 gels partly dehydrated at temp. up to 500° were tested for adsorptive power (I) over 10% H_2SO_4 at room temp. For unheated samples (I) varies according to method of prep. and age. It falls but little up to 250°, but is much less at 500°, which reduces the effective surface. Similar tests show that (I) is considerable for a siliceous earth, but very small for crushed rocks consisting of SiO_2. Ignition at 1000° does not affect the structure as shown by *X*-ray analysis, but (I) is destroyed. There is no sign of tridymite rays. At higher temp. cristobalite is formed. Al_2O_3 gel still absorbs 20% H_2O after heating at 500° and (I) is still evident after heating at 1000°. Definite interference rings were not found below 1000°, when those of corundum appeared. The region of stability of γ-Al_2O_3 is thus more limited than is usually believed. Bauxite adsorbs much less H_2O than Al_2O_3 gel, and böhmite, Al_2O_3,H_2O, is the principal product. Fe_2O_3 gels heated at 200° show considerable absorption, but at 250° transformation into hæmatite occurs, with a sharp reduction in the H_2O adsorbed. Samples of natural limonite etc. studied were found to be solid solutions of α-Fe_2O_3,H_2O (goethite) and H_2O. C. I.

Morphology of chemical reactions in colloidal media. IV. Significance of auto-form catalysis and form catalysis in colloidal media in explanation of morphological phenomena. F. M. Schemjakin (Kolloid-Z., 1933, 64, 324—327; cf. this vol., 780).—The formation of periodic and similar structures in gels is discussed in relation to biological phenomena. E. S. H.

Shaking (thixotropy) effect with cellulose solutions followed by vapour-pressure measurements. M. Ulmann (Z. physikal. Chem., 1933, 166, 147—155).—The v.p. (*p*) of colloidal dispersions of cryst. cellulose acetate (I) in glacial AcOH is initially $>$ that of the pure solvent, but on keeping falls to that val. This change is reversible, *p* being raised again by shaking. This effect is absent with mol. dispersion of (I) in AcOH. R. C.

Cinematographic swelling analysis in the dark field by means of the micro-manipulator. I. Mechanism of swelling of cellulose threads, starch grains, and similar structures. K. Hess and B. Rabinovitsch (Kolloid-Z., 1933, 64, 257—268).—A cinematographic study of the swelling of cellulose, starch, wool, silk, and gelatin indicates that the liquid penetrates the skin of the colloidal substances and reacts with the contents, forming a liquid system which is under considerable internal pressure. The internal liquid is ejected when the skin is punctured by the micro-manipulator. E. S. H.

Mechanism of enzyme action. XI. Cryolysis and charging with gas of lyophilic colloids. I G. Weiss and F. F. Nord (Z. physikal. Chem., 1933, 166, 1—15).—The increase in the surface tension, γ, of 10^{-4} to 10^{-6}% aq. Na oleate (I) caused by absorption of C_2H_4 or C_2H_2 is $>$ otherwise if the solution has previously been frozen. The γ–concn. curves of frozen and unfrozen solutions intersect at about 10^{-3}%. Absorption of N_2O depresses γ. For 10^{-6} to 1% ovalbumin (II) solutions γ is increased by absorption of C_2H_4 and C_2H_2, and, to a smaller extent, by the absorption of N_2O; in each case the increase is greater if the solution has previously been frozen. Gelatin (III) sols behave similarly. The solvent power for C_2H_4 and C_2H_2 of solutions of (I), (II), and (III) is usually increased by a preliminary freezing. The above observations are correlated with changes in the degree of dispersity in accordance with Nord's theory of cryolysis. R. C.

Plant colloids. XXXIV. Particle sizes of oxidised starches, determined by the osmotic and chemical methods. M. Samec (Kolloid-Z., 1933, 64, 321—323; cf. this vol., 811).—Fair agreement is reached in the determination of the mol. wt. of six sol. starches by osmometry and by neutralisation of the acid groups formed by oxidation. E. S. H.

Physical chemistry of starch and bread making. XIII. Comparative investigation of peptisation of various native starches with much water. J. R. Katz and T. B. van Itallie (Z.

physikal. Chem., 1933, **166**, 27—42; cf. this vol., 903).—In the peptisation the changes in the vol. of decantate, *v*, in the % of doubly-refracting granules, and in the *X*-ray diagram in general run parallel. When the end state has approx. been reached at a given temp. the proportion of granules peptised increases with rise of temp. On peptisation the original spectrum is replaced by a *V*-spectrum. The changes in *v*, the proportion of sol. starch, and the *X*-ray diagram indicate that there is a temp. below which no peptisation occurs. The granules in a given specimen of starch differ in their resistance to peptisation. The above parallelism is not, however, always quite perfect, suggesting that peptisation is a complex phenomenon which is the resultant of several inter-related processes. R. C.

Displacement of equilibrium by variation of mass. J. E. Verschaffelt (Compt. rend., 1933, **197**, 683—684).—An error in Etienne's calculation (cf. this vol., 783) is pointed out. C. A. S.

Conditions of equilibria between two phases. G. Antonoff (Kolloid-Z., 1933, **64**, 336—337).—Polemical (cf. Taubmann, this vol., 222). E. S. H.

Influence of the methyl, ethyl, and phenyl radicals on the association of salicylic acid derivatives. K. Kalinowski (Rocz. Chem., 1933, **13**, 384—398).—The mol. polarisations of Ph, Et, and Me salicylate in C_6H_6 at 40·2° are respectively 256·8, 207·5, and 153·4; the mols. are of the dipole type, and are increasingly associated as the concn. rises and the temp. falls. In solutions containing both Ph and Et salicylate association is > for each ester separately, and occurs between both similar and dissimilar mols. R. T.

Dissociation constant of hypochlorous acid: glass-electrode potential determinations. J. W. Ingham and J. Morrison (J.C.S., 1933, 1200—1205).—Potentiometric titration of aq. HOCl with aq. NaOH indicates that the apparent dissociation const., K', $=3·47\times10^{-8}$ at 18°. It is calc. that the true const., K, is $2·95\times10^{-8}$. D. R. D.

Ionisation constant of monochloroacetic acid, at 25°, from conductance measurements. B. Saxton and T. W. Langer (J. Amer. Chem. Soc., 1933, **55**, 3638—3645).—The conductances of 0·00008—0·031*N*-HCl, $\cdot CH_2Cl\cdot CO_2H$, and their Na salts have been determined. The data are consistent with Shedlovsky's extension of Onsager's equation. The val. $K_a=1·396\times10^{-3}$ is derived for the thermodynamic ionisation const. of $CH_2Cl\cdot CO_2H$. At concn. > 0·01*N*, this val. decreases. From new data for AcOH $K_a=1·759\times10^{-5}$. J. G. A. G.

Dissociation of acids in salt solutions. VII. Dissociation constants and activity functions of hydroxy- and ketonic acids in sodium and potassium chloride solutions. E. Larsson (Z. physikal. Chem., 1933, **166**, 241—253; cf. this vol., 780).—The introduction of OH at the α-C atom of AcOH, $EtCO_2H$, $Pr^{\beta}CO_2H$, or $Bu^{\beta}CO_2H$ or at the β-C atom of a fatty acid, and the introduction of OEt or OPh into AcOH raise —log ϕ, at the higher ionic concns. Substitution of OH in the γ or ε position in a fatty acid has no effect. Exchange of two H atoms in the α position in a fatty acid for O markedly increases —log ϕ, but exchange in the β position has only a small effect. It is doubtful if ketonic acids are present as such in solution. R. C.

Ionisation constants [at 25°] of methylated quinolines and of saturated bases isolated from petroleum distillates. W. A. Felsing and B. S. Biggs (J. Amer. Chem. Soc., 1933, **55**, 3624—3625).—The data refer to sixteen mono-, di-, and tri-methylquinolines. In the Me_1 series, location of the Me on the N-ring leads to higher ionisation consts. Max. vals. of K are obtained with Me at position 2 and positions 2 and 6 in the Me_1 and Me_2 series, respectively. J. G. A. G.

Cuprammonium solution. VI. Equilibrium composition. VII. Effect of sucrose on copper concentration. N. Ishii (J. Soc. Chem. Ind., Japan, 1933, **36**, 487—488B, 488—490B).—VI. Cuprammonium solution prepared by the air-bubbling process contains an excess of Cu which ppts. on keeping. The equilibrium [Cu] increases with increasing $[NH_3]$ and with falling temp. At const. temp. $[Cu]=k[NH_3]^{0·702}$ in which concns. are in mg.-mol. per 100 c.c.

VII. Recorded data show the increase in the equilibrium [Cu] caused by the addition of sucrose. At const. temp. and $[NH_3]$, $[Cu]=a+b[\text{sucrose}]$. The absorption spectrum is slightly affected. A. G.

Electrochemistry of complex cuprous–halogen anions. S. von Náray-Szabó and Z. Szabó (Z. physikal. Chem., 1933, **166**, 228—240).—Solutions containing the above ions prepared by electrolysis with a Cu anode of 1—6*M* aq. solutions of KCl, NaCl, HCl, $CaCl_2$, KBr, and KI have been examined. From the relation of the potential of a Cu electrode in the chloride solutions to the $[Cu^{\cdot}]$ and $[Cl']$ the complex ion has been shown to be $CuCl_3''$. The ratio of the activity of $Cu^{\cdot}$ to the $[CuCl_3'']$ is const. for a given total ionic concn., Γ. The variation of the activity coeff. of $CuCl_3''$, γ, with Γ is given by $-\log\gamma=0·234\sqrt{\Gamma}$, from which the dissociation const., $(Cu^{\cdot})(Cl')^3/(CuCl_3'')$ is calc. to be $14·5\times10^{-7}$. R. C.

Complex compounds in Eder's solution. G. H. Cartledge and S. L. Goldheim (J. Amer. Chem. Soc., 1933, **55**, 3583—3594).—Partition and f.-p. data suggest that complex formation in Eder's solution involves the following: $2HgCl_2+2C_2O_4''\rightleftharpoons Hg_2Cl_2(C_2O_4)_2''+2Cl'$, $HgCl_2+Cl'\rightleftharpoons HgCl_3'$, and $Hg_2Cl_4+Cl'\rightleftharpoons Hg_2Cl_5'$. This scheme harmonises the apparently contradictory reaction velocity data obtained with Eder solutions by various workers using corresponding ranges of concns. Other formulations do not accord with the results. J. G. A. G.

Amphoteric hydrated oxides, their compounds of higher mol. wt., and solutions thereof. XIX. Hetero- and *iso*-polytungstic acids, particularly periodotungstic acids. G. Jander and H. Witzmann (Z. anorg. Chem., 1933, **214**, 145—157; cf. this vol., 580).—Diffusion measurements have been undertaken to elucidate the mode of formation of the periodotungstic acids described by Rosenheim (A., 1899, ii, 743), whose preparative and analytical results are confirmed. The diffusion coeff. of the anions in solutions 0·05M with respect to both Na_2WO_4 and $Na_2H_3IO_6$ corresponds with WO_4'' at p_H 9—8, and with HW_6O_{21}''''' in solutions more acid than p_H 6. At p_H 1·5, in presence of excess of H_5IO_6, condensation takes place with formation of the readily hydrolysable $H_5[I(WO_4)_6]$. The constitution of complex tungstic and molybdic acids is discussed. F. L. U.

Activity coefficients of hydroxyl ion in solutions of calcium hydroxide at 30°. E. P. Flint and L. S. Wells (Bur. Stand. J. Res., 1933, **11**, 163—171).—The e.m.f. of the cell $H_2|Ca(OH)_2(c)|KCl$ (saturated)|HgCl+Hg has been measured at 30° for vals. of c between 0·050 and 1·199 g. CaO per litre. The p_H vals. and activity coeffs. of OH′ are recorded. The data lead to $K_w = 1{\cdot}72 \times 10^{-14}$. H. J. E.

[Free] energy of formation of aluminium oxide from its elements. W. D. Treadwell and L. Terebesi (Helv. Chim. Acta, 1933, **16**, 922—939).—From existing thermal data the free energy of formation of Al_2O_3 is calc. for the range 293·1—2600° abs. The val. is 371·1 kg.-cal. per mol. at 298·1° abs. Measurements of the e.m.f. of the Al–Cl_2 cell at 380—460° and of the Al–O_2 cell at 1118—1378° abs. lead to concordant vals. F. L. U.

Heat capacities of sodium carbonate and hydrogen carbonate and of silver carbonate at low temperatures. C. T. Anderson (J. Amer. Chem. Soc., 1933, **55**, 3621—3623).—The entropies calc. from sp.-heat data within the range 53·5—295° abs. by means of the Debye and Einstein functions are Na_2CO_3 32·5, $NaHCO_3$ 24·4, and Ag_2CO_3 40·0 g.-cal. per 1°. J. G. A. G.

Calcium nitrate. IV. Heats of dilution of solutions of calcium nitrate in water. W. W. Ewing and A. N. Rogers (J. Amer. Chem. Soc., 1933, 55, 3603—3609).—Heats of dilution of 1·39—19·55M-$Ca(NO_3)_2$ have been determined and the total and partial heats of dissolution calc. The partial heats of dissolution of H_2O calc. from v.-p. determinations by means of Kirchhoff's equation are consistent with the calorimetric vals. J. G. A. G.

Transformation of solid ammonium chloride near —30°. A Smits and C. H. MacGillavry (Z. physikal. Chem., 1933, **166**, 97—112).—Dilatometric investigation has shown that the transformation is practically discontinuous, being almost completed within a few hundredths of a degree (cf. A., 1930, 986). There is, however, hysteresis. It is inferred that the transformation is heterogeneous, but that the way is paved for it by a homogeneous transformation below the transition region. R. C.

Thermal and X-ray characterisation of lattice faults in zinc oxide. R. Fricke and P. Ackermann (Z. anorg. Chem., 1933, **214**, 177—188).—The heat of dissolution in aq. HF of ZnO prepared by heating rhombic $Zn(OH)_2$ increases as the temp. and time of its prep. decrease. A difference of 1·3 kg.-cal. per mol. has been observed. X-Ray examination shows the higher energy content to be associated with incompleteness of the crystal lattice. F. L. U.

Thermal equilibrium of acetanilide and certain organic compounds. K. Hrynakowski and F. Adamanis (Rocz. Chem., 1933, **13**, 448—453).—The fusion diagrams for NHPhAc with antipyrine, BzOH, quinine, $NHPh_2$, phenacetin, quinol, menthol, $CO(NH_2)_2$, α-$C_{10}H_7{\cdot}NH_2$, salipyrine, salol, and ethylurethane indicate complete miscibility of the fused constituents and absence of compound formation. R. T.

Thermal analysis of binary systems containing organic nitrates. T. Urbański (Rocz. Chem., 1933, **13**, 399—434).—The fusion diagrams for mannitol hexanitrate (I) and p-$C_6H_4Me{\cdot}NO_2$ (II), p-$OMe{\cdot}C_6H_4{\cdot}NO_2$ (III), p-$OEt{\cdot}C_6H_4{\cdot}NO_2$ (IV), and 1-$C_{10}H_7{\cdot}NO_2$ (V) indicate the formation of unstable 1 : 2 compounds with (II), (III), and (IV), and a 1 : 1 compound with (V). Neither compound nor solid solution formation is found in the systems: pentaerythritol tetranitrate (VI) or (I)–o-$C_6H_4Cl{\cdot}NO_2$, m-$C_6H_4(NO_2)_2$ (VII), 3 : 5-dinitroanisole, 2 : 4-$C_6H_3Cl(NO_2)_2$, 1 : 3 : 5-$C_6H_3(NO_2)_3$, 2 : 4 : 6-$C_6H_2Me(NO_2)_3$, $C_{10}H_8$, $CO(NPhMe)_2$, and $CO(NPhEt)_2$; erythritol tetranitrate (VIII)–(I), (II), (VI), and (VII); (VI)–(I), (II), (III), and (V). The solubility of the above nitrates in org. solvents increases in the order (VI)<(I)<(VIII). Secondary reactions take place between (I) or (II) and $C_{10}H_8$ or $CO(NPhR)_2$, with the production of NO_2- or NO-compounds. R. T.

Liquidus in the system diphenylamine–centralite [s-diphenyldiethylcarbamide]. I. L. Médard. **II.** M. Giua and G. Guastalla. **III.** L. Médard (Chim. et Ind., 1933, **30**, 277—280).—I. In agreement with previous results (A., 1932, 376) an equimol. compound, m. p. 37·5°, is indicated by m.-p. observations. The contrary result obtained by Giua and Guastalla (B., 1933, 333) is ascribed to supercooling and the slow rate of formation of the compound. Centralite forms two compounds with H_2SO_4, containing 0·5 mol. and 2 mols. of H_2SO_4, with m.p. 75° and 71°, respectively.

II. Evidence is adduced that m.-p. and f.-p. curves yield concordant results. It is considered that supercooling is immaterial in determining the form of the curve, and that the existence of a compound of the type described by Médard is improbable.

III. The error resulting from supercooling varies and is particularly great in the neighbourhood of a eutectic. H. F. G.

Acetic acid–acetate solutions. A. W. Davidson and W. Chappell (J. Amer. Chem. Soc., 1933, 55, 3531—3537).—The solubility of $Sr(OAc)_2$ in pure AcOH (14—122°) lies between the vals. for the Ca and Ba salts. $Sr(OAc)_2$,AcOH exists below 113°. The solubility of $Ni(OAc)_2$ at 30° has no definite val. This is attributed to the presence of colloidal constituents which persist until > 15% of NH_4OAc has been added, when const. vals. are obtained and the solid *phase* is $Ni(OAc)_2$,NH_4OAc,2AcOH. In general, NH_4OAc lowers the solubility of $Ni(OAc)_2$. F.-p. depression curves are discussed. J. G. A. G.

Calcium aluminates. III. Crystallisation of calcium aluminate solutions at 90°. G. Assarsson (Z. anorg. Chem., 1933, **214**, 158—166).—The equilibrium diagram at 90° is similar to that previously observed at 20° and 40° (A., 1932, 583). The

presence of $4CaO,Al_2O_3,13{\cdot}5H_2O$, $3CaO,Al_2O_3,6H_2O$, $2CaO,Al_2O_3,9H_2O$, and Al hydroxide in the solid phase was established. The last-named occurs partly as gel, and partly as microcryst. aggregates having the average composition $Al_2O_3,3$—$3{\cdot}5H_2O$.
F. L. U.

Equilibria between water vapour and vanadium and its oxides. M. KOBAYASHI (Bull. Chem. Soc. Japan, 1933, 8, 231—245).—The oxidation-reduction method has been applied to the determination of the equilibria between H_2O and the phases $V+VO$ and $VO+V_2O_3$ at H_2O v.p. between $1{\cdot}07\times10^{-3}$ and $6{\cdot}65\times10^{-7}$ atm. The reactions involved are $V+H_2O=VO+H+56{\cdot}4$ kg.-cal., and $2VO+H_2O=V_2O_3+H_2+29{\cdot}6$ kg.-cal. The O pressures at various temp., and the free energies and heats of formation of the oxides, have been calc. H. F. G.

System sodium carbonate–calcium carbonate–water. C. R. BURY and R. REDD (J.C.S., 1933, 1160—1162).—From 15° to 37°, the stable double salt is gaylussite, $Na_2CO_3,CaCO_3,5H_2O$; from 40° to 95° it is pirssonite, $Na_2CO_3,CaCO_3,2H_2O$. D. R. D.

Isothermal equilibrium $CaCO_3$ + aq. NH_4NO_3. A. GUYER and H. SCHÜTZE (Helv. Chim. Acta, 1933, 16, 904—913).—Equilibria have been determined at 25°, 40°, 60°, 80°, and 95°, using 0·5—10*M*-NH_4NO_3. The results are in accord with the measured hydrolysis of NH_4NO_3, vals. of which are recorded. F. L. U.

Thermal investigation of calcium silicophosphates. G. BEHRENDT and H. WENTRUP (Arch. Eisenhüttenw., 1933—1934, 7, 95—102).—An optical pyrometric device for observing very small heat effects in taking heating and cooling curves up to 2000° is described and the results obtained for the equilibria in the CaO–P_2O_5 (*A*) and CaO–P_2O_5–SiO_2 (*B*) systems are described. In *A* max. on the liquidus occur at 1760° ($4CaO,P_2O_5$) and 1775° ($3CaO,P_2O_5$); these compounds form a eutectic with one another at 1568° and 57·4% CaO. The former yields a eutectic with CaO at 1655° and 62·8% CaO, and the latter undergoes a polymorphic transformation at 1460—1480°. In *B* the compound $5CaO,P_2O_5,SiO_2$ shows a well-defined peak in the liquidus surface at about 1900°; it forms a ternary eutectic at 1600° with CaO and $4CaO,P_2O_5$ and a quasi-binary system with $2CaO,P_2O_5$ and with $4CaO,P_2O_5$. A. R. P.

System CaO–FeO–SiO_2. N. L. BOWEN, J. F. SCHAIRER, and E. POSNJAK (Amer. J. Sci., 1933, [v], 26, 193—284).—The system is characterised by three ternary compounds: $CaFeSi_2O_6$ (hedenbergite, stable below 965°), $2CaO,FeO,2SiO_2$ (iron-akermanite, stable below 775°), and $CaFeSiO_4$, the only one stable in contact with liquid. The min. temp. of existence of liquid is 1093°. Of some thirty invariant points, seven are ternary, but there is no ternary eutectic. There are several solid solutions, including wollastonite (I)–$FeSiO_3$, which extends to 76% $FeSiO_3$, and hedenbergite–$FeSiO_3$, which extends to 80% $FeSiO_3$; the latter is stable only at low temp., and at 940—980° is transformed into the (I) series; with a higher $FeSiO_3$ content orthosilicate and tridymite are formed. The principal orthosilicate solid solutions are Ca–Fe olivines (II) extending from Fe_2SiO_4 (fayalite) through $CaFeSiO_4$ to 59% Ca_2SiO_4. (I) solid solutions and (II) co-exist under certain conditions. The inversion temp. of (I) is 1150°. Neither α- nor β-(I) (solid) dissolves appreciable quantities of CaO or SiO_2. The optical and *X*-ray diffraction properties of many of the solid phases have been determined. The results are discussed in reference to the formation and composition of the minerals concerned. H. F. G.

Determination of high-frequency conductivity of uni-univalent electrolytes. E. GLOWATZKI (Ann. Physik, 1933, [v], 18, 217—232).—The method of Rieckhoff and Zahn (A., 1929, 512) has been improved, and used to determine the conductivity change at high frequencies (3×10^8 Hertz) of HCl and NaCl solutions. Deviations are found from theory for uni-univalent electrolytes. A. J. M.

Electrolytic solutions. VI. Conductance of sodium triphenylstannide, sodium triphenylgermanide, and sodium triphenylmethide in liquid ammonia. C. A. KRAUS and W. H. KAHLER. **VII. Conductance of sodium trimethylstannide and of the sodium salts of phenols and thiols in liquid ammonia.** C. A. KRAUS and E. G. JOHNSON. **VIII. Conductance of ternary salts in liquid ammonia.** C. A. KRAUS and P. B. BIEN. **IX. Conductance of salts in benzene.** R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1933, 55, 3537—3542, 3542—3546, 3609—3614, 3614—3620).—VI. The conductances of $NaSnPh_3$, $NaGePh_3$, and $NaCPh_3$ at dilutions between 59 and 59,000 in liquid NH_3 show that although the solutions are unstable at very low concns. these salts are strong electrolytes, the dissociation const. of $NaSnPh_3$ being approx. four times that of $NaBrO_3$. Earlier conclusions (this vol., 907) receive additional support.

VII. The effects of ion size and constitution on the properties of the electrolyte have been investigated. From the dissociation consts., NaOPh $3{\cdot}82\times10^{-4}$, β-$C_{10}H_7{\cdot}ONa$ $6{\cdot}5\times10^{-4}$, α-$C_{10}H_7{\cdot}ONa$ $8{\cdot}08\times10^{-4}$, EtSNa $22{\cdot}5\times10^{-4}$, PhSNa $36{\cdot}0\times10^{-4}$, and $NaSnMe_3$ 36×10^{-4} (approx.), it is inferred that, in general, the most highly ionised electrolytes are those which have the largest ions, the configuration of which is such that the charges are most completely screened by surrounding atoms or groups. The salts are not sufficiently strong electrolytes to conform to the Debye–Hückel relation and the mass-action effect increases as *K* decreases.

VIII. The data at −33° for concn. $>10^{-4}N$ show that the salts are, in general, weaker electrolytes than those in VII. The conductivity of $CPh_2{\cdot}ONa_2$ almost coincides with that of $CPh_2{\cdot}ONa$ at low concns., but the results cannot be interpreted on the basis of a simple binary or ternary equilibrium. The importance of the constitutional factor is emphasised by the very low conductivity of $CHPh_2{\cdot}ONa$ as compared with that of $CPh_2{\cdot}ONa$. $(NPh)_2K_2$ behaves as a ternary salt, and in accordance with the Debye–Hückel theory, the conductivity is much < for the binary salts. It appears that the anion of the ternary salt $Na_2(SnPh_2)_2$ dissociates partly into $SnPh_2'$.

IX. By means of an improved technique (cf. this vol., 230) conductivity data for 0·03—$10^{-6}N$-tetra*iso*-

amyl ammonium picrate, thiocyanate, fluoride, chloride, bromide, and iodide in C_6H_6 at 25° have been obtained. Conductance min. occur at concn. between 10^{-4} and $10^{-5}N$ and the rise in conductivity with increasing dilution of solutions $< 10^{-5}N$ agrees with the requirements of the law of mass action. Consistent with the absence of solvation, the apparent sizes of ions are: $I' > Br' > Cl' > F'$. The relation between the form of the conductivity curves and the structure of the electrolytes is discussed. J. G. A. G.

Conductivity of tetramethylammonium salts in methyl and ethyl alcohol. T. H. Mead, O. L. Hughes, and (Sir) H. Hartley (J.C.S., 1933, 1207—1214).—The conductivities of 0·0001—0·0015*N*-NMe_4 chloride, bromide, picrate, thiocyanate, nitrate, iodide, and perchlorate in MeOH, and of the first five in EtOH, at 25°, have been determined. The mobility of $NMe_4^{\cdot}$ is 70·1 in MeOH and 28·3 in EtOH. Deviations from the Debye–Hückel–Onsager equation are discussed. D. R. D.

Determination and conductance of sulphuric acid in anhydrous acetic acid. W. C. Eichelberger and V. K. La Mer (J. Amer. Chem. Soc., 1933, 55, 3635—3638).—The conductivity curve for H_2O–AcOH mixtures has a sharp max. at 18% AcOH. H_2SO_4 in anhyd. AcOH is determined by conductimetric titration with $Ba(OAc)_2$. Conductivity data for H_2SO_4 in anhyd. AcOH are recorded. J. G. A. G.

Conductivity of ferric chloride in non-aqueous solution. E. Wertyporoch and I. Kowalski (Z. physikal. Chem., 1933, 166, 205—218).—The mol. conductivity, λ, of solutions of $FeCl_3$ in the lower alkyl chlorides increases with the dilution when *c*, the concn., is < about 0·003 mol. per litre, but at moderate concns. varies little with *c* owing to the formation of such complexes as $[Fe(EtCl)_n][FeCl_6]$. In solutions in higher alkyl chlorides stable complexes are formed and λ remains const. even at the lowest concns. On keeping these solutions λ increases; this is due to the formation of unsaturated hydrocarbons which are incorporated in the cation, this change being less rapid with primary than with *iso*chlorides. Addition of C_6H_6 to $FeCl_3$ solutions in EtCl or EtBr increases λ owing to formation of ethylbenzenes. For solutions in BzCl and AcCl λ is comparatively high, the $FeCl_3$ entering into salt-like complexes in which the cation contains carbonyl compounds. Solutions in CH_2PhCl, $CHPhCl_2$, and $CPhCl_3$ have a very small λ. For solutions of $AlCl_3$ in the higher alkyl chlorides λ increases with *c* because HCl is readily lost, forming unsaturated hydrocarbons which are added to the cation. $BeCl_2$ and $ZrCl_4$ give conducting solutions in EtBr. R. C.

Potential of the silver–silver iodate electrode at 25°. J. N. Pearce and V. I. Wirth (J. Amer. Chem. Soc., 1933, 55, 3569—3571).—From the e.m.f. of the cell $Hg,Hg_2Cl_2|0\cdot01—0\cdot2M\text{-}KCl|0\cdot01—0\cdot2M\text{-}KIO_3|AgIO_3,Ag$, the potential of the Ag, $AgIO_3$, IO_3' electrode is found to be 0·3569 volt. J. G. A. G.

Thallous bromide. F. Ishikawa and Y. Terui (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 755—758).—The e.m.f. of the reversible cell Tl,Hg|TlBr (solid), 0·1*M*-KBr, HgBr (solid)|Hg at 25° is 0·7945 volt. The mol. heat of formation of TlBr (solid) is −41·51 kg.-cal. The solubility product of TlBr is $3\cdot88\times10^{-6}$. H. F. G.

Effect of glass containers on the electromotive force of Weston normal cells. G. W. Vinal and M. L. Howard (Bur. Stand. J. Res., 1933, 11, 255—275).—Solubility of glass containers changes the acidity of the electrolyte, and hence the e.m.f. of the cell. The effect is emphasised by adding powdered glass to the $HgSO_4$ paste. It is greatest for Pb sealing-in glass. The use of fused quartz cells is suggested. Impurities [CdO, PbO, $Al_2(SO_4)_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, and H_3BO_3], added to the $HgSO_4$ paste, altered the hysteresis effect and the temp. coeff. of the cell. H. J. E.

Variation with concentration of Volta potential in systems $Ag|Ag_{aq}^{\cdot}$ and $Cu|Cu_{aq}^{\cdot\cdot}$. M. Andauer and E. Lange (Z. physikal. Chem., 1933, 166, 219—227).—In the system $Ag|Ag_{aq}^{\cdot}$ the Volta potential, $\Delta\psi$, has been measured for concns. of 0·1 to $10^{-9}N$. The val. of $d\Delta\psi/d \log c$ is about 0·070 volt, showing that the surface potential of the solution does not change by > 0·01 volt for a tenfold change in $[Ag^{\cdot}]$. For the system $Cu|Cu^{\cdot\cdot}$ $d\Delta\psi/d \log (Cu^{\cdot\cdot})$ is approx. 0·029 volt. R. C.

Exchange between atoms and ions of a metal. O. Erbacher (Z. physikal. Chem., 1933, 166, 23—26).—In the exchange which occurs when Pb or Bi is in contact with a solution of one of its salts, local action is largely or entirely absent if the metal has previously been etched with HNO_3 (cf. this vol., 468); probably the kinetic exchange involves only a monat. surface layer. R. C.

Electrocapillary experiments. I. G. Walters (Phil. Mag., 1933, [vii], 16, 617—625).—Electrocapillary curves for Hg in aq. KCl (0·02*N*—saturated), 0·5*N*-KI, 0·5*N*-KI+0·5*N*-KCl, and in EtOH saturated with KCl have been determined. In EtOH the max. is much depressed and is flatter. This is accounted for by the very low ion concn. in the EtOH solution. H. J. E.

Measurement of oxidation–reduction potentials in glacial acetic acid solutions. J. B. Conant and B. F. Chow (J. Amer. Chem. Soc., 1933, 55, 3745—3751).—The oxidation–reduction potentials of benzoquinone, tetrachlorobenzoquinone, indo-*o*-cresol, indothymol, and *o*-cresol-indophenol can be measured in AcOH by the method of mixtures or by titration of the oxidant with $Cr(OAc)_2$. The vals. of E^0_h (calc. from results obtained in a series of buffers of const. ionic strength) plotted against $(p_H)^{AcOH}$ give a straight line with the theoretical slope. The relation of the $(p_H)^{AcOH}$ scale to Hammett and Deyrup's acidity function (A., 1932, 921) is discussed briefly. H. B.

Electrolytic reduction potential of organic compounds. XVI. *p*-Aminoazobenzene. M. Shikata and I. Tachi (J. Agric. Chem. Soc. Japan, 1933, 9, 207—213).—The electrolytic reduction potential of *p*-aminoazobenzene (I), which is more negative than that of azobenzene, is more positive in lower than in higher concn. at any p_H. The two vals. obtained refer to a dissociated and an undissociated form. The reduction potential of the quinonoid form is more positive than that of the azoid form, and that of the dissociated more positive than that of the undissociated form. The calc. solubility of (I) in H_2O at 25° is $2{\cdot}815 \times 10^{-4}$ g.-mol. per litre. Ch. Abs.

Electrolytic reduction potentials of organic compounds. XVII. Dimethylaminoazobenzene. I. Tachi (J. Agric. Chem. Soc. Japan, 1933, **9**, 227—234).—Vals. are more negative at higher concns., except at $p_H < 2{\cdot}2$. Ch. Abs.

Potential of free radicals of the triphenylmethyl type in glacial acetic acid solutions. J. B. Conant and B. F. Chow (J. Amer. Chem. Soc., 1933, **55**, 3752—3758).—Methods previously described (this vol., 1121) are applied to the determination of the oxidation–reduction potentials of CPh_3, benzyl- and phenyl-xanthyl, and their halochromic salts (cf. A., 1925, ii, 874). H. B.

Oxidation–reduction potential of ascorbic acid. R. Wurmser and J. A. de Loureiro (Compt. rend. Soc. Biol., 1933, **113**, 543—544).—The conflicting opinions as to whether ascorbic acid (I) is capable or incapable of forming a thermodynamically reversible oxidation–reduction system arise from the fact that it forms two such systems of different levels of potential. In one of these a stable (II) and in the other an unstable (III) oxidised form is produced. (III) passes slowly into (II). In oxidation–reduction systems of r_H 17 or greater, (I) is readily reduced by the donation of 2 H, and in systems of lower r_H, by very slow donation of 4 H. Nutr. Abs. (*m*)

Theory of cathodic evolution of hydrogen. J. Hoekstra (Z. physikal. Chem., 1933, **166**, 76—79).—Volmer's theory (A., 1930, 1376) is criticised. R. C.

Theory of cathodic evolution of hydrogen. M. Volmer (Z. physikal. Chem., 1933, **166**, 80).—Hoekstra's criticisms (cf. preceding abstract) are refuted. R. C.

Overvoltage. VI. Mechanism of the transfer of electrolytic hydrogen and oxygen through thin sheets of platinum and palladium. A. L. Ferguson and G. Dubpernell (Trans. Electrochem. Soc., 1933, **64**, 253—279; cf. A., 1932, 1208).—$2N$-H_2SO_4 is electrolysed between Pt or Pd foil electrodes which form the end-walls of the cell and the backs of which are in contact with electrolyte in separate external compartments. During electrolysis the relations between the potentials of the front and back of such an electrode are very irregular: the potential of the back may follow closely variations in that of the front or it may remain const. irrespective of such variations for a long period and then perhaps change suddenly towards the potential of the front. Experiments under various conditions indicate that electrolytically liberated H and O do not diffuse through solid metals, but only through definite pores, and that transference of potential to the back of an electrode occurs only if the metal is porous. This view is supported by the observation that whether such transference occurs or not depends on the particular specimen of metal used, irrespective of whether it is acting as cathode or anode. Also such transference of potential is often accompanied by detectable acidification of H_2O in contact with the back of the electrode. Microscopic blisters formed on the front of the electrode (and to a smaller extent on the back) at higher c.d. are attributed to gas liberated from electrolyte in the pores within the metal. The nature of the porosity and the bearing of the results on theories of overvoltage are discussed. H. J. T. E.

Theory of overvoltage. O. Essin (Z. physikal. Chem., 1933, **166**, 270—272).—Erdey-Grúz and Volmer's theory of overvoltage is capable of accounting for the connexion between overvoltage and $[H^{\cdot}]$ more satisfactorily than any other theory if the velocity of the opposing reaction is taken into account. R. C.

Polarisation currents due solely to changes in electrode area. K. E. Glidden and W. A. Patrick (J. Amer. Chem. Soc., 1933, **55**, 3594—3602).—On the assumption that the current between a fixed and an expanding Hg surface in aq. Hg_2SO_4 is due to adsorption of $Hg^{\cdot}$ by sp. rather than electrostatic forces, the data indicate that the adsorption of $Hg^{\cdot}$ rises to a const. val. at concn. $> 0{\cdot}00013M$-Hg_2SO_4. The lowering of interfacial tension between Hg and aq. Hg_2SO_4 suggests the formation of an oriented unimol. layer of charged particles (Hg_2SO_4) at the Hg surface. J. G. A. G.

Electrochemical theory of corrosion. O. P. Watts (Trans. Electrochem. Soc., 1933, **64**, 219—244).—The fundamental basis and implications of the theory are critically discussed in relation to recent experimental work. Unpublished data of Rummele and Sobota (1932) for single potentials of metals and potentials for liberation of H_2 on them in N-H_2SO_4 and N-Na_2SO_4 are given. Unpublished work of Krombholtz on the effect of dissolved O_2 and H_2 on single potentials of metals in $0{\cdot}1N$-K_2SO_4 and on residual currents is referred to. H. J. T. E.

Electrochemical behaviour of iron in corrosion cells. I. Iron electrode carrying no external current. II. Cathode. III. Current-carrying capacity. H. L. Lochte and R. E. Paul (Trans. Electrochem. Soc., 1933, **64**, 23—40, 41—47, 49—55).—I. Variations of the single potential of Fe wires with time in various electrolyte solutions, and the effects of electrode size, temporary H_2 evolution, rate of stirring, p_H, O_2 concn., and nature of anions present are shown by potential–time curves. The observed single potential is regarded as a mean val. resulting from polarisation of the anodic and cathodic half-elements constituting the metal surface. Half-elements nobler than H_2 can be removed by immersion in $5N$-HCl, and after this or other suitable treatment Fe acts as an indicator electrode towards $H^{\cdot}$ in acid solutions and in deaërated neutral or alkaline solutions. With respect to their influence on the potentials, anions fall into two classes: those which, like Cl', form only sol. $Fe^{\cdot\cdot\cdot}$ corrosion products; and those like PO_4''' which yield insol. products. Anions of the PO_4''' type lead to nobler potentials and inactivity of the electrode in aërated solutions. When both types of ion are present the effect depends on their proportions.

II. The polarisation of Fe wires in $0{\cdot}1N$-NaCl and

-Na_3PO_4 rises notably with increase of c.d., especially in the latter case. During decrease of c.d. in 0·1*N*-NaCl there is a break in the c.d.–potential curve, the polarisation increasing again at low c.d. and local action occurring. The c.d. at this point corresponds with the crit. c.d. required to protect Fe from corrosion.

III. If dissolved O_2 is absent or anions of the Cl′ type are present, the anodic polarisation of Fe at a c.d. likely in corrosion cells is very small, and corrosion is limited by the cathodic polarisation. In the presence of anions of the PO_4''' type in aërated solutions both anodic and cathodic polarisations increase so rapidly with c.d. that little damage can be done. With mixtures of the two types of anion in aërated solutions the effect depends on the ratio of their concns. and on the sp. anions present, but the anode tends to become more active with time, since anions of the Cl′ type accumulate there, whilst those of the PO_4''' type are kept back as insol. corrosion products. In actual corrosion cells the c.d. is probably always very small, but the anodic val. may be as high as 0·1 milliamp. per sq. cm. in special cases. H. J. T. E.

Relations between affinity and reaction velocity. O. Dimroth (Angew. Chem., 1933, **46**, 571—576).—A lecture. E. S. H.

Spark ignition of low inflammable gas mixtures. II. Spectrographic examination of the ignition spark. K. Yumoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 246—255).—For mixtures of air with $< 5\%$ H_2 or $< 10\%$ CO, the igniting power of a short spark (< 4 mm.) which shows a band spectrum is $>$ that of a spark showing a spark spectrum. In long sparks (10—12 mm.) the igniting power is greatest on the portions of the spark where the heads of the N_2 band appear strongly, and especially on the negative side of the spark where the heads of the first negative band are superimposed on the enhanced positive band. With 0·3% N_2 in CO–O_2 mixtures (CO=7%) the N_2 bands are still bright, and coincide with the max. igniting power of the spark, but no conclusion is reached as to whether the excited N_2 and N_2 mols. are directly concerned with the ignition. J. W. S.

Ignition of gases. VIII. Ignition by a heated surface: (*a*) Mixtures of ethane, propane, or butane with air; (*b*) mixtures of ethylene, propylene, or butylene with air. C. A. Naylor and R. V. Wheeler (J.C.S., 1933, 1240—1247; cf. A., 1931, 1240).—The relative ignition temp. and lags in ignition in a quartz bulb at 600—750° were measured for mixtures of air with C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, or C_4H_8. For C_2H_6–air mixtures CH_2O and C_2H_4 are formed during the lag period. Prior addition of these did not shorten the lag, but addition of EtI or EtBr did so. In C_2H_4–air mixtures CH_2O is formed during the lag. For the olefines the ignition temp. falls as the mol. wt. increases. Results are compared with those for CH_4. H. J. E.

Oxidation of triethylphosphine. W. H. Thompson and N. S. Kelland (J.C.S., 1933, 1231—1236; cf. this vol., 917).—The lower crit. explosion pressure of PEt_3, measured from 42° to 100°, was of the order of 12—25 mm. The effect of vessel diam. and added inert gases indicated a chain reaction, with deactivation at the walls. Deactivation can also occur in the gas phase. The slow reaction below the lower limit was probably a wall reaction. The reaction mechanism is discussed. H. J. E.

Polymerisation of gaseous formaldehyde. R. Spence (J.C.S., 1933, 1193—1197).—The reaction at 19—22° on a Pyrex glass surface covered with polymeride was unimol. above approx. 200 mm. pressure. At lower pressures it becomes bimol., and ultimately multimol. Reaction is more rapid on clean glass. At below 50° depolymerisation is very slow. The velocity of this process was measured at 85° (cf. Trautz and Ufer, A., 1926, 821). H. J. E.

Thermal decomposition of trinitrotriazidobenzene and other polynitropolyazidobenzenes. O. Turek (Chim. et Ind., 1933, **29**, Spec. no., 883—887).—The thermal decomp. at different temp. of 1 : 3-dinitro- (improved prep.) and 1 : 3 : 5-trinitro-2 : 4 : 6-triazido- (I) and of 2 : 4 : 6-trinitro-1-azido-benzene (improved prep.) was studied, and the temp. coeffs. and energies of activation are calc., these differing little for the three substances. Interaction of *o*-N_3 and -NO_2 groups produces N_2 and *o*-NO groups. The greater stability of (I) is attributed to its symmetry. A. A. L.

Decomposition of hydrogen peroxide by potassium ferro- and ferri-cyanides. B. S. Srikantan and A. R. Rao (J. Indian Chem. Soc., 1933, **10**, 299—307).—The decomp. of H_2O_2 by $K_4Fe(CN)_6$ is complicated. Reaction of H_2O_2 with $K_3Fe(CN)_6$ is unimol. and is preceded by an induction period, the duration of which is inversely proportional to the concn. of ferricyanide and decreases with rise of temp. The temp. coeff. is about 2·3. Light does not accelerate the reaction, but leads to the formation of Prussian-blue, which acts as centres for the reaction to start, thus eliminating the induction period. An intermediate complex between H_2O_2 and $K_3Fe(CN)_6$ may be formed. E. S. H.

Velocity of alcoholysis of esters of dibasic acids. Z. H. Patel and H. E. Watson (J. Indian Inst. Sci., 1933, **16**, A, 55—67).—The velocity of alcoholysis of the Me and Et esters of oxalic, malonic, succinic, adipic, suberic, azelaic, sebacic, tartaric, and malic acids with EtOH and MeOH in presence of HCl has been studied dilatometrically at 30°. With the symmetrical acids the reaction is unimol., although a slight deviation is observed with $H_2C_2O_4$. The two ester groups in malic acid react at different rates. In the series of unsubstituted acids $H_2C_2O_4$ has the greatest velocity coeff. and malonic acid has the smallest; the vals. for the remaining acids are equal. The reaction velocity is approx. proportional to the concn. of the catalyst (HCl). The equilibrium const. increases slightly from $H_2C_2O_4$ to adipic acid. E. S. H.

Stability of ethylene glycol in acid solution. F. E. Brown and C. E. Headington (Iowa State Coll. J. Sci., 1933, 7, 383—386).—At 107° $C_2H_4(OH)_2$ decomposes very slowly in aq. H_2SO_4 (< 20 wt.-%); the rate increases to 44% in 3 hr. for 35% H_2SO_4. At 107° in presence of HCl in low concn. decomp. occurs;

with 25% HCl at 107°, 54% decomposes in 3 hr. Rise of temp. rapidly increases the rate of decomp. Increase in pressure (H_2) had no effect. Ch. Abs.

Velocities of esterification of alcohols in formic acid. II. A. Kailan and N. H. Friedmann (Monatsh., 1933, 62, 284—316).—The velocity of esterification (v_e) at 15° of EtOH, $Pr^{\alpha}OH$, $Pr^{\beta}OH$ (I), $Bu^{\alpha}OH$ (II), CHMeEt·OH, *sec.*- and *tert.*- (III) -amyl alcohols, $CH_2Pr^{\beta}\cdot CH_2\cdot OH$, and octan-α- and -β-ol (IV) in anhyd. HCO_2H and in presence of "0·104—1·017 mol." H_2O per kg. 100% acid (w_0), both with and without HCl catalysis, has been determined by the f.-p. method (A., 1929, 655). For solutions of C_6H_6, BzOH, $CHCl_3$, and various alkyl formates in HCO_2H the val. of the cryoscopic const. is $<2·73$, the val. calc. from the heat of fusion (Zanninovitch–Tessarin), and for w_0=0·3—2·1 it is 2·44° and is independent of the H_2O concn. With all the above alcohols esterification is complete. In the uncatalysed reaction as w_0 is increased from 0·19 to 1·11, v_e for all the alcohols, except (IV), decreases, by 27% for primary, 19—25% for *sec.*, and 51% for (III). The ratio of v_e for primary, *sec.*-, and *tert.*-alcohols is 1 : 0·27 : 0·25 and 1 : 0·30 : 0·17, respectively, for the two vals. of w_0. No appreciable differentiation is observed between the various primary alcohols, but branching of the chain decreases v_e by about 10%. For w_0=0·1 and 1, v_e for (I) is about 14 and 22% > that for (II), respectively, and that of (III) is approx. twice that of *tert.*-BuOH. In the presence of 0·0007 mol. HCl per kg. of 100% acid and when w_0=0·1, v_e for *sec.*- and *tert.*-alcohols is increased 4·4 and 2·7 times, respectively, and the retarding action of H_2O is now greater, v_e for *sec.*- and *tert.*-alcohols being reduced by 72% and 76%, respectively, as w_0 increases from 0·1 to 1·0, and in the catalysed reaction v_e for (IV) is also reduced by 59%. The temp. coeff. for (I) is the same in both acids, v_e being > doubled when t is increased from 15° to 25°. After reduction to the same temp. v_e in HCO_2H, HCO_2H+HCl (w_0=0·1 and 1·0) is, respectively, 15,000—20,000, 8000—10,000, and 2000 times the val. in AcOH under similar conditions (A., 1932, 1210). J. W. B.

Influence of substitution on the velocity of hydrolysis of benzylidene chloride. F. Asinger and G. Lock (Monatsh., 1933, 62, 323—343).—The vals. of the ψ-unimol. velocity coeff. k for the irreversible hydrolysis of the following substituted benzylidene chlorides have been determined in H_2O–$COMe_2$ (1 : 1) at 50° or in H_2O–EtOH (1 : 1) at 83·5°. All are prepared by the action of PCl_5 on the appropriate aldehyde: $CHPhCl_2$, *o*- and *p*-chloro-, *m*- and *p*-methyl-, *o*-, *m*-, and *p*-nitro-, m-*chloro*-, b.p. 105°/11 mm., 235—237°/738 mm., o-*methyl*-, b.p. 105—107°/11 mm., 2 : 5- and 2 : 6-dichloro-, 3 : 5-*dichloro*- (this vol., 1162), 2 : 3 : 6-*trichloro*-, m.p. 83°, b.p. 145—150°/12 mm., and 2 : 4 : 6-*trimethyl*- (I), m.p. 37°, b.p. 139—140°/13 mm., -*benzylidene chloride*. In 50% aq. EtOH at 83·5° (determined directly or converted from the vals. in $COMe_2$ at 50°, hydrolysis in dil. EtOH occurring about five times as fast as in $COMe_2$) the vals. of the half-change periods (min.) are, respectively: 2, 97, 5, 0·9, 0·027, 10,760, 3207, 7476, 168, 0·3, 2563, 6785, 4925, 123,600, and 0·0025. Thus the retarding action of Cl substitution is in the order $m>o\gg p$, that of NO_2 $o>p>m$, whereas the accelerating action of Me is in the order $p>o>m$. These results, especially the rapid hydrolysis of (I), render untenable the steric hindrance theory previously suggested (A., 1932, 345). Since k is independent of the concn. and of $[H^{\cdot}]$ it is suggested that an unstable intermediate CHPhCl·OH first formed decomposes into PhCHO and HCl. The ratio $k_{\text{unsubstituted}}/k_{\text{substituted}}$ for 4-Cl-, 2 : 6-Br_2- (Cl_2-), 4-NO_2-, and 4-Me substituents in CH_2PhCl is 0·62, 0·12, 0·07, 10·6, and for $CHPhCl_2$ 0·004, 0·00029, 0·00027, and 71·4, respectively. Thus the retarding or accelerating action of substituents is greater in the benzylidene than in the benzyl series. J. W. B.

Pseudo-bases and compounds with reactive groups. Conductivity changes in systems of crystal-violet base and carboxylic acids. R. Rebek and G. Mandrino (Coll. Czech. Chem. Comm., 1933, 5, 317—330).—The velocity of salt-formation in systems of the type crystal-violet base–org. acid–$COMe_2$ at 25° has been determined conductometrically. In general, the velocity is the higher the stronger is the acid. Discrepancies are attributed to the fact that the vals. taken for the dissociation consts. of the acids refer to aq. solutions. Data, including conductivities of $COMe_2$ solutions, are given for the even fatty acids up to C_{18}, the dicarboxylic acids up to C_5, and for fumaric, maleic, and benzoic acids. D. R. D.

Kinetics of decomposition of trichloroacetic acid. II. Mechanism of decomposition of acid in aniline solutions. H. W. Patwardhan and A. N. Kappanna (Z. physikal. Chem., 1933, 166, 51—58; cf. A., 1932, 475).—The decomp. at 60—80° in NH_2Ph, and in NH_2Ph–C_6H_6 and NH_2Ph–PhMe mixtures, is unimol. in respect of the acid and bimol. in respect of NH_2Ph, and the temp. coeff., independent of the composition of the solvent, is 3·0. The hydrocarbons merely reduce the NH_2Ph concn. and have no effect on the decomp. The decomp. of the acid occurs either by activation by collision with two NH_2Ph mols., or by slow formation by a triple collision between two NH_2Ph mols. and an acid mol. of an intermediate compound which rapidly decomposes. R. C.

Mode of formation of chlorohydrins. VI. Higher homologues of ethylene chlorohydrin. H. Nilsson and L. Smith (Z. physikal. Chem., 1933, 166, 136—146; cf. A., 1920, i, 658).—The rates of hydrolysis of the homologues in neutral and alkaline solution at 18° have been determined and used to ascertain the proportions of the isomerides in the mixtures obtained by addition of HCl to C_2H_4 oxides. Substitution of Me for H considerably increases the rate of hydrolysis in alkaline solution, but has little effect on the rate in neutral solution. Michael's rule (A., 1900, i, 321) is confirmed. R. C.

Influence of nuclear substituents on side-chain reactions. I. W. S. Nathan and H. B. Watson (J.C.S., 1933, 1248—1252; cf. this vol., 890).—The relation obtained already is shown to apply to the dipole moments of compounds of the type PhX, and the crit. increments of the side-chain reactions of

C_6H_6 derivatives, with X as a nuclear substituent. With X in the *m*-position, halogen derivatives show deviations. With X in the *p*-position, electromeric effects cause complications, but otherwise the relation holds. H. J. E.

Mechanism of bimolecular reactions in solution. Addition of methyl iodide to pyridine in several solvents. W. H. Thompson and E. E. Blandon (J.C.S., 1933, 1237—1240).—The reaction kinetics were studied in $CHCl_3$, $PhNO_2$, CCl_4, and anisole as solvents at 40—60°, and in the gas phase at 215°, and the energies of activation were calc. The reaction rate in solution or in the gas phase was 10^{-4} to 10^{-6} of that for hypothetical gas reactions with the same activation energies. The rate was lowest in CCl_4 and highest in $PhNO_2$, the activation energy being greatest in $PhNO_2$. H. J. E.

Kinetics of the decomposition of the dichlorosuccinic acids. H. V. W. Robinson and D. T. Lewis (J.C.S., 1933, 1260—1262).—The reactions of $C_4H_4O_4Cl_2$ and *iso*-$C_4H_4O_4Cl_2$ with aq. KOH at 25° are bimol. The velocity coeff. for the *iso*-acid falls during the reaction, due to conversion into the normal form. In aq. solution at 70—90° the decomp. is unimol. The velocity is unaltered by added Na_2SO_4. Energies of activation were calc. Holmberg's results (J. pr. Chem., 1892, **46**, 394) were confirmed. H. J. E.

Mechanism of substitution in organic compounds. Elimination of bromine from bromoacetic acid and the bromoacetates. H. M. Dawson and N. B. Dyson (J.C.S., 1933, 1133—1143; cf. this vol., 234).—The replacement of Br by OH in $CH_2Br·CO_2H$ or bromoacetates may take place in one or two stages, but the primary stage in all cases involves the liberation of Br as Br′. Measurements of the rate of this process have been made under conditions which eliminate the disturbances due to products of reaction and to variations in the reaction medium. The results obtained with solutions containing (*a*) undissociated mols. of acid, (*b*) ions, (*c*) mols.+ions show that four independent reactions are involved and that the reaction velocity in general may be expressed by $v=v_1+v_2+v_3+v_4=k_1[A']+k_2[A']^2+k_3[HA]+k_4[HA].[A']$. Any one of the four reactions may be made predominant by varying the conditions. In special circumstances the general equation reduces to simple forms which facilitate the determination of the velocity coeffs. The mol.–ion mixtures obtained by mixing equiv. solutions of acid and salt show a max. on the velocity–composition curve. The influence of reaction products on the course of the reaction is discussed.

Action of hydrogen chloride on propyl alcohol. Relation between reaction velocity and electrostatic activity. S. Kilpi (Z. physikal. Chem., 1933, **166**, 285—304).—The rates of reaction of HCl with PrOH and of hydrolysis of PrCl have been measured in PrOH–H_2O mixtures at 96·5° and 110°. The rate of the former reaction varies with [HCl] according to the same equation as represents the variation of the activity of HCl with electrolyte concn. according to the Debye–Hückel theory. With increase in [PrOH] in the solvent the velocity coeff. increases by an amount of the same order as the increase in electrostatic activity of the HCl calc. by Born's equation (Z. Physik, 1920, **1**, 45). The temp. coeff. is independent of the composition of the solvent and is equal to that for the action of HCl on EtOH. The rate of hydrolysis of PrCl is independent of the electrolyte concn., which agrees with Brönsted's theory of complex formation (A., 1925, ii, 681). Referred to the stoichciometric H_2O concn. the rate of hydrolysis in solvent mixtures rich in PrOH is approx. const., independent of the composition of the solvent, and, since the electrostatic activity of a neutral mol. is independent of the dielectric const. of the solvent, agrees with the electrostatic activity of the reactant. Ionic diameters calc. from the velocity data by means of the Debye–Hückel theory are of an acceptable order of magnitude and vary with the composition of the solvent. R. C.

Kinetics of transformation of halogencalkylamines into heterocyclic compounds. V. Effect of phenyl group on ring opening and closing. H. Freundlich and G. Salomon (Z. physikal. Chem., 1933, **166**, 161—178; cf. A., 1926, 1010).—The conversion of $CHPhCl·CH_2·NH_2$ in alkaline solution into styreneimine hydrochloride, followed by determinations of [Cl′], follows the unimol. law and has the temp. coeff. 3·7 between 0° and 11°. The reverse reaction in HCl solution, which occurs only at $p_H<4$, is bimol., with the temp. coeff. 1·8 between 25° and 35°. $CHPhBr·CH_2·NH_2,HBr$ rapidly changes into the styreneimine salt in neutral aq. or EtOH solution, which is partly accounted for by the high velocity coeff. of ring closing and the weakness of the base. The introduction of Ph into chloroalkylamines at the C atom to which the Cl is attached greatly increases the rate at which Cl is eliminated and weakens the Ph·CN linking in the styreneimine formed. Measurements with $CH_2Cl·CHPh·NH_2$ indicate that only a Ph group in the α-position to the Cl increases the mobility of the latter. R. C.

Homogeneous catalysis of gaseous reactions. (A) Influence of iodine on the decomposition of acids, esters, ketones, and halides. (B) Influence of iodine on the decomposition of simple aliphatic amines and of hexane. S. Bairstow and C. N. Hinshelwood (J.C.S., 1933, 1147—1155, 1155—1160; cf. A., 1930, 1130).—(A) At 450° I catalyses the homogeneous decomp. of HCO_2Me, forming CH_4+CO_2 (29%) and MeOH+CO (71%). The further decomp. of MeOH is also catalysed, and follows the reactions (1) $MeOH=2H_2+CO$, (2) $H_2+I_2=2HI$, (3) $MeOH+2HI=CH_4+H_2O+I_2$. At 500°, MeOAc decomposes like an ether, forming MeCHO and CH_2O, which decompose further into CH_4+CO and H_2+CO, respectively. The reaction is catalysed by I. The decomp. of HCO_2H, AcOH, Et halides, $COMe_2$, and COMeEt is not catalysed by I. The kinetics are complex.

(B) I catalyses the decomp. of $NHEt_2$, $NHMe_2$, NEt_3, and NMe_3 at 400—550°. For NEt_3 the rate is proportional to the catalyst concn., but in the other cases falls with increasing concn. It is considerably greater for $NHEt_2$ or NEt_3 than for $NHMe_2$ or NMe_3.

The effect of I for NH_2Et or C_6H_{14} at 520—545° is small. The reaction mechanism and the analogy with the catalysed decomp. of ethers, aldehydes, and esters is discussed. H. J. E.

Flame phenomena of carbon monoxide. A. R. J. P. Ubbelohde (J.C.S., 1933, 972—977).—Observations have been made on the influence of H_2O vapour, H_2, and certain metals and salts on a flame of dry CO burning in dry O_2. The CO flame was lit in air and inserted in the O_2 chamber. As self-drying proceeded the flame gradually lengthened and was finally extinguished. With added H_2 the height of the flame increased as the mol. fraction of H_2 decreased. A method of determining H_2 in other gases down to mol. fractions of 10^{-7} is suggested. The formation of O_3, H_2O_2, and N oxides is shown not to be due to photosynthesis or the decomp. of H_2O_2. The effect of the vapours of alkali halides and Pt differs from that of H_2. W. R. A.

Polybasic acids as catalysts for reduction of ammoniacal silver solutions with phosphorous acid. B. Blaser (Z. physikal. Chem., 1933, **166**, 64—75).—If a mixture of a HNO_3 solution of H_3PO_3 and $AgNO_3$ is made ammoniacal, the amount of Ag separating, *w*, is very small, but if certain acids of high basicity, such as the phosphoric acids or citric acid, are present, *w* is considerably increased. The effect of the acid passes through a sharp max. with increase in its concn., and at high concns. is negligible. Some acids have no effect. As little as 3×10^{-6} g. of H_3PO_4 has a detectable catalytic action. The ratio H_3PO_3 : added H_3PO_4 for max. *w* is largely independent of the dilution and temp. For a given H_3PO_4 concn. *w* passes through a max. with increasing H_3PO_3 concn. R. C.

Ozone as an oxidising catalyst. VI. Action of diluents, of light, and of autoxidation catalysts. VII. Ozonation of hydriodic acid in solution. E. Briner and H. Biedermann (Helv. Chim. Acta, 1933, **16**, 1119—1124, 1125—1130; cf. this vol., 680).—VI. Dilution of ozonised O_2 with N_2 or CO_2 results in diminished catalytic activity of the O_3, but to a smaller extent than when the same degree of dilution is effected by lowering the total pressure. In the oxidation of $NaHSO_3$ or PhCHO the effect of ultra-violet radiation is superposed on that of O_3. The presence of other catalysts, whether positive or negative, diminishes the catalytic effect of O_3 in the oxidation of aq. $NaHSO_3$.

VII. Oxidation of aq. HI by ozonised O_2 is markedly increased in presence of AcOH, as well as by increasing [HI]. In no case does the oxidation yield exceed 100%. F. L. U.

Anti-oxidative action of thyroxine and of substances resembling thyroxine. L. de Caro (Z. physiol. Chem., 1933, **219**, 257—266).—Thyroxine (I), thyronine, di-iodothyronine, di-iodotyrosine, quinol, and toluquinol inhibit oxidation of Na oleate and linoleate (II), and delay decolorisation of carotene (III) in (II). The antagonism (I)-(III) is independent of the thyroid-like action of (I). The anti-oxidative action is probably due to phenolic OH and may be linked with complex formation with heavy metals (Fe, Cu), since KCN has a similar action. J. H. B.

Supposed chain mechanism of the formation of water from detonating gas in presence of platinum-black. B. Foresti (Ateneo Parmense, 1932, 4, 805—812; Chem. Zentr., 1933, i, 1567).—Reduction of WO_3 to W_2O_5 in presence of Pt observed by Kobosev and Anochin occurs only if the WO_3 and Pt are intimately mixed and the temp. is $\ngtr$50—60°; the presence of a small quantity of H_2O is favourable. Reduction takes place only at the catalytic surface and is due to adsorbed activated H_2. A. A. E.

Chain reactions in heterogeneous catalysis. B. Foresti (Ateneo Parmense, 1932, 4, 401—407; Chem. Zentr., 1933, i, 1567).—Thermal effects at the catalyst in the hydrogenation of C_2H_4 have been studied by means of a differential microcalorimeter. The reaction is exothermic and of the calc. order; Bennewitz and Neumann's view is therefore incorrect. Reaction in heterogeneous catalysis occurs exclusively at the surface. A. A. E.

Physical state of solid catalysts. E. Audibert and A. Raineau (Compt. rend., 1933, **197**, 596—598).—The *d* of a catalytic sample of any substance is always $<$ that of the same when non-catalytic; *e.g.*, catalytic Cu had *d* 7·60 and 7·52±0·5, whilst the *d* calc. from the *X*-ray structure of ordinary Cu is 8·9. Also the *X*-ray pattern of catalytic Cu is always blurred, indicating slight variations in the crystal lattice. Both deviations from normal disappear, with the catalytic activity, on prolonged heating, *e.g.*, for Cu after 6 hr. at 500—700°. It is concluded that for catalytic activity there must be increased distances between the atoms at certain points, which are the "active centres." C. A. S.

Nature of activated carbons. II. E. Berl and L. Reinhardt (Z. physikal. Chem., 1933, **166**, 81—96; cf. A., 1932, 217).—Determinations of the size and shape of the primary particles in various carbons have shown that these properties do not solely determine the activity of a C. Experiments on the change in particle shape on ignition of active C and the treatment of C with K have shown that the activity is a property of unsaturated C atoms at lattice irregularities in the sense of Smekal's "loose places" and Taylor's "active centres." The most active C would therefore consist of free C atoms, *i.e.*, amorphous C; since this is incapable of existence activation must aim at producing unsaturated C atoms on the surface of the primary C particles. The edge C atoms also make a contribution to the activity which varies with the particle shape, and the fall in this contribution, owing to the growth of the primary particles in the direction of the planes of the leaflets, is responsible for the decrease in activity of the C when heated at 1000—1500°. R. C.

Catalytic reduction of magnetic sand.—See B., 1933, 832.

Connexion between centres active in adsorption and catalytic activity. (Measurements with active iron.) R. Klar (Z. physikal. Chem., 1933, **166**, 273—284).—The adsorption of C_2H_4, C_2H_6, and H_2 by samples of Fe of various activities at 0—50° has been measured, the results for C_2H_4 being used to determine the no. of active centres, *n*; the hydrogenation of C_2H_4 on the same catalysts has also been studied. The results show that no direct comparison between n and the catalytic activity is admissible; the quality of the active centres must be taken into consideration. The rate of reaction is determined by reduction in the activation energy as a result of the adsorption of the reacting substances. R. C.

Catalysis. P. Sabatier (Chim. et Ind., 1933, **29**, Spec. no., 868).—Experiments on the diffraction of electrons at the surface of Ni in the presence of H_2 at low pressures (A., 1931, 12) are considered to support the intermediate compound theory of catalysis. A. A. L.

Synthesis of benzine.—See B., 1933, 773.

Anodic behaviour of nickel. III. K. Georgi (Z. Elektrochem., 1933, **39**, 736—743; cf. A., 1932, 1093).—The rate of dissolution of Ni in N-HCl increases proportionately to the amount of 30% H_2O_2 added. In N-H_2SO_4 the rate first increases linearly, but falls very rapidly between 0·3 and 0·6% H_2O_2. $FeCl_3$ added to N-HCl resembles H_2O_2, but in N-H_2SO_4 containing $Fe_2(SO_4)_3$, Ni behaves as a noble metal. CrO_3 in N-HCl resembles H_2O_2; in N-H_2SO_4 it resembles $Fe_2(SO_4)_3$. Simultaneous potential measurements are recorded. Results are correlated with and support the author's theory of active centres on the electrode. H. J. E.

***KZ*, *KG*$_{\text{I}}$, and *KG*$_{\text{II}}$ during the formation of the cathode deposit.** A. Glazunov and J. Janoušek (Chim. et Ind., 1933, **29**, Spec. no., 739—742).—In the electrolysis of $AgNO_3$ with flat electrodes the no. of centres of crystallisation increases with increasing c.d. and with diminishing concn. of the electrolyte. The latter is considered to be due to the action of the combined forces KG_{I}, normal to the cathode and along the lines of force, and KG_{II} parallel to the cathode surface, since the crystals are shown to grow in both these directions. A. A. L.

Relation between the direction of growth of the cathode deposit and the form of the lines of electric force. A. Glazunov and O. Rada (Chem. et Ind., 1933, **29**, Spec. no., 736—738).—When $AgNO_3$ is electrolysed in shallow vessels with obstacles between the cathode and anode Ag is deposited along the direction of the theoretical lines of force. A. A. L.

Electrolytic reduction of ketones in glacial acetic acid. I. Reduction of aromatic ketones. S. Swann, jun. (Trans. Electrochem. Soc., 1933, **64**, 245—252).—In H_2SO_4–AcOH solution $COPh_2$ was electrolytically reduced at all cathode materials tried at 60—90°, the main identifiable product being benzpinacolin, but no reduction occurred at room temp. The best yields of purest product were obtained at an Fe cathode at 0·3 amp. per sq. cm. in a solution containing 30% H_2SO_4. H. J. T. E.

Amino-acids and related compounds. VII. Oxidation of amino-acids. Y. Takayama (Bull. Chem. Soc. Japan, 1933, **8**, 213—230).—The ease of oxidation at a PbO_2 anode of a no. of NH_2-acids in 0·33M solution in 2N-H_2SO_4, as indicated by the rate of evolution of NH_3, falls in the order (a) glycine, valine, glutamic acid, alanine; (b) leucine, aspartic acid; (c) tyrosine (I), phenylalanine (II), the members in each group differing but little from one another. In the case of (I), (II), tryptophan, and histidine humin is formed after a time and the solution darkens; with lysine and proline darkening but no humin formation takes place. Carbonyl derivatives could not in general be isolated. H. F. G.

Photographic reciprocity law failure for radiations of different wave-length. J. H. Webb (J. Opt. Soc. Amer., 1933, **23**, 316—323).—The relation between intensity, time of exposure, and density of image has been investigated for rapid blue-sensitive and panchromatic plates, using various Hg lines from 3650 to 6910 Å. The simple reciprocity law does not apply, but the form of the curves is in all cases identical when the points of equal time of exposure are made to coincide. Curves are given for intermittent light of various frequencies. D. R. D.

Silver chromate [in photographic emulsions]. Lüppo-Cramer (Z. wiss. Phot., 1933, **32**, 129—130).—Ag_2CrO_4 emulsion in gelatin gives on exposure a latent image which can be physically developed. Development is greatly hastened if the exposed plate is treated with 0·1% aq. KI. More conc. solutions, KBr, or KCl cause fogging. The emulsion has a max. sensitivity to yellow light. J. L.

Photographic effect of *X*-rays. G. W. Brindley and F. W. Spiers (Phil. Mag., 1933, [vii], **16**, 686—691).—The density of blackening, D, was proportional to the intensity of monochromatic X-radiation, I, for vals. of $D < 1·4$. The variation of D with I was measured by an absorption method, the films providing the absorbing medium. H. J. E.

Chemical action of Röntgen rays. P. Günther (Angew. Chem., 1933, **46**, 627—631).—A lecture.

Relative effects produced by 200-kv. Röntgen rays, 700-kv. Röntgen rays, and γ-rays. II. Effects on iodides, Eder's solution, and photographic film. H. Q. Woodard, E. H. Quimby, and H. R. Downes (Amer. J. Roentgenol., 1933, **29**, 308—326).—When the radiation output is standardised by ionisation measurements the effect produced (liberation of I, pptn. of HgCl, or darkening of film) varies with the quality of the radiation. The variation is different for different substances. Ch. Abs.

Decomposition of ethyl chlorothioncarbonate in darkness and by the action of light. A. Berthoud and D. Porret (Helv. Chim. Acta, 1933, **16**, 939—942).—Freshly prepared ClCS·OEt undergoes very little decomp. at room temp., but more on heating. The action is not influenced by light. In the prep. by Delépine's method ($CSCl_2$+EtOH in Et_2O) a catalyst appears gradually to be formed which accelerates the decomp. F. L. U.

Response of a photographic emulsion to α-rays. T. R. Wilkins and R. N. Wolfe (J. Opt. Soc. Amer., 1933, **23**, 324—332).—The equation $D=D_{\text{max.}}(1-e^{-c_1N})$ holds for commercial emulsions of any thickness. The data indicate that an α-particle must actually hit a grain in order to affect it, a fact which may be utilised for the determination of grain-size. Plates may be temporarily desensitised to the luminescence produced by α-rays in air by means of an aq. solution containing 10 g. of $K_2Cr_2O_7$ and 4 c.c. of conc. H_2SO_4 per litre. D. R. D.

Attempt to prepare a chloride or fluoride of xenon. D. M. Yost and A. L. Kaye (J. Amer. Chem. Soc., 1933, 55, 3890—3892).—Experiments affording negative results are described. J. G. A. G.

Double nitrate of copper and ammonium. J. Milbauer and J. Doškař (Chim. et Ind., 1933, 29, Spec. no., 787).—No true Cu NH_4 nitrate exists. If solutions are mixed in the ratio 1 mol. $Cu(NO_3)_2,6H_2O$ to 12 mols. NH_4NO_3 and evaporated with agitation a blue cryst. product is obtained. This, however, contains only entrained Cu, which is readily removed by recrystallisation. C. I.

Existence of ammoniates of double salts. G. Spacu and P. Spacu (Z. anorg. Chem., 1933, **214**, 113—142).—Tensimetric experiments have established the existence of *compounds* of NH_3 with double chlorides as follows (figures denote no. of mols. of NH_3 combined with 1 mol. of the respective double salts): Rb_2CuCl_4 10, 5, 3, 2, 1; $CsCuCl_3$ 10, 5, 1; Cs_2CuCl_4 10, 6, 3, 2; $Cs_3Cu_2Cl_7$ 13, 10; Cs_2CoCl_4 9, 5, 2, 1; $CsNiCl_3$ 1; K_2FeCl_5 11, 6, 5, 2; $KAuCl_4$ 10, 3, 2; $RbAuCl_4$ 13, 12, 5, 4, 3; $CsAuCl_4$ 11, 10, 6, 5, 4, 3; K_2ZnCl_4 12, 5, 3, 1; $(NH_4)_2ZnCl_4$ 11, 10, 5, 4, 2; $(NH_4)_3ZnCl_5$ 12, 6; $(NH_4)_4CdCl_6$ 13, 12, 4. The above are distinguished from the NH_3 compounds with the simple heavy metal chlorides by their composition, colour, heat of formation, and NH_3 pressures. Ephraim's statement (A., 1917, ii, 319; 1919, ii, 291) that combination of NH_3 with double salts requires a preliminary decomp. of the latter is incorrect. F. L. U.

Hydrazinates of silver halides. H. Gall and H. Roth (Z. anorg. Chem., 1933, **214**, 201—208; cf. A., 1932, 919).—By the action of a dry EtOH solution of the appropriate base on a dry C_5H_5N (or 2-C_5H_4NMe) solution of AgX, the following *compounds* have been obtained: $3AgCl,N_2H_4$; $3AgBr,N_2H_4$; $AgBr,N_2H_4$; $2AgI,N_2H_4$; $AgCl,NHPh{\cdot}NH_2$; $AgBr,NHPh{\cdot}NH_2$. F. L. U.

Change in constitution of tricalcium phosphate on fusion. A. Travers and Bauer (Helv. Chim. Acta, 1933, **16**, 918—922).—An account of work previously published (this vol., 794). F. L. U.

Zinc phosphate cement. F. Halla and A. Kutzelnigg (Z. Stomatol., 1933, **31**, 177—181; Chem. Zentr., 1933, i, 2524).—ZnO and 89% H_3PO_4 afford a product giving *X*-ray lines of $Zn_3(PO_4)_2,4H_2O$ (hopeite); free ZnO is also present. A. A. E.

Reactions in the solid state at higher temperatures. X. Course of the reaction. W. Jander and W. Scheele (Z. anorg. Chem., 1933, **214**, 55—64; cf. A., 1932, 128).—The theory is advanced that, in the reaction between two solid particles, an amorphous or pseudomorphic reaction skin is first formed; from this crystals of the product form. Mixtures of $BaCO_3+MoO_3$, $BaCO_3+WO_3$, $ZnO+Cr_2O_3$, and $ZnO+Al_2O_3$ were heated at 250—550°, and the adsorption of Me-violet and fuchsin on the product was examined. At the temp. of incipient reaction adsorption increased (amorphous skin formation). At higher temp. it fell (cryst. product). Reaction zones are illustrated by photomicrographs of Mg_2TiO_4, formed from MgO and TiO_2 at 1500°. H. J. E.

Electrometric studies of the precipitation of hydroxides. X. Action of ammonia on solutions of potassium mercuri-iodide, and mercuric bromide, nitrate, sulphate, and perchlorate. XI. Constitution of ammoniacal solutions of (*a*) silver nitrate, (*b*) silver oxide. H. T. S. Britton and (Miss) B. M. Wilson (J.C.S., 1933, 1045—1049, 1050—1053).—X. In the action between NH_3 and $HgBr_2$ the NH_3 caused pptn. at a lower p_H than with NaOH. The composition of the ammoniated ppt. varied somewhat and did not correspond with either "fusible" or "infusible" white ppt., or with the bromide of Millon's base. K_2HgI_4 did not react unless sufficient NaOH was added to raise the p_H by 1; then the Nessler colour is produced followed by a ppt. $Hg(NO_3)_2$, in dil. HNO_3, gave a white ppt. with 2 mols. of NH_3. $Hg(ClO_4)_2$ and 2 mols. of NH_3 reacted to give a pale yellow ppt. With $HgSO_4$ in the presence of H_2SO_4, the p_H vals. are comparable with those prevailing with NaOH. In all cases the ppt. is an ammoniacal basic salt of variable composition. Control of the composition by variation of conditions is discussed.

XI. The variation in p_H during the addition of NH_3 and of NaOH to $AgNO_3$ has been investigated by means of a glass electrode. The p_H curves are given for both hydroxides in various concns. The formation of $Ag(NH_3)_2NO_3$ in solution is indicated and the mobility of $Ag(NH_3)_2^+$ is 62·0. By a glass electrode titration of an NH_3 solution of Ag_2O with HNO_3 a p_H curve is obtained; the base $Ag(NH_3)_2OH$, stronger than NH_4OH, is formed. W. R. A.

Reactions in the solid state. M. Paić (Arh. Hemiju, 1933, 7, 114—119).—The *X*-ray spectra of the products indicate the following reactions between solid substances: $HgSO_4+2HgO\longrightarrow 3HgO,SO_3$; $3HgO,2SO_3,2H_2O$ (I)$+3HgO\longrightarrow 2(3HgO,SO_3)+2H_2O$; $HgSO_4+HgS\longrightarrow\beta\text{-}HgSO_4,HgS$; $HgSO_4+HgI_2\longrightarrow HgSO_4,HgI_2$; (I)$+HgI_2\longrightarrow 3HgO,HgI_2,2SO_3+2H_2O$. (I) also reacts with HgS, yielding unidentified products. R. T.

Borates and boron. L. Hackspill (Helv. Chim. Acta, 1933, **16**, 1099—1118; cf. this vol., 894).—A lecture reviewing recent work. F. L. U.

Production of large artificial graphite crystals. A. Goetz, A. B. Focke, and A. Faessler (Physical Rev., 1932, [ii], 39, 168—170).—Unicryst. flakes of Ceylon graphite, treated with HF and HCl to remove SiO_2 and Fe, are suspended in a 3% solution of gum dammar in C_6H_6 and allowed to settle in an inhomogeneous electromagnetic field. Evaporation of the C_6H_6 leaves an artificial crystal of considerable rigidity. L. S. T.

Transformation of diamond into graphite. E. Szarvasy and B. Lányi (Math. Nat. Anz. ung. Akad. Wiss., 1932, 48, 137—146; Chem. Zentr., 1933, i, 1564).—Diamond powder heated for 7 hr. at 1370° gives non-transparent black crystals, but no Debye–Scherrer graphite lines appear; these lines appear after heating at 1600°, but diamond lines are still present after heating at 1750°, although not at 2000°.

A. A. E.

Fission of carbon monoxide on iron oxide and iron. H. A. Bahr and V. Jessen (Ber., 1933, 66, [*B*], 1238—1247; cf. Gluud *et al.*, A., 1929, 1409).—Fe_2C (9·7% C) can very probably be prepared pure from Fe and CO at as low a temp. as possible ($\nless$ 225°); at 230—400°, a mixture of Fe_2C and Fe_3C with free C probably results, whereas at $>$ 400° only Fe_3C (6·68% C) is produced. Carbonised products obtained by means of Fe oxide always contain O; detection of combined C by hydrogenation with H_2 is not quite trustworthy in this case and must be performed at 255—260°. Products obtained with Fe at $\nless$ 330° are free from O; at higher temp. the oxidising action of the liberated CO_2 is observed. Hydrogenation of combined C with H_2 can take place at 280—290°. Carbide formation from CO and Fe occurs relatively rapidly; subsequently, the main reaction is the separation of free C.

H. W.

Iodine and aqueous solutions of ammonia. E. Chirnoagă and E. Chirnoagă (Z. anorg. Chem., 1933, 214, 167—176).—When boiling aq. NH_3 is added to powdered I and the mixture shaken, no $N_2H_3I_3$ is formed, but a solution of I in aq. NH_4I. If $[NH_3] \ngtr 2\%$ NH_4IO_3 is also present. The ratio (free I/I′) is about 1 and is independent of the concn. Part of the I is present as ultramicrons and can be pptd. by $Al^{\cdots}$ or $Th^{\cdots\cdot}$. F. L. U.

[Preparation and properties of] ammonium azide. W. S. Frost, J. C. Cothran, and A. W. Browne (J. Amer. Chem. Soc., 1933, 55, 3516—3518).—The solubility in H_2O, C_6H_6, Et_2O, EtOH, and MeOH at 0—40° and the *d* of the saturated solutions have been determined. Solid NH_4N_3 has d^{20} 1·3459 and the v.p. between 15° and 134° is given by $\log p_{mm.} = -3428{\cdot}6/T + 11{\cdot}325$. Dissociation of the vapour is indicated. J. G. A. G.

Constitution of azoimide and azides. A. Hantzsch (Ber., 1933, 66, [*B*], 1349—1354).—Alkyl azides show discontinuous or selective absorption and are non-electrolytes. Since aryl azides have the structure $\overset{N}{\underset{N}{\vdots}}{>}NAr$, and N^V exists only in O compounds or NH_4 salts, alkyl esters are $\overset{N}{\underset{N}{\vdots}}{>}NAlk$. To N_3H the cyclic structure is also assigned by reason of its analogy with N_3Alk and its existence in H_2SO_4 as the trisulphate, incompatible with the possession of N^V. Since the liquid acid is associated, the structure is expanded to $HN{<}\begin{smallmatrix}N & \cdots\cdots & N\\ \vdots & & \vdots\\ N & \cdots\cdots & N\end{smallmatrix}{>}NH$. The alkali and NH_4 salts are electrolytes with continuous or general absorption in which the positive metals, as cations, are equally bound to all the negative atoms as anions. Only feebly positive metals are united in their salts to a single atom, and then, as ψ-salts, differ markedly in absorption from true salts. Since all true azides correspond with the *sym.* type and, in general, *sym.* are more stable than *asym.* complexes, it is assumed that N_3' is *sym.* and is thus distinct from nearly all other anions in the absence of a central atom. Cyanoazide is more strongly absorbent than any other azide, is hydrolysed normally to $N_3CO{\cdot}NH_2$ and N_3CO_2H, and therefore contains 2CN; it is $NC{\cdot}N{<}\begin{smallmatrix}N & \cdots\cdots & N\\ \vdots & & \vdots\\ N & \cdots\cdots & N\end{smallmatrix}{>}N{\cdot}CN$.

H. W.

Oxidation of phosphorus by water at high temperatures and under pressure. I. Red phosphorus. II. Yellow phosphorus. I. N. Buschmakin, M. V. Risakov, and A. V. Frost. **III. Phosphine. IV. Phosphorous acid.** I. N. Buschmakin and A. V. Frost (J. Appl. Chem. Russ., 1933, 6, 577—587, 588—606, 607—612, 613—620).—I. The reaction of oxidation of red P by H_2O takes place in two stages, liquefaction and oxidation of the products. The former stage consists of the reactions: $P_4+6H_2O=2H_3PO_3+2PH_3$; $P_4+8H_2O=2H_3PO_4+2PH_3+2H_2$; $P_4+12H_2O=4H_3PO_3+6H_2$; $P_4+16H_2O=4H_3PO_4+10H_2$; its duration falls from 2 hr. at 280° to 4 min. at 400°, and in presence of NiO catalyst to 4 min. at 280°. The second stage, which is practically completed in 3 hr., consists of the reactions: $H_3PO_3+H_2O=H_3PO_4+H_2$; $4H_3PO_3=3H_3PO_4+PH_3$; $PH_3+3H_2O=H_3PO_3+3H_2$; $PH_3+4H_2O=H_3PO_4+4H_2$; the velocity of these reactions is unaffected by NiO. The relative concns. of H_2O and P depend on the dimensions of the apparatus used, a certain optimum val. existing in each case. Under optimum conditions complete dissolution of P is obtained, to yield H_2 containing traces of PH_3 and P, and 20—25% solutions of H_3PO_4 with only traces of PH_3 and H_3PO_3. The process is unaffected by varying the partial H_2 pressure from 100 to 350 atm.

II. Yellow P is converted into H_3PO_4 as above, at 325°, and in presence of 1% of NiO. Apparatus is described for prep. on a technical scale.

III. PH_3 undergoes oxidation to H_3PO_3 and H_3PO_4 according to the equations given above. The reactions are catalysed by Ag and Cu_3P_2.

IV. Anhyd. H_3PO_3 decomposes at 280° as follows: $4H_3PO_3=3H_3PO_4+PH_3$. At higher temp. the reaction $PH_3+3H_2O=H_3PO_3+3H_2$ takes place, the necessary H_2O being obtained by dehydration of H_3PO_4. In presence of small quantities of H_2O the reaction commences at 330°, and proceeds as above, whilst with excess of H_2O the extremely slow reaction $H_3PO_3+H_2O=H_3PO_4+H_2$ takes place. A no. of oxides have no catalytic action on this reaction, but rapid and quant. conversion is attained in 30 min. at 350° by adding excess of aq. NH_3, when pure NH_4 phosphate crystallises on cooling. R. T.

Metaphosphoric acid. A. Travers and Chu (Helv. Chim. Acta, 1933, 16, 913—917).—In a mixture of aq. phosphoric acids containing excess of 10% NH_4Cl, $ZnSO_4$ ppts. only $H_4P_2O_7$ when the p_H is adjusted to 3·7—4·7, whilst H_3PO_4 is quantitatively pptd. as $ZnNH_4PO_4$ at p_H 7·0. Pptn. of HPO_3 is prevented by the NH_4Cl. Using this method of separation it is shown that no $H_4P_2O_7$ is formed either by the action of P_2O_5 on H_2O at 0° or by dissolving the product obtained by heating $(NH_4)_2HPO_4$ to dull redness. "Glacial metaphosphoric acid" of commerce consists of a mixture of H_3PO_4 with a (probably tri-)metaphosphate of Na. F. L. U.

The two forms of phosphorous acid. R. Dolique and A. Grangiens (Compt. rend., 1933, 197, 618—620).—Results obtained by Dubrisay's method (cf. A., 1918, ii, 368), with a solution of stearic acid in vaseline oil as dropping fluid, show that the acid produced by adding $\frac{1}{n}PCl_3$ to H_2O is at first preponderantly $P(OH)_3$ or $PHO(OH)_2$ according as n is $>$ or $<$ 50—75; more conc. or more dil. solutions tend to the same equilibrium mixture on keeping (cf. A., 1925, ii, 316). C. A. S.

Phosphorous fluorochlorides. H. S. Booth and A. R. Bozarth (J. Amer. Chem. Soc., 1933, **55**, 3890).—Fluorination of PCl_3 by SbF_3 in the presence of $SbCl_5$ yields PF_3 together with smaller quantities of the colourless *gases* PF_2Cl, b.p. −48°, m.p. −166°, and $PFCl_2$. 50% of a mixture of PCl_3 and PF_3 is converted into PF_2Cl and $PFCl_2$ by passage over porcelain at 200°. J. G. A. G.

Interaction of phosphorus bromide and chloride. I. A. Renc (Rocz. Chem., 1933, **13**, 454—463).—Mixtures of PCl_5 and PBr_5 in the proportions 1 : 5 to 1 : 1 yield red crystals, of composition $PCl_{0{\cdot}26}Br_{5{\cdot}63}$—$PCl_{2{\cdot}55}Br_{5{\cdot}97}$, and a light red liquid. When the ratio is 5·5 : 4·5 to 3 : 2 the mixture consists of two liquid phases, one light red, and the other deep red, composition $PCl_{2{\cdot}47}Br_{5{\cdot}80}$—$PCl_{3{\cdot}15}Br_{5{\cdot}71}$. Mixtures in the ratios 7 : 3 to 9 : 1 yield three phases: yellow crystals, $PCl_{4{\cdot}22}Br_{0{\cdot}80}$—$PCl_{4{\cdot}65}Br_{0{\cdot}35}$, a deep red liquid, $PCl_{3{\cdot}21}Br_{3{\cdot}94}$—$PCl_{3{\cdot}4}Br_{3{\cdot}3}$, and a light red liquid. R. T.

Action of nitric acid on hypophosphoric acid. B. Blaser (Z. physikal. Chem., 1933, **166**, 59—63).—Pure HNO_3 does not oxidise $H_4P_2O_6$ at the b.p., but catalyses its hydrolysis: $H_4P_2O_6+H_2O=H_3PO_3+H_3PO_4$. The H_3PO_3 formed is not attacked even by boiling 86% HNO_3. The hydrolysis of H_3PO_2 in aq. HNO_3 and HCl at 40° is unimol.; conc. HNO_3 is a weak acid. R. C.

Sulphur monoxide. II. Preparation and properties of pure sulphur monoxide. H. Cordes and P. W. Schenk (Z. anorg. Chem., 1933, **214**, 33—43; cf. this vol., 475).—SO was prepared at a SO_2 pressure of 10 mm. by using a more powerful discharge. The formula was proved by analysis ($2SO \rightarrow S+SO_2$). SO is inert towards O_2 at room temp. It reacts when sparked, but not explosively at the low pressures used. SO attacks Hg, Fe, Cu, and brass rapidly, but not rubber. With H_2O, S and polythionic acids, and with aq. KOH a strongly reducing solution, are formed. By inflating a rubber bladder in a glass vessel containing SO at a low pressure it could be compressed to 40 mm. pressure. The odour of SO resembles that of S heated just below its ignition point. H. J. E.

Complex and internally complex compounds of quinquivalent molybdenum. A. Rosenheim and C. Nernst (Z. anorg. Chem., 1933, **214**, 209—224; cf. A., 1932, 484).—The following *compounds*, prepared from $MoCl_5$, are described: with pyrocatechol ($C_6H_4O_2=P$),
$(NH_4)_2H[MoOP_3],0{\cdot}5PH_2,3H_2O$;
$KH_2[MoOP_3],0{\cdot}5PH_2,4H_2O$;
$(CN_3H_6)_2[Mo(OH)_3P_2],3H_2O$;
$(CN_3H_6)_2H[MoOP_3],5H_2O$;
$(C_5H_6N)_2H[MoOP_3],2H_2O$;
$(C_5H_6N)H[Mo(OH)_3P_2]$; $Tl_2[Mo(OH)_3P_2]$; with salicyclic acid or its Me ester,
$(C_5H_6N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_4\cdot CO_2]$,
$(C_9H_8N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_4\cdot CO_2]$,
$Mo(OH)_2Cl_2(O\cdot C_6H_4\cdot CO_2Me)$; with 2-hydroxy-*m*-toluic acid, $(C_5H_6N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_3Me\cdot CO_2]$,
$(C_9H_8N)_2[Mo_2(OH)_5Cl_5O\cdot C_6H_3Me\cdot CO_2]$; with phenols,
$MoCl_2(OPh)_3$, $MoCl_2(O\cdot C_6H_4Me)_3$ *m*- and *p*-,
$Mo(OH)Cl_2(SPh)$, $Mo(OH)Cl_2(O\cdot C_{10}H_7)_2$ (β);
also $[(CH_2)_6N_4H]_3[Mo_2O_3Cl_7],6H_2O$,
$(C_5H_6N)_2[Mo_2O_3Cl_4(C_2O_4)],2H_2O$,
$(C_9H_8N)_2[Mo_2O_3Cl_4(C_2O_4)],H_2O$,
$(NH_4)_3[(MoO_2)_2(HCO_2)_5],0{\cdot}5HCO_2NH_4,0{\cdot}5H_2O$, and
$K_3[(MoO_2)_2(HCO_2)_5],0{\cdot}5HCO_2H,0{\cdot}5H_2O$. Complex and internally complex Mo^{V} compounds present a close analogy with those of Nb and Ta, not with those of As and Sb. F. L. U.

Polonium. E. Rona (Pharm. Presse, 1932, 37, Wiss.-prakt. Heft, 168—170; Chem. Zentr., 1933, i, 1599).—A review of properties and application to biological problems. A. A. E.

Interaction of saturated solutions of potassium chromate and manganous chloride. H. Wunschendorff and (Mme.) P. Valier (Compt. rend., 1933, **197**, 584—585).—On adding a boiling saturated solution of K_2CrO_4 to one of $MnCl_2$ as long as a ppt. is formed the red ppt. first formed turns black. The latter is well washed and boiled out with H_2O, giving a red solution which on evaporation to a syrup and finally over $CaCl_2$ gives ruby crystals of $MnCr_2O_7$, whilst the black ppt. is $Cr_2(MnO_3)_3$ (cf. A., 1907, i, 961; 1910, ii, 299). C. A. S.

Bromine fluoride, BrF. O. Ruff and A. Braida (Z. anorg. Chem., 1933, **214**, 81—90).—BrF was prepared by the interaction of Br and F at 10°, and was purified from Br, BrF_3, and BrF_5 by fractional condensation. It is also formed in the interaction of Br with BrF_3 or BrF_5 (cf. A., 1932, 133). It forms a reddish-brown gas and a dark red liquid, b.p. approx. 20°, f.p. −33°. At 50° it decomposes rapidly into BrF_3, BrF_5, and Br. The formula was established from the gas density and analysis. The liquid Br fluorides are partly miscible. Only traces dissolve in liquid Br. H. J. E.

BrF_3. O. Ruff and A. Braida (Z. anorg. Chem., 1933, **214**, 91—93; cf. A., 1932, 707).—The v.p. was measured between −5° and 80°. The b.p. (extrapolated) is 127±1°, and the heat of vaporisation approx. 10 kg.-cal. per mol. The high val. for the Trouton const. (25·3) indicates association of liquid BrF_3. H. J. E.

Extraction of rhenium from molybdenite. E. Kronmann, V. Bibikova, and M. Askenova (Z. anorg. Chem., 1933, **214**, 143—144; cf. A., 1932, 1224).—Experimental details are given. F. L. U.

Rhenium. M. Prettre (Bull. Soc. chim., 1933, [iv], 53, 669—681).—A lecture on the extraction, properties, determination, and compounds of Re.

Rhenium trichloride. W. Geilmann, F. W. Wrigge, and W. Biltz (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1932, 579—587; Chem. Zentr., 1933, i, 1598—1599).—$ReCl_4$, when heated in an indifferent gas, affords $ReCl_3$, which is purified by sublimation in vac. at 500—550°. It forms reddish-black lustrous crystals, apparently trigonal; the magnetic susceptibility at 20° is $-0{\cdot}13\times10^{-6}$. $ReCl_3$ is only slightly ionised in aq. solution. Characteristic reactions are described. Heating with KCl in vac. at 600° affords K_2ReCl_6 and Re. A. A. E.

Magnetic and *X*-ray investigations of the ageing of hydrated ferrous oxide. O. Baudisch and L. A. Welo (Naturwiss., 1933, **21**, 659—660).—Freshly prepared FeO,H_2O will reduce alkali nitrates only in the presence of O_2, and at the same time any oxidisable compound present may be oxidised. In the absence of O_2 the FeO,H_2O remains unchanged, and will not effect these reactions. This power is also lost with keeping under anaërobic conditions. FeO,H_2O kept for some days and oxidised by the air gives a ferromagnetic red Fe_2O_3,H_2O, the space lattice of which corresponds with α-Fe_2O_3. Since it is ferromagnetic, γ-Fe_2O_3 must be present. FeO,H_2O changes into compounds with less H_2O on keeping, the H_2O previously combined chemically being now held by adsorption. In presence of O_2, H_2O is eliminated even at room temp., and breaks up according to the equation $H_2O \longrightarrow H + O(H_2O_2)$, a reaction which is not possible with the aged compound, which will not therefore react as above. A. J. M.

Iron chloride and other metallic chlorides in the Friedel–Crafts reaction. E. Wertyporoch [with I. Kowalski and A. Roeske] (Ber., 1933, **66**, [*B*], 1232—1238).—Measurements of electrical conductivity and transport nos. of $FeCl_3$ in EtCl, EtBr, $\mathrm{Pr}^{\alpha}\mathrm{Cl}$, $\mathrm{Pr}^{\beta}\mathrm{Cl}$, $\mathrm{Bu}^{\alpha}\mathrm{Cl}$, $\mathrm{Bu}^{\beta}\mathrm{Cl}$, *n*- and *iso*-amyl chloride, *n*-$C_6H_{13}Cl$, BzCl, and AcCl, supported by the behaviour in individual cases after addition of C_6H_6, C_6Et_6, COPhMe, or $COPh_2$, lead to the conclusion that the production of alkyl- or acyl-benzenes from hydrocarbons and alkyl or acyl chloride in presence of $FeCl_3$, as in the case of $AlCl_3$ or $AlBr_3$, is due to the production of a conducting, ternary complex in which a loosening of the halogen linking in the alkyl (acyl) chloride and of the H linking in the hydrocarbon occurs; stabilisation occurs by elimination of HCl and production of alkyl-(acyl-)benzene. The complex formation is much less complete than with the freely sol. $AlCl_3$ or $AlBr_3$ and the yields of alkylbenzenes are very poor. The amounts of CH_2Ph_2, $CHPh_3$, CPh_3Cl, COPhMe, and $COPh_2$ obtained by use of $FeCl_3$ are about half those obtained in presence of $AlCl_3$. The high conductivity of HCl in MeCN is increased by dissolution of $ZnCl_2$, apparently owing to complex formation. $ZrCl_4$ is slightly sol. in EtBr and causes conversion of C_6H_6 into C_6Et_6. $BeCl_2$ in EtBr does not react with C_6H_6, but, at higher temp., behaves towards $CPhCl_3$ in the same manner as $AlCl_3$. Even under increased pressure and temp., the chlorides of Hg, Tl, Th, Ti, and Sn do not cause reaction between C_6H_6 and EtBr or C_6H_6 and $CHCl_3$ in the sense of the Friedel–Crafts change. H. W.

Hexacyanocobaltic acid and *n*-propyl alcohol. F. Hölzl, W. Brell, and G. Schinko (Monatsh., 1933, **62**, 349—358; cf. A., 1931, 944, 1382).—By passing HCl gas into a solution of $H_3[Co(CN)_6]$ (I) in $\mathrm{Pr}^{\alpha}\mathrm{OH}$ (II) is obtained the *oxonium* salt $[Co(CN)_6](H_2O\mathrm{Pr}^{\alpha})_3$ (of type $[A]R_3$), and tensimetric measurements with the efflorescent product also indicate the existence of the salts $[A]H_2R$ and $[A]HR_2$. The continuous rate of fall of acid titre observed when (I) is heated in (II) at 98° is increased and becomes irregular in the presence of increasing amounts (0—10%) of H_2O, indicating the sequence of reactions (1) esterification of (I) to a carbylamine complex (which occurs in H_2O-free media); (2) fission of free HCN (accelerated by H_2O); (3) and (4) a two-stage hydrolysis of the carbylamine; (5) introduction of aquo-groups in place of NC; and (6) the formation of highest complexes. In 98% $\mathrm{Pr}^{\alpha}\mathrm{OH}$ after 42 hr. a violet *compound* $[(H_2O)_2(NC)_3Co{\cdot}CN{\cdot}Co{\cdot}CN\mathrm{Pr}^{\alpha}(CN)_3(OH_2)]H \rightleftharpoons [(HO)(NC)_3H_2OCo{\cdot}CN{\cdot}Co{\cdot}CN\mathrm{Pr}^{\alpha}(CN)_3(OH_2)]H_2$ is isolated, and from the 90% $\mathrm{Pr}^{\alpha}\mathrm{OH}$ solution the dark red *compound* $[(H_2O)(NC)_4Co{\cdot}CN{\cdot}Co(CN)_4(OH_2)]H_3 \rightleftharpoons [(HO)(NC)_4Co{\cdot}CN{\cdot}Co(CN)_4(OH)]H_5$ is obtained, which gives no carbylamine, a $NH_2\mathrm{Pr}^{\alpha}$ odour with alkali, and loses 9·17% H_2O in a vac. to give the compound $[(CN)_3{\vdots}Co{\vdots}(CN)_3{\vdots}Co{\vdots}(CN)_3]H_3$. J. W. B.

Constitution of nitro–aquo–cobaltic salts. J. Meyer and O. Rampoldt (Z. anorg. Chem., 1933, **214**, 1—15; cf. A., 1926, 925).—From *cis*- and *trans*-$[Co\ en_2ClNO_2]$ salts (I) (Werner, A., 1901, i, 512) the *cis*- and *trans*-forms of the *compounds* $[Co\ en_2(H_2O)(NO_2)](SO_3{\cdot}C_{10}H_6{\cdot}NH_2)_2$ (II) and its trihydrate were prepared. Action of H_2SO_4, H_2SeO_4, HNO_3, and $H_2C_2O_4$ on (II) gave the corresponding *cis*- and *trans*-salts of these acids. All were anhyd. The *d*- and *l*-*cis* forms of (II) were isolated by hydration of the corresponding forms of (I). The two optically active forms gave identical crystals, differing from the inactive form. The *compounds*, *trans*-$[Co(NH_3)_4(H_2O)(NO_2)](SO_3{\cdot}C_{10}H_6{\cdot}NH_2)_2$ and *trans*-$[Co(NH_3)_4(NO_2)I]I$ were prepared. The constitution is discussed. H. J. E.

Nickel nitrites of bivalent metals. A. Ferrari and R. Curti (Gazzetta, 1933, **63**, 499—506; cf. A., 1932, 483).—The *compounds* $Ba_2[Ni(NO_2)_6]$, $Sr_2[Ni(NO_2)_6]$, and $Pb_2[Ni(NO_2)_6]$, the prep. of which is described, have a cubic structure very similar to that of K_2PtCl_6, with 4 mols. per unit cell and *a* 10·67, 10·54, and 10·55 Å., respectively. The corresponding Ca_2, Ba Sr, Ba Ca, and Sr Ca compounds could not be obtained. O. J. W.

Bivalent rhodium. H. Reihlen and W. Hühn (Z. anorg. Chem., 1933, **214**, 189—195).—Na_2 or Na H *salts* of the acids $H_2[Rh(SO_3)_2]$, $H_4[Rh(SO_3)_2SO_4]$, and $H_6[Rh_2(SO_3)_4SO_4]$, in which Rh is bivalent, have been obtained by the action of aq. Na_2SO_3 or $NaHSO_3$ on $RhCl_3$. F. L. U.

Complex compounds. A. A. Grinberg (Ann. Inst. Platine, 1933, No. 10, 47—64).—The results of physico-chemical research on the co-ordination compounds of the Pt group are discussed. R. T.

Complex platinum compounds. I. I. Tscherniaev (Ann. Inst. Platine, 1933, No. 10, 33—46).—The work of the Institute since 1918 is reviewed. R. T.

Spectroscopic analysis of minerals with the acetylene–air burner. A. K. Russanov (Z. anorg. Chem., 1933, **214**, 77—80).—A method of introducing finely-powdered minerals into a C_2H_2–air stream, which then burns at a jet, is described. Reproducible flame conditions, suitable for quant. spectrum analysis, are obtained. 0·005 Rb or 0·004% Cs was detectable. H. J. E.

Determination of rock constituents by semi-micro-methods. (Miss) W. C. A. Guthrie and (Miss) C. C. Miller (Min. Mag., 1933, **23**, 405—415).—Details are given of the method of working on separate portions of 0·1 g. Analyses are given of crinanite, olivine-dolerite, olivine-basalt, and a plastic clay; compared with standard analyses made on the same materials they show no loss in accuracy. L. J. S.

Indirect chemical determination of minerals in a polished surface by "spotting." G. Gutzeit, M. Gysin, and R. Galopin (Arch. Sci. phys. nat., 1933, [v], **15**, 192—196).—The application of org. reagents is described. C. W. G.

Fluorescence indicators. K A. Jensen (Z. anal. Chem., 1933, **94**, 177—179).—14 new fluorescent indicators for acidimetry, covering the p_H range 0·0—11, are described. The use of an ultra-violet lamp (cf. this vol., 242) is recommended. J. S. A.

Titration with fluorescence indicators. S. Malowan (Chem.-Ztg., 1933, **57**, 755).—Acid–alkali titrations of coloured or turbid liquids can be carried out in ultra-violet light, using methylumbelliferone as indicator. E. H. S.

Application of the thermionic valve in potentiometric titration. K. Masaki and O. Hirabayashi (Bull. Chem. Soc. Japan, 1933, **8**, 245—254).—The grid of the valve is rendered positive with respect to the filament, and the resulting grid current is employed to polarise the Pt electrodes. Part of the grid current is shunted in order to maintain a const. p.d. between the electrodes up to the equivalence point. The approach to the end-point is clearly indicated, and it is therefore unnecessary to plot the readings. Typical results for a variety of titrations are given. H. F. G.

Electrometric determination of halogens. J. L. Tremblay (Arch. phys. biol., 1932, **10**, 67—73; Chem. Zentr., 1933, i, 2282—2283).—The potentiometric determination of Br′ and I′ in presence of much Cl′ has been studied. Cl′ in serum can be determined without previous destruction of protein if the p_H is sufficiently far removed from the isoelectric point (4·7). A. A. E.

Determination of iodine liberated from iodides by nitrous acid. A. Guerbet (J. Pharm. Chim., 1933, [viii], **18**, 258—262).—Following the liberation of I by HNO_2 and extraction of the I by $CHCl_3$, the addition of $NaHCO_3$ to the $CHCl_3$ extract renders the subsequent titration with $Na_2S_2O_3$ inaccurate owing to the small but significant formation of NaOI which reacts with $Na_2S_2O_3$ to form $NaHSO_4$. Substitution of Na_2SO_3 for $Na_2S_2O_3$, however, enables an accuracy of ±0·5% to be attained. F. O. H.

Use of glycerol in iodometry. A. T. Bawden and S. K. Dyche (Ind. Eng. Chem. [Anal.], 1933, **5**, 347).—I may be weighed, without loss by volatilisation, by adding a quantity to a solution of glycerol (2 vols.) and saturated aq. KI (1 vol.) and noting the increase of wt. An open vessel may be used. E. S. H.

Colorimetric determination of fluorine. W. D. Armstrong (Ind. Eng. Chem. [Anal.], 1933, **5**, 300—302).—F′ is determined by comparing its fading action on the colour of Fe^{III} acetylacetone with that of a similar solution to which has been added a known amount of F′, thus eliminating differences due to acidity. E. S. H.

Acidimetric determination of sulphide and hydrosulphide in presence of one another. K. A. Jensen and O. V. Rasmussen (Z. anal. Chem., 1933, **94**, 180—183).—The accuracy of Podreschetnikov's method (cf. B., 1926, 154) is enhanced by titrating the Na_2S to an end-point at p_H 9·6—10, using thymolphthalein (I) as indicator. The sample is dissolved in H_2O, treated with $BaCl_2$ or $SrCl_2$, and an aliquot part titrated with 0·1N-HCl, using (I); 10 c.c. of CH_2O solution are added and titration is continued with phenolphthalein. J. S. A.

Photometric investigation of Nessler reaction and Witting method for determination of ammonia in sea-water. H. E. Wirth and R. J. Robinson (Ind. Eng. Chem. [Anal.], 1933, **5**, 293—296).—Photometric investigation of the colours developed by four Nessler reagents at low NH_3 concns. in H_2O and sea-H_2O shows that, whilst all the reagents have a non-sensitive region in H_2O, Treadwell's reagent has no non-sensitive region in sea-H_2O. It is possible to determine 0·003 mg. N as NH_3 without the device of adding known amounts of NH_3. The sensitivity of the Treadwell reagent increases with increasing [Cl′]. There is no error due to adsorption in determining NH_3 in sea-H_2O by Witting's method. E. S. H.

Determination of nitrogen in calcium cyanamide in presence of nitrate.—See B., 1933, 827.

Determination of phosphorus in copper and copper–zinc alloys.—See B., 1933, 792.

Electrolytic determination of arsenic. F. N. Moerk (Trans. Electrochem. Soc., 1933, **64**, 173—186).—An improved form of the electrolytic modification of the Gutzeit method for the determination of small amounts of As has been developed, and the influence of varying the operating conditions has been examined. Under the standardised conditions recommended for the highest accuracy the time required for the test is notably shortened. H. J. T. E.

Determination of silver and copper in alloys.—See B., 1933, 792.

Qualitative analysis with small quantities. IV. Detection of alkaline-earth metals. A. J. Scheinkmann and A. B. Politzschuck (Z. anal. Chem., 1933, **94**, 192—193).—Ca, Sr, and Ba carbonates are dissolved by warming with NH_4OAc. Ca may then be pptd. by $K_4Fe(CN)_6$, Ba by cold Na_2SO_4, and Sr by boiling the filtrate from the Ba pptn. J. S. A.

Detection of barium, strontium, and calcium in the course of systematic analysis. J. Brintzinger and H. Brintzinger (Z. anal. Chem., 1933, **94**, 166—170).—Ba, Sr, and Ca are pptd. by addition of conc. H_2SO_4 to the (conc.) filtrate from group II. $CaSO_4$ is extracted with hot dil. HCl and yields characteristic crystals of $CaSO_4,2H_2O$ when evaporated on a micro-slide. $SrSO_4$ and $BaSO_4$ are reduced to sulphides on a Pt wire in the reducing flame, dissolved in HCl, and Ba is pptd. with H_2SiF_6. The solution is evaporated to dryness, K_2CrO_4 added, and Sr pptd. with KIO_3. J. S. A.

Indirect colorimetric determination of calcium. E. M. Emmert (Plant Physiol., 1933, **8**, 469—473).—The method is based on the fact that in NH_3-free solutions of $Fe^{\cdot\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, and PO_4''', addition of NaOH ppts. Fe and Mg as hydroxides and Ca as $Ca_3(PO_4)_2$. The reduction in PO_4''' content of the solution is thus a measure of the $Ca^{\cdot\cdot}$ present, and is determined by the Mo-blue method. Org. matter may be removed by ignition. Al, if present, reacts similarly to Fe. If the $[PO_4''']$ is high relative to $[Ca^{\cdot\cdot}]$ the accuracy of the method is lessened. This is obviated by preliminary addition of known amounts of Ca. A. G. P.

Quantitative spectrographic studies of co-precipitation. II. Group II elements with barium sulphate. L. Waldbauer and E. St. C. Gantz (Ind. Eng. Chem. [Anal.], 1933, **5**, 311—313).—When solutions of sulphates are added to aq. $BaCl_2$, the sulphates of Ca, Sr, and Cd, but not those of Be, Mg, or Zn, are co-pptd. with $BaSO_4$. When CdI_2 is used there is evidence of preferential adsorption of I' or CdI_4''. E. S. H.

Determination of magnesium. C Brioux (Rapport, Inst. Recherches Agron. Paris, 1932, 177; Proc. Internat. Soc. Soil Sci., 1933, **8**, 119).—To avoid co-pptn. of Mg during the removal of Fe and Al by aq. NH_3 in the presence of much NH_4 salts, double pptn. or the use of a very slightly alkaline solution is recommended. If Ca is present in Mg solutions during pptn. of the latter as $MgNH_4PO_4$ the Ca phosphate also pptd. is insol. in NH_4 citrate. Vals. for Mg obtained by a single pptn. as $MgNH_4PO_4$ are unduly high. The ppt. is redissolved in HCl and repptd. by addition of a min. of aq. NH_3. No further addition of NH_4 phosphate is made. A. G. P.

Reagent for magnesium: 5-*p*-acetamidophenylazo-8-hydroxyquinoline. G Gutzeit, R. Monier, and R. Bachoulkova-Brun (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 203—206).—An alkaline solution of this substance (prep. described) gives a violet colour with $Mg^{\cdot\cdot}$ in dilutions $\nless 1:10{,}000$. $Sn^{\cdot\cdot}$ and metals giving coloured ppts. with alkali hydroxides must be absent. $Ca^{\cdot\cdot}$ decreases the sensitivity of the test, but other metals do not interfere. Solid carbonates containing Mg give the colour with the reagent in EtOH. R. S. C.

Ignition of magnesium ammonium phosphate. VIII. S. J. Kiehl and H. B. Hardt (J. Amer. Chem. Soc., 1933, **55**, 3555—3560; cf. this vol., 352).—During the process of losing H_2O in the early stages of ignition, $MgNH_4PO_4,6H_2O$ has the property of attaching firmly within its structure certain volatile org. compounds which, if present, later decompose with the deposition of graphitic C. The luminescence or flash during the ignition of $MgNH_4PO_4,6H_2O$ and $MgNH_4PO_4,H_2O$ is due to the large evolution of heat which accompanies the rapid crystallisation of $Mg_2P_2O_7$ at 550—600°. The transformation is slower and occurs without the flash at 500°. J. G. A. G.

Quantitative analysis of the hydrogen sulphide group. J. Kunz (Helv. Chim. Acta, 1933, **16**, 1044—1049).—A scheme of separation based on pptn. by H_2S in presence of graded concns. of HCl is described. F. L. U.

Accuracy of lead analyses. L. T. Fairhall (J. Ind. Hyg., 1933, **15**, 289).—A reply to the criticisms of the author's methods by Kehoe and co-workers (cf. this vol., 1200). F. O. H.

Detection and determination of small amounts of inorganic substances by colorimetric methods. N. Strafford (Inst. Chem., 20 Feb., 1933, 36 pp.).—A review, with outlines of the procedures recommended for a no. of metals. The depth of colour produced in the Kastle–Meyer method of determining Cu is independent of the Cu content of the solution, as the reaction is purely catalytic, and the method is therefore of little val. H. F. G.

Detection and determination of small quantities of mercury. F. Cucuel (Mikrochem., 1933, **13**, 321—364).—A review.

Asbestos in permanganate titrations. R. W. Curtis and J. Finkelstein (Ind. Eng. Chem. [Anal.], 1933, **5**, 318—319).—Filter-paper reacts with $0{\cdot}1N$-$KMnO_4$, but asbestos does not. E. S. H.

Bunsen's method [of analysis of oxides]. New apparatus. K. Braddock-Rogers and K. A. Krieger (Ind. Eng. Chem. [Anal.], 1933, **5**, 342—344).—The accuracy of Bunsen's method for the decomp. and analysis of $KMnO_4$, Pb_3O_4, PbO_2, and MnO_2 is confirmed. HBr and HCl are of equal val. in this reaction. The use of $Na_2S_2O_3$ is preferred to H_3AsO_3 in the determination. A modified apparatus is described. E. S. H.

Organic reagents in qualitative analysis. I. Separation of iron, chromium, and aluminium. L. Lehrman, E. A. Kabat, and H. Weisberg (J. Amer. Chem. Soc., 1933, **55**, 3509—3511).—Excess of 10% aq. $(CH_2)_6N_4$ completely ppts. $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Cr^{\cdot\cdot\cdot}$ from boiling aq. solutions of $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, and $Zn^{\cdot\cdot}$ containing excess of NH_4NO_3. The degree of separation is such that 1 mg. of one metal is detected in the presence of 100 mg. of another. J. G. A. G.

Precipitation of iron as basic acetate. P. Wegner, C. Cimerman, and M. Gorni (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 157—158).—$FeOAc(OH)_2$ is pptd. at $p_H < 6$, the optimum val. of the latter being 4·2. C. W. G.

Application of sodium salt of *p*-toluenesulphonchloroamide ("chloramine") in volumetric analysis. A. S. Komarovski, V. F. Filonova, and I. M. Korenman (J. Appl. Chem. Russ., 1933, **6**, 742—748).—p-$C_6H_4Me{\cdot}SO_2NClNa$ (I) can be applied in place of I for titrating $Fe(CN_6)''''$,

CNS', N_2H_4, H_3PO_2, and CS_2. The titre of 0·1004*N*-(I) remained const. during 40 days, and fell to 0·0991*N* after 90 days. R. T.

Adaptation of the dimethylglyoxime–benzidine test for cobalt to the usual scheme of qualitative analysis. A. W. Scott (J. Amer. Chem. Soc., 1933, **55**, 3647—3648).—The mixture of NiS and CoS is dissolved in HCl containing HNO_3. The liquid is evaporated. There are then added successively dil. AcOH, 1 g. NaOAc, 0·5 c.c. of 0·5% benzidine in EtOH, and excess of dimethylglyoxime in EtOH. Ni is removed by filtration. A red filtrate indicates Co. The method is satisfactory with concn. of Ni times ≯ 50-fold that of Co. J. G. A. G.

Determination of antimony in copper alloys.—See B., 1933, 792.

Colorimetric determination of bismuth. C. Mahr (Z. anal. Chem. 1933, **94**, 161—166; cf. this vol., 1025).—A dil. HNO_3 solution of the sample is treated with excess of solid $CS(NH_2)_2$ (I). $Fe^{\cdots}$ if present is first reduced by N_2H_4. Pptd. compounds of (I) with heavy-metal salts are filtered off, washed with a saturated solution of (I) in dil. HNO_3, and the filtrate is diluted to a definite vol. The yellow colour is compared with that produced in a solution of known Bi content. 0·01% Bi in Pb or Cu may be determined. Addition of KF destroys the yellow coloration produced by Sb if present. J. S. A.

Potentiometric determination of gold in alkaline solutions with vanadyl sulphate. C. del Fresno and E. Mairlot (Z. anorg. Chem., 1933, **214**, 73—76; cf. this vol., 800).—$NaAuO_2$ may be determined with 0·1*N*-$VOSO_4$ at 30—70° in presence of 7·5—30% alkali. The reaction is $AuO_2'+3VO^{\cdot\cdot}+8OH'=Au+3VO_3'+4H_2O$. H. J. E.

Spot method for the approximate determination of platinum. N. A. Tananaev and G. T. Michaltschischin (Z. anal. Chem., 1933, **94**, 188—192).—0·002 c.c. of a 0·01% Pt solution is added to a drop of saturated aq. $TlNO_3$ absorbed on filter-paper, and treated with a drop of acid $SnCl_2$. The deep orange coloration produced is compared with that given by the solution under examination. One or other solution is so diluted that the intensities are matched. Au and Pd interfere; the stain produced is sol. in aq. NH_3. J. S. A.

Delayed relay for thermostats. J. Korpiun and A. Geldbach (Z. Elektrochem., 1933, **39**, 755—756).—In the valve circuit described a controlled time lag from a fraction of a sec. to several min. occurs in breaking the heating current circuit. Fouling of the Hg contact of the thermoregulator is thereby avoided. H. J. E.

Adjustable temperature regulator. W. G. Parks (Ind. Eng. Chem. [Anal.], 1933, **5**, 357).—The height of the Hg can be varied by adjusting a plunger fitted to a side tube, thus avoiding the necessity of removing Hg when the temp. is to be changed. E. S. H.

Camera for Laue spectrograms. R. Stratta (L'Ind. Chimica, 1933, **8**, 986—987).—A simple form of camera with centering device is described. H. F. G.

Sodium lamp. W. A. N. Markwell (Perf. Ess. Oil Rec., 1933, **24**, 294—295).—Two glow electrodes (W), surrounding an electron-emitting material, are contained in an atm. of inert gas together with some Na. The electrodes provide the necessary heat during the starting period (20 sec.), and are then switched off. The discharge then takes place through the Na. The emitting surface is about 10×15 mm. and of the total intensity, about 99% is due to Na-*D* line. Little heat is generated and radiation is const. in intensity. E. H. S.

Origin and development of absolute colorimetry by means of grey solutions. A. Thiel (Z. anal. Chem., 1933, **94**, 170—177).—A review. Polemical. Procedure to avoid possible deterioration of the grey solutions is discussed. J. S. A.

Interferometry. II. Construction, testing, and use of reflexion echelons for the visible and ultra-violet regions. W. E. Williams (Proc. Physical Soc., 1933, **45**, 699—726).—Details of the construction and method of testing reflexion echelons are considered, different methods of mounting being compared. A method for using the instrument for wave-length measurements is described. The echelon provides an alternative method of standardising length units in terms of light wave-lengths. J. W. S.

Rotating chamber for interferometric determination of refractive indices of solutions. A. Kruis and W. Geffcken (Z. physikal. Chem., 1933, **166**, 16—22).—The construction and manipulation are described. R. C.

***X*-Ray method for quantitative comparison of crystallite orientation in cellulose fibres.** W. A. Sisson and G. L. Clark (Ind. Eng. Chem. [Anal.], 1933, **5**, 296—300).—The method described is based on the assumption that the distribution of the crystallites around the pencil of *X*-rays is proportional to the distribution of intensity around the 002 diffraction ring. A microdensitometer with rotating stage is used for the intensity measurements. Results for three grades of cotton are given. E. S. H.

Tyndallmetric examination of filtered liquors. A. B. Cummins and M. S. Badollet (Ind. Eng. Chem. [Anal.], 1933, **5**, 328—332).—The turbidity of the filtrate is determined photometrically from the intensity of the Tyndall beam produced in it under standard conditions. The application of the method to refining of sugar is discussed and results are given. E. S. H.

Micro-absorption spectra. C. R. Naeser and B. S. Hopkins (Ind. Eng. Chem. [Anal.], 1933, **5**, 358).—A simple procedure is described. E. S. H.

Silver filter for ultra-violet light. G. C. Brock (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 563—566).—The filter is prepared from a lantern slide, which is exposed, developed to a brown colour, and then the emulsion stripped and supported between two plates of "Uviol" glass or "Vita-glass." The filtering action, attributed to the presence of colloidal Ag, is superior to that of sputtered or chemically deposited films. Max. transmission occurs at about 3000 Å. J. W. S.

Conditions for securing accuracy in spectrophotometry. F. Twyman and G. F. Lothian (Proc. Physical Soc., 1933, 45, 643—662).—Basic principles in the design and use of spectrophotometers are discussed. The applications of absorption photometry to chemistry are considered and the photographic, visual, and photo-electric methods compared. The uses of spectrophotometry as a means of describing a radiation, especially in connexion with colorimetry, the comparison of light sources, and quant. spectrum analysis, are also discussed. J. W. S.

Device for measuring intensity of illumination [in plant work]. H. R. Rosen and W. M. Roberds (Science, 1933, 78, 241—242). L. S. T.

Measurement of critical potentials with a screened grid valve. F. L. Arnot (J. Sci. Instr., 1933, 10, 294—295).—A 4-electrode wireless valve containing a trace of Hg may be used. C. W. G.

Calibration and salt error of the antimony electrode. Its application in soil reaction measurements. N. J. King (Ind. Eng. Chem. [Anal.], 1933, 5, 323—327).—Calibration of the Sb electrode in many series of buffer solutions shows a linear relation between e.m.f. and p_H between p_H 3·0 and 12·0. Contrary results of previous investigators have been due to the presence of KCl. The use of the Sb electrode in N-KCl is recommended in soil studies, the salt error having been determined. E. S. H.

Standard-cell comparator. A specialised potentiometer. H. B. Brooks (Bur. Stand. J. Res., 1933, 11, 211—231).—The difference between the e.m.f. of the cell under test and that of the reference cell is added automatically (algebraically) to the e.m.f. of the latter. The e.m.f. is thus indicated directly. H. J. E.

Suitability of some rectifier photo-cells for the measurement of daylight. H. H. Poole and W. R. G. Atkins (Sci. Proc. Roy. Dublin Soc., 1933, 20, 537—546).—Under conditions specified the cells appear to be suitable for approx. comparative measurements. H. G. R.

Selenium rectifier photo-electric cell. V. N. Lepeshinskaya (J. Exp. Theor. Phys., U.S.S.R., 1932, 2, 388—392). Ch. Abs.

Use of gas-filled photo-electric cells in photometric measurements. T. D. Gheorghiu (Ann. Physique, 1933, [x], 20, 133—242).—A detailed description is given of a spectrophotometer in which two photo-cells of known characteristics are used, one being employed for control purposes to permit the use of an unstable light source. The accuracy of the arrangement is discussed in detail. Beer's law holds for solutions of $CuSO_4$, but not for $CuCl_2$ or for alkaline solutions of Cu tartrates and Cu racemate. The deviations are attributed to the presence of complex ions. At equal concn., Cu *d*- and *l*-tartrates absorb the Hg green line equally, but the racemate is more transparent and a mixture of equal parts of *d*- and *l*-tartrate solutions much more opaque. The absorption min. is the same for *d*- and *l*-tartrates and racemate, but that of the mixture is at a lower wavelength. The significance of these results is discussed. J. W. S.

Improved form of mercury distiller. P. G. N. Nayar, V. V. Rao, and B. Dasannacharya (Indian J. Physics, 1933, 17, 91—93).—An apparatus dispensing with the auxiliary vac. pump is described. N. M. B.

Improved chain-packed distilling column. S. T. Schicktanz (Bur. Stand. J. Res., 1933, 11, 89—92).—The column is 250 cm. long and is packed with jeweller's brass locket chain, size nos. 13—18. From 1500 c.c. of a 50 mol.-% mixture of C_6H_6 and $C_2H_4Cl_2$ (b.p. 3·42° apart), a distillate of 450 c.c. of pure C_6H_6 and a residue of 350 c.c. of pure $C_2H_4Cl_2$ were obtained. D. R. D.

Automatic water still. H. B. Gordon (Ind. Eng. Chem. [Anal.], 1933, 5, 357).—The still, designed for a small laboratory, can be made from simple apparatus. E. S. H.

Variable-control still head for laboratory columns. S. C. Rothmann (Ind. Eng. Chem. [Anal.], 1933, 5, 338—339). E. S. H.

Modified Soxhlet [extractor]. T. R. Liston and W. M. Dehn (Ind. Eng. Chem. [Anal.], 1933, 5, 306). E. S. H.

Mechanically operated burette. C. H. Whitnah (Ind. Eng. Chem. [Anal.], 1933, 5, 352—354).—The apparatus is designed to add aq. NaOH to a reaction mixture as required to maintain a const. e.m.f. over periods up to several days. E. S. H.

Microburette for potentiometric micro-analysis. H. L. Lochte and A. Hoover (Ind. Eng. Chem. [Anal.], 1933, 5, 335).—The apparatus can be used for potentiometric titrations with 1 c.c. or less of 0·1—0·01N solutions. E. S. H.

Continuous air-lift extractor. Application to determination of benzoic acid. R. P. Chapman and L. P. Hammett (Ind. Eng. Chem. [Anal.], 1933, 5, 346—347).—Continuous circulation of the solvent (CCl_4) through the solution to be extracted and through 0·1N-NaOH is caused by a current of air. E. S. H.

Ground-glass junctions. H. L. Baumbach (Ind. Eng. Chem. [Anal.], 1933, 5, 349).—A hollow cone of sheet Cu is used. The inside of the cone is used for grinding the taper and the outside for grinding the socket. E. S. H.

Measurement of viscosity by oscillating columns. S. Venkataraman (Indian J. Physics, 1933, 17, 25—42).—A new method for liquids, by measuring photographically the damping of their oscillations in a tube, is described. Data are obtained for CCl_4, CS_2, $CHCl_3$, EtOAc, C_6H_6, PhMe, AcOH, C_5H_5N, xylene, and H_2O. N. M. B.

Microvolumetric procedure. A. Romwalter (Mitt. berg.-hüttenmänn. Abt. Hochsch. Sopron, 1932, 4, 67—76; Chem. Zentr., 1933, i, 1482).—A simple apparatus for the determination of the vol. of gas evolved in reactions involving a few mg. of substances is described. A. A. E.

Copper to glass seals. H. de Laszlo (J. Sci. Instr., 1933, 10, 296—297).—Cu tubing is turned down to a feather edge, coated with $Na_2B_4O_7$, and sealed to the inside of a glass tube. C. W. G.

Silicon tetrafluoride volatilisation. W. D. Armstrong (Ind. Eng. Chem. [Anal.], 1933, 5, 315—317).—A simplified apparatus for the evolution and collection of SiF_4 in quant. analysis is described.
E. S. H.

Preparation of permeable extraction thimbles for laboratory filtration. F. J. Williams (Ind. Eng. Chem. [Anal.], 1933, 5, 322). E. S. H.

Multiple steam-bath. W. L. Beuschlein and W. M. Dehn (Ind. Eng. Chem. [Anal.], 1933, 5, 327).
E. S. H.

Circulator for ice water. L. L. English (Ind. Eng. Chem. [Anal.], 1933, 5, 351). E. S. H.

Use of pump as gas sampler. R. C. Lee (Ind. Eng. Chem. [Anal.], 1933, 5, 354—356).—The advantages of a metal plunger pump are discussed.
E. S. H.

Air trap for water lines. L. Lehrman and E. A. Kabat (Ind. Eng. Chem. [Anal.], 1933, 5, 358).
E. S. H.

Simple automatic pressure regulator. C. C. Coffin (J. Amer. Chem. Soc., 1933, 55, 3646—3647).—The device described has been used for obtaining const. temp. between 210° and 280° with the vapour of boiling Hg. J. G. A. G.

Automatic pressure regulators for vacuum distillation. II. Sulphuric acid as a manostat fluid. E. B. Hershberg and E. H. Huntress (Ind. Eng. Chem. [Anal.], 1933, 5, 344—346; cf. this vol., 480).—A modified apparatus is described, in which H_2SO_4 replaces Hg as a manostat liquid. In view of the increased viscosity of H_2SO_4, the diam. of the column should be about four times that used with Hg. Evolution of gas is negligible when H_2SO_4 (d 1·71) is used. E. S. H.

Micropyknometer for determination of displacements of isotopic ratio in water. E. S. Gilfillan and M. Polanyi (Z. physikal. Chem., 1933, 166, 254—256).—A pyknometer by means of which 10^{-5} to 10^{-2} mg. may be weighed is described. R. C.

Apparatus for taking samples of gas at the moment of explosion. A. G. Suvorov (J. Appl. Chem. Russ., 1933, 6, 753—754).—Apparatus is described. R. T.

Influence of surface tension on hydrometer readings. B. Scheda (Chem. Fabr., 1933, 6, 413—414).—An example of the error introduced by surface tension variation in hydrometer readings is in the apparent alteration of d for distilled H_2O as determined by the hydrometer, if a trace of oil is floating on the surface. Determinations of d for aq. solutions are on this account uncertain in the third or fourth decimal point. By the construction of pairs of hydrometers of which the capillarity consts. are in a fixed ratio the error can be corr. An example of the use of such pairs is in the determination of d for dil. EtOH solutions, when results obtained in this way closely approach those given by the pyknometer. C. I.

Geochemistry.

Presence of formaldehyde in rain and dew and its formation by photo-oxidation of organic compounds and the problem of carbon assimilation. N. R. Dhar and A. Ram (J. Indian Chem. Soc., 1933, 10, 287—298).—CH_2O does not appear to be formed in atm. electrical discharges. Dew contains more CH_2O than rain-H_2O (about 0·0015 g. per litre). Numerous org. substances yield CH_2O when exposed to sunlight and air; in some cases CH_2O is believed to be a direct product of photo-oxidation, whilst in others it may be obtained from the photosynthesis of the energy-rich CO_2 and H_2O produced by photo-oxidation. The relation between respiration and photosynthesis in plants is considered, and a theory of C assimilation is advanced. E. S. H.

Characteristics of bore-hole waters in the Karachukhur district. I. Tolbin (Azerbaid. Neft. Choz., 1933, No. 3, 56—62).—The primary salt content (Palmer) increases from 72 to 97% in the fourth horizon of the Apsheron peninsula. d decreases with stratigraphic depth from 1·143 to 1·042. The alkalinity of some horizons increases from roof to wings. The secondary Palmer alkalinity content is $< 0·1\%$. The waters are hard. The primary alkalinity begins in the wings of the fifth and sixth horizons.
Ch. Abs.

Meteoric iron and silica-glass from the meteorite craters of Henbury (Central Australia) and Wabar (Arabia). L. J. Spencer [with M. H. Hey] (Min. Mag., 1933, 23, 387—404).—Meteorite craters are not merely percussion indentations; they are explosion craters due to the sudden vaporisation of part of the material, both of the meteorite and of the earth's crust, at the high temp. developed by the impact. The meteoric irons from both localities are of exactly the same type, namely, a medium octahedrite containing Ni 7·3%, with little Co, Cu, and S; d 7·69. They are found scattered outside the craters, the larger masses showing the normal octahedral lamellar structure of a single crystal, whilst in the smaller twisted masses there is a partial obliteration of this structure with granulation of the kamacite (transformation of α-Fe into γ-Fe at 850°). These are only weathered remnants of larger masses torn asunder by the explosions. The associated iron-shale, representing the weathered product, contains Fe_2O_3 78·45, FeO 8·32, NiO 5·28, CoO 0·32, etc., and consists of a mixture of limonite, hæmatite, magnetite, and trevorite ($NiFe_2O_4$).

SiO_2-glass, of rare occurrence in nature, shows a remarkable development at Wabar, building the rims of the meteorite craters. A snow-white highly vesicular glass, formed by the fusion and boiling of the clean desert sand, contains SiO_2 92·88% with small amounts of Ti, Al, Fe, Mn, Mg, Ca, Sr, Na, K, H_2O; d 2·10, n 1·468. Bombs of this material shot out from the craters are coated with a thin skin of black SiO_2-glass free from bubbles and containing Fe_2O_3 0·28, FeO 5·77, NiO 0·35 (Fe : Ni as in the meteorite); d

2·24, n 1·500. Embedded in some of the vesicular SiO_2-glass are numerous ($\ngtr 2\times10^6$ per c.c.) polished spheres (0·003—0·14 mm. diam.) of Ni–Fe containing Ni 8·8%. These represent a rain of molten metal into a pool of boiling SiO_2. The vaporisation of Fe, Ni, and SiO_2 indicates temp. up to about 3500°. At Henbury the SiO_2-glass is less abundant, and being formed from a ferruginous sandstone it is less pure; SiO_2 68·88%, d 2·31, n 1·545. L. J. S.

Biological detection of radioactivity of rocks. O. Muck (Strahlenther., 1933, **46**, 378—383; Chem. Zentr., 1933, i, 2429).—The reaction depends on the vasoconstriction of probed nasal mucous membrane after contact of the human body with radioactive material. A. A. E.

Geochemistry of boron. II. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., 1932, 528—545; Chem. Zentr., 1933, i, 2074—2075; cf. this vol., 928).—Numerous determinations of B in eruptive rocks and minerals, sedimentary rocks, sea-H_2O, weathering products, and soils have been carried out. Magmatic rocks usually contain $\ngtr$ 0·0005—0·001% B_2O_3. High vals. are obtained for sea salts and sediments. B is also contained in siliceous skeletons of sea organisms and in coral. The origin of B and Cl in the sea is discussed. A. A. E.

Crystal chemistry of the silicates. F. Machatschki (Geol. För. Stockholm Förh., 1932, **54**, 447—470; Chem. Zentr., 1933, i, 1575).—The chief structural types of silicates are discussed. A. A. E.

Bismuthite. M. A. Peacock (Z. Krist., 1933, **86**, 203—211).—Well-developed crystals of bismuthite occur at Tasna (Bolivia) associated with pyrite, mispickel, jamesonite (?), and metavauxite. The bismuthite is orthorhombic holohedral, $a:b:c=$ 0·9862 : 1 : 1·0493, and contains Bi 76·51, Sb 3·58, S 20·07%. C. A. S.

Minerals from the gorge of the Lieser near Spittal (Carinthia). H. Heritsch (Z. Krist., 1933, **86**, 253—269; cf. this vol., 892).—The following minerals occur near the junction of pegmatite with garnet-gneiss, amphibolite, and eclogite: (I) dark green hornblende, d 3·15, $a:b:c=$0·5406 : 1 : 0·2829, β 73° 52′, n_α 1·651, n_β 1·659, $n_\gamma-n_\alpha$ 0·022; (II) pistacio-green epidote, $a:b:c=$1·589 : 1 : 1·791, and 1·636 : 1 : 1·868, β 63° 48′ and 63° 57′, n_β 1·731; (III) greyish-green clinozoisite, d 3·28, n_α 1·715, n_β 1·722, $n_\gamma-n_\alpha$ 0·014; (IV) bluish-green zoisite, n_β 1·703; (V) plagioclase (albite-oligoclase), d 2·63, n_α 1·535, n_β 1·540, $n_\gamma-n_\alpha$ 0·009; (VI) pyrrhotite, d 4·63, Fe 60·50, Ni 0·74, S 38·06%; (VII) clove-brown axinite, d 3·280, $a:b:c=$1·170 : 1 : 0·778 and 1·204 : 1 : 0·897, α 96° 18′ and 97° 59′, β 99° 14′ and 99° 54′, γ 104° 13′ and 103° 51′, n_α 1·686, n_β 1·693, $n_\gamma-n_\alpha$ 0·010. Analyses of (I), (III), (V), and (VII) are (in that order): SiO_2 44·25, 37·57, 63·61, 41·39; TiO_2 0·55, 0·18, 0, 0; Al_2O_3 10·09, 28·20, 21·56, 18·31; Fe_2O_3 4·09, 6·61, 1·07, 0·65; FeO 14·54, 1·87, 0·15, 8·12; MnO 0·19, 0·12, trace, 2·70; MgO 9·76, 0, 0·12, 1·64; CaO 11·34, 23·56, 2·30, 20·13; Na_2O 0·63, 0·08, 9·42, 0·22; K_2O 1·41, 0·01, 1·29, 0·05; B_2O_3 0, 0, 0, 5·37; H_2O 3·44, 1·93, 0·63, 1·80. There also occur in small quantities blue asbestiform hornblende, graphite (in the pegmatite), chalcopyrite, specular iron, analcite, and perhaps natrolite. The paragenesis indicates deposition from gradually cooling H_2O. C. A. S.

Anapaite, ainigmatite, and eudidymite. C. Palache (Z. Krist., 1933, **86**, 280—291).—Anapaite, $Ca_2Fe(PO_4)_2,H_2O$ (cf. A., 1902, ii, 268; 1903, ii, 303), is triclinic, $a:b:c=$0·8575 : 1 : 0·9401, α 108° 56′ 40″, β 104° 5′ 40″, γ 78° 25′ 24″. Ainigmatite (or cossyrite) (cf. A., 1929, 1223) is triclinic, $a:b:c=$1·0014 : 1 : 0·5853, α 97° 2·5′, β 96° 49·5′, γ 112° 26·5′. Eudidymite is monoclinic, $a:b:c=$1·7103 : 1 : 1·8951, β 76° 42′. Previous results are discussed. C. A. S.

Frequent presence of pyrite crystals in the diatoms of lacustrine chalk: their probable bacterial origin. E. Joukowsky (Arch. Sci. phys. nat., 1933, [v], **15**, 182—185).—Descriptions are given. C. W. G.

Indium and scandium in pegmatite. H. Romeyn, jun. (J. Amer. Chem. Soc., 1933, **55**, 3899—3900).—Preliminary. The samples contain 1·0—2·8% In and 0·5—1·2% Sc. J. G. A. G.

Recent limestones. J. Pia (Tsch. Min. Petr. Mitt., 1933, Ergänz.-Bd., 1—420).—A comprehensive treatise with review of the extensive literature on the deposition of $CaCO_3$ from solution. This takes place under a variety of conditions (abiogenic, physiological, and org.) and with many kinds of resulting products. L. J. S.

Petrography and petrology of the Mount Devon diabase porphryry. G. A. Muilenburg and S. S. Goldich (Amer. J. Sci., 1933, [v], **26**, 355—367).—The dike was extruded as a porphyritic magma, large crystals of basic plagioclase having been formed prior to intrusion. Secondary products were formed by the action of hydrothermal solutions derived probably from the main reservoir from which the magma was extruded. The secondary change is regarded as an end phase of the primary intrusion. H. F. G.

Portlandite, a new mineral from Scawt Hill, Co. Antrim. C. E. Tilley (Min. Mag., 1933, **23**, 419—420).—The larnite–spurrite rock occurring at the contact of dolerite and chalk contains in cavities colourless hexagonal plates with d 2·23, n_ω 1·575, n_ϵ 1·547, and the spacings a 3·64, c 4·85 Å. These characters together with microchemical tests identify the mineral with $Ca(OH)_2$, which has been previously found in Portland cement briquettes (Ashton and Wilson, A., 1927, 402). The mineral is associated with afwillite, and both have evidently been derived by the hydration of larnite and spurrite. L. J. S.

Piedmontite in quartz-muscovite-schist from New Zealand. F. J. Turner (Min. Mag., 1933, **23**, 416—418).—A reddish schist from Shotover valley, western Otago, thought to be coloured with hæmatite, when examined in micro-sections was found to contain piedmontite. Details are given of the optical characters. L. J. S.

Forms under which platinum and allied metals occur in nature. O. E. Zvjagintzev (Ann. Inst. Platine, 1932, No. 10, 14—33).—A discussion. R. T.

Malayan soils. I. Introduction. H. A. Tempany. **II. Classification and properties.** J. H. Dennett (Malay. Agric. J., 1933, 21, 345—361).—The composition and conditions of formation of these soils are discussed. A. G. P.

Lithology and palæobotany of certain British coals. R. Crookall (Fuel, 1933, 12, 276—279).—The conditions under which the original plant débris was deposited are discussed in relation to the formation of the different lithological types (fusain, durain, clarain, and vitrain) in British coals. The important factors in this process were (*a*) the level at which the waters stood in relation to the accumulating plant débris, and (*b*) the plant parts present. Numerous lenticles of fusain indicate that, during the accumulation of the plant débris, the general level of the peat-like matter approximated to that of the swamp waters, so that masses of débris were frequently exposed to sub-aërial decay. In some cases the rarity of durain is to be correlated with the scarcity of Lycopods in the flora of the immediate roofs of the co-extensive seams. The fragile nature of some coals may be due to the high proportion of clarain and fusain (*e.g.*, Kent coals), or to the exceptional development of cleat. A. B. M.

Organic Chemistry.

Nature of valencies in organic chemistry. G. Urbain (Bull. Soc. chim., 1933, [iv], 53, 637—652).—A lecture.

Theory of free radicals of organic chemistry. E. Hückel (Faraday Soc., Sept., 1933, Advance proof; cf. this vol., 890). R. S. C.

Chemistry of radicals with tervalent carbon. K. Ziegler (Faraday Soc., Sept., 1933, Advance proof).—The tendency to dissociation of substituted ethanes is influenced by both the unsaturation and the size of the substituents. The latter factor operates by increasing the distance separating the ethane C atoms. Published work is reviewed and it is stressed that quant. data are essential for further progress. R. S. C.

Free radicals and ions as factors in chemical change. T. M. Lowry (Faraday Soc., Sept., 1933, Advance proof).—A summary is given of the ways in which C·C linkings may rupture and of the methods used for investigation of the problem. R. S. C.

Use of free methyl and ethyl in chemical synthesis. F. A. Paneth [with H. Loleit and W. Lautsch] (Faraday Soc., Sept., 1933, Advance proof).—By decomp. of the Pb compounds Me, Et, and CH_2Ph (but not Pr, Bu, CH_2, or Ph) radicals are obtained in low concn. Me or Et radicals with cold As, Sb, or Bi mirrors give $AsMe_3$, $(AsMe_2)_2$, $(AsMe)_5$, $AsEt_3$, $(AsEt_2)_2$, $(AsEt)_5$, $SbMe_3$, $(SbMe_2)_2$, m.p. 17·5°, $SbEt_3$, $BiMe_3$, and $BiEt_3$. With hot mirrors an increased proportion of the less volatile mono- and di-alkyl compounds is formed, together with $(SbEt_2)_2$ and $(BiMe_2)_2$. *$SbEt_2O_2H$* is prepared. R. S. C.

Preparation of tetramethylmethane (neopentane) and determination of its physical constants. F. C. Whitmore and G. H. Fleming (J. Amer. Chem. Soc., 1933, 55, 3803—3806).—CMe_4, b.p. 9·4°/760 mm., f.p. −19·5° (corr.), is conveniently prepared in 42—50% yield from MgMeCl and $Bu^{\gamma}Cl$ in PhMe at 45—50°. Numerous physical data are given. H. B.

Hexamethylethane. F. C. Whitmore, C. J. Stehman, and J. M. Herndon (J. Amer. Chem. Soc., 1933, 55, 3807—3809).—C_2Me_6, m.p. 101°, is obtained in 10% yield from MgMeCl and $CMe_3{\cdot}CMe_2Br$ (I) in xylene at 60°, in 18—19% yield from $MgBu^{\gamma}Cl$ and AgBr in Et_2O, and in 50% yield from $ZnMe_2$ and (I) in xylene. Other methods tried are summarised. H. B.

Antimony trichloride as reagent for the ethylenic linking. S. Sabetay (Compt. rend., 1933, 197, 557—559).—30% $SbCl_3$–$CHCl_3$ solution with ethylenic compounds or certain aldehydes gives yellow, brown, red, or blue (much less intense than with carotenoids) colours and usually a pink, yellow, or brown ppt. The reaction is negative for saturated or aromatic (otherwise saturated) compounds, and for styrene, cinnamic and crotonic acids, allyl alcohol, and C_2HCl_3. Bases give white ppts. Et octinenoate gives a pink ppt. R. S. C.

Preparation of Δ^{α}- and *iso*-butene. H. Pines (J. Amer. Chem. Soc., 1933, 55, 3892—3893).—Pure Δ^{α}-butene is obtained when $Bu^{\alpha}OH$ is passed at the rate of 75 g. per hr. through a glass tube filled with Al_2O_3 at 375—425°. The discrepancy between this result and that of Matignon *et al.* (this vol., 693) is probably due to the method of analysis used by the last-named. Pure *iso*butene is prepared by Ipatiev's method (A., 1903, i, 594). H. B.

Polymerisation of diolefines with olefines. II. Function of Δ^{β}-pentene in the polymerisation of isoprene. C. A. Thomas and W. H. Carmody (J. Amer. Chem. Soc., 1933, 55, 3854—3856).—Polymerisation of pure isoprene (I) by solid $AlCl_3$ occurs slowly and gives an insol. polymeride (II). When dry HCl is passed into a mixture of (I), $AlCl_3$, and naphtha, (II) and sol. polymeride (III) result; the amount of (III) produced is related to the quantity of the hydrochloride of (I) formed [when sufficient of this is used to dissolve all the $AlCl_3$, (III) is the sole product]. The yield of (III) is also increased with other mutual solvents ($PhNO_2$, EtOAc) for (I) and $AlCl_3$. The function of Δ^{β}-pentene in the polymerisation previously studied (A., 1932, 830) is to act as a "solubiliser" for the $AlCl_3$. The mechanism of polymerisation of (I) is discussed (cf. Houtz and Adkins, this vol., 600). H. B.

Ozonisation of lycopene. Formation of lævulic acid and lævulaldehyde. H. H. Strain (J. Biol. Chem., 1933, 102, 151—155).—Ozonisation of lycopene (I) yields, according to the conditions, lævulaldehyde [*bis*-2 : 4-*dinitrophenylhydrazone,* m.p.

235·5—236·5° (corr.)] or lævulic acid [2 : 4-dinitrophenylhydrazone, m.p. 203—205·5° (corr.); β-*naphthylhydrazone*, m.p. 136·5° (corr.)], the max. yield of the latter being 1·32 mols., thus confirming Karrer's formula for (I). Citral, but not xanthophyll, forms the same products under similar conditions.
R. S. C.

Fluorination of organic compounds. III. Action of fluorine on organic compounds. W. Bockemüller (Annalen, 1933, **506**, 20—59; cf. A., 1931, 611).—*n*-Hexadecane (1 mol.) and F (1 mol.) (prep. by electrolysis of fused KHF_2 described in detail) in CCl_4 at 15° give a *fluorohexadecane*, b.p. 104—112°/0·2 mm., m.p. 7° (previous softening). $PrCO_2H$ (or PrCOCl) similarly affords (at 0°) a mixture of β- and γ-fluorobutyric acids, b.p. 80—98°/13 mm. [from which a p-*phenylphenacyl* ester (I), m.p. 92°, is prepared], since hydrolysis (aq. NaOH) gives $CHMe{:}CH{\cdot}CO_2H$ and γ-butyrolactone; some γγγ-trifluorobutyric acid is also produced, since treatment of the original product with aq. $NaHCO_3$ and subsequent distillation gives a residue containing $({\cdot}CH_2{\cdot}CO_2H)_2$. α-*Fluorobutyric acid*, b.p. 90°/13 mm. [p-*phenylphenacyl* ester, m.p. 91·5°, not identical with (I)], is obtained by hydrolysis (dil. HCl) of its *Et* ester, b.p. 138—141° (prepared from $CHBrEt{\cdot}CO_2Et$ and AgF–CaF_2 at 150°). (I) is also prepared from the hydrolysis product of the similar fluorination of $Pr{\cdot}CO{\cdot}OAc$. $Pr^{\beta}CO_2H$ is fluorinated to (mainly) β-*fluoro*iso*butyric acid*, b.p. 80—82°/13 mm. *cyclo*Hexane and F in CCl_2F_2 at −80° give cyclo*hexyl fluoride*, b.p. 100°, and higher F-compounds. C_2Cl_4 and F similarly afford (mainly) $C_2Cl_4F_2$, b.p. 91°, m.p. 26·5° (cf. Booth *et al.*, A., 1932, 496), some C_2Cl_5F, m.p. about 100°, a trace of CCl_3F, and some *octachlorodifluorobutane*, b.p. 139—142°/13 mm. [which may be formed thus: $C_2Cl_4+F_2 \longrightarrow \cdots CCl_2{:}CCl_2 \cdots F_2 \longrightarrow \cdots CCl_2{\cdot}CCl_2{\cdot}CCl_2{\cdot}CCl_2 \cdots F_2 \longrightarrow ({\cdot}CCl_2{\cdot}CCl_2F)_2$]. *n*-$\Delta^{\alpha}$-Hexadecene and F in CCl_4 at 15° give *difluorohexadecane*, b.p. 103—106°/0·2 mm.; oleic acid (II) affords a *difluorostearic acid* (III), m.p. 81° (softens at 80°) [in one case, using (II) from a different source, an *isomeride*, m.p. 95°, was also produced], whilst elaidic acid furnishes a *difluorostearic acid*, m.p. 84—85°, which differs from (III). In all these cases, substitution occurs also. $CHMe{:}CH{\cdot}CO_2H$ and F in CCl_4 at 0° afford two αβ-*difluorobutyric acids*, m.p. 81° (IV), and b.p. 100—102°/13 mm. (V), and an *acid*, $C_8H_{12}O_4F_2$ [*Me_2* ester (VI), b.p. 105—115°/0·5 mm.]. (IV) and (V) are hydrolysed (aq. NaOH) to α-*fluorocrotonic*, m.p. 112°, and impure α-fluoro*iso*crotonic acid, respectively, whilst (VI) and MeOH–KOH give an unsaturated *acid*, $C_8H_{10}O_4$, m.p. 240—244° (decomp.).

Fluorination of C_6H_6 in CCl_4 does not give simple substitution products, but yields a F-containing tar; PhBr, *p*-$C_6H_4Br_2$, *m*-$C_6H_4(NO_2)_2$, and benzoquinone behave similarly. BzOH and F in CCl_4 at 15° afford an amorphous product (the F content of which increases with time of fluorination); in presence of Br at 0°, CO_2H is eliminated and fractions, b.p. 110—120°/13 mm., and 150—160°/13 mm., of the composition $C_6H_6Br_2F_4$ and $C_6H_6Br_3F_3$, respectively, are isolated. These are partly converted by Zn-Cu into aromatic compounds which yield non-homogeneous bromofluoronitro-compounds. In the above fluorinations, the F is diluted with about an equal vol. of CO_2.
H. B.

Preparation of *iso*propyl bromide from *iso*propyl alcohol. E. A. Werner (J.S.C.I., 1933, **52**, 285—286T).—Experiments on the prep. of $Pr^{\beta}Br$ (I) : $Pr^{\beta}OH+KBr+H_2SO_4=Pr^{\beta}Br+KHSO_4+H_2O$, have shown that if the anhyd. alcohol is used, or < 10% of H_2O is present, the yield of alkyl bromide is poor (about 38%) on account of the simultaneous production of much propylene (II). With greater dilution the formation of (II) can be completely suppressed, and although this tends to suppress esterification of the alcohol, the yield of (I) is considerably increased at the expense of formation of (II). Thus a yield of pure (I), b.p. 60—61°, equal to 73·5% was obtained by heating at 90—115° a mixture of $3Pr^{\beta}OH,H_2O$ 100 g., H_2SO_4 150 g., and $NaBr,2H_2O$ 210 g. No (II) was formed.

Sorbyl chloride [α-chloro $\Delta^{\beta\delta}$-hexadiene]. II. T. Reichstein and G. Trivelli (Helv. Chim. Acta, 1933, **16**, 968—975; cf. A., 1932, 498).—Sorbyl chloride [α-chloro-$\Delta^{\beta\delta}$-hexadiene] (I), b.p. 45·5°/12 mm. (improved prep.), and NaOPh in Et_2O yield o-$\Delta^{\beta\delta}$-*hexadienylphenol*, b.p. 100°/0·2 mm., hydrogenated (PtO_2–Et_2O) to *o*-*n*-hexylphenol and a neutral substance, b.p. 72°/0·2 mm., which is not Ph hexadienyl ether. (I), Mg, and CO_2 in Et_2O afford an unsaturated acid hydrogenated to immediately homogeneous α-ethyl-*n*-valeric acid and a hydrocarbon $C_{12}H_{18}$ (II), b.p. 90—95°/11 mm., which is the main product when Mg–Cu is used in absence of CO_2. Hydrogenation of (II) does not lead to *n*-dodecane. Ozonisation of (II) and subsequent oxidation with $KMnO_4$ yields $({\cdot}CH_2{\cdot}CO_2H)_2$. (II) is probably a mixture of δε-divinyl-$\Delta^{\beta\zeta}$-octadiene and δ-vinyl-$\Delta^{\beta\zeta\theta}$-decatriene.
H. W.

Analysis of liquid organic substances by the conductometric method. K. Šandera (Chim. et Ind., 1933, **29**, Spec. no., 231—234).—The mixture of org. liquids is saturated with a suitable electrolyte, and the conductivity of the solution determined. The method is standardised by measurements with mixtures of known concn., and has been applied to mixtures of H_2O and EtOH (using $CaSO_4$, K_2SO_4 or KCl), H_2O and MeOH (using $CaSO_4$) and pentane and MeOH (using KCl as electrolyte).
J. W. S.

Tschugaev reaction for dehydrating alcohols. F. C. Whitmore and C. T. Simpson (J. Amer. Chem. Soc., 1933, **55**, 3809—3812).—The Tschugaev method (A., 1900, i, 129) applied to *n*- and *iso*-amyl alcohols gives Δ^{α}-pentene and $CH_2{:}CHPr^{\beta}$, respectively; octyl alcohol furnishes almost equal amounts of Δ^{α}- and Δ^{β}-octene. No rearrangement occurs. The Na (K) xanthate is best prepared from an excess of the alcohol and equimol. quantities of NaOH (KOH) and CS_2 or equimol. amounts of the reactants in Et_2O–CCl_4. *n*-$AlkO{\cdot}CS_2Me$ are relatively stable to heat; they can be distilled in vac.
H. B.

Hexacyanocobaltic acid and *n*-propyl alcohol. —See this vol., 1131.

Configuration-specific esterification of *sec*.-alcohols in presence of brucine or strychnine.

R. Wegler (Annalen, 1933, 506, 77—83; cf. A., 1932, 1094).—Treatment of *dl*-CHPhMe·OH, $CHPhPr^{\beta}{\cdot}OH$, and CHPhEt·OH with Ac_2O in presence of brucine and CCl_4 gives (—)-acetates; the (—)-antipode is esterified more readily in each case. CHMeBu·OH affords a (+)-acetate and is thus configuratively related to the above series; the opposite antipode is esterified more readily with CHMeEt·OH, $OH{\cdot}CHMe{\cdot}CH_2Ph$, and *cyclo*hexylmethylcarbinol (I). Except for (I), the residual alcohol is dextrorotatory. (+)-Benzoates are obtained (using BzCl) from the above and $CHMePr^{\beta}{\cdot}OH$ (II), CHPhBu·OH, *cyclo*hexylpropylcarbinol, *cyclo*hexylethylcarbinol, $OH{\cdot}CHPr^{\beta}{\cdot}CH_2Ph$, and $CHBuPr^{\beta}{\cdot}OH$; some of the residual alcohols are dextro- and some lævo-rotatory. All the above alcohols [except (II)] and CHEtPr·OH, CHEtBu·OH, and $OH{\cdot}CHEt{\cdot}CH_2Ph$ give (+)-benzoates in presence of strychnine; (II) affords a (—)-benzoate. H. B.

Rearrangement of *tert.*-butylmethylcarbinol (pinacolyl alcohol). II. Dehydration. F. C. Whitmore and P. L. Meunier (J. Amer. Chem. Soc., 1933, 55, 3721—3722; cf. this vol., 486).—Dehydration of $CHMeBu^{\gamma}{\cdot}OH$ over H_3PO_4 on SiO_2 gel at 300°/2500 lb. pressure gives $CMe_2{:}CMe_2$ and $CH_2{:}CMePr^{\beta}$ in the ratio 2 : 1, together with 3% of the normal dehydration product, $CH_2{:}CHBu^{\gamma}$. H. B.

Dehydration of *tert.*-alcohols containing a neopentyl system. II. Methyl*iso*propyl*tert.*-butyl-, methyldi*tert.*-butyl-, and methylethylneopentyl-carbinols. F. C. Whitmore and K. C. Laughlin (J. Amer. Chem. Soc., 1933, 55, 3732—3738).—Dehydration of $CMeEtBu^{\gamma}{\cdot}OH$ with 2-$C_{10}H_7{\cdot}SO_3H$ gives the same mixture of olefines as is obtained using I (A., 1932, 1232). Dimethyl*tert.*-amylcarbinol, b.p. 86·5°/60 mm., obtained in 78% yield from MgMeCl and $CMe_2Et{\cdot}CO_2Et$, is similarly dehydrated to (mainly) βγγ-trimethyl-Δ^{α}-pentene, b.p. 107·5—108·7°, and < 6% of βγγ-trimethyl-Δ^{γ}-pentene (formed by rearrangement of a Me group). MgMeCl and $COPr^{\beta}Bu^{\gamma}$ [prepared (*a*) by oxidation (CrO_3) of $CHPr^{\beta}Bu^{\gamma}{\cdot}OH$, (*b*) from $COMeBu^{\gamma}$, MeI, and $NaNH_2$ in Et_2O–C_6H_6, and (*c*) $COPr^{\beta}_2$, $NaNH_2$, and Me_2SO_4 in PhMe] give $CMePr^{\beta}Bu^{\gamma}{\cdot}OH$, b.p. 62°/12 mm., which is dehydrated (2-$C_{10}H_7{\cdot}SO_3H$) to γγ-dimethyl-β-*iso*propyl-Δ^{α}-butene and βγγδ-tetramethyl-Δ^{α}-pentene (rearrangement product) in the ratio 3 : 1, and a trace of βγδδ-tetramethyl-Δ^{β}-pentene (by normal dehydration involving the Pr^{β} group). $CMeBu^{\gamma}_2{\cdot}OH$, b.p. 122·5—123°/100 mm., m.p. 42°, from MgMeCl and $COBu^{\gamma}_2$, is dehydrated to > 90% of γγ-dimethyl-β-*tert.*-butyl-Δ^{α}-butene and some unidentified material of low b.p. Methylethylneopentylcarbinol, b.p. 62—62·5°/14 mm., from MgEtBr and Me neopentyl ketone, is dehydrated without rearrangement to (mainly) γεε-trimethyl-Δ^{β}-hexene, < 5% of ββδ-trimethyl-Δ^{γ}-hexene, and a trace of δδ-dimethyl-β-ethyl-Δ^{α}-pentene. The structures of the olefines are proved by ozonolysis. The results show the great tendency of *tert.*-alcohols to dehydrate without rearrangement; this is in marked contrast to the related primary and *sec.*-alcohols containing the neopentyl group, which dehydrate mainly with rearrangement (cf. *loc. cit.*). H. B.

Trialkylethinylcarbinols. D. D. Coffman, J. C. Y. Tsao, L. E. Schniepp, and C. S. Marvel (J. Amer. Chem. Soc., 1933, 55, 3792—3796).—Mg cetyl bromide and $CH_2{:}CBr{\cdot}CH_2Br$ in Et_2O and N_2 give 14·8% of β-*bromo*-Δ^{α}-*nonadecene*, b.p. 168—172°/0·5 mm., m.p. 10—10·5°, converted by $NaNH_2$ in xylene into Δ^{α}-*nonadecinene*, b.p. 144°/1·5 mm., m.p. 37—38° (*Hg* derivative, m.p. 96—97°). This is converted as described previously (A., 1928, 988) into *tri*-Δ^{α}-*nonadecinylcarbinol* (I), m.p. 71—72° (the *Me ether*, m.p. 44—45°, prepared from the ·OMgBr derivative and Me_2SO_4, could not be cleaved by liquid Na–K alloy), which with AcOH–conc. H_2SO_4 gives *di*(*tri*-β-*ketononadecylmethyl*) *ether* (?), m.p. 56—58°. (I) and 40% HBr or AcBr in Et_2O or C_6H_6 give a *compound*, m.p. 37—38°, which is not the expected bromide; (I), $SOCl_2$, and C_5H_5N afford a *compound*, m.p. 40—42°. Mg Δ^{α}-propinyl bromide (II) and Et_2CO_3 yield *tri*-Δ^{α}-*propinylcarbinol*, m.p. 134—135°, which is reduced (H_2, PtO_2, EtOH) to $CPr^{\alpha}_3{\cdot}OH$, and is converted by PCl_5 in C_6H_6 into a *compound*, $(C_{10}H_9Cl)_2$, m.p. 153—154° (violent decomp.), the Cl of which is not removed by "mol." Ag. $COPr_2$ and (II) give *di*-n-*propyl*-Δ^{α}-*propinylcarbinol* (III), b.p. 196—197°, also reduced to $CPr^{\alpha}_3{\cdot}OH$, which with PCl_5 or $SOCl_2$ affords liquid products which decompose on distillation. Me ethers could not be prepared from (I) or (III) and MeOH–conc. H_2SO_4. H. B.

Determination of the configuration of polyhydroxy-compounds. B. Englund (Svensk Kem. Tidskr., 1933, 45, 196—202).—A crit. review of methods of determining structure from complex formation with H_3BO_3 and As compounds. R. P. B.

Stability of ethylene glycol in acid solution.—See this vol., 1123.

Oxidation of αβ-glycols by lead tetra-acetate and periodic acid. P. Karrer and R. Hirohata (Helv. Chim. Acta, 1933, 16, 959—962).—Comparative examination of the oxidation of βε-dimethyl-*n*-hexane-βγ-diol and α-phenyl-β-methylpropane-αβ-diol shows HIO_4 to be the more suitable reagent for operation in H_2O; otherwise $Pb(OAc)_4$ is probably to be preferred by reason of the subsequent ready removal of Pb salts. H. W.

Partial acetonisation of sugars and sugar alcohols. III. αβ-*iso*Propylidene-*d*-mannitol and partly acylated derivatives of *d*-mannitol. L. von Vargha (Ber., 1933, 66, [*B*], 1394—1399; cf. this vol., 490).—*d*-Mannitol is converted by $COMe_2$, H_3BO_3, and conc. H_2SO_4 into αβ-iso*propylidenemannitol* δε-*borate* (I), m.p. (indef.) 75—90°, converted by evaporation with MeOH into αβ-iso-*propylidene*-d-*mannitol* (II), m.p. 167°, $[\alpha]_D^{20}$ +3·48° in H_2O. The position of the alkyl group in (II) follows from the non-identity of (II) with γδ-*iso*propylidene-*d*-mannitol, the conversion of (II) by CPh_3Cl in C_5H_5N into ζ-*triphenylmethyl*-αβ-iso*propylidene*-d-*mannitol*, m.p. (indef.) 45—55°, $[\alpha]_D^{20}$ +3·29° in $CHCl_3$ [also obtained from (I)], by $COMe_2$ and anhyd. $CuSO_4$ into αβεζ-di*iso*propylidene-*d*-mannitol, m.p. 122°, $[\alpha]_D^{25}$ +1·2° in H_2O, and by $COMe_2$–conc. H_2SO_4 into tri*iso*propylidene-*d*-mannitol. The δε position of $:B(OH)_2$ is preferred, since any other eventuality involves the possibility of introducing a further $\colon CMe_2$ or $\colon B(OH)_2$. (II) and Ac_2O in C_5H_5N afford αβ-iso*propylidene*-d-*mannitol* γδεζ-*tetra-acetate* (III), m.p. 107°, $[\alpha]_D^{20}$ +28·04° in $CHCl_3$, whilst (II), BzCl, and C_5H_5N give αβ-iso*propylidene*-d-*mannitol* γδεζ-*tetra-benzoate* (IV), m.p. 114°, $[\alpha]_D^{23}$ +47·84° in $CHCl_3$. αβεζ-*Di*iso*propylidene*-d-*mannitol* γδ-*diacetate* (V) has m.p. 123°, $[\alpha]_D^{20}$ +26·72° in $CHCl_3$. Hydrolysis of (III) by 70% AcOH at 50° leads to d-*mannitol* γδεζ-*tetra-acetate*, m.p. 92°, $[\alpha]_D^{20}$ +31·61° in $CHCl_3$, +26·0° in H_2O. Similar hydrolysis of (IV) and (V) leads, respectively, to d-*mannitol* γδεζ-*tetrabenzoate*, $[\alpha]_D^{25}$ +52·56° in $CHCl_3$, and d-*mannitol* γδ-*diacetate*, m.p. 139°, $[\alpha]_D^{25}$ +45·32° in H_2O. H. W.

Formation of cyclic acetals from aldehydes or ketones and alkylene oxides. M. T. Bogert and R. O. Roblin, jun. (J. Amer. Chem. Soc., 1933, **55**, 3741—3745).—Ethylene oxides (0·25 mol.) react with COR_2 or RCHO (0·2 mol.) in presence of anhyd. $SnCl_4$ (0·01 mol.) at 40—45° to give 25—35% yields of the $\colon CR_2$ and $\colon CHR$ ethers of the ethylene glycols; increases in the amount of $SnCl_4$ or rise of temp. cause the formation of "polymeric" material. Traces of ethers are formed using $ZnCl_2$, $FeCl_3$, $SbCl_3$, $AlCl_3$, or $SnCl_4,4H_2O$, but no appreciable reaction occurs with $CaCl_2$, NH_4Cl, HCl, H_2SO_4, or $POCl_3$. The benzylidene, heptylidene, *methylhexylmethylene*, b.p. 97° (all b.p. are corr.)/23 mm., and *phenylmethylmethylene*, b.p. 103·5—104·5°/23 mm., m.p. 62° (corr.), *ethers* of $(\cdot CH_2\cdot OH)_2$ and the *benzylidene*, b.p. 118°/23 mm., *heptylidene*, b.p. 102·5—103·5°/23 mm., *methylhexylmethylene*, b.p. 102°/23 mm., and *phenylmethylmethylene*, b.p. 105°/23 mm., *ethers* of $OH\cdot CHMe\cdot CH_2\cdot OH$ are described. H. B.

Formation of alkyl nitrites in dilute solutions. Butyl and amyl nitrites. W. A. Noyes (J. Amer. Chem. Soc., 1933, **55**, 3888—3889).—A convenient method of prep. of Bu^{α} and amyl nitrites is given. In the production of $EtO\cdot NO$, the EtOH functions as an acid and the HNO_2 as a base. H. B.

Phosphoric esters of xylose and of 5-methyl-*iso*propylidenexylose. Their bearing on the nature of the pentose of yeast nucleic acid. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, **102**, 347—355).—*iso*Propylidenexylose and $POCl_3$ in cold C_5H_5N give a product, which with hot 2*N*-H_2SO_4 affords *xylose-5-phosphoric acid* [*Ba* salt (I), $[\alpha]_D^{22}$ about +5·0° in H_2O; *Na* salt, $[\alpha]_D^{22}$ about +3·2° in H_2O and about +4·8° in half-saturated borax solution]. *iso*Propylidenexylose 5-benzoate and 5-acetate afford (probably 5-)*phosphoric acids* (*Ba* salts), which, when hydrolysed, give probably (I). 5-Methyl-1 : 2-*iso*propylidenexylose (II) gives a 3-*phosphoric acid* [*Ba* salt (impure), $[\alpha]_D^{22}$ +4·0° in H_2O], which with BaO in MeOH gives only (II), no migration having occurred. (I) is shown by reduction to give a γ-glucoside. R. S. C.

Preparation of aliphatic mercaptans and sulphonic acids of high mol. wt. G. Collin, T. P. Hilditch, P. Marsh, and A. F. McLeod (J.S.C.I., 1933, **52**, 272—275T).—Improved methods of prep. are given for higher alkyl mercaptans (I) from the corresponding halides, and for oxidation of (I) to the corresponding sulphonic acids (II), which are isolated as Na salts. Nearly theoretical yields of (I) are obtained when the halides are heated in an autoclave at 130—160° with dry EtOH–NaSH saturated with H_2S. The simple (I) oxidise extremely readily to disulphides (III), even by exposure to air. The (I) or (III) are best oxidised to (II) by $KMnO_4$ in $COMe_2$ or AcOH, or by CrO_3 in AcOH; the soft soap-like, hygroscopic (II) may be "salted out" from the aq. solutions of the oxidation products by means of aq. HCl, and are then best converted into the cryst. Na salts for analysis. The following are described: n-*octadecyl*, m.p. 56°, and n-*dodecyl mercaptan*, m.p. 18—20°; α-*thiolpalmitic acid*, m.p. 82°, θ(or ι)-*thiolstearic acid*, liquid; *di*-n-*octadecyl*, m.p. 62·5°, *di*-n-*hexadecyl*, m.p. 54°, and *di*-n-*dodecyl disulphide*, m.p. 32°. By oxidation of (I) or (III) the following products were obtained: from *n*-octadecyl mercaptan or disulphide, *Na* n-*octadecylsulphonate* and a neutral *compound*, m.p. 112°; from *n*-hexadecyl, *Na* n-*hexadecylsulphonate* and a neutral *compound*, m.p. 95°; from *n*-dodecyl, *Na* n-*dodecylsulphonate* and traces of a neutral *compound*, m.p. 71°; from α-thiolpalmitic acid, a Na_1 salt, probably $C_{14}H_{29}\cdot CH(SO_3Na)\cdot CO_2H$.

Preparation and properties of anhydrous acetic acid. W. C. Eichelberger and V. K. La Mer (J. Amer. Chem. Soc., 1933, **55**, 3633—3634).—Large quantities of AcOH are best purified by refluxing with CrO_3 in amount slightly > required to react with H_2O present, distilling, and dehydrating with $B(OAc)_3$. AcOH, m.p. 16·60°±0·01, has sp. conductivity $1{\cdot}4\times 10^{-8}$ reciprocal ohm at 25°.

J. G. A. G.

Elimination of bromine from bromoacetic acid and bromoacetates.—See this vol., 1125.

Preparation of nonoic acid and its catalytic reduction to nonaldehyde. H. Paillard and A. Demolis (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 131—137).—The yield of nonoic acid (I) obtained by alkali fusion of undecenoic acid varies from 20 to 77% being greatest with KOH (3 parts) at 350° (time of fusion, 35 min.). (I) is best reduced to nonaldehyde (70% yield) by passage with HCO_2H over $MnCO_3$ on pumice at 330—350° and atm. pressure. $MnCO_3$ on SiO_2 gel and $Mn(OH)_2$ are ineffective, and CO–H_2O mixtures (1 : 1) cannot replace HCO_2H.

R. S. C.

Isomeric [fatty acid] esters. J. R. Ruhoff and E. E. Reid (J. Amer. Chem. Soc., 1933, **55**, 3825—3828).—Numerous physical data are determined for fifteen esters, $R\cdot CO_2R'$, where R=H—*n*-$C_{14}H_{29}$ and R′=*n*-$C_{15}H_{31}$—Me. The following are new: Pr^{α} *tridecoate*, b.p. 194°/30 mm., m.p. −5·74°; n-*amyl undecoate*, b.p. 193°/30 mm., m.p. −21·17°; n-*hexyl decoate*, b.p. 193°/30 mm., m.p. −17·67°; n-*nonyl heptoate*, b.p. 193°/30 mm., m.p. −11·14°; n-*decyl hexoate*, b.p. 193°/30 mm., m.p. −19·29°; n-*undecyl valerate*, b.p. 193·5°/30 mm., m.p. −23·14°; n-*tridecyl propionate*, b.p. 195°/30 mm., m.p. −0·42°; n-*pentadecyl formate*, b.p. 201·5°/30 mm., m.p. 13·69°.

H. B.

Addition of hydrogen bromide to olefines. Undecenoic acid. J. C. Smith (Nature, 1933, **132**, 447; cf. this vol., 805).—HBr passed into 10% solution of undecenoic acid in light petroleum gave 70—80% yields of practically pure κ-bromoundecoic acid: when O_2 is removed by H_2 or by addition of $NHPh_2$, a mixed product in which the ι-Br-acid predominates is obtained. L. S. T.

Capillary fractionation of fatty acids. R. Dubrisay (Chim. et Ind., 1933, **29**, Spec. no., 1045—1047; cf. A., 1932, 1198).—Considerable fractionation of mixtures of two acids, *e.g.*, oleic, arachidic, or stearic and lauric acids, or a purification of crude oleic acid, can be effected by producing a lather in an aq. 0·1% solution of the mixed soaps and separating the froth, which is richer in the more surface-active constituent, from the remainder. E. L.

Radical interchange of alkyl orthoformates. H. W. Post and E. R. Erickson (J. Amer. Chem. Soc., 1933, **55**, 3851—3854).—$CHCl_3$ (1 equiv.), NaOR (R=Et or Pr) (1·5 equivs.), and NaOR′ (R′=Pr, Bu, *n*- and *iso*-amyl) (1·5 equivs.) give mixtures of $CH(OR)_3$, $OR'{\cdot}CH(OR)_2$, $OR{\cdot}CH(OR')_2$, and $CH(OR')_3$. Equilibrium mixtures of the four esters are obtained also when mixtures of $CH(OR)_3$ and $CH(OR')_3$ are kept at room temp. for 1 month. $OPr{\cdot}CH(OEt)_2$ in presence of P_2O_5 gives all four possible esters, whilst $CH(OPr)_3$ and EtOH afford $CH(OEt)_3$ (2·1%), $OPr{\cdot}CH(OEt)_2$ (42%), $OEt{\cdot}CH(OPr)_2$ (40%), $CH(OPr)_3$ (15·9%), EtOH, and PrOH. The reaction $CH(OEt)_3+EtSH \rightleftharpoons EtOH+SEt{\cdot}CH(OEt)_2$ occurs at room temp. H. B.

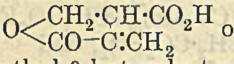
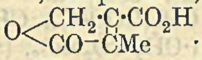
Fixation of Sb_2O_3 by monohydroxy-monoacids. Volmar and Duquénois (Compt. rend., 1933, **197**, 599—600; cf. this vol., 376).—Only α-OH-acids react with Sb_2O_3, the reaction velocity being greatest with *tert.*-OH. The following are described: *Na antimonyl glycollate* ($+H_2O$), and *α-hydroxybutyrate*, and *Na* ($+2H_2O$), and *K antimonyl α-hydroxy*iso*butyrate*. A. A. L.

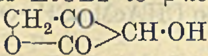
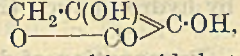
Benzyl compounds of α-hydroxy-acids and their application to syntheses. I. Derivatives of glycollic acid. H. O. L. Fischer and B. Gohlke (Helv. Chim. Acta, 1933, **16**, 1130—1142).—The chlorides of benzyloxy-acids are condensed with OH-acid, alcohols, etc. in the presence of *tert.* bases and the CH_2Ph group is removed from the product by hydrogenation in presence of Pd. $CH_2Cl{\cdot}CO_2H$ is converted by a large excess of $CH_2Ph{\cdot}ONa$ in $CH_2Ph{\cdot}OH$ at 150° into *benzyloxyacetic acid*, b.p. 136°/0·2 mm., which with PCl_5 in $CHCl_3$ affords *benzyloxyacetyl chloride* (I), b.p. 81°/0·2 mm. (*benzyloxyacetanilide*, m.p. 49°). (I), $OH{\cdot}CH_2{\cdot}CO_2H$ and $NPhMe_2$ in $CHCl_3$ give *benzylglycollylglycollic acid*, b.p. 151°/0·05 mm., m.p. 59° after softening at 55—56°, whence (Pd–H_2–AcOH) glycollylglycollic acid, m.p. 97—99°. (I) and *iso*propylideneglycerol yield iso*propylideneglyceryl benzyloxyacetate*, b.p. 152—153°/0·04 mm., whence iso*propylideneglyceryl hydroxyacetate*, b.p. 91°/0·05 mm., hydrolysed by 12·5% AcOH to *glyceryl α-hydroxyacetate* (*Ac_2* derivative, b.p. 118°/0·05 mm.). Glycerol yields non-cryst. *glyceryl tribenzyloxyacetate* and non-cryst. *glyceryl trihydroxyacetate* (*Ac_3*, b.p. 177—180°/0·05 mm., and *Bz_3*, m.p. 83—85° after softening at about 78°, derivatives). β-Di*iso*propylidenefructose is converted into the 6-*benzyloxyacetate*, m.p. 84°, and 6-*hydroxyacetate*, m.p. 128°, $[\alpha]_D^{21}$ −30·65° in $CHCl_3$. *iso*-Propylideneglucose gives the 3 : 5 : 6-*tribenzyloxyacetate*, m.p. 73°, whence the non-cryst. 3 : 5 : 6-*trihydroxyacetate* and *glucose* 3 : 5 : 6-*trihydroxyacetate*. Glucose gives the *pentabenzyloxyacetate*, hydrogenated to the non-cryst. *pentahydroxyacetate*. H. W.

Optical rotations of configuratively related methoxypropiono- and β-methoxybutyro-nitriles. P. A. Levene and R. E. Marker (J. Biol. Chem., 1933, **102**, 297—302).—Et lactate, $[M]_D^{25}$ −7·55°, with MeI–Ag_2O gives *Et* l-*α-methoxypropionate*, b.p. 142°, $[M]_D^{20}$ −119·6°, hydrolysed to the corresponding *acid*, b.p. 92°/15 mm., $[M]_D^{25}$ −80·7°, whence, by way of the chloride and amide, the *nitrile*, b.p. 115°/735 mm., $[M]_D^{20}$ −117·5°, was obtained. *Et* l-β-*hydroxybutyrate*, b.p. 74°/12 mm., $[M]_D^{25}$ −33·0° (from the acid, $[M]_D^{25}$ −25·0° in H_2O), gives similarly l-β-*methoxybutyric acid*, b.p. 115°/15 mm., $[M]_D^{25}$ −13·7° (*Et* ester, b.p. 165°, $[M]_D^{25}$ −10·6°), and the *nitrile*, b.p. 129°/740 mm., $[M]_D^{25}$ +13·9°. The rotation contributions of the CO_2H, CO_2Et, and (probably) CN groups are of opposite order in the two series. R. S. C.

Titanium potassium oxalate. L. Stuckert (Chem.-Ztg., 1933, **57**, 754—755).—Ti K oxalate (I) may be prepared on the technical scale by treating TiO_2 with highly-conc. aq. NaOH at 300—400° and finally at 600—650°, and converting the K_2TiO_3 formed into (I) by dissolving in the theoretical amount of aq. $H_2C_2O_4$. The yield is 90—96%. E. S. H.

Carbon syntheses with malonic and related acids. I. A. Michael and J. Ross (J. Amer. Chem. Soc., 1933, **55**, 3684—3695).—Paracetaldehyde (I), $CHMe(CO_2H)_2$, Ac_2O, and AcOH at 100° (bath) followed by gentle ebullition give tiglic (II) and *β-acetoxy-α-methylbutyric acid* (III), b.p. 147—150°/10 mm.; possible reaction mechanisms are discussed. Distillation of (III) at atm. pressure affords (II). The above reagents with a little conc. H_2SO_4 give *γ-hydroxybutane-*ββ*-dicarboxylic acid* (IV), m.p. 135° (decomp.), and its β-lactone (V). (IV) decomposes when heated at the m.p. (vac. or atm. pressure) to MeCHO and $CHMe(CO_2H)_2$, whilst (V) at >100°/vac. passes into α-methyl-β-butyrolactone, b.p. 80°/15 mm. (lit. 67°/21 mm.) [distillation of the free acid in a vac. gives (II)]. (I), $CHEt(CO_2H)_2$, Ac_2O, and AcOH afford α-ethylcrotonic and a little β-acetoxy-α-ethylbutyric acid (?), b.p. 156—160°/10 mm. Prolonged interaction of paraformaldehyde (VI), ethane-ααβ-tricarboxylic acid (VII), Ac_2O, and AcOH at room temp. and subsequent heating gives paraconic and a little itaconic acid; (I) and (VII) similarly yield *β-carboxy-γ-methylparaconic acid*, m.p. 165°. (VI), *s*-$C_2H_2(CO_2H)_4$, Ac_2O, and AcOH afford the *γ-dilactone* (VIII), m.p. 178° (decomp.), of αδ-dihydroxybutane-βγγ-tricarboxylic acid, which when heated gives the *γ-dilactone* (IX), m.p. 138°, of αδ-dihydroxybutane-βγ-dicarboxylic acid (X). When (IX) is boiled with 2 equivs. of NaOH, approx. equal amounts of two stereoisomeric Na_2 salts are formed; the more sol. salt gives (IX) on acidification, whilst the less sol. *Na_2* salt

($+8H_2O$) affords (after drying and decomp. with Et_2O–HCl) the *γ-monolactone*, m.p. 122°, of the *meso*-form of (X). Distillation of the syrupy residue from the prep. of (VIII) at 20 mm. gives a mixture of (IX) and an unsaturated *isomeride*, m.p. 165°, which may be  $O<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CO-C{:}CH_2\end{matrix}$ or  $O<\begin{matrix}CH_2\cdot C\cdot CO_2H\\ CO-CMe\end{matrix}$. α-Carboxy-α-methyl-β-butyrolactone (XI), prepared from MeCHO, $CHMe(CO_2H)_2$, and Ac_2O–conc. H_2SO_4 (cf. Meldrum, J.C.S., 1908, **93**, 605), decomposes when heated to the relatively stable α-methyl-β-butyrolactone. The thermal decomp. and properties of (XI) and related β-lactonic acids (lit.) are discussed: the results show that an intramol. strain in β-lactone rings can be only one of the energy factors which determine physical and chemical stability of such rings. Deductions made solely from Baeyer's strain theory are, therefore, erroneous. H. B.

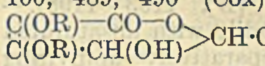
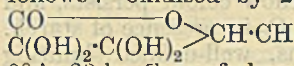
Oxytetronic acid, the simplest substance of the ascorbic acid type. F. Micheel and F. Jung (Ber., 1933, **66**, [*B*], 1291—1292).—Treatment of Et benzoyloxyacetate with K (Na is without action, whilst $NaNH_2$ affords $OH\cdot CH_2\cdot CO\cdot NH_2$ and EtOBz) leads with loss of EtOBz to β-*keto-αγ-dihydroxy*-n-*butyrolactone* (I),  $\begin{matrix}CH_2\cdot CO\\ O\text{——}CO\end{matrix}>CH\cdot OH$ or  $\begin{matrix}CH_2\cdot C(OH)\\ O\text{————}CO\end{matrix}\gg C\cdot OH$, m.p. 153°, which closely resembles ascorbic acid, but has no antiscorbutic action. With NaOH and phenolphthalein 1 OH is immediately determinable. (I) powerfully reduces $AgNO_3$ in acid solution and reacts with I (2 atoms per mol.). H. W.

C_4-Saccharic acids. VII. Preparation and resolution of *dl-threo*-αβ-dihydroxybutyric acid. J. W. E. Glattfeld and J. W. Chittum (J. Amer. Chem. Soc., 1933, **55**, 3663—3668).—*dl-threo*-αβ-Dihydroxybutyric acid (I), best prepared by oxidation of crotonic acid (II) with $AgClO_3$ and OsO_4 at room temp. (cf. Braun, A., 1929, 293), is resolved by brucine into forms of $[\alpha]_D$ +15·1° and −15° and by quinidine (cf. Morrell and Hanson, J.C.S., 1904, **85**, 197) into forms of $[\alpha]_D$ +15·45° and −15·5° (mean vals.). During the prep. of (I) by oxidation of (II) with $KClO_3$ and OsO_4 (A., 1927, 1054), a compound $C_4H_8O_4,C_4H_7O_4K$ [m.p. 104—107°, when prepared from (I) and its K salt], is produced. H. B.

Substances produced by action of moulds. II. Constitution of glauconic acids. H. Sutter and N. Wijkman (Annalen, 1933, **505**, 248—254; cf. A., 1931, 523).—Glauconic acid I (I), $C_{19}H_{22}O_4$, contains 1 active H (Zerevitinov); glauconic acid II and the thermal fission product $C_{11}H_8O_6$ have none. The NO_2-derivative of (I) is an ester and regenerates (I) on hydrolysis. The aldehyde $C_7H_{12}O$ (II), obtained by thermal decomp. of (I), readily gives a H_2-*derivative*, b.p. 63—64°/50 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 123°), oxidised by CrO_3–H_2SO_4 to a hexoic acid [? (III); p-*phenylphenacyl ester*, m.p. 65° (diffuse)] and by Ag_2O to hexane-γ-carboxylic acid (III), b.p. 103°/11 mm. (*amide*, m.p. 104—105°). Oxidation of (II) with O_3 gives EtCHO and COEt·CHO; it is therefore CHEt:CEt·CHO.

H. A. P.

Syntheses of *d*- and *l*-ascorbic acid (vitamin-*C*). T. Reichstein, A. Grüssner, and R. Oppenauer (Helv. Chim. Acta, 1933, **16**, 1019—1033; cf. this vol., 1035).—*d*-Xylose (I) is converted into its phenylosazone and thence by means of PhCHO into *d*-xylosone (II) [more readily prepared from (I) and H_2O_2 and purification through the Pb salt]. (II) is transformed by HCN–H_2O in presence of KCN and N_2 followed by hydrolysis with HCl into d-*ascorbic acid* (III), m.p. 187—189° (decomp.), $[\alpha]_D^{23}$ −48·3° in MeOH [conveniently purified through the *brucine* salt, m.p. 209° (corr., decomp.)]. *l*-Ascorbic acid (IV), m.p. 187—189° (corr., decomp.), $[\alpha]_D^{23}$ +48° in MeOH, is obtained similarly from *l*-xylose. Admixture of equal amounts of (III) and (IV) leads to dl-*ascorbic acid*, m.p. 168—169° (corr.). (III) does not show marked antiscorbutic action. d-*Saccharomonolactone monohydrate*, m.p. (indef.) 85—90° according to the rate of heating, l-*gulonolactone*, m.p. 185—187° (corr., slight decomp.), l-*gulonamide*, m.p. 124·5—125·5°, which is not successfully degraded to *l*-xylose by OCl′, and *d*-galacturonic acid are incidentally described. H. W.

Constitution of ascorbic acid. R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith (J.C.S., 1933, 1270—1290).—A detailed account of work summaries of which have already appeared [A., 1932, 548, 982, 987 (Cox); this vol., 100, 489, 490 (Cox), and 594]. Ascorbic acid,  $\begin{matrix}C(OR)-CO-O\\ C(OR)\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot OH$ (I; R=H), m.p. 192° [*Ca*, $[\alpha]_D^{19}$ +91° in H_2O, and *brucine*, m.p. 216—217° (decomp.), salts], is proved to be the enolic form of 3-keto-*l*-gulofuranolactone. The main evidence is as follows: oxidised by 2I in acid solution (I) gives  $\begin{matrix}CO\text{————}O\\ C(OH)_2\cdot C(OH)_2\end{matrix}>CH\cdot CH(OH)\cdot CH_2\cdot OH$, $[\alpha]_{5780}$ +56°→0° in 28 hr. [loss of absorption band similar to that of $(HO\cdot\ddot{C}\cdot CO_2H)_2$], further oxidised by NaOI to $H_2C_2O_4$ and *l*-threonic acid [also by $KMnO_4$ oxidation of (I)], methylated to *Me trimethyl*-l-*threonate*, b.p. 120°/13 mm., $[\alpha]_{5780}^{18}$ +49° in MeOH (*amide*, m.p. 78°, $[\alpha]_{5780}^{20}$ +68° in MeOH), and oxidised by HNO_3 (*d* 1·2) to *d*-tartaric acid. With CH_2N_2 at −5° (I) gives dimethylascorbic acid (*Ba* salt) [(I) R=Me], which with saturated NH_3 in MeOH at 35° gives the *amide* $C_8H_{15}O_6N+MeOH$, m.p. 124°, $[\alpha]_{5780}$ −24° in 50% H_2O–MeOH, formed (contrary to Micheel and Kraft, this vol., 489) by addition of NH_3 at the ·O· linking; and converted into tetramethylascorbic acid (II) by Ag_2O–MeI. Ozonolysis of (II) gives the neutral ester $CO_2Me\cdot CO\cdot O\cdot CH(CO_2Me)\cdot CH(OMe)\cdot CH_2\cdot OMe$, which with NH_3–MeOH gives $(\cdot CO\cdot NH_2)_2$, 3 : 4-dimethyl-*l*-threonamide, and the epimeric 3 : 4-dimethyl-*l*-erythronamide, whereas hydrolysis with 0·27*N*-$Ba(OH)_2$ gives the Ba salts of the corresponding acids. Structures for the various $NHPh\cdot NH_2$ derivatives are given. Only (I) is consistent with *X*-ray and absorption spectra data. *Me dimethoxymaleate*, b.p. 85°/0·03 mm. (absorption band at 255 mμ, ε 6000), is prepared from the $(OH)_2$-acid by CH_2N_2 followed by Ag_2O–MeI. J. W. B.

Synthesis of *d*-glycuronic acid. L. Zervas and P. Sessler (Ber., 1933, **66**, [*B*], 1326—1329).—Condensation of 1 : 2-*iso*propylidene-*d*-glucofuranose with PhCHO and P_2O_5 affords 3 : 5-benzylidene-1 : 2-

*iso*propylidene-α-*d*-glucofuranose (I), m.p. 149—150° (corr.), $[\alpha]_D^{20}$ +23·1° in $CHCl_3$, probably identical with the compound of Brigl *et al.* (A., 1932, 1115). Oxidation of (I) with $KMnO_4$ in slightly alkaline solution leads to 3 : 5-*benzylidene*-1 : 2-iso*propylidene*-α-d-*glycuronic acid* (II), m.p. 170° (corr.), $[\alpha]_D^{20}$ +30·3° in $COMe_2$, catalytically converted (H_2–Pd black–EtOH) into 1 : 2-iso*propylidene*-α-d-*glycuronic acid* (III), m.p. 147° (corr.), $[\alpha]_D^{20}$ −9·2° in H_2O (initial val.). (II) or (III) is readily hydrolysed by dil. acid to *d*-glycurone, m.p. 177° (corr.), $[\alpha]_D^{20}$ +19·4° in H_2O. H. W.

Oxidation of δ-ketogluconic acid with nitric acid in presence of vanadium. W. E. Barch (J. Amer. Chem. Soc., 1933, 55, 3653—3658).—Oxidation of Ca δ-ketogluconate with HNO_3 (2—4 mols.) in presence of a little Na_3VO_4 at 100° (bath) gives (after gas evolution ceases) *d*- (I) (14·2—27·8%) and *dl*- (II) (0—8·5%) -tartaric acids, trihydroxyxyloglutaric acid (III) (0—5·9%), and $H_2C_2O_4$ (IV) (11·4—17·3%). Fission of the chain occurs on both sides of the CO group, and 50% of the original mol. is converted into (I)+(IV). (II) arises from (III). It is suggested that the oxidation involves the formation of unstable nitrates which then lose HNO_2. H. B.

Fats and thiolacetic acid. G. Axberg and B. Holmberg (Ber., 1933, 66, [*B*], 1193—1198).—$SH\cdot CH_2\cdot CO_2H$ (I) combines readily with unsaturated fats and fatty acids to preparatively uninviting products. The reaction can be used in determining the I val. by treating the fat with excess of (I) in air or CO_2 at room temp., dissolving the product in AcOH, adding I solution until a yellow colour persists, and titrating excess of I by $Na_2S_2O_3$ in presence of starch. Under the stated conditions, well-defined limiting vals. are invariably obtained after 12 hr. These vals. agree closely with, but are usually slightly >, the Hübl I vals. Rise of temp. leads to less trustworthy results and should be used only in the case of solid fats to ensure only liquid phases. The choice of CO_2 or air appears immaterial. Technical (I) may replace the pure material, but the use of specimens with high acid equiv. appears inadvisable. H. W.

Raman effect and problems of constitution. IV. Carbonyl frequencies and molecular constitution. K. W. F. Kohlrausch and A. Pongratz (Ber., 1933, 66, [*B*], 1355—1369; cf. this vol., 144).—Measurements are recorded of the ·CO· frequencies for the compounds R·CHO, R·COMe, $R\cdot CO_2H$, $R\cdot CO_2Me$, $R\cdot CO_2Et$, R·COCl, HCO_2R, $ClCO_2R$ (R=H, Me, Et, Pr^α, Bu^α, Bu^β, *n*-amyl, *n*-hexyl, *n*-heptyl, Pr^β, CHMeEt, CMe_3, CMe_2Et). The frequencies are const. and independent of the length of the side-chain and may therefore be regarded as characteristic of X in R·CO·X. The frequency heights have no direct connexion with the wt. of X, but depend on the nature of the atom or group of atoms directly united to CO; they are due therefore to a typical constitutive effect exerted by the vicinal atom on the strength of the C:O linking. In the compounds Me·CO·X, $CH_2R\cdot CO\cdot X$, $CHR_2\cdot CO\cdot X$, and $CR_3\cdot CO\cdot X$ (X=OH, OMe, OEt, Me, Cl, H) a slight effect is attributable to branching of the chain in the α-position, but the change is negligible in comparison with that exercised by the vicinal atom. With unsaturated materials, such as $CH_2R\cdot CO\cdot X$, $>C:CH\cdot CO\cdot X$, Ph·CO·X (X=OH, OEt, OMe, Me, H) a more marked effect is observed when conjugation is possible. In the compounds $(CO_2Me)_2$, $(CO_2Et)_2$, $CH_2(CO_2Me)_2$, $CH_2(CO_2Et)_2$, $CH(CO_2Me)_3$, $CH(CO_2Et)_3$, $C(CO_2Et)_4$, $(\cdot CH_2\cdot CO_2Me)_2$, $(\cdot CH_2\cdot CO_2Et)_2$, and $CO_2Me\cdot CH(CH_2\cdot CO_2Me)_2$, the conjugation of 2 CO leads to marked exaltation, which diminishes when CH_2 separates 2 CO and disappears when 2 CH_2 are interposed. Accumulation of CO groups at the same C atom causes a further feeble exaltation. Possibly the supposed symmetry is not quite complete in certain cases. Observations with $COMe\cdot CO_2H$, $COMe\cdot[CH_2]_2\cdot CO_2H(Me)(Et)$, $COMe\cdot CMe_2\cdot CO_2Me$, and $CO_2Et\cdot CH_2\cdot C(CO_2Et):CH\cdot CO_2Et$ are recorded. The work of Hayashi (this vol., 764) on Ac_2, CH_2Ac_2, $[CH_2]_2Ac_2$, and *m*-$C_6H_4(OH)_2$ is not confirmed. H. W.

β-Hydroxymethyl-Δ$^\alpha$-buten-γ-one. H. Gault and L. A. Germann (Compt. rend., 1933, 197, 620—621).—In the prep. of $CH_2Ac\cdot CH_2\cdot OH$ (cf. G.P. 223,207), there is also formed β-*hydroxymethyl*-Δ$^\alpha$-*buten*-γ-*one*, b.p. 92—95°/15 mm. (dibromide), identified by hydrogenation (Ni) to $CHAcMe\cdot CH_2\cdot OH$. H. A. P.

Preparation of diacetyl. A. K. Plisov (J. Appl. Chem. Russ., 1933, 6, 739—741).—In the prep. of Ac_2 from COMeEt and $EtNO_3$ higher yields are obtained by treating the CAcMe:N·OH (I) with HNO_3 without isolation of (I). R. T.

Determination of the mol. wt. of carbohydrates. A. Beiser and H. Pringsheim (Ber., 1933, 66, [*B*], 1296—1298; cf. this vol., 149).—Contrary to Berner, it is maintained that the principle of additivity is not applicable to cryoscopic determinations of mol. wt. when EtOH is present in dil. solution. In very dil. solution, α-methylglucoside and sucrose appear colloidal in boiling H_2O, whereas they yield normal vals. at higher concn. (cf. Hess *et al.*, this vol., 47). In consequence of lack of knowledge of the state of solution at different concn. and temp., such measurements should not form the basis of theoretical conclusions in carbohydrate chemistry. Application of the osmometric method to the determination of the mol. wt. of di- (I) and tetra- (II) -amylose is not admissible, since the stabilising EtOH distils during the experiments (*loc. cit.*). The transformation of (II) into (I) by displacement of p_H towards the alkaline side could not be confirmed in cryoscopic measurements. H. W.

3- and 5-Methylxylose. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, 102, 331—346).—*iso*Propylidenexylose 5-benzoate, m.p. 83·5—84·5°, is probably homogeneous, but with MeI–Ag_2O gives, probably by partial migration, 3-*methyl*iso*propylidenexylose* 5- (I) (about 70%), m.p. 64—65·5°, $[\alpha]_D^{20}$ −50·2° in $CHCl_3$, and 5-*methyl*iso*propylidenexylose 3-benzoate* (II) (about 20%), b.p. 164—167°/0·1 mm., $[\alpha]_D^{20}$ −33·0° in $CHCl_3$, and 3 : 5-dimethylxylose, a syrup. (II) with BaO in MeOH gives 5-*methyl*iso*propylidenexylose* (III), m.p. 80·5—81·5° (lit. 78°), $[\alpha]_D^{20}$ −20·2° in H_2O, hydrolysed by 0·1*N*-H_2SO_4 to 5-*methylxylose* (IV), a syrup, $[\alpha]_D^{20}$ +32·8° $\longrightarrow$ +36·4°

in 4 hr. in H_2O [p-*bromophenylosazone*, m.p. 170—171° (decomp.), $[\alpha]_D^{20}$ $-50° \longrightarrow -30°$ in 24 hr. in C_5H_5N–EtOH (2 : 3)], which reduces cold Fehling's solution. (I) gives similarly 3-*methyl*iso*propylidenexylose*, a syrup, $[\alpha]_D^{27}$ $-54·1°$ in H_2O, and 3-*methylxylose* (V), m.p. 103—104°, $[\alpha]_D^{20}$ $+55·2° \longrightarrow +14·8°$ in 4 hr. in H_2O [p-*bromophenylosazone*, m.p. 153—155° after sintering and decomp. at 142—143°, $[\alpha]_D^{20}$ $+6·0 \longrightarrow -14·0°$ in 24 hr. in C_5H_5N–EtOH (2 : 3)], which reduces slightly warm Fehling's solution. *iso*Propylidenexylose affords 5-*triphenylmethyl*iso*propylidenexylose*, m.p. 118—119°, $[\alpha]_D^{25}$ $+10·5°$ in $CHCl_3$, which with MeI–Ag_2O gives 5-*triphenylmethyl*-3-*methyl*iso*propylidenexylose*, a syrup, $[\alpha]_D^{22}$ $-40·9°$ in $CHCl_3$, hydrolysed by cold HBr–AcOH to (V). 5-*p*-Toluenesulphonyl*iso*propylidenexylose (VI) and NaOMe at 20—25° give 1 : 2-iso*propylidene*-3 : 5-*anhydroxylose*, b.p. 63—65°/0·1 mm., m.p. 16·9—17·3°, $[\alpha]_D^{20}$ $+11·7°$ in $CHCl_3$ and $+14·7°$ in H_2O. This, or (VI), with hot NaOMe gives (III). *iso*Propylidenexylose or (IV) affords 3 : 5-dimethyl*iso*propylidenexylose, $[\alpha]_D^{22}$ $-46·9°$ in H_2O [p-*bromophenylosazone*, m.p. 107—108·5°, $[\alpha]_D^{22}$ $-46° \longrightarrow -30°$ in C_5H_5N–EtOH (2 : 3)], whence by hydrolysis and oxidation 2 : 3-dimethylxylolactone (*p*-bromophenylhydrazide, m.p. 95—96°, $[\alpha]_D^{20}$ $+6·0°$ in EtOH) was obtained. The glucoside formation of (IV) and (V) consists of a single and double reaction, respectively.

R. S. C.

Derivatives of *iso*propylidenexylose. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1933, **102**, 317—330).—*iso*Propylidenexylose (modified prep.) gives the following derivatives: 5-*benzoate* (possibly impure), m.p. 83·5—84·5°, $[\alpha]_D^{20}$ $+5·5°$; 5-p-$C_6H_4Me·SO_2$, m.p. 133—134°, $[\alpha]_D^{20}$ $-13·0°$; 3 : 5-*diacetate*, a syrup, $[\alpha]_D^{20}$ $-6·1°$; 3-*acetate* 5-*benzoate*, m.p. 84·5—85·5°, $[\alpha]_D^{22}$ $-26·5°$; 3-p-$C_6H_4Me·SO_2$ 5-*acetate*, m.p. 84·5—85°, $[\alpha]_D^{20}$ $-33·0°$, and 5-*benzoate*, m.p. 94·5—95·5°, $[\alpha]_D^{20}$ $-64·0°$; 5-p-$C_6H_4Me·SO_2$ 3-*acetate*, a syrup, $[\alpha]_D^{20}$ $-17·9°$, and 3-*benzoate*, m.p. 86—87°, $[\alpha]_D^{20}$ $-37·0°$; 5-*iodide*, m.p. 108—109°, $[\alpha]_D^{22}$ $-40°$; 5-*nitrate*, m.p. 115·5—116·5°, $[\alpha]_D^{20}$ $-24·8°$; 5-*carbobenzyloxy*-, m.p. 90—91°, $[\alpha]_D^{20}$ $+7·5°$, hydrolysed by dil. alkali, but not by dil. acids. The structures are proved by reaction of the 5-*p*-$C_6H_4Me·SO_2$ derivatives with NaI. All [α] are in $CHCl_3$.

R. S. C.

Acetone [*iso*propylidene] derivatives of *d*-ribose. P. A. Levene and E. T. Stiller (J. Biol. Chem., 1933, **102**, 187—201).—Owing to steric causes, ribose, pure $COMe_2$, and H_2SO_4 (0·2%) give abnormally 2 : 3-iso*propylideneribofuranose* (I), b.p. 110—117°/0·05 mm. (*acetate*, b.p. 119—121°/0·1 mm.), and (probably) 2 : 3-iso*propylidene*-1 : 5-*anhydroribofuranose* (II), b.p. 55—60°/0·05 mm., m.p. 61—62°, $[\alpha]_D^{28}$ $-64·35°$ in MeOH. With HCl there is formed also a *substance*, $C_8H_{12}O_4$, m.p. 93—94°, b.p. 105—115°/0·07 mm. The structure of (I), and thus of (II), is proved by the following reactions. By Purdie's method (I) gives *methyl*-2 : 3-iso*propylidene*-5-*methylriboside*, b.p. 62—65°/0·03 mm., hydrolysed by HCl–MeOH at 70° to *methyl*-5-*methylriboside* (III), b.p. 70—77°/0·12 mm., and by 0·04*N*-HCl at 100° to 5-*methylribofuranose* (IV) [p-*bromophenylosazone*, m.p. 161—162° (decomp.), $[\alpha]_D^{26}$ $-48°$ in EtOH–C_5H_5N (3 : 2)]. The rate of glucoside formation by (III) proves its furanose structure. (III) gives by Purdie's method *methyltrimethylribofuranoside*, b.p. 68°/0·05 mm., hydrolysed to the known 2 : 3 : 5-trimethylribose, whence the corresponding γ-lactone was obtained by Br–H_2O. (I) and *p*-$C_6H_4Me·SO_2Cl$ in C_5H_5N at 37° give abnormally the 1 : 5-$(C_6H_4Me·SO_2)_2$ derivative, m.p. 122—123°, whence 1-p-*toluenesulphonyl*-2 : 3-iso*propylideneribose* 5-*iodide*, m.p. 120°, $[\alpha]_D^{23}$ $+84·6°$ in $CHCl_3$, and 5-*nitrate*, m.p. 156°, were obtained. (II) is stable to NaOI, Fehling's solution (until hydrolysed by acid), and NaOMe at 125°.

R. S. C.

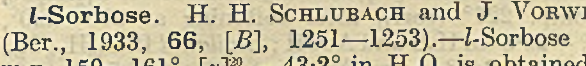
Distinction of keto- from aldo-hexoses. A. Castiglioni (Z. anal. Chem., 1933, 94, 96—101).—An improved form of Tollens' test. A 0·1—0·8% solution of the sugar is heated with 5 vols. of HCl (*d* 1·09—1·18), best to 70°. A reddish-brown coloration develops rapidly with ketoses, slowly with aldoses. Fructose and sucrose may be detected in presence of a large excess of glucose, lactose, or galactose.

J. S. A.

Behaviour of hexoses in presence of animal charcoal and iron phosphate complexes. K. Wunderly (Helv. Chim. Acta, 1933, 16, 1013—1018).—*d*-Fructose (I) and *d*-glucose do not suffer decomp. in the presence of animal C and absence of O_2; $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $MgHPO_4$, or alkali phosphate buffering in the region p_H 4·5—7·5 is without influence. (I) in presence of alanine (II) suffers more decomp. in presence of C than in the system (I)–(II). Admixture of $KFe(C_2O_4)_2$ and $Na_4P_2O_7$ gives a complex which expedites the O-free decomp. of the system (I)–*dl*-alanine.

H. W.

Action of acetic anhydride and sulphuric acid on *iso*propylideneglucose. H. H. Schlubach, W. Rauchenberger, and A. Schultze (Ber., 1933, 66, [*B*], 1248—1251; cf. Schultze, Diss., Hamburg, 1930).—The action of Ac_2O–H_2SO_4 at 0° on *iso*propylideneglucose triacetate leads to *iso*propylideneglucose penta-acetate (I), m.p. 140°, $[\alpha]_D^{18}$ $+60·4°$ in $CHCl_3$, identical with the product obtained by Brigl *et al.* (this vol., 810) by means of $ZnCl_2$. The $\vdots CMe_2$ is eliminated by alkali with unusual ease. NH_3–EtOH converts (I) into *iso*propylideneglucose in poor yield. NH_3–Et_2O gives small amounts of an *isomeride*, m.p. 140°, $[\alpha]_D^{18}$ $+3·0°$ in $CHCl_3$ (? α- and β-forms). Dil. HCl in AcOH hydrolyses (II) to non-cryst. glucose tetra-acetate (II), $[\alpha]_D^{18}$ $+32°$ in $CHCl_3$, converted by the successive action of MeI and Ag_2O, Me_2SO_4, and 7% HCl into 2 : 3 : 5 : 6-tetramethylglucose, $[\alpha]_D^{19}$ $-30°$ in $CHCl_3$. Liquid HCl transforms (I) into acetochloro-γ-glucose, converted by Ag_2CO_3 and $COMe_2$–H_2O into (II). (I) is therefore


$$OAc·CH_2·CH(OAc)·\underbrace{CH·[CH·OAc]_2·CH}_{O}·O·CMe_2·OAc.$$

H. W.

***l*-Sorbose.** H. H. Schlubach and J. Vorwerk (Ber., 1933, 66, [*B*], 1251—1253).—*l*-Sorbose (I), m.p. 159—161°, $[\alpha]_D^{20}$ $-43·2°$ in H_2O, is obtained in 50—75% yield by the action of *B. xylinum* on sionin (technical sorbitol) if the concn. of AcOH in the solution is increased to 0·5% to prevent infection. (I) is transformed by Ac_2O–H_2SO_4 into an unstable, brown syrup, whereas use of $ZnCl_2$ under defined conditions leads to a Ac_5 derivative (II) (probably *keto*-l-*sorbose* 1 : 3 : 4 : 5 : 6-*penta-acetate*), m.p. 96·5—97·5°, $[\alpha]_D^{18}$ +2·9° in $CHCl_3$. Attempts to transform (II) into an acetohalogenosorbose led to non-cryst. material. H. W.

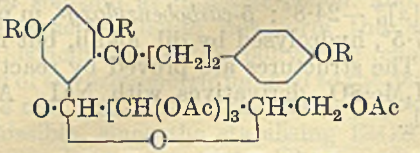
Microscopical detection of fructose. M. Wagenaar (Pharm. Weekblad, 1933, 70, 1029—1034).—The solid sugar, suspended in a 2% solution of α-$C_{10}H_7$·OH in glycerol, is treated with conc. H_2SO_4, whereby the crystals of a ketose are coloured bluish-violet. It is possible to detect 1% of sucrose in glucose, arabinose, maltose, or galactose and 0·1% in lactose. It is not possible to differentiate fructose, sucrose, and raffinose. S. C.

β-4-Glucosido-β-glucosan and 4-galactosido-β-glucosan. P. Karrer and J. C. Harloff (Helv. Chim. Acta, 1933, 16, 962—968; cf. A., 1932, 46).—Acetobromocellobiose and $NHMe_2$ in $CHCl_3$ at room temp. afford *dimethylaminocellobiose hepta-acetate*, m.p. 210—211°, $[\alpha]_D^{18}$ −10·1° in $CHCl_3$; the corresponding *methiodide* is transformed by $Ba(OH)_2$ into *cellobiose anhydride* [β-4-*glucosido*-β-*glucosan*] (I) (*hexa-acetate*, m.p. 144°, $[\alpha]_D^{17}$ −46·24° in $CHCl_3$). (I) is not affected by emulsin, but is transformed by the enzyme from *Helix pomatia* into glucose and β-glucosan (II) (triacetate, m.p. 110°). Similarly, acetobromolactose yields *dimethylaminolactose hepta-acetate*, m.p. 154°, $[\alpha]_D^{18}$ −21·37° in C_6H_6, converted successively into the *methiodide* and 4-*galactosido*-β-*glucosan* (*hexa-acetate*, m.p. 206°, $[\alpha]_D^{18}$ −38·89° in $CHCl_3$), hydrolysed to galactose and (II). H. W.

Heart glucosides. II. Genuine glucosides of *Digitalis lanata*, digilanids *A*, *B*, and *C*. A. Stoll and W. Kreis (Helv. Chim. Acta, 1933, 16, 1049—1098; cf. this vol., 877).—Fresh *lanata* leaves are ground with $(NH_4)_2SO_4$ to a uniform paste; the press-cake is extracted with EtOAc and the extract conc. to a viscous mass at ≯ 35°/vac. The residue is triturated with Et_2O until it is mainly solid and then digested with boiling Et_2O. Tannins are removed from the residue by treatment with $Pb(OH)_2$ in MeOH–H_2O. The filtrate is greatly conc. at a low temp., thereby yielding a ppt. of " total digilanids " (I), which, after repeated crystallisation from MeOH, has m.p. 245—248° (decomp.) when rapidly heated. (I) consists of an isomorphous mixture of three glucosides separable into its components by fractional distribution between MeOH–H_2O and $CHCl_3$–MeOH; full details are given for operation with homogeneous mixtures and also in presence of an intermediate solid phase. Thus are obtained: *digilanid* A, $C_{49}H_{76}O_{19}$, m.p. 245—248° (decomp.), $[\alpha]_D^{20}$ +31·9° in 95% EtOH, +23·2° in dioxan, hydrolysed by H_2SO_4 in EtOH–H_2O to digitoxigenin, m.p. 250° (corr.), $[\alpha]_D^{20}$ +18·1° in MeOH, digitoxose (II), and *digilanidobiose*, $C_{12}H_{22}O_9$, decomp. 227° (corr.) after softening at 215—220°, $[\alpha]_D^{20}$ +29·8° in H_2O and AcOH; *digilanid* B, $C_{49}H_{76}O_{20}$, m.p. 245—248° (corr., decomp.), $[\alpha]_D^{20}$ +36·7° in 95% EtOH, +31·8° in dioxan, hydrolysed to gitoxigenin, m.p. 232° (corr.), $[\alpha]_D^{20}$ +36·1°±2° in MeOH (II), glucose (III), and AcOH; *digilanid* C, $C_{49}H_{76}O_{20}$, m.p. 245—248° (decomp.), $[\alpha]_D^{20}$ +33·4° in 95% EtOH, +22·6° in dioxan, hydrolysed to digoxigenin, m.p. 220° (corr.), $[\alpha]_D^{20}$ +23·2° in MeOH, (II), (III), and AcOH. H. W.

Natural glycosides. V. Ruberythric acid. E. T. Jones and A. Robertson. **VI. Hexose residue of phloridzin.** A. Müller and A. Robertson (J.C.S., 1933, 1167—1169, 1170—1172).—V. With MeI–Ag_2O in $COMe_2$ the Ac_7 derivative (I), m.p. 260°, of alizarin-β-gentiobioside (II) +$6H_2O$, m.p. 96—98°, and anhyd., m.p. 178—180° (prep. by modification of Zemplén and Müller's method, A., 1929, 1281), gives its *Me ether*, m.p. 240°, hydrolysed by HCl in MeOH–AcOH to 1-*O*-methylalizarin. When treated with 5% aq. NaOH a suspension of (I) in MeOH affords (II). Alizarin-β-cellobioside (III), m.p. 260° (Ac_8 derivative, m.p. 143—145°, becoming solid at 170—180°, and remelting at 224—225°), is similarly prepared. Ruberythric acid (IV) is not identical with (II), (III), or alizarin-2-β-maltoside, but is hydrolysed by emulsin to alizarin (V) and a pentose (phloroglucinol and orcinol reactions) and is probably a pentosido-β-glucoside. Hepta-acetylprimeverose (by a modification of Helferich and Rauch's method, A., 1927, 859) with Ac_2O and saturated HBr in AcOH gives *hexa-acetylprimeverosidyl bromide* (amorphous), converted by (V), quinoline, and Ag_2O into the Ac_7 derivative, m.p. 241°, of alizarin-β-primeveroside, not identical with the Ac derivative of (IV).

VI. Hydrolysis of phloridzin (I) with 0·2*N*-H_2SO_4 affords phloretin and glucose. With MeI and K_2CO_3 in boiling $COMe_2$ (I) gives its Me_3 ether +H_2O (II), sintering at 73°, m.p. 75—76° (lit. 63—65°), further methylated (MeI–Ag_2O) to the *Me_7 ether*, which is hydrolysed in $COMe_2$ by 10% H_2SO_4 to *O*-trimethylphloretin (III) and 2 : 3 : 4 : 6-tetramethylglucose, thus indicating the pyranose structure. With *O*-tetra-acetyl-α-glucosidyl bromide, Ag_2O, and quinoline at 30—35° (III) gives O-*tetra-acetyltrimethylphloridzin* (IV, R=Me), m.p. 94—95°, $[\alpha]_{5461}^{21}$ −44·64° in $CHCl_3$, hydrolysed by 0·5*N*-NaOMe in MeOH in a freezing mixture to (II), all these products being



(IV.) (I, R=H, Ac=H; II, R=Me, Ac=H)

identical with specimens similarly prepared from the natural product (I). Either synthetic or natural (II) is hydrolysed by emulsin in aq. EtOH at 37° to (III) and glucose. (I) is therefore a β-glucopyranose. J. W. B.

Alcoholytic degradation of starch. E. Berner and F. Melhus (Ber., 1933, 66, [*B*], 1333—1338; cf. this vol., 937, 938).—Trihexosan, obtained by the action of glycerol (I) on starch at 205° (cf. Pictet *et al.*, A., 1922, i, 987), contains about 4% of combined (I); assuming the reaction to be alcoholysis, the mean mol. wt. of the degraded product is 2000—2500. Treatment of starch with (I) at 180° during 40 hr. yields a mixture of α- and β-glycerylglucoside (II). $[\alpha]_D$ about +60°, transformed into the *hexa-acetate*, $[\alpha]_D^{17}$ +56·9° in C_6H_6, and thence by NaOH and

Me_2SO_4 into the *Me_6 ether*, b.p. 127°/0·1 mm., $[\alpha]_D^{20}$ +59·9° in $CHCl_3$, hydrolysed by 2*N*-HCl to 2 : 3 : 4 : 6-tetramethyl-α-glucose, m.p. 83°, $[\alpha]_D^{20}$ +83·2° in H_2O (final val.); at 210°, degradation is accompanied by loss of H_2O. Reaction occurs at 130° in presence of H_3PO_4. $C_2H_4(OH)_2$ and starch at 180° during 24 hr. yield a mixture of glycylglucosides, $[\alpha]_D$ +77·8°, converted into their penta-acetates (α-*form*, m.p. 66°, $[\alpha]_D^{20}$ +143·0° in C_6H_6, +123·3° in EtOH). In absence of catalyst, starch is little acted on by MeOH, whereas methylated starch (OMe=39%; [α] +186° in $CHCl_3$) is readily converted into a mixture of 2 : 3 : 6-trimethyl-α- and -β-glucoside, b.p. 115°/0·04—0·05 mm., $[\alpha]_D^{20}$ +60·8° in H_2O. Starch is readily degraded by PhOH and $CH_2Ph{\cdot}OH$. H. W.

Solubility of inulin. E. YANOVSKY and R. M. KINGSBURY (J. Amer. Chem. Soc., 1933, **55**, 3658—3663).—The solubility of dahlia inulin (I) in H_2O and 50% EtOH at various temp. is considerably < that of chicory inulin (II) (cf. Wolff and Geslin, A., 1920, i, 424). (I) and (II) both exist in two modifications having differing solubilities. The more sol. form of (II) (obtained by crystallisation from aq. EtOH) gradually changes into the less sol. stable form. The presence of fructose increases the solubility of (I), but has no effect with (II), whilst " sol." inulin (A., 1931, 776) does not affect either solubility. Inulin is slowly deposited from supersaturated solutions until normal solubility is reached. H. B.

Inulin and inulinases. XIII. P. OHLMEYER and H. PRINGSHEIM (Ber., 1933, **66**, [*B*], 1292—1295; cf. A., 1932, 934).—Schlubach's method of purifying inulin (I) (A., 1932, 1021) can be shortened by keeping the 5% solution for some days at room temp. instead of freezing it. The final product (55% yield) has $[\alpha]_D^{20}$ —40·2° in H_2O, 0·035% ash, and does not reduce Fehling's solution. Quant. hydrolysis of (I) with *Aspergillus* inulinase yields 90—92% of cryst. fructose (II). The mother-liquors contain 1·5% of glucose (III) (as determined *loc. cit.*) and this val. is confirmed by separation of residual (II) as the phenylmethylosazone. The hypothesis that the production of (III) arises from isomerisation of γ-fructose in an acid medium is not supported by the observation that the same proportion of (III) results from hydrolysis with 0·05*N*-H_2SO_4 or by enzyme action at p_H 3·8 or 6·0. Further, the theoretical ratio of (II) to (III) is observed when sucrose is subjected to enzymic hydrolysis under the same conditions as (I). Although it appears improbable that (III) arises from impurities in (I) the question is not regarded as settled. H. W.

Influence of iodine on the decomposition of simple aliphatic amines and of hexane.—See this vol., 1125.

Reaction of nitrogen trichloride with Grignard reagents. G. H. COLEMAN, M. A. BUCHANAN, and W. L. PAXSON (J. Amer. Chem. Soc., 1933, **55**, 3669—3672).—NCl_3 reacts with RMgX (R=Et, Pr^β, Bu^α, *sec.*-Bu, Bu^γ, *n*-amyl, Ph, $\cdot CH_2Ph$, $\cdot CH_2{\cdot}CH_2Ph$; X=Cl, Br, I) in Et_2O to give N_2, NH_3, NH_2R, and NHR_2 (small yield); with $CH_2Ph{\cdot}MgCl$, a trace of $N(CH_2Ph)_3$ is also formed. The yield of NH_2R decreases in the order X=Cl, Br, I. The yields of amines are generally considerably smaller than with NH_2Cl (A., 1928, 622; 1929, 431). Methods of analysis (lit. and modifications) of solutions of NCl_3 are compared. H. B.

Alkylation of secondary amines with aldehydes and ketones. A. SKITA, F. KEIL, and H. HAVEMAN (Ber., 1933, **66**, [*B*], 1400—1411; cf. A., 1928, 1120, 1228; 1930, 327).—Hydrogenation of *sec.* amines (I) in presence of aldehydes is a general method for the prep. of *tert.* amines (II), but the yields are greatly reduced if (I) contains a branching of the C chain in the α-position to N. With aromatic aldehydes the production of (II) depends on the mol. wt. of (I). In general, the proximity of Ph to N diminishes the capacity of alkylation. Reaction between (I) and ketones (III) depends on the mol. wt. and constitution of both reactants. (I) of medium mol. wt. with >NMe react with (III) containing ·COMe. Replacement of Me by Et or higher radical greatly reduces the reactivity, as does a branch in the C chain in α-position to N. In *o*-methyl*cyclo*hexanone the CO is greatly protected by Me, but the influence is not so obvious in the *m*- and *p*-isomerides. The following compounds are described: ethyl*iso*amylamine, b.p. 124—128°, from MeCHO and *iso*amylamine or NH_2Et and *iso*valeraldehyde (IV), whence *ethyl*iso*amylheptylamine*, b.p. 112—113°/11 mm. (*H oxalate*, m.p. 75—76°), and *-γη-dimethyloctylamine*, b.p. 136—137°/11 mm. (*H oxalate*, m.p. 81—82°); di*iso*amylamine, from (IV) and NH_3 in presence of Ni, whence *ethyl-*, b.p. 75—78°/11 mm. (*picrate*, m.p. 95—96°; *picrolonate*, m.p. 114—115°; *methiodide*, m.p. 148·5—149·5°), and *butyl-di*iso*amylamine* (V), b.p. 100—103°/11 mm. (*picrate*, m.p. 117—118°) [(V) is also prepared by use of crotonaldehyde and is formed from MeCHO through $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$]; *di*iso*amyl-γη-dimethyloctylamine*, b.p. 161—162°/12 mm. (*H oxalate*, m.p. 112—113°); *ethyl-*, b.p. 186—188°/10 mm. (*H oxalate*, m.p. 94—95°), and iso*amyl-*, b.p. 208°/13 mm. (*H oxalate*, m.p. 100—101°), *-di-γη-dimethyloctylamine*; *tri-γη-dimethyloctylamine*, b.p. 237—239°/12 mm. (*H oxalate*, m.p. 105—106°); n-*propyldi*iso*propylamine*, b.p. 145—147° (*picrate*, m.p. 120—121°); *di-α-methylpropylheptylamine*, b.p. 249—252° (*picrolonate*, m.p. 105—106°); diphenyl-methylamine; -ethylamine (*Br_2*-compound, m.p. 107—108°); -n-*propylamine*, b.p. 154°/12 mm. (*Br_2*-compound, m.p. 76—77°); -n-*butylamine*, b.p. 164°/11 mm. (*Br_2*-compound, m.p. 56—57°); -iso*butylamine*, b.p. 156—157°/11 mm.; *methyl-*iso*propyl-α-methylpropylamine*, b.p. 132—133° (*picrate*, m.p. 142—143°); *-di-α-methylpropylamine*, b.p. 155—157° (*picrate*, m.p. 92—93°); *-α-methylpropyl-α′-methylbutylamine*, b.p. 170—172° (*picrolonate*, m.p. 130—131°; *picrate*, m.p. 87—88°); *-α-methylpropyl-α′-methylamylamine*, b.p. 192—193° (*picrolonate*, m.p. 98—99°); *-α-methylpropyl-α′-methylhexylamine*, b.p. 211—213° (*picrolonate*, m.p. 99—100°); *-α-methylpropyl-α′-methylheptylamine*, b.p. 224—225°; *-α-methylpropyl*cyclo*hexylamine*, b.p. 208—209° (*picrate*, m.p. 110—111°); *-α-methylpropyl-*p*-methyl*cyclo*hexylamine*, b.p. 221—222° (*picrolonate*, m.p. 138—139°); *-α-methylpropyl-*m*-methyl*cyclo*hexylamine*, b.p. 218—219° (*picrate*, m.p. 92—93°); *ethyl*iso*propyl-α-methylpropylamine* (*picrate*, m.p. 118°); *ethyl*iso*propyl*iso*amylamine* b.p.

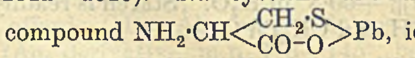
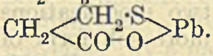
163—164°/762 mm. (*picrate*, m.p. 60—61°); *iso-propyldiisoamylamine*, b.p. 206—208° (*picrate*, m.p. 80—81°). *Methyl-α-methylpropyl-α′-ethylpropylamine*, b.p. 168—171°/744 mm. (*picrolonate*, m.p. 115—116°), is obtained from $COEt_2$ and $NHMe\cdot CHMeEt$, from COMeEt and $NHMe\cdot CHEt_2$ and from CH_2O and $NH(CHMeEt)\cdot CHEt_2$. *Methyl-α-ethylpropylamine*, b.p. 106—107° (*H oxalate*, m.p. 142—143°), and *α-methylpropyl-α′-ethylpropylamine*, b.p. 150—152° (*picrolonate*, m.p. 187—188°), are incidentally described. H. W.

Diaminobutanes. I. *dl*-αβ-Diaminobutane; αβ-diamino-β-methylpropane (*dl*-αβ-diaminopropane). E. STRACK and H. SCHWANEBERG (Ber., 1933, **66**, [*B*], 1330—1333; cf. A., 1932, 727).—The best yields of diamines from aminonitriles are obtained when reduction (H_2–Pd or Na–abs. EtOH) is effected in very dil. solution. The following salts of *dl*-αβ-diaminobutane are described: hydrochloride, m.p. 189—190°; *sulphate*, m.p. > 300°; chloroplatinate, decomp. > 250°; *chloroaurates*, $R,2HAuCl_4,H_2O$ [$R=C_4H_{12}N_2$], m.p. 199—200° after softening at 190°, $R,2AuCl_3$, decomp. 217° after softening at 212°, R,HAu_2Cl_5, decomp. 195—200°; picrate, decomp. 256° after softening at 200°; *picrolonate*, decomp. 267—269°; *salts*, $R,HgCl_2$, m.p. 190°, and $R,3HgCl_2$, m.p. 147°; *Bz_2*, m.p. 186°, and *di*-m-*nitrobenzoyl*, m.p. 198°, derivatives. αβ-Diamino-β-methylpropane gives a hydrochloride, m.p. 303°, picrolonate, decomp. 260—262° after softening at 256°; *mercurichloride*, m.p. 151—152°; chloroplatinate, m.p. 270°; chloroaurates, $R',2HAuCl_4,2\cdot 5H_2O$ ($R'=NH_2\cdot CH_2\cdot CMe_2\cdot NH_2$), m.p. 135° (sealed tube) or m.p. (anhyd.) 233°, and $R,2AuCl_3$, m.p. 228°; picrate, m.p. (anhyd.) 241° ($+H_2O$), decomp. 235° after softening at 230°; *sulphate*, m.p. > 300°; *Bz_2*, m.p. 182·5° after softening at 180°, and *di*-m-*nitrobenzoyl*-, m.p. 174° after softening at 171°, derivatives. H. W.

Autoxidation of amino-acid derivatives and their degradation by ozone. II. F. BERGEL and K. BOLZ (Z. physiol. Chem., 1933, **220**, 20—26; cf. this vol., 494).—α-Dimethylamino*iso*butyric acid (from α-bromobutyric acid and $NHMe_2$) on autoxidation in presence of animal C undergoes 100% decomp. into CO_2, $NHMe_2$, and $COMe_2$, under conditions in which α-amino*iso*butyric acid is completely resistant. All types of NH_2-acids in H_2O are attacked by O_3 with the formation of products similar to those obtained by autoxidation. J. H. B.

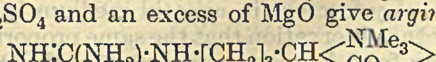
Behaviour of carbamide derivatives, amino-acids, and peptides towards animal charcoal. K. WUNDERLY (Helv. Chim. Acta, 1933, **16**, 1009—1013).—$CO(NH_2)_2$, biuret, barbituric acid, urethane, phenylurethane, hydantoic acid, and diketopiperazine are unaffected when heated in dil. aq. solution with animal or sugar C. In 24 hr. at 80° serine, sarcosine, *dl*-glycylglycine, and *dl*-leucylglycylglycine are deaminated to the extent of 20%, 5%, 40%, and 8%, respectively. H. W.

Deamination of glycine by pyrocatechol derivatives and identification of glyoxylic acid as intermediate product. H. K. BARRENSCHEEN and W. DANZER (Z. physiol. Chem., 1933, **220**, 57—60).—Methylamino- (I), amino- (II), and ethylamino-acetopyrocatechol (III) are inferior to adrenaline in catalysing the deamination of glycine in presence of O_2. (II) and (III) are better than (I) at p_H 6·8 and equal to pyrocatechol (IV); at 7·7 they are less active than (IV) owing to their low solubility. $CHO\cdot CO_2H$ was isolated as the 2 : 4-dinitrophenylhydrazone from the deamination products, indicating $NH_2\cdot CH_2\cdot CO_2H \longrightarrow NH{:}CH\cdot CO_2H \longrightarrow CHO\cdot CO_2H+NH_3$. J. H. B.

Lead compounds of glycine, cysteine, and β-thiolpropionic acid. R. KLEMENT (Ber., 1933, **66**, [*B*], 1312—1315).—Na cysteine and $Pb(OH)_2$ afford the compound  $NH_2\cdot CH{<}\genfrac{}{}{0pt}{}{CH_2\cdot S}{CO-O}{>}Pb$, identical with that of Bauer *et al.* (this vol., 940). $SH\cdot CH_2\cdot CH_2\cdot CO_2H$ (I) and $Pb(OAc)_2$ or $SH\cdot CH_2\cdot CH_2\cdot CO_2Na$ and $Pb(OH)_2$ afford the *salt* $Pb{:}[\cdot S\cdot CH_2\cdot CH_2\cdot CO_2]_2{:}Pb$, converted by boiling 2*N*-Na_2CO_3 into $PbCO_3$, (I), and the *compound*  $CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot S}{CO-O}{>}Pb$. Pb in Pb glycine (II) is in complex union with NH_2, since (II) is unaffected by liquid NH_3, whereas anhyd. $Pb(OAc)_2$ yields the unstable *substance* $Pb(OAc)_2,NH_3$. H. W.

Preparation of glycyltaurine and glycylcysteic acid. J. WHITE (J. Biol. Chem., 1933, **102**, 249—251).—$CH_2Br\cdot COBr$ (I) and taurine in *N*-NaOH at 0° give *glycyltaurine*, cryst. (50% yield). (I) does not condense with cysteic acid. Diglycylcysteine and $Br–H_2O$ at 0° give a 91% yield of *glycylcysteic acid*, cryst. R. S. C.

Oxidation of *d*-glutamic acid by chromic acid and by acid permanganate. E. J. H. CHU and C. L. TSENG (J. Chinese Chem. Soc., 1933, **1**, 46—50).—*d*-Glutamic acid with hot $Na_2Cr_2O_7–H_2SO_4$ or $KMnO_4–H_2SO_4$ during 6—7 hr. affords $(\cdot CH_2\cdot CO_2H)_2$, CO_2, and NH_3. J. L. D.

Protein problem: methylation of arginine. W. ZIMMERMANN and A. CANZANELLI (Z. physiol. Chem., 1933, **219**, 207—214).—Arginine salts with Me_2SO_4 and an excess of MgO give *arginine-α-betaine* (I),  $NH{:}C(NH_2)\cdot NH\cdot[CH_2]_3\cdot CH{<}\genfrac{}{}{0pt}{}{NMe_3}{CO—}{>}O$ [*diflavianate*, m.p. 190° (decomp.); *dipicrate*, m.p. 168—169°; *sesquichloroaurate*, m.p. 195—197°]. Hydrolysis of (I) with aq. $Ba(OH)_2$ yields $CO(NH_2)_2$ and ornithine-α-betaine (II) [*diflavianate*, m.p. 240—242° (decomp.); *dipicrate*, decomp. 118—120°, or ($+H_2O$) m.p. 91°]. δ-Benzoylornithine with Me_2SO_4 and MgO and subsequent hydrolysis with 50% H_2SO_4 gave (II) in poor yield. Arginine carbonate with Me_2SO_4 and $BaCO_3–Ba(OH)_2$ (cf. Engeland and Kutscher, A., 1913, i, 194) affords trimethylarginine (III) [*diflavianate* (IV), decomp. 225—228°; *dichloroaurate*, m.p. 174°]. Hydrolysis of (IV) with aq. $Ba(OH)_2$ for 5 hr. eliminates 2 Me with the $CO(NH_2)_2$ radical and gives (?) α-methylornithine [*flavianate*, m.p. 222—223° (decomp.); *picrate*, m.p. 205—206°], not identical with δ-methylornithine or its piperidone (*flavianate*, m.p. 260—262°; *picrate*). Hydrolysis of (IV) with aq. $Ba(OH)_2$ for 2 hr. yields, without loss of Me, a trimethylcitrulline [*flavianate*, m.p. 235°

(decomp.); *picrate*, decomp. 214—216°]. (III) is always formed in methylation if the mixture becomes acid, probably owing to transformation of (I) primarily formed. J. H. B.

Racemisation and oxidation of cystine in acid solution. J. C. Andrews (J. Biol. Chem., 1933, **102**, 263—268).—Cu'' (but no other substance) catalyses the aërial oxidation of cystine (I) to cysteic acid in HCl, but not in H_2SO_4 or H_3PO_4. H_3PO_4 racemises (I) faster than does HCl or H_2SO_4. R. S. C.

Mesocystine. H. S. Loring and V. du Vigneaud (J. Biol. Chem., 1933, **102**, 287—295).—Details are given for the prep. of *dl*- [*phenylcarbamido*-derivative, m.p. 195—196° (corr.); *diformyl* derivative, m.p. 196—198°, resolved by the strychnine salt] and *meso-cystine*, decomp. 200—218° [*diformyl* derivative, m.p. 192—193° (corr.) (*strychnine* salt, $+4H_2O$, m.p. 133—135°, anhyd., decomp. 175—176°, $[\alpha]_D^{26}$ −21·5° in H_2O, irresolvable)]. R. S. C.

Decomposition of the phenylhydantoin of cystine. J. C. Andrews and (Miss) K. C. Andrews (J. Biol. Chem., 1933, **102**, 253—262).—The phenylhydantoin of cystine [*l*- (I), m.p. 114·5°, $[\alpha]_D^{25}$ −155° in $COMe_2$; *dl*-, m.p. 177°] (modified prep.) is slowly racemised by hot, dil. acid, and is decomposed by hot H_2O and rapidly by dil. NaOH to 3-phenyl-5-methylenehydantoin, Na_2S, and S, the reaction being catalysed by Pb or glass. (I) and Br–H_2O at 0° give the *phenylhydantoin hydrobromide* of cysteic acid, m.p. 138°, $[\alpha]_D^{27}$ −41·4° in $COMe_2$, decomposing very readily to give, amongst other products, SO_4''. R. S. C.

Condensation of bromal hydrate with aliphatic amides. B. H. Yelburgi (J. Indian Chem. Soc., 1933, **10**, 383—390).—Condensation of bromal hydrate with the appropriate aliphatic amides gives the bromalamide, converted by Ac_2O–NaOH into the anhydrodi-derivative and by reduction (Zn–AcOH) into the bromoethylene compound. The following have been prepared: *bromalformamide*, m.p. 139—140° (*Ac*, m.p. 107—108°, *Bz*, m.p. 139°, and *anhydrodi*-derivatives, m.p. 170°); *Me*, m.p. 106°, *Bz*, m.p. 122°, and *anhydrodi*-derivatives of bromalacetamide, m.p. 183—185°; *bromalpropionamide*, m.p. 174° (*Ac*, m.p. 96—98°, *Bz*, m.p. 113—115°, *Me*, m.p. 85—87°, and *anhydrodi*-derivatives, m.p. 192°); *Ac*, m.p. 96—98°, *Bz*, m.p. 122°, *Me*, m.p. 101°, and *anhydrodi*-derivatives of bromoalbutyramide, m.p. 155°; *bromal*-iso*butyr*-, m.p. 156° (*Ac*, m.p. 141—143°, *Bz*, m.p. 131—132°, *Me*, m.p. 135°, and *anhydrodi*-derivatives, m.p. 155°); -iso*valer*-, m.p. 149° (*Ac*, m.p. 140—142°, *Bz*, m.p. 98—100°, *Me*, m.p. 115—117°, and *anhydrodi*-derivatives, m.p. 130—132°); -*hexo*-, m.p. 146° (*Ac*, m.p. 120—122°, *Bz*, m.p. 132—134°, *Me*, m.p. 105—107°, and *anhydrodi*-derivatives, m.p. 153°); -*hepto*-, m.p. 142° (*Ac*, m.p. 135—136°, *Bz*, m.p. 126°, and *Me* derivatives, m.p. 93—95°); -*octo*-, m.p. 139° (*Ac*, m.p. 129°, *Bz*, m.p. 108—110°, *Me*, m.p. 85°, and *anhydrodi*-derivatives, m.p. 166°); and -*nono*-, m.p. 139° (*Ac*, m.p. 121°, *Bz*, m.p. 123—126°, and *Me* derivatives, m.p. 72—74°), -*amide*; β-*tribromo-α-chloroethyl-formamide*, b.p. 80°/15 mm., -*acetamide*, b.p. 76°/8 mm., -*acetchloroimide*, b.p. 138°/25 mm., -*propionamide*, b.p. 120°/19 mm., and -*butyramide*, b.p. 126°/15 mm.; β-*dibromoethyleneacet*-, m.p. 82°, -*propion*-, m.p. 84—86°, -*butyr*-, m.p. 78—80°, iso*butyr*-, m.p. 80—82°, -iso*valer*-, m.p. 68—70°, -*hexo*-, m.p. 74—75°, -*octo*-, m.p. 115°, and -*nono*-, m.p. 63—64°, -*amide*; and β-*bromoethylene*-iso*valer*-, m.p. 71—74°, -*hexo*-, m.p. 61—63°, -*octo*-, m.p. 67—71°, and -*nono*-, b.p. 148°/10 mm., -*amide*. F. R. S.

Synthesis of *l*-asparagine from *l*-glutamine. M. Bergmann, L. Zervas, and L. Salzmann (Ber., 1933, **66**, [*B*], 1288—1290; cf. A., 1932, 935).—Benzylcarbonato-*l*-aspartic anhydride is converted by $CH_2Ph{\cdot}OH$ at 100° mainly into the *CH_2Ph H* ester $CO_2H{\cdot}CH_2{\cdot}CH(NH{\cdot}CO_2{\cdot}CH_2Ph){\cdot}CO_2{\cdot}CH_2Ph$, m.p. 84—85°, transformed successively into the corresponding *chloride*, m.p. 81—82°, and *amide*, m.p. 132° (corr.), which, when treated with Pd-black and H_2 in MeOH, gives PhMe, CO_2, and *l*-asparagine, $[\alpha]_D^{17}$ +20·6° in 0·1*N*-HCl. Similarly benzylcarbonato-*d*-glutamic anhydride is transformed successively into the non-cryst. α-*CH_2Ph* ester, its *chloride*, *amide*, m.p. 123° (corr.), and *d*-glutamine, m.p. 184—185°, $[\alpha]_D^{19}$ +8·0° in H_2O. H. W.

Thiocarbamyl chloride. Thiocyanic acid. M. Battegay and E. Hégazi (Helv. Chim. Acta, 1933, **16**, 999—1008).—Treatment of a saturated solution of NH_4CNS in H_2O at −5° with 50—60% H_2SO_4 in amount not quite sufficient to liberate HCNS completely, followed by extraction with ether so as to produce a $\not>$ 20% solution and treatment of the dried extract with HCl, leads to *thiocarbamyl chloride* (I), $NH_2{\cdot}CSCl$, decomp. 75—80°, which with H_2O and bases suffers the change $NH_2{\cdot}CSCl \longrightarrow HCl+HSCN$. With alcohols (I) affords alkoxythioformamides, $OR{\cdot}CS{\cdot}NH_2$, of which the following are described: Me, m.p. 42—43°; Et, m.p. 40—41°; Pr^β, m.p. 79—80°; Bu^a, m.p. 20—21°; Bu^β, m.p. 51—53°; $OH{\cdot}CH_2{\cdot}CH_2$, m.p. 68—69°. With excess of (I) dithioallophanates are obtained. With MeOH methylthiolformamide is also produced, indicating the equilibrium $NH_2{\cdot}CSCl \rightleftharpoons HCl+S{:}C{\cdot}NH$. With PhOH (I) gives phenylxanthamide and p-*hydroxythiobenzamide*, m.p. 175° (decomp. with production of *p*-$CN{\cdot}C_6H_4{\cdot}OH$), mixed with a small proportion of the *o*-isomeride, m.p. 117—118°. H. W.

Action of sodium on aliphatic diazo-compounds. E. Müller and H. Disselhoff (Naturwiss., 1933, **21**, 661).—CPh_3Na with EtOH- and H_2O-free CH_2N_2 (A., 1930, 1027) yields an explosive Na compound which with BzCl gives a *substance*, $C_8H_6ON_2$, not identical with diazoacetophenone. Similarly diphenyldiazomethane affords an Et_2O-sol. compound which on decomp. with H_2O yields a *substance*, $C_{32}H_{26}N_2$, not identical with diphenylketazine. CPh_3Na also reacts with PhN_3 (cf. A., 1901, i, 678). F. O. H.

Formation of free radicals from aliphatic azo-compounds. F. O. Rice and B. L. Evering (J. Amer. Chem. Soc., 1933, **55**, 3898—3899; cf. Leermakers, this vol., 1039).—Measurements of the rate of disappearance (method: A., 1932, 1108) of the active fragments obtained from β-azopropane (in $COMe_2$) indicate the formation of a fragment of relatively long life. H. B

Preparation and application of organomagnesium compounds without use of ether. II. Action of magnesium on alkyl and aryl chlorides. P. SCHORIGIN, V. ISSAGULIANZ, and A. GUSSEVA (Ber., 1933, **66**, [*B*], 1426—1431).—Mg and 1-$C_{10}H_7Cl$ react vigorously at 200—220° with copious sublimation of $C_{10}H_8$ and production of 10—13% of $C_{10}H_7\cdot MgCl$. Boiling CH_2PhCl and Mg react very energetically with evolution of HCl and formation of a glassy mass probably due to a condensing action of $MgCl_2$ similar to that of $AlCl_3$, $FeCl_3$, or $SnCl_4$. Bu^aCl, *iso*-$C_5H_{11}Cl$, and *n*-$C_8H_{17}Cl$ react moderately violently near their b.p.; the intermediate organomagnesium compounds are completely decomposed, with the formation of R·R, RH, and R—H, leaving a residue probably of $MgCl_2$ and Mg. The formation of organo-Mg derivatives is placed beyond doubt by the production of nonoic acid from *n*-$C_8H_{17}Cl$ and Mg in CO_2, although $(CH_2)_2O$ is without action. Treatment of RCl with Mg activated by I and PhCHO affords CHPhBz·OH. Moderation of the reaction between *iso*-$C_5H_{11}Cl$ or Bu^aCl and Mg by addition of PhMe gives the corresponding *p*-alkyltoluenes characterised by oxidation to terephthalic acid; this change is not caused by $MgCl_2$. The compound, m.p. 209—211° (A., 1931, 1411), is *p*-phenyldiphenyl. H. W.

Action of sodium on gallium trimethyl and gallium dimethyl chloride in liquid ammonia. C. A. KRAUS and F. E. TOONDER (J. Amer. Chem. Soc., 1933, **55**, 3547—3554; cf. this vol., 599).—In liquid NH_3 at −33°, the reaction $2GaMe_3,NH_3+Na=[GaMe_3]_2NH_2Na+0{\cdot}5H_2+NH_3$ (I) is accompanied by $2GaMe_3,NH_3+2Na=[GaMe_3]_2Na_2+2NH_3$ (II) to the extent of 0—30%, depending on the conditions. With Li and liquid NH_2Et at −33°, the reactions are $GaMe_3,NH_2Et+Li=GaMe_3,NHEtLi+0{\cdot}5H_2$ and the analogue of (II). $Na_2[GaMe_3]_2$ reacts with NH_4Br: $Na_2[GaMe_3]_2+2NH_4Br=2GaMe_3,NH_3+2NaBr+H_2$, whereas $Li_2[GaMe_3]_2$ decomposes during the evaporation of the NH_2Et as follows: $Li_2[GaMe_3]_2+2NH_2Et\longrightarrow 2GaMe_3,NHEtLi+H_2$. With one equiv. of Na the reaction $GaMe_2Cl+Na=GaMe_2+NaCl$ (III) is followed by the formation of $GaMe_2,NH_3$, which decomposes after the evaporation of the solvent: $GaMe_2,NH_3=GaMe_2\cdot NH_2+0{\cdot}5H_2$. With two equivs. of Na, (III) is followed by the slow reaction $GaMe_2,NH_3+Na=GaMe_2,NaNH_2+0{\cdot}5H_2$ and $GaMe_2,NH_3$ is regenerated on the addition of NH_4Br. J. G. A. G.

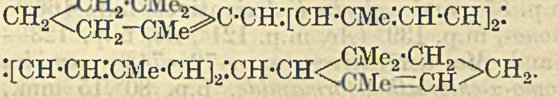
New hydrocarbons of the *cyclo*pentane series and their passivity towards catalytic dehydrogenation. N. D. ZELINSKI, S. E. MICHLINA, and M. S. EVENTOVA (Ber., 1933, **66**, [*B*], 1422—1426).—*cyclo*Pentanone (I) and *n*-$C_6H_{13}\cdot MgBr$ yield 1-n-*hexyl*-cyclo*pentan*-1-*ol*, b.p. 120—121°/15 mm., converted by heating with cryst. $H_2C_2O_4$ into n-*hexyl*cyclo*pentene*, b.p. 204—205°/740 mm., which is reduced (Pt–C at 200°) to n-*hexyl*cyclo*pentane* (II), b.p. 204—206°/748 mm. *n*-$C_8H_{17}\cdot MgCl$ and (I) yield 1-n-*octyl*cyclo*hexan*-1-*ol*, converted successively into n-*octyl*cyclo*pentene* and n-*octyl*cyclo*pentane* (III), b.p. 133—134°/26 mm. Mg *cyclo*pentyl chloride and powdered trioxymethylene give cyclo*pentylmethyl alcohol*, b.p. 162—163°/753 mm., converted by red P and I into an iodide (IV), b.p. 75°/19 mm., which with Na in Et_2O affords *dicyclo*-[0 : 1 : 3]-hexane and a non-homogeneous mixture converted by Pd–C at 300° into Ph_2 and αβ-*di*-cyclo*pentylethane*, b.p. 206—207°/748 mm. (IV) is therefore a mixture of *cyclo*pentylmethyl and hexyl iodide. (II) and (III) are stable in presence of Pt–C at 300°. H. W.

Kinetics of a diene synthesis. A. WASSERMANN (Ber., 1933, **66**, [*B*], 1392—1394).—By periodic measurement of the intensity of colour, the reaction between *p*-benzoquinone and *cyclo*pentadiene (I) is shown to be bimol. in *n*-C_6H_{14}, CCl_4, C_6H_6, EtOH, and AcOH. That between (I) and *cyclo*pentadienequinone is also bimol. H. W.

Kinetics of the irreversible catalysis of *cyclo*hexene and the *cyclo*hexadienes. N. D. ZELINSKI and G. S. PAULOV (Ber., 1933, **66**, [*B*], 1420—1422; cf. A., 1925, i, 122).—In presence of Pd sponge at 35°, *cyclo*hexene, b.p. 83·5° (corr.), is converted into C_6H_6 and *cyclo*hexane; the reaction, measured by periodic titration with Br in $CHCl_3$, is sesquimol. $\Delta^{1:3}$- and $\Delta^{1:4}$-*cyclo*Hexadiene react vigorously in contact with Pd (Pt) sponge; the first violent action $2C_6H_8=C_6H_{10}+C_6H_6$ is followed by the slower change, $3C_6H_{10}=C_6H_6+2C_6H_{12}$. H. W.

1-Methyl*dicyclo*-[1 : 2 : 2]-heptane and its behaviour during catalytic dehydrogenation and hydrogenation. Fission of the *cyclo*pentane ring by catalytic hydrogenation. N. D. ZELINSKI, B. A. KAZANSKI, and A. F. PLATE (Ber., 1933, **66**, [*B*], 1415—1419).—*endo*Methylenetetrahydrobenzaldehyde (I), b.p. 71—72°/9 mm., is transformed through the hydrazone into 2-*methyl*dicyclo-[1 : 2 : 2]-Δ^5-*heptene* (II), b.p. 115·5—117°/750 mm. Hydrogenation of (I) (Pt sponge or, preferably, Pd sponge) leads to endo*methylenehexahydrobenzaldehyde*, b.p. 62—64°/12 mm., similarly converted into 2-*methyl*dicyclo-[1 : 2 : 2]-*heptane* (III), b.p. 125—126·5°/761 mm., which is stable towards $KMnO_4$. Hydrogenation of (II) as gas at 130° (Pt–C) gives a product, b.p. 120—124°/727 mm., not completely identical with (III), whereas at room temp. (EtOH–Pd sponge) the product is homogeneous and identical with (III). Passage of (III) over Pt–C at 300 in H_2 leads to addition of 2H and formation of the saturated system C_nH_{2n}. One of the pentamethylene rings suffers fission in contact with Pt giving a monocyclic *cyclo*pentane hydrocarbon which may undergo further rupture of the ring. *cyclo*-Pentane is almost quantitatively transformed into *n*-pentane by passage over Pt–C at 300° in H_2. H. W.

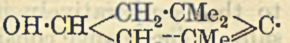
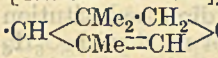
Vegetable colouring matters. LII. Constitution of α-carotene. P. KARRER, R. MORF, and O. WALKER. **LIII. Xanthophyll and violaxanthin.** P. KARRER, A. ZUBRYS, and R. MORF (Helv. Chim. Acta, 1933, **16**, 975—977, 977—979).—LII. Ozonisation of α-carotene (I), separated from β-carotene by $Ca(OH)_2$, leads to geronic acid and a somewhat smaller amount of *iso*geronic acid. (I) is therefore



$$CH_2{<}\begin{matrix}CH_2\cdot CMe_2\\ CH_2{-}CMe\end{matrix}{>}C\cdot CH{:}[CH\cdot CMe{:}CH\cdot CH]_2{:}$$

$${:}[CH\cdot CH{:}CMe\cdot CH]_2{:}CH\cdot CH{<}\begin{matrix}CMe_2\cdot CH_2\\ CMe{=}CH\end{matrix}{>}CH_2.$$

By reason of its acidity, fuller's earth is unsuitable for the purification of (I).

LIII. Elucidation of the structure of (I) (see above) leads to the constitution  $OH\cdot CH<\begin{smallmatrix}CH_2\cdot CMe_2\\ CH_2\text{--}CMe\end{smallmatrix}>C\cdot$ $\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot[CH{:}CH\cdot CH{:}CMe]_2\cdot CH{:}CH\cdot$  $\cdot CH<\begin{smallmatrix}CMe_2\cdot CH_2\\ CMe\text{==}CH\end{smallmatrix}>CH\cdot OH$ for xanthophyll (II). The *sec.* OH groups in (II) are characterised by reduction of (II) from grass or stinging nettles to perhydroxanthophyll, which is oxidised by CrO_3 in AcOH to perhydroxanthophyll diketone (*disemicarbazone*, m.p. 158°). H. W.

Carotene. V. Formation of geronic acid by ozonisation of carotene, dihydrocarotene, and related compounds. H. H. STRAIN. **VI. Hydrogenation of α- and β-carotene.** J. H. C. SMITH (J. Biol. Chem., 1933, 102, 137—150, 157—160; cf. A., 1932, 619).—V. The yield of geronic acid (I) obtained by ozonisation of (*a*) carotene or dihydrocarotene, or (*b*) β-ionone, β-*cyclo*citral, or β-*cyclo*geranic acid, varies widely according to the conditions, the max. being (*a*) 0·67 and (*b*) 0·78 mol. (I) is best determined as 2 : 4-*dinitrophenylhydrazone*, m.p. 133—134° (corr., decomp.), decomposed by alkalis and rapidly hydrolysed by the $NaHSO_3$ compound of glyoxal in AcOH. α-Ionone similarly gives *iso*geronic acid (5—8% only) [2 : 4-*dinitrophenylhydrazone*, m.p. 140—141° (corr.)]. Citralcyanoacetic acid and H_3PO_4 give chiefly α-*cyclo*citral.

VI. α- and β-Carotene in AcOH or AcOH–*p*-menthane absorb 11 mols. of H_2 (PtO_2), if the solvent has not come into contact with rubber or tap-grease. R. S. C.

Significance of tautomerism and of reactions of aromatic compounds in the electronic theory of organic reactions. C. K. INGOLD (J.C.S., 1933, 1120—1127).—The internal polar properties of atoms or groups are classified according to (1) time-dependence or (2) mechanism. The characteristics distinguished in (1), viz., polarisation (dipole moment μ) and polarisability (deformation coeff. α), differ in dimensions by an amount corresponding with the dimensions of an electric force ($m=\mu+\alpha F$). The effects categorised in (2) differ in the source of their energy. The zero moment of alkyl groups in hydrocarbons (polarisation) coupled with the reactivity of the latter towards electrophilic (electron-seeking) reagents (polarisability) necessitates the recognition of an "inductomeric" in addition to an inductive effect, the two being distinguished by their time-dependence. Similarly the tautomeric mode of electron displacement is split up into electromeric (*E*, polarisability, time-variable) and mesomeric (*M*, permanent polarisation, originally designated electronic strain) effects. Anomalous orientation (*op*-substitution coupled with nuclear deactivation) in aromatic substitution by electrophilic reagents, and the decrease in strength of BzOH by a *p*-OMe substituent, despite the electron-attracting dipole of their latter, are considered from this point of view. The driving power of the inductive effect (octet stability) is quantum mechanical, but the energy of the mesomeric effect is regarded as arising from a form of wave-mechanical degeneracy, evidence being adduced in support of this view. J. W. B.

Influence of nuclear halogens on aromatic side-chain reactivity. G. M. BENNETT (J.C.S., 1933, 1112—1114).—On the basis of results previously summarised (this vol., 499), various side-chain velocity data, and the strengths of halogeno-substituted anilines and benzoic acids, it is suggested that, contrary to hitherto accepted ideas, the electromeric effect (*E*) of the halogens decreases in the order F>Cl>Br>I. *E* is regarded as an ethenoid or butadienoid polarisation in the Ph nucleus promoted by the electron-repelling outer field of the halogen atom (*loc. cit.*). J. W. B.

Effect of nuclear halogen substituents on triad prototropic systems in relation to aromatic side-chain reactions. C. W. SHOPPEE (J.C.S., 1933, 1117—1120).—Results previously summarised (A., 1930, 912; 1931, 834; 1932, 384) and side-chain velocity data (lit.) show that the effect of halogen substituents anticipated on the basis of the order of their $-I$-effects, F>Cl>Br>I, is inverted in all cases except for the mobility of prototropic systems activated by aryl groups. The last type of reaction is unique in that both the postulated reaction phases, (*a*) the approach of the negative (catalytic) ion, and (*b*) the cationisation of the mobile H, are facilitated by electron-recession. It is suggested that other aromatic side-chain reactions involve two rate-affecting phases of opposite polar types (cf. Baker, *infra*) and hence for type *B* reactions (electron-recession) the velocity coeffs. for ambipolar ($-I$, $+T$) substituents should pass through a max. In the curves connecting relative velocities and the series I, Br, Cl, F (increasing $-I$, diminishing $+T$) the position of the max. may vary according to the way in which mol. circumstances weight the opposing polar phases, and data illustrating each type of curve are cited. Similar curves for type *A* reactions (electron accession) exhibit min., indicating the probable existence of two or more reaction mechanisms, each possibly complex. J. W. B.

Anomalies in the reactivities of side-chain halogens with special reference to reaction mechanism. J. W. BAKER (J.C.S., 1933, 1128—1133).—The ψ-unimol. velocity coeffs. (10^3k, min.$^{-1}$) for the reaction (I) $CH_2RX+C_5H_5N\longrightarrow CH_2R\cdot\overset{\oplus}{N}C_5H_5\}\overset{\ominus}{X}$, and (II) $+NH_2Ph\longrightarrow CH_2R\cdot NHPh+HX$, previously determined (A., 1932, 744, 1241), indicate that the reaction requires electron-accession to (*A*), or recession from (*B*), the side-chain when $R=p\text{-}Y\cdot C_6H_4\cdot$ and $p\text{-}Y\cdot C_6H_4\cdot CO\cdot$, respectively, the nature of R thus predisposing the mol. to react mainly by one or the other type of mechanism. The observed velocity of side-chain reactions is probably determined by two (or more) rate-affecting factors of opposite polar types (cf. Shoppee, preceding abstract) and (for X=Br) evidence for this view is adduced from (*a*) the influence of ambipolar substituents on 10^3k for I*A* (I, 3·3; Br, 3·0, Cl, 3·2; H, 4·4) and II*A* (45, 41, 44, and 35, respectively); (*b*) the effect of *m*- (10^3k 1·36) and *p*- (1·56) -NO_2 substituents on I*A*; (*c*) the relative facilitating and retarding effects of unipolar substituents (accelerating influence of group > its retarding influence on a reaction of opposite polar type; (*d*) the results of Dawson and Dyson (this vol., 1125); and (*e*) the effect of base concn. on the reaction velocity of I*A* (10 mols., 10^3k 4·4; 20 mols. 8·2) and I*B* (10 mols. 6·5; 20 mols. 11). The effect of varying X (Cl, Br, or I) on *k* is discussed and possible mechanisms for the reactions are suggested. J. W. B.

Hydrogenation of aromatic compounds at temperatures close to their decomposition [points] in presence of catalysts. V. IPATIEV (J. Amer. Chem. Soc., 1933, 55, 3696—3701).—C_6H_6 and $C_6H_4Me_2$ are not hydrogenated at 400—450°/65—100 atm. using MoO_3 catalysts; $C_6H_4Me_2$ decomposes to C_6H_6 and PhMe. Hydrogenation of $C_{10}H_8$ at $\ngtr$ 450°/65—80 atm. (initial pressure) using NiO, Fe_2O_3, and MoO_3 catalysts gives 1 : 2 : 3 : 4-tetrahydronaphthalene (I) almost exclusively; reaction proceeds (probably) 9 : 10-H_2-$\longrightarrow$1 : 4-H_2-$\longrightarrow$(I). Above 450°, the (I) formed decomposes into C_6H_6 hydrocarbons; with Ni catalysts naphthens are formed, showing that some mols. of the monocyclic aromatic compounds are hydrogenated during this decomp. Similar hydrogenation of PhOH in presence of MoO_3, Fe_2O_3, or CuO gives 10—30% of *cyclo*hexane. Thiophen has no effect on the rate of destructive hydrogenation of $C_{10}H_8$, but decreases the yield of hydrocarbons during the reduction of PhOH. H. B.

Catalytic oxidation of benzene to maleic acid. J. S. SALKIND and S. ZOLOTAREV (J. Appl. Chem. Russ., 1933, 6, 681—684).—Air is passed through C_6H_6 at 15°, the vapour is heated to 360°, and passed over V_2O_5 catalyst at 410—430°, when 14—17% yields of $(\text{:}CH\cdot CO_2H)_2$ (I) are obtained. The issuing gas contains in addition $(\text{:}CH\cdot CO)_2O$, CO_2, benzoquinone, and unchanged C_6H_6, which is recovered by adsorption on cooled SiO_2 gel. The process consists probably of the reactions: $C_6H_6\longrightarrow PhOH\longrightarrow p\text{-}C_6H_4(OH)_2\longrightarrow$benzoquinone$\longrightarrow$(I). R. T.

Action of aluminium bromide on benzene. E. WERTYPOROCH and H. SAGEL (Ber., 1933, 66, [*B*], 1306—1312).—Protracted action of $AlBr_3$ on C_6H_6 at 18° gives a liquid (I) and an oily (II) layer. Fractional distillation of (I) affords no evidence of PhMe or PhEt, but yields a liquid $C_7H_6O_5$ with a phenolic odour which contains 2 OH (Zerevitinov), is stable towards $KMnO_4$, and is hydrogenated to a mixture of phenols; phenyl*cyclo*hexane, Ph_2, and *o*-diphenyl*cyclo*hexane are identified. (II) yields PhOH but not $C_{10}H_8$, a *phenyl*cyclo*hexanediol*, m.p. 178—179°, and a phenyl*cyclo*hexanol, *cyclo*hexane, and a mixture of phenylated methyl*cyclo*pentanes and *cyclo*hexanes. H. W.

ψ-Halogens. XXII. Reaction of metallic salts with iodine and bromine in presence of benzene. L. BIRCKENBACH and J. GOUBEAU (Ber., 1933, 66, [*B*], 1280—1287; cf. A., 1932, 1120).—The salt is covered with C_6H_6 and treated with small, successive quantities of I or Br at room temp. until the colour persists. Substitution in the C_6H_6 is observed in the presence of salts of Ag, Hg^{II}, and Au^{I} and to a smaller extent in that of Cu^{I} or Cu^{II}, but not of Zn, Cd, Tl^{I}, or Pb^{II} even after addition of $AlCl_3$. Reasons are advanced for attributing the success of the reaction to the comparatively non-polar type of the active salts. The change consists in a primary, equilibrated formation of a mixed halogen the action of which on C_6H_6 is facilitated by $AlCl_3$. A direct substitution is excluded, since I or Br does not react with C_6H_6 in presence of Na_2CO_3 or CaO and the rate of the observed reaction depends greatly on the anion. Reaction between $AgNO_3$ and I is accelerated by HNO_3. Conc. H_2SO_4 is helpful in the cases of I and Ag_2SO_4, Hg_2SO_4, and $HgSO_4$, but not of $PbSO_4$. The main product of the change is invariably PhBr or PhI, the other component of the mixed halogen seldom appearing in the final product. Small amounts of $PhNO_2$ and PhOAc, respectively, are observed in the actions with $AgNO_3$ and I or Br and AgOAc with Br. H. W.

Electrochemical experiments with *p*-fluorotoluene and *p*-fluorobenzoic acid; di-*p*-fluorobenzoyl peroxide and its decomposition. F. FICHTER and J. ROSENZWEIG (Helv. Chim. Acta, 1933, 16, 1154—1158).—*p*-C_6H_4FMe is immediately converted by electrolytic oxidation into *p*-$C_6H_4F\cdot CO_2H$ (I), degradation with formation of CO_2 also occurring; the formation of *p*-$C_6H_4F\cdot CHO$ cannot be detected. *p*-$C_6H_4F\cdot CO_2Na$ in MeOH, like other aromatic acids with CO_2H attached directly to the nucleus, does not undergo Kolbe's electrosynthesis, the F being incapable of protecting the nucleus from oxidation. *Di*-p-*fluorobenzoyl peroxide*, m.p. 97°, slow decomp. 99—100°, from *p*-$C_6H_4F\cdot COCl$ in Et_2O and BaO_2,H_2O, is converted at 250° into 4 : 4′-difluorodiphenyl mixed with more complex condensation products and regenerated (I). H. W.

Monochlorination of *m*-nitrotoluene. W. E. EVISON (J.S.C.I., 1933, 52, 275—276T).—*m*-$C_6H_4Me\cdot NO_2$ is smoothly chlorinated (Fe catalyst) to a mixture of Cl_1- and Cl_2-derivatives which cannot be separated by distillation. On reduction it gives an oil which contains 30% of 6-chloro-*m*-toluidine; a part of this base crystallises, whilst the remainder is isolated as oxalate, picrate, or sulphate. The dichloroamino-compounds are easily removed, as their hydrochlorides are almost completely hydrolysed by H_2O; 2 : 5-dichloro-*m*-toluidine appears to preponderate in the basic mixture which is thus separated. About 21% of the 2-Cl- and small quantities of the 4-Cl-isomerides can then be isolated as their Ac derivatives, by acetylating and fractionating the residual oil. From the oxidation product of the mixed chloronitrotoluenes, 4-chloro-3-nitrobenzoic acid is most easily isolated, and is present to the extent of 10—15%.

Absorption spectra of 2 : 4 : 6-trinitrotoluene. M. M. PAVLIK (Chim. et Ind., 1933, 29, Spec. no., 245—259).—The photochemical decomp. of 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ (I) has been followed by investigation of the absorption spectra and extinction coeffs. of the fused compound and of its solutions in org. solvents before and after exposure to light. The absorption spectra of its decomp. products, *o*- and *p*-quinoxime, have also been investigated. The quantities of these compounds produced in (I) can be determined by spectrum analysis. Thermal decomp. and the action of alkalis lead to products similar to those of the photochemical decomp.

J. W. S.

Volume effects of alkyl groups in aromatic compounds. I. Influence of 2 : 6-dinitration on a group ·CR_1R_2Alk. II. Influence of a group ·CR_1R_2Alk on vicinal substitution. R. J. W. Le Fèvre (J.C.S., 1933, 977—980, 980—984).—I. The expectation, based on scale drawings (cf. this vol., 557), that spatial interference of the Pr^{β} with the adjacent NO_2 groups in 1 : 4 : 6 : 3 : 5-$C_6HMePr^{\beta}R(NO_2)_2$ would lead to geometrical isomerism has not been realised where R is OH, OAc, OBz, Cl, or Br, all attempts at fractionation of 4 : 6-dinitrocarvacrol, m.p. 121—122°, its acetate, m.p. 74—75°, and benzoate, m.p. 100—101°, proving unsuccessful. The reported existence of isomeric 3 : 5-dinitro-2-chloro- or -bromo-*p*-cymenes (cf. A., 1889, 493) is disproved, the sole nitration product being in each case the cryst. form, which was obtained in almost quant. yield and gave 3 : *5-dinitro-2-piperidino*-p-*cymene*, m.p. 123—124°, with $C_5H_{11}N$. Attempts to realise a similar interference with the ·CMe_3 group in the artificial musks were frustrated by their lack of reactivity. "Musk xylol" [1 : 3 : 5 : 2 : 4 : 6-$C_6Me_2Pr^{\beta}(NO_2)_3$] could not be oxidised to a carboxylic acid and did not react with aromatic aldehydes, although 2 : 4 : 6-trinitro-*m*-xylene readily gives 2 : 4 : 6-*trinitro*-1 : 3-*distyrylbenzene*, m.p. 145—146°. "Musk ambrette" [1 : 3 : 2 : 4 : 6 : 5-$C_6MePr^{\beta}(NO_2)_3$·OMe] could not be demethylated and reacts only very slowly with $C_5H_{11}N$ to give the *piperidino*-derivative, $C_{16}H_{22}O_6N_4$, m.p. 184°.

II. Preferential substitution of *p*-cymene in the 2-position is confirmed, 70%, 59%, and 54% of homogeneous 2-substituted derivatives being isolated on nitration, chlorination, and bromination, respectively. Current electronic theories require preferential 3-substitution, and it is suggested that the steric effect of the Pr^{β} group is the disturbing factor. p-*Cymene*-3-*carboxylic acid*, m.p. 82—83° (from 3-bromocymene, Mg, and CO_2), and 2-p-*cymeneazo*-β-*naphthol*, m.p. 131—132°, are described.

H. A. P.

Nitration of 4-nitro-*o*-tolyl *p*-toluenesulphonate. F. H. Curd and A. Robertson (J.C.S., 1933, 1166—1167).—With HNO_3 (*d* 1·5) at room temp. 4-*nitro*-o-*tolyl* p-*toluenesulphonate*, m.p. 123—124° (from 4-nitro-*o*-cresol, *p*-C_6H_4Me·SO_2Cl, and anhyd. Na_2CO_3), gives the corresponding 2-*nitro*-p-*toluenesulphonate*, m.p. 120—121°, but with conc. H_2SO_4–HNO_3 (*d* 1·5) at $< 40°$ or 0°, 4 : 5-*dinitro*-o-*tolyl* 2-*nitro*-p-*toluenesulphonate* (I), m.p. 125—126°, is obtained. With piperidine at 100° or 10% KOH in aq. EtOH, (I) gives 4 : 5-*dinitro*-p-*cresol*, m.p. 115° (and 2-nitro-*p*-toluenesulphonic acid), the *Me ether*, m.p. 80—81°, of which is converted by H_2SO_4–HNO_3 into 3 : 4 : 5-trinitro-2-methoxytoluene, identical with a specimen prepared from 4-nitro-2-methoxytoluene (A., 1901, i, 590), and is reduced by $SnCl_2$–HCl–MeOH to 5-*nitro*-2-*methoxy*-p-*toluidine*, m.p. 152°, from which 5-nitro-2-methoxytoluene is obtained by elimination of the NH_2 group by diazotisation.

J. W. B.

Catalytic oxidation of acenaphthene in solution. R. Duckert (Arch. Sci. phys. nat., 1933, [v], 15, 244—263, 343—371).—The % oxidation of acenaphthene (I) to naphthalic acid (II) and acenaphthenequinone (III) (9 : < 1) is (*a*) at atm. pressure, 0 without and < 2 with a catalyst in absence of a solvent, (*b*) at 200° and 8 kg. per sq. cm. initial pressure, in absence of a solvent, < 5, (*c*) at 175—300° and 2—8 kg. per sq. cm. with various catalysts in H_2O, AcOH, PhCl, or $C_6H_4Cl_2$, 2—24 [best with $Mn(NO_3)_2$ in $C_6H_4Cl_2$ at 300° and 3—5 kg. per sq. cm.]. Decomp., always considerable, is very great in case (*b*). The method of separation of (II) and (III) from much (I) and resin is modified.

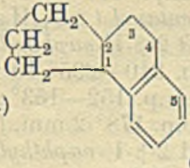
R. S. C.

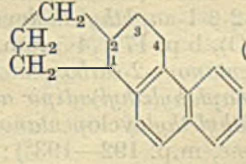
Rearrangements of polyinenes. V. Reactions of 1 : 1′-bis-(1 : 3-diphenylindenyl). M. T. Goebel and C. S. Marvel (J. Amer. Chem. Soc., 1933, 55, 3712—3715).—1 : 1′-Bis-(1 : 3-diphenylindenyl) (I) (this vol., 57), also prepared by the action of *s*-$C_2Me_4Br_2$ on the Na alkyl (II) from 1 : 3-diphenylindene and 40% Na–Hg, is oxidised ($K_2Cr_2O_7$–AcOH or O_2 in boiling xylene) to *o*-$C_6H_4Bz_2$ and is cleaved slowly by 1% Na–Hg and readily with 40% Na–Hg or liquid Na–K alloy to (II). (II) and $ClCO_2Me$ give *Me* 1 : 3-*diphenylindene*-1-*carboxylate*, m.p. 99—100°; the free acid could not be obtained by hydrolysis or from (II) and CO_2. Reduction (HI, P, AcOH) of (I) affords 1 : 3-diphenylhydrindene. (I) dissolves in xylene to a faint yellow solution which deepens in colour when heated in absence of air and then fades on cooling; continued heating and cooling changes (I) into a gummy solid. The above reactions show that (I) dissociates into an unstable free radical and is a new type of hydrocarbon containing an active C·C linking.

H. B.

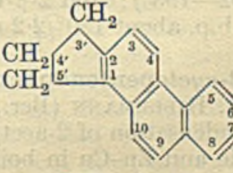
Polycyclic compounds related to sterols. I. G. A. R. Kon (J.C.S., 1933, 1081—1087).—12-*Methyl*- (I), b.p. 157°/16 mm., and 11-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (II), b.p. 133°/2·8 mm., 1 : 2-cyclo*pentano*- (III), b.p. 138°/19 mm., and 1 : 2-cyclo*pentano*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (IV), b.p. 128°/12 mm., 1 : 2-(5′-*methyl*cyclo*pentano*)-, (?) (V), b.p. 141—145°/2 mm., and 1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (?) (VI), b.p. 142°/2 mm., are prepared. On dehydrogenation with Se (I) and (II) give phenanthrene with ease, (III) and (IV) give 4 : 5-*benzohydrindene*, b.p. 118°/0·5 mm. (*picrate*, m.p. 108°), the latter with some difficulty, (V) gives 5′-*methyl*-1 : 2-$\Delta^{1':3'}$(or $\Delta^{1':4'}$)-cyclo*pentadienophenanthrene* (cf. VII), m.p. 182° [*picrate*, m.p. 199—200° (decomp.)] (reduction of this with Na and 95% EtOH did not give pure products), and (IV) gives 1 : 2-$\Delta^{1':3'}$(or $\Delta^{1':4'}$)-cyclo*pentadienophenanthrene*, b.p. 182—183° (*picrate*, m.p. about 124°), and 1 : 2-*cyclo*pentenophenanthrene (VII) ("1 : 2-*cyclo*-

(III.)



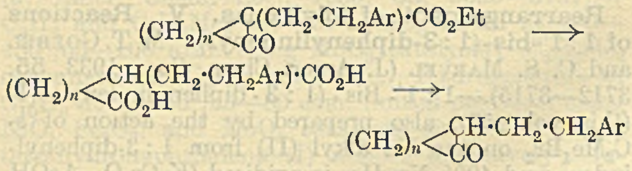


(VI.)



(VII.)

pentanophenanthrene " of Ruzicka, this vol., 820; cf. *ibid.*, 710), m.p. 135—136° [*picrate*, m.p. 133—134°; $C_6H_3(NO_2)_3$ *compound*, m.p. 165·5°], apparently identical with the "Diels hydrocarbon." In synthesising the compounds (I)—(VI) modifications of Bardhan and Sen-Gupta's phenanthrene synthesis (A., 1932, 1241) were used, the yield of the 2-β-arylethyl*cyclo*-pentanones or -hexanones being much improved by hydrolysis of the 2-carboxylic esters with $Ba(OH)_2$ or KOH and re-cyclisation of the resulting dicarboxylic acid :



$$(\mathrm{CH_2})_n\!<\!\begin{array}{l}\mathrm{C(CH_2\cdot CH_2Ar)\cdot CO_2Et}\\ \mathrm{CO}\end{array} \longrightarrow (\mathrm{CH_2})_n\!<\!\begin{array}{l}\mathrm{CH(CH_2\cdot CH_2Ar)\cdot CO_2H}\\ \mathrm{CO_2H}\end{array} \longrightarrow (\mathrm{CH_2})_n\!<\!\begin{array}{l}\mathrm{CH\cdot CH_2\cdot CH_2Ar}\\ \mathrm{CO}\end{array}$$

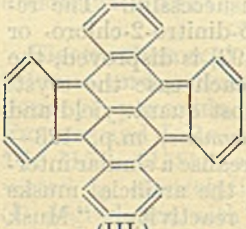
Introduction of the Me group is effected with MgMeI or, if on a C atom common to two rings, by alkylation of the 2-alkyl*cyclo*ketones by the $NaNH_2$ method (cf. A., 1927, 666). The following are described : α-(β-*phenylethyl)pimelic acid*, m.p. 64—65°; 1-*methyl*-2-β-*phenylethyl*cyclo*hexanol*, b.p. 140°/3 mm.; 2-*methyl*-2-β-*phenylethyl*cyclo*hexanone*, b.p. 152°/4 mm. (*semicarbazone*, m.p. 178°) (from 2-methyl*cyclo*hexanone, $NaNH_2$, and $CH_2Ph\cdot CH_2Br$); 2-*methyl*-2-β-*phenylethyl*cyclo*hexanol*, b.p. 159°/3 mm.; *Et* 2-β-*phenylethyl*cyclo*pentanone-2-carboxylate*, b.p. 192°/6 mm. (*semicarbazone*, m.p. 163°); α-(β-*phenylethyl*)-*adipic acid*, m.p. 97—98°; 2-β-*phenylethyl*cyclo*pentanone*, b.p. 163°/13 mm. [*semicarbazone*, m.p. 213° (decomp.)]; 1-*methyl*-2-β-*phenylethyl*cyclo*pentanol*, b.p. 134—135°/5 mm. (dehydrated by heat to an unsaturated *hydrocarbon*, $C_{14}H_{18}$, b.p. 120°/7 mm.); 2-β-*phenylethyl*cyclo*pentanol*, b.p. 131°/1·5 mm.; β-1-*naphthylethyl bromide* (VIII) (from the alcohol and 30% HBr–AcOH), b.p. 172°/20 mm.; *Et* 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanone-2-carboxylate*, b.p. 227°/4 mm. [from K derivative of Et 5-methyl*cyclo*pentanone-2-carboxylate and (VIII) in $C_6H_4Me_2$]; α-*methyl*-α′-(β-1-*naphthylethyl)adipic acid*, m.p. 155—156°; 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanone*, b.p. 222—225°/10 mm. (*semicarbazone*, m.p. 171—172°); 5-*methyl*-2-β-1-*naphthylethyl*cyclo*pentanol* (? $C_{18}H_{22}O$ or $C_{18}H_{24}O$), b.p. 177°/4·5 mm.; *Et* 2-β-1′-*naphthylethyl*-cyclo*pentanone-2-carboxylate*, b.p. 210—235°/10 mm.; α-(β-1-*naphthylethyl)adipic acid*, m.p. 152—153°; 2-β-1′-*naphthylethyl*cyclo*pentanone*, b.p. 178°/2 mm. (*semicarbazone*, m.p. 192—193°); and 2-β-1′-*naphthylethyl*-cyclo*pentanol* (?), b.p. about 180°/2·2 mm.

H. A. P.

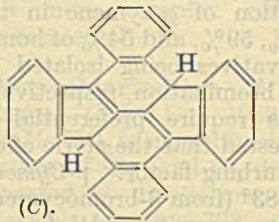
3′-Methyl-1 : 2-*cyclo*pentenophenanthrene. E. Bergmann and H. Hillemann (Ber., 1933, 66, [*B*], 1302—1306).—Condensation of 2-acetylphenanthrene with $CH_2Br\cdot CO_2Me$ and Zn–Cu in boiling C_6H_6 leads to *Me* β-*hydroxy*-β-2-*phenanthrylbutyrate*, m.p. 107—109°, dehydrated by 85% HCO_2H to *Me* β-2-*phenanthrylcrotonate*, m.p. 147—148°, which is reduced ($Pd–BaSO_4–H_2$) to *Me* β-2-*phenanthrylbutyrate*, m.p. 76—78° [corresponding *acid* (I), m.p. 125—127°]. (I) is transformed by the successive action of $SOCl_2$ and $AlCl_3$ in $PhNO_2$ into 6 : 7-(1′ : 2′-*naphtha*)-3-*methylhydrind*-1-*one*, m.p. 135—136°, reduced (Zn–Hg, conc. HCl) to 3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* (II), m.p. 126—127° (*picrate*, m.p. 130—131°). Although identity is not at present claimed, (II) is closely similar to the hydrocarbon obtained by Diels by dehydrogenation of cholesteryl chloride by Se (this vol., 1047). Analyses of the picrate, m.p. 120—122° after darkening at 117°, appear to indicate $C_{18}H_{16}$.

H. W.

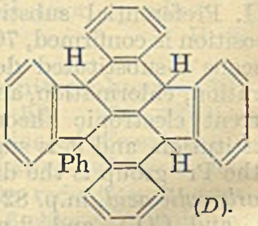
Coloured hydrocarbons. Blue hydrocarbon and related colourless hydrocarbons. M. Badoche (Ann. Chim., 1933, [x], 20, 200—284).—Mainly a detailed account of results previously summarised (A., 1932, 375, 507). Of the hydrocarbons formed by the action of Na on dehydrorubrene $C_{42}H_{26}$ (I), *A*, m.p. 302°, and its stereoisomeride B_1, m.p. 338°, and *D*, m.p. 286—287°, are sol. in Et_2O, whereas *C*, [(II) in A., 1932, 507], m.p. 400°, and the blue hydrocarbon (III), m.p. 465° [together with unchanged (I)], are insol., and are separated by long fractional crystallisation from CS_2. For short reaction periods (10 days) *A* and *B* are the main products, but on prolonged action (3 months) these are replaced by (III), *C*, and *D*. Spectrophotometric data (visible and ultra-violet) for these hydrocarbons and for dihydro-, tetraphenyl-, and ψ-rubrene indicate their close relationship, all being characterised by a group of three bands. On the basis of these data and known types of reaction of Na with benzenoid hydrocarbons the structures here given are provisionally assigned :



(III.)



(*C*).



(*D*).

D forming an intermediate between the two groups of hydrocarbons into which *A* and *B*, and (III) and *C*, respectively, fall.

J. W. B.

Steric hindrance. VIII. J. von Braun and E. Anton [with C. Kemény] (Ber., 1933, 66, [*B*], 1373—1378; cf. A., 1932, 1242).—*cyclo*Pentylmethylamine, prepared in > 90% yield from the acid and N_3H in $CHCl_3$, is converted into the *Bz* (I) derivative, b.p. 185°/0·7 mm., m.p. 75°, transformed by PCl_5 at 100° into cyclo*pentylmethyl chloride* (II), b.p. 60°/50 mm. The homogeneity of (II) follows from its successive conversion by way of the iodide, *cyanide*, b.p. 110—115°/80 mm., acid, and its chloride into *cyclo*pentylacetamide, m.p. 144°. (II) reacts very slowly with $NHEt_2$, piperidine, or NaOPh. *cyclo*Pentylacetonitrile is reduced by Na–EtOH to β-cyclo*pentylethylamine*, b.p. 158—159° [non-hygroscopic *hydrochloride*, m.p. 195°; *picrate*, m.p. 142°; *Bz* (III) derivative, b.p. 184°/0·2 mm., m.p. 62°], whence β-cyclo*pentylethyl chloride*, b.p. 84—86°/60 mm., which is little reactive. 2 : 3 : 3-Trimethyl*cyclo*pentylamine (dihydro-β-campholenamine; dihydro*iso*lauronamine) yields a *Bz* derivative (IV), b.p. 184°/0·4 mm., m.p. 50°, converted by PCl_5 into

2 : 3 : 3-*trimethyl*cyclo*pentylmethyl chloride*, b.p. 73°/14 mm., which reacts with difficulty with piperidine. Interaction of N_3H with *iso*campholic or α-campholenic acid affords 2 : 2 : 3-*trimethyl*cyclo*pentylmethylamine*, b.p. 71—73°/12 mm. (*picrate*, decomp. 222° after darkening at 205°; *chloroaurate*; *chloroplatinate*, decomp. 245°); the *Bz* derivative (V), b.p. 185°/0·3 mm., m.p. 92°, and PCl_5 yield an *imidochloride*, b.p. 150—152°/14 mm., converted by distillation under atm. pressure into 2 : 2 : 3-*trimethyl*cyclo*pentylmethyl chloride*, b.p. 60°/12 mm. (corresponding *bromide*, b.p. 73°/13 mm.). 1 : 4 : 5 : 5-Tetramethyl*cyclo*pentylmethylamine (VI) (from campholonitrile, Na, and EtOH) gives a Bz derivative (VII), transformed by PCl_5 into a mixture of 1 : 4 : 5 : 5-tetramethyl*cyclo*pentylmethyl chloride and a hydrocarbon $C_{10}H_{18}$ (VIII), b.p. 54—55°/14 mm., 175°/756 mm. (VI) does not smoothly lose NH_3 when distilled with H_3PO_4. Successive treatment of (VI) with Me_2SO_4–NaOH and then with KI affords 1 : 4 : 5 : 5-*tetramethyl*cyclo*pentylmethyltrimethylammonium iodide*, decomp. 310—312°; the corresponding hydroxide when distilled with or without alkali yields almost exclusively 1 : 4 : 5 : 5-*tetramethyl*cyclo*pentylmethyldimethylamine*, b.p. 91°/12 mm., $[\alpha]_D^{16}$ +72·8° (*picrate*, m.p. 176°), transformed by syrupy H_3PO_4 in CO_2 into the *hydrocarbon* $C_{10}H_{18}$, b.p. 154—157°/760 mm., not identical with (VIII). Comparative hydrolyses of the Bz derivatives with 38% HCl at 120° during 4 hr. indicate the possibility of the separation of types (II) and (I) from (IV), but not of (IV) from (V). There seems little possibility in this direction of utilising the varying reactivity of Cl in the chlorides. H. W.

Nitration of disulphonanilides. F. Bell and R. Cohen (J.C.S., 1933, 1290).—Mononitration of *di*-m-*nitrobenzenesulphonanilide*, m.p. 189°, is accomplished with fuming HNO_3 (conc. HNO_3 has no action); treatment of the resultant product with conc. H_2SO_4 gives di-*m*-nitrobenzenesulphon-*m*-nitroanilide and *m*-nitrobenzenesulphon-*p*-nitroanilide. *Di*-m-*nitrobenzenesulphon*-p-*toluidide*, m.p. 199°, is similarly nitrated to the 2-*nitro*-p-*toluidide*, m.p. 208°, which with conc. H_2SO_4 gives m-*nitrobenzenesulphon-2-nitro*-p-*toluidide*, m.p. 136°. *Di*-m-*nitrobenzenesulphon*-o-*toluidide*, m.p. 226°, affords the 4-, m.p. 221°, and 6- (I), m.p. 185°, -*nitro*-o-*toluidides*; (I) is converted by piperidine into m-*nitrobenzenesulphon*-6-*nitro*-o-*toluidide*, m.p. 148°. H. B.

Polyhalogenodinitrobenzenes. S. S. Joshi and S. M. Sane (J. Indian Chem. Soc., 1933, **10**, 459—463).—With the appropriate amine, 1-chloro-4-bromo-2 : 6-dinitrobenzene gives 4-bromo-2 : 6-dinitro-aniline, m.p. 159°, -diphenylamine, m.p. 122°, -*dimethylamine*, m.p. 119°, and -*phenylpiperidine*, m.p. 110°, 4 : 4′-*dibromo*-2 : 6 : 2′ : 6′-*tetranitrodiphenyl*-p-*phenylenediamine*, m.p. > 300°, 3-*bromo-5-nitrophenoxazine* (from *o*-aminophenol), m.p. 179°, and 5-*bromo-7-nitro-2-phenyl-ψ-aziminobenzene* (from NH_2NHPh), m.p. 199°; the 4-I-compound gives 4-*iodo*-2 : 6-*dinitro-aniline*, m.p. 175°, -*dimethylaniline*, m.p. 100°, -*diphenylaniline*, m.p. 135°, and -*phenylpiperidine*, m.p. 99°, 3-*iodo-5-nitrophenoxazine*, m.p. 210°, and 5-*iodo-7-nitro-2-phenyl-ψ-aziminobenzene*, m.p. 209°. 1-Chloro-2-bromo-4 : 6-dinitrobenzene yields 2-*bromo*-4 : 6-*dinitrophenylpiperidine*, m.p. 127°, and 7-*bromo-5-nitro-2-phenyl-ψ-aziminobenzene*, m.p. 174°, whilst the 2-I-compound forms 2-*iodo*-4 : 6-*dinitro-aniline*, m.p. 158°, -*diphenylamine*, m.p. 144°, and -*dimethylaniline*, m.p. 112°, 2 : 2′-*di-iodo*-4 : 6 : 4′ : 6′-*tetranitrodiphenyl*-p-*phenylenediamine*, m.p. > 300°, 7-*iodo-5-nitro-2-phenyl-ψ-aziminobenzene*, m.p. 192°, and 3 : 5-dinitrophenoxazine, m.p. 214—215°. F. R. S.

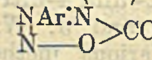
Reaction of formaldehyde with diphenylamine. D. Craig (J. Amer. Chem. Soc., 1933, 55, 3723—3727).—$NHPh_2$ (1·5 mols.), 36% CH_2O (0·19 mol.), and conc. HCl (1 c.c.) in EtOH (250 c.c.) at 40—100° (bath) give (mainly) 4 : 4′-dianilinodiphenylmethane (I), m.p. 122—123° [synthesised (Ullmann method) from 4 : 4′-diaminodiphenylmethane and *o*-$C_6H_4Cl{\cdot}CO_2H$]; resins are produced with equiv. amounts or excess of CH_2O. Equimol. quantities of CH_2O and $NHPh_2$ in C_6H_6 give tetraphenyldiaminomethane (II), m.p. 104—105° [the specimen prepared by Houben and Arnold (A., 1908, i, 533) is probably contaminated with (I)], which is hydrolysed (dil. acid) to CH_2O and $NHPh_2$, but with $NHPh_2$ and a little conc. HCl in EtOH passes into (I); with dry HCl alone, resinification occurs. Hydrogenolysis of (II) using a Cu chromite catalyst gives $NHPh_2$ (main product), NPh_2Me, and (I). The *compound* $(NPh_2Me,HCl)_2,ZnCl_2$ has m.p. 186—188° (decomp.). H. B.

Condensation of ethyl propylacetoacetate with aromatic amines. II. G. V. Jadhav (J. Indian Chem. Soc., 1933, **10**, 391—394).—Et *n*-propylacetoacetate has been heated with further aromatic amines (cf. A., 1931, 1407). Except with *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$, *s*-diarylcarbamides were obtained together with the acetoacetarylamide, but α-$C_{10}H_7{\cdot}NH_2$ gave only $CO(NH{\cdot}C_{10}H_7)_2$, m.p. 296°. The following appear to be new: n-*propylacetoacet*-β-*naphthylamide*, m.p. 115—116°, -o-*phenetidide*, m.p. 90—91°, -p-, m.p. 95—96°, and -m-*hydroxyanilide*, m.p. 223—224° (*Ac* derivative, m.p. 165°), -o-, m.p. 83—84°, -m-, m.p. 88—89°, and -p-*chloroanilide*, m.p. 123—124°, and -m-, m.p. 95—96°, and -p-*nitroanilide*, m.p. 118—119°. F. R. S.

Nitration of aceto-α-naphthalide and preparation of 2- and 4-nitro-α-naphthylamines. H. H. Hodgson and J. Walker (J.C.S., 1933, 1205—1207).—Various methods of mononitration of α-$C_{10}H_7{\cdot}NHAc$ are investigated (cf. A., 1924, i, 637); the use of HNO_3 (*d* 1·42) at 5—10° affords the best yield (87%) and purest product. Hydrolysis (50% H_2SO_4–EtOH) of the nitration mixture, dissolution of the 2- (I) and 4- (II) -nitro-α-naphthylamines in $PhNO_2$, and passage of dry HCl through the solution give the hydrochloride of (II); addition of conc. H_2SO_4 to the filtrate ppts. the sulphate of (I). The free bases are obtained by trituration of the salts with H_2O. Superheated steam removes the slowly volatile (I) from its mixture with (II). The f.-p. diagram of 2-nitroaceto-α-naphthalide [best prepared by partial hydrolysis (EtOH–NaOH) of (III) (below)] and the 4-NO_2-isomeride (IV) [prepared readily from (II) and Ac_2O in AcOH] indicates the existence of the 1 : 1-compound (III), m.p. 171°, described by Lellmann and Remy (A., 1886, 754), and of a metastable eutectic containing about 60 mols.-% of (IV). 2-Nitro-α-naphthol and (I) readily crystallise together in equimol. proportion; the f.-p. diagram does not indicate 1 : 1-compound formation. H. B.

Manufacture of *p*-aminodiphenyl and derivatives thereof.—See B., 1933, 857.

Formation of azides from the *N*-nitroso-derivatives of hydrazo-compounds. G. Longo (Gazzetta, 1933, 63, 463—471).—Arylhydrazinecarboxylates, $NHAr\cdot NH\cdot CO_2R$ (I) are prepared from $NHAr\cdot NH_2$ and $ClCO_2Me$(or Et) in presence of C_5H_5N; with $NaNO_2$ and AcOH they yield *N*-NO-derivatives, $NAr(:NO)\cdot NH\cdot CO_2R$ (II), and with CrO_3 substituted benzeneazocarboxylates,, $NAr:N\cdot CO_2R$ (III). When heated with 10% NaOH, (II) give the azides ArN_3 in very small yield, with N_2 and decomp. products. The following are described: *Me*, m.p. 180°, and *Et*, m.p. 198—199°, p-*nitrophenylhydrazinecarboxylates* [*NO*-derivatives, m.p. 125—126° and 110—111° (decomp.)]; *Me*, m.p. 84—85°, and *Et*, m.p. 74—75°, p-*nitrobenzeneazocarboxylates*; *Me* 2 : 4-*dinitrophenylhydrazinecarboxylate*, m.p. 138°; *Me*, m.p. 110—111°, and *Et*, m.p. 105°, p-*bromophenylhydrazinecarboxylate* [*NO*-derivatives, m.p. 92° and 104—105° (decomp.)]; *Me* p-*bromobenzeneazocarboxylate*, m.p. 75—76°; *Me* p-*tolylhydrazinecarboxylate*, m.p. 112° [*NO*-derivative, m.p. 55—56° (decomp.); *Et* ester, m.p. 88°, no NO-derivative]; *Me* p-*tolueneazocarboxylate*, m.p. 29—30°. Formyl-*p*-nitrophenylhydrazine forms with amyl nitrite and HCl the N-*NO*-derivative, m.p. 109—110° (decomp.). For *p*-bromo- and *p*-nitro-phenylsemicarbazide the new m.p. 223° and 220° are found. Attempts to prepare compounds of type $NAr:N\cdot C(OH):NOH$ and $NHAr\cdot NH\cdot C(OH):NOH$ from (III) and (I), respectively, or from the corresponding amides, failed.
E. W. W.

Reaction between diazonium salts and trinitromethane. G. Ponzio (Gazzetta, 1933, 63, 471—478).—The formula $R\cdot N_2\cdot NO:C(NO_2)_2$ (A., 1915, i, 1012) is preferred to that proposed by Quilico (this vol., 59) for the products from diazonium salts and nitroformates; their decomp. products cannot be formulated $R\cdot N(NO)\cdot N:CO$ (Quilico, *loc. cit.*), for they have none of the properties of the N(NO) and N:CO groupings. The formulation  $\begin{matrix}NAr:N\\ |\qquad\ \\ N\text{---}O\end{matrix}\!>\!CO$, as *anhydrides of oximinoarylazocarboxylic acids*, on the other hand, explains their stability to heat, and to H_2O, EtOH, NH_2Ph, etc., and the fact that *p*-nitrobenzenediazonium nitroformate when treated with KOH+MeOH or KOH+EtOH gives quantitatively the *K* salts of Me and Et *N*-nitroso-*p*-nitrophenylhydrazinecarboxylates (cf. preceding abstract).
E. W. W.

Supercrystallinity of *p*-azoxybenzoic acid.—See this vol., 1108.

Constitution of *o*-hydroxyazo-compounds. K. von Auwers (Annalen, 1933, 505, 283—295).—Polemical (cf. this vol., 828, 946). Arguments in favour of the azoid structure are advanced.
H. A. P.

Action of chlorine on the nitrobenzeneazoacetoacetates. F. D. Chattaway and D. R. Ashworth (J.C.S., 1933, 1143—1146).—The action of Cl_2 on nitrobenzeneazoacetoacetates (αβ-diketo-*n*-butyrate-α-nitrophenylhydrazones) differs considerably from that of Br (cf. this vol., 705); the course of the reaction is affected by the position of the NO_2-group and by the solvent. Thus, $p\text{-}NO_2\cdot C_6H_4\cdot NH\cdot N:CAc\cdot CO_2Et$ (I) and Cl_2 in AcOH give *Et α-chloroglyoxylate-2-chloro-4-nitrophenylhydrazone*, m.p. 120°, also obtained similarly from *Et* 2-*chloro-4-nitrobenzeneazoacetoacetate*, m.p. 109°. In dry $CHCl_3$, *Et α-chloroglyoxylate*-p-*nitrophenylhydrazone* (II), m.p. 192°, results, but in AcOH–NaOAc the N-*Cl*-derivative (III), m.p. 67°, of (II) is formed. (III) and KI in aq. AcOH give (II). Cl could not be introduced into the Ac group of (I). *Et* 2 : 6-*dichloro-4-nitrobenzeneazoacetoacetate*, m.p. 104°, and Cl_2 in AcOH afford *Et α-chloroglyoxylate*-2 : 6-*dichloro* - 4 - *nitrophenylhydrazone*, m.p. 124°. $o\text{-}NO_2\cdot C_6H_4\cdot NH\cdot N:CAc\cdot CO_2Et$ (IV) and Cl_2 in $CHCl_3$ give *Et* o-*nitrobenzeneazo-γ-chloroacetoacetate*, m.p. 149°, whilst *Et* 4-*chloro-2-nitrobenzeneazoacetoacetate* (V), m.p. 127°, affords *Et* 4-*chloro-2-nitrobenzeneazo-γ-chloroacetoacetate*, m.p. 131°. In AcOH–NaOAc, (IV) and (V) furnish *Et α-chloroglyoxylate-4-chloro-2-nitrophenylhydrazone*, m.p. 108°. *Et α-chloroglyoxylate*-m-*nitrophenylhydrazone*, m.p. 158°, is obtained from $m\text{-}NO_2\cdot C_6H_4\cdot NH\cdot N:CAc\cdot CO_2Et$ and Cl_2 in $CHCl_3$; in AcOH or AcOH–NaOAc, viscous liquids result. The above benzeneazoacetoacetates are prepared from the requisite diazonium salt and $CH_2Ac\cdot CO_2Et$ (cf. *loc. cit.*). *Et* p-*nitro*-, m.p. 135°, 2-*chloro-4-nitro*-, m.p. 134°, and 2 : 6-*dichloro-4-nitro*-, m.p. 127°, -*benzeneazo-γ-chloroacetoacetates*, prepared from the appropriate diazonium salt and $CH_2Cl\cdot CO\cdot CH_2\cdot CO_2Et$, are converted by EtOH–KOAc into Et 4-hydroxy-1-*p*-nitrophenyl-, -1-2′-*chloro-4′-nitrophenyl*-, m.p. 188°, and -1-2′ : 6′-*dichloro-4′-nitrophenyl*-, m.p. 197°, -*pyrazole-3-carboxylate*, respectively. *Et* 2-*chloro-4-nitro*-, m.p. 130°, and 2 : 6-*dichloro-4-nitro*-, m.p. 112°, -*benzeneazo-γ-bromoacetoacetates* are prepared from the corresponding azoacetoacetates and Br. Et α-aminoglyoxylate-*p*-nitrophenylhydrazone, -2 : 6-*dichloro-4-nitrophenylhydrazone*, m.p. 182°, -4-*chloro-2-nitrophenylhydrazone*, m.p. 141°, and -m-*nitrophenylhydrazone*, m.p. 158°, are obtained from the corresponding α-Cl-derivatives and EtOH–NH_3. H. B.

Rearrangements of phenyl ethers. Action of aluminium chloride on phenyl butyl ethers. R. A. Smith (J. Amer. Chem. Soc., 1933, 55, 3718—3721).—Equal wts. of $PhOBu^{\beta}$ (I) and $AlCl_3$ at room temp. for a few days give > 50% of *p*-*tert.*-$Bu\cdot C_6H_4\cdot OH$, also obtained similarly from *tert.*-BuOPh (II), and when (II) is boiled for a few hr. *sec.*-BuOPh (III) and $AlCl_3$ give *p*-*sec.*-$Bu\cdot C_6H_4\cdot OH$. (I) and (III) do not rearrange when boiled for 10 hr. H. B.

Aromatic compounds of fluorine. XVII. Fluoronitroanisoles. G. Schiemann and T. B. Miau (Ber., 1933, 66, [*B*], 1179—1187; cf. A., 1932, 1247).—Treatment of *o*-fluoroanisole (I) (improved prep.) with HNO_3 of differing concn., also in presence of AcOH and, particularly, of Ac_2O, affords 2-*fluoro-4-nitroanisole* (II), m.p. 104·6°. Repetition of the procedure of Holmes and Ingold (A., 1926, 831) leads only to (II) in addition to (I), and the compound, m.p. 52—52·5°, should be deleted from the lit. The constitution of (II) is established by converting 4-nitro-*o*-anisidine, m.p. 116° (prepared by reducing 2 : 4-dinitroanisole with H_2S–NH_3 or by successive nitration and hydrolysis of acet-*o*-anisidide), into 5-*nitro*-2-*methoxybenzenediazonium fluoborate*, decomp. 173°, which affords (II) when heated. Treatment of (I) with H_2SO_4–HNO_3 (*d* 1·51) at −5° to 0° yields 2-*fluoro*-4 : 6-*dinitroanisole* (III), b.p. 164—165°/10 mm., also obtained similarly from (II); prolongation of, or rise in temp. during, the reaction causes partial hydrolysis with production of 2-*fluoro*-4 : 6-*dinitrophenol* (IV), m.p. 102°. Similarly, *o*-fluorophenetole affords 2-*fluoro*-4 : 6-*dinitrophenetole*, b.p. 168°/13 mm., and (IV). The fluorodinitroanisole of Holmes and Ingold (*loc. cit.*) is probably impure (II) or partly hydrolysed (III). *p*-Fluoroanisole is transformed by conc. H_2SO_4–HNO_3 (*d* 1·51) into 4-*fluoro*-2 : 6-*dinitroanisole*, m.p. 81·7—82·7°, and 4-fluoro-2 : 6-dinitrophenol, m.p. 50—50·2°. Contrary to Holmes and Ingold (*loc. cit.*), elimination of F is not observed during reduction of fluoronitro-compounds. Thus (II) is converted by conc. HCl–$SnCl_2$ into 2-*fluoro*-p-*anisidine*, m.p. 82·6° (*hydrochloride*, decomp. 180—200°), whilst (III) gives 6-*fluoro*-4-*nitro*-o-*anisidine*, m.p. 108·5° (*Bz* derivative, m.p. 99—100°).

[With W. Winkelmüller.] 4-Nitro-*o*-phenetidine is transformed into 5-*nitro*-2-*ethoxybenzenediazonium fluoborate*, decomp. 171°, which, when heated, gives 2-*fluoro*-4-*nitrophenetole*, m.p. 77°, in poor yield.
H. W.

Oxidation of *s*-tri-iodophenol. W. H. Hunter and M. L. Morse (J. Amer. Chem. Soc., 1933, **55**, 3701—3705).—Oxidation of *s*-$C_6H_2I_3$·OH (I) with $K_3Fe(CN)_6$ (10 equivs.) in dil. KOH gives a large amount of Lautemann's Red (chromopolydihalogenophenylene oxide), a small quantity of 2 : 6 : 2′ : 6′-*tetra-iododiphenoquinone* (II) [isolated through the corresponding *quinol*, m.p. 260—265° (decomp. at 245°)], and an unstable compound (not isolated); phenoxyquinones are not produced. Oxidation with PbO_2 in C_6H_6 gives amorphous material and 50% of unchanged (I). Oxidation does not occur with $NaNO_2$ in AcOH or N_2O_3 in CCl_4; replacement of I by NO_2 occurs. The product from (I) and CrO_3–AcOH contains 86% of 2 : 6-di-iodo-*p*-benzoquinone [+ a little (II) and amorphous material]; *s*-$C_6H_2Cl_3$·OH and *s*-$C_6H_2Br_3$·OH give 97 and 74%, respectively, of the dihalogenoquinone. The type of radical formed from (I) is discussed (cf. A., 1926, 839). H. B.

Mono- and di-bromo-derivatives of *m*-cresol. II. R. C. Huston and W. J. Peterson (J. Amer. Chem. Soc., 1933, **55**, 3879—3882).—Br (1 mol.) is added to *m*-cresol (1 mol.) in cold oleum (23% SO_3), the mixture kept for 24 hr., diluted with H_2O, and then heated to 180°; steam distillation (mixture kept at 180—210°) gives (mainly) 2-bromo-*m*-cresol (I), m.p. 58·5—59° [Me ether, m.p. 39·5—40° (lit. 35·5—36·5°); *benzoate*, m.p. 59—60°; *benzenesulphonate*, m.p. 70—71°; p-*toluenesulphonate*, m.p. 85—85·5°], 6-bromo-*m*-cresol (II) (*benzoate*, m.p. 87·5—88°; *benzenesulphonate*, m.p. 92—93°; p-*toluenesulphonate*, m.p. 72·5—73°), and 2 : 6-*dibromo*-m-*cresol* (III), b.p. 114—116°/4 mm. (*benzoate*, m.p. 89·5—90°; *benzenesulphonate*, m.p. 94—95°; p-*toluenesulphonate*, m.p. 122—123°). (I), (III), and 2 : 4 : 6-tribromo-*m*-cresol (*benzoate*, m.p. 84—85°; *benzenesulphonate*, m.p. 117—117·5°; p-*toluenesulphonate*, m.p. 113—114°) are obtained from Br (1 mol.) and *m*-cresoldisulphonic acid in alkaline solution and subsequent distillation of the acidified product in superheated steam. (III) is also prepared by deamination of its 4-NH_2-derivative and by bromination of *m*-cresol-*p*-sulphonic acid in alkaline solution (and subsequent steam distillation). (I) and (II) are also prepared from the amino-*m*-cresols. (I) is brominated in CCl_4 to (probably) 2 : 6- and 2 : 4-dibromo-*m*-cresol (*benzoate*, m.p. 81—81·5°; *benzenesulphonate*, m.p. 92—92·5°; p-*toluenesulphonate*, m.p. 89·5—90°). H. B.

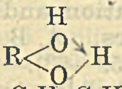
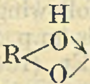
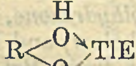
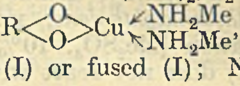
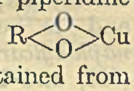
β-Arylaminocrotonarylamides. I. J. K. Thomson and F. J. Wilson (J.C.S., 1933, 1262—1263).—Contrary to Jadhav (A., 1930, 1426), *s*-diarylcarbamides and not β-arylaminocrotonarylamides are obtained (in poor yield) from $CH_2Ac·CO_2Et$ and *p*-OMe·C_6H_4·NH_2, *p*-OEt·C_6H_4·NH_2, *o*-, *m*-, and *p*-C_6H_4Cl·NH_2, and *m*-4- and *p*-xylidines. The following (also prepared from NH_2Ar and $COCl_2$ in PhMe) are described: s-*dianisyl*-, m.p. 234—235°; *s*-diphenetyl-, m.p. 232—233° (lit. 225—226°); s-*di*-o-, m.p. 238—239°, -m-, m.p. 245—246°, and -p-, m.p. 306—307° (sealed hard-glass tube; in soft-glass tubes the m.p. is much lower and is accompanied by decomp.), -*chlorophenyl*-; s-*di*-2 : 4-, m.p. 263—265°, and -2 : 5-, m.p. 285° (sealed tube), -*dimethylphenylcarbamides*. H. B.

β-Naphthol derivatives. I. Preparation and identification of some β-naphthol ethers. A. B. Wang (J. Chinese Chem. Soc., 1933, **1**, 59—63).—Interaction of β-$C_{10}H_7$·ONa and alkyl halides in boiling EtOH afford the following β-naphthyl alkyl ethers, the *picrates* of which (m.p. in parentheses) are described: Me (118°); Et (104·5°); Bu^{α} (67°); Bu^{β} (80·5°); sec.-*Bu*, m.p. 34° (85°); *n*-amyl (64°) *iso*amyl (90·5°); cyclo*hexyl*, m.p. 116° (125°); benzyl (122°). β-Naphthyl methylene ether, m.p. 134°, does not form a picrate. J. L. D.

Synthesis and resolution of *dl*-phenyl-2-methoxy-α-naphthylmethylamine. F. E. Ray and W. A. Moomaw (J. Amer. Chem. Soc., 1933, **55**, 3833—3838).—*Ph* 2-*methoxy*-α-*naphthyl ketone* (I), m.p. 125° (corr.) [*phenylhydrazone*, m.p. 183·5° (corr.), obtained from (II) (below) and NHPh·NH_2 in EtOH–AcOH], is obtained from BzCl, β-$C_{10}H_7$·OMe, and $AlCl_3$ in CS_2, or by hydrolysis of its *ketimine* (II), m.p. 98—99° [the *hydriodide*, m.p. 180° (corr.), is prepared from Mg 2-methoxy-α-naphthyl iodide (III) and PhCN]. 1-*Iodo*-2-*methoxynaphthalene*, m.p. 88°, is prepared by methylation (Me_2SO_4, 10% alkali) of the iodonaphthol. (I) does not react with NH_2OH and is reduced (Na–Hg) to *phenyl*-2-*methoxy*-α-*naphthylcarbinol*, m.p. 98° (corr.), also prepared from (III) and PhCHO. MeOBz and (III) give (mainly) (I) and some *diphenyl*-2-*methoxy*-α-*naphthylcarbinol*, m.p. 202—203° (corr.). Reduction (2% Na–Hg and EtOH in Et_2O–C_6H_6) of (II) affords dl-*phenyl*-2-*methoxy*-α-*naphthylmethylamine* (IV), m.p. 102° (corr.) [hydrochloride, m.p. 237—240° (decomp.); iso*propylidene*, m.p. 162° (corr.), *benzylidene*, m.p. 98° (corr.), and N-*Ac*, m.p. 186·5—187°, derivatives], which is resolved by *l*-malic acid into *d*-, $[\alpha]_D^{23}$ +197° in Et_2O, and *l*-, $[\alpha]_D^{23}$ —202° in Et_2O, forms. (IV) is much more stable than the 2-OH-analogue (cf. this vol., 389). β-$C_{10}H_7$·OMe does not react with PhCHO and NH_3 (cf. *loc. cit.*). H. B.

Substitution in resorcinol derivatives. Bromo-derivatives of resorcinol methyl ethers. M. S. Iyengar and H. S. Jois (J. Mysore Univ., 1931, 5, 232—234).—Bromination of dialkoxy-benzaldehyde or -benzoic acid yields, in addition to large quantities of 5-Br-derivatives, small quantities of Br_2-derivatives. Thus 2 : 4-$C_6H_3(OMe)_2$·CO_2H or 2 : 4-$C_6H_3(OMe)_2$·CHO also affords 4 : 6-dibromoresorcinol Me_2 ether; the (OEt)(OMe) compounds afford the 1-Et 3-Me ethers. Ch. Abs.

Preparation of 3 : 4-dihydroxytoluene from 3-amino-*p*-cresol by diazotisation. J. B. Aschkinazi (J. Appl. Chem. Russ., 1933, 6, 730—738).—3 : 4-$C_6H_3Me(OH)_2$ (I) is obtained in 82·5—87·5% yield by diazotising 3-amino-*p*-cresol and hydrolysing the product with 65% H_2SO_4 at 153°, and distillation with steam preheated at 160°. (I) may be determined by pptn. as the Pb salt. A solution of (I) in abs. EtOH becomes blue on pouring without mixing on to EtOH–NaOEt; under these conditions *o*-$C_6H_4(OH)_2$ gives a green coloration. R. T.

Co-ordination compounds of 2 : 2′-dihydroxydiphenyl. O. L. Brady and E. D. Hughes (J.C.S., 1933, 1227—1230).—The physical properties of 2 : 2′-dihydroxydiphenyl (I) suggest that it is  $R{<}\overset{\overset{H}{|}}{O}{\searrow}{\underset{O}{}}{\nearrow}H$ (in this and subsequent formulæ, R= ·C_6H_4·C_6H_4·). (I) and TlOAc in aq. EtOH–NH_3 give the *Tl* derivative,  $R{<}\overset{\overset{H}{|}}{O}{\searrow}{\underset{O}{}}{\nearrow}Tl$ (II), m.p. 227°, which is converted by aq. NaOH or KOH (not aq. NH_3) into the *Tl_2* salt, $R(OTl)_2$ (III). A cold aq. solution of (II) contains Tl˙. (II) is decomposed by boiling $CHCl_3$ or C_6H_6 to (I) and (III); it is readily sol. in fused (I), $CHCl_3$ containing an excess of (I), and in fused mixtures of (I) and camphor or $C_{10}H_8$. In these last cases, further co-ordination probably occurs. (I) and $TlEt_2$·OH in C_6H_6 give the *mono(diethylthallium)* derivative,  $R{<}\overset{\overset{H}{|}}{O}{\searrow}{\underset{O}{}}{\nearrow}TlEt_2$, m.p. 191° (decomp.), an aq. solution of which contains $TlEt_2$ ions; the mol. wt. in camphor is high, indicating association. (I), NH_2Me, and $Cu(OAc)_2,H_2O$ in EtOH give the *compound*,  $R{<}\genfrac{}{}{0pt}{}{O}{O}{>}Cu{\genfrac{}{}{0pt}{}{\swarrow NH_2Me}{\nwarrow NH_2Me}}$, which also dissolves in $CHCl_3$+(I) or fused (I); NH_2Pr and piperidine afford *compounds* containing 1 mol. of  $R{<}\genfrac{}{}{0pt}{}{O}{O}{>}Cu$ and 1 mol. of amine. The *compound* obtained from (I) and an ammoniacal solution of $Cu(OAc)_2$ contains 3 mols. of (I) and 2 mols. of NH_3 per 1 atom of Cu. This dissolves in $CHCl_3$ to an olive-green solution which decomposes slowly at room temp. and more rapidly at the b.p.; the decomp. is facilitated by $COMe_2$ and the resultant product appears to be a mixture of $(C_6H_4)_2O_2Cu$, $(C_6H_4)_2O_2Cu(NH_3)_2$, and $(C_6H_4)_2O_2Cu(H_2O)_2$. (I), $Cu(OAc)_2$, and an excess of aq. NH_3 give a *compound*, $[(C_6H_4)_2O_2H]_2Cu(NH_3)_2,2H_2O$, (approx. composition), which when dried over conc. H_2SO_4 affords a *complex*, $[(C_6H_4)_2O_2H]_2Cu(NH_3)_2,H_2O$ (approx. composition). H. B.

Relation of electromeric effects and relative polarisabilities of halogens. R. Robinson (J.C.S., 1933, 1114—1117).—A criticism of the views of Baddeley and Bennett (this vol., 499). When two electromeric processes are opposed and one of them is concerned with a hetero-enoid system terminating in a halogen atom, then the resistance offered by the latter is not a question of the extent of its electromeric displacement under normal conditions, but will depend on the deformability of the halogen atom. The order of polarisability or deformability is doubtless I>Br>Cl>F. H. B.

Influence of nuclear substituents on side-chain reactions.—See this vol., 1124.

Triphenylvinyl mercaptan. C. F. Koelsch and G. Ullyot (J. Amer. Chem. Soc., 1933, 55, 3883—3884).—Mg triphenylvinyl bromide and S give *triphenylvinyl mercaptan* (I), m.p. 110—111° (*Me ether*, m.p. 109·5—110°; *benzoate*, m.p. 192—193°), which reacts only in the ·SH form, is hydrolysed ($AcOH–H_2SO_4$) to $CHPh_2$·COPh, and is oxidised (alkaline $KMnO_4$) to *di(triphenylvinyl) disulphide*, m.p. 179·5—180·5° [also formed from (I), NH_2OH, HCl, and NaOAc in EtOH]. H. B.

Preparation of 4 : 4′-tetraethyldiamino-2 : 2′-dimethoxytriphenylcarbinol. W. R. Brown and F. A. Mason (J.C.S., 1933, 1269—1270).—*m-Methoxydiethylaniline*, b.p. 146—148°/14 mm. (from *m*-NEt_2·C_6H_4·OH, Me_2SO_4, and MeOH–KOH), PhCHO, and conc. HCl give *4 : 4′-tetraethyldiamino-2 : 2′-dimethoxytriphenylmethane*, m.p. 114°, which is oxidised by tetrachloro-*p*-benzoquinone in Et_2O to the carbinol, m.p. 115°. The carbinyl chloride resembles brilliant-green and shows no tendency to form the corresponding xanthen. *as*-Phthaloyl chloride, *m*-NMe_2·C_6H_4·OMe [? *m*-NEt_2·C_6H_4·OMe], and $AlCl_3$ give (probably) rhodamine-*B* and not the 4′ : 4″-tetra-alkyldiamino-2′ : 2″-dimethoxydiphenylphthalide. H. B.

Constitution of triarylmethyl compounds. A. Hantzsch and A. Burawoy (Ber., 1933, 66, [*B*], 1435—1441).—In reply to Petrenko-Kritschenko (this vol., 1048), it is shown that colourless, ester-like triarylmethyl compounds and coloured triarylmethyl salts exist. The acid residue is non-ionic in the former, ionic in the latter. Coloured triarylmethyl ions are quinonoid, containing conjugated systems which are responsible for the bands causative of dark colour. All "carbonium" theories according to which the peripheral residues of the triarylmethyl ions possess the same function in each individual ion do not explain the colour or the regularities of the absorption and are therefore to be discarded, particularly since they depend on the improbable assumption that a C atom and not a positive group is the site of the charge. H. W.

Retropinacolin rearrangement. I. W. E. Bachmann (J. Amer. Chem. Soc., 1933, 55, 3857—3859).—Dehydration of $CPh_3·CHPh·OH$ [acetate, m.p. 151° (lit. 131°)] with 1 in AcOH gives $CPh_2:CPh_2$. αβββ-*Tetra*-p-*tolylethyl alcohol*, m.p. 161—162°, similarly affords tetra-*p*-tolylethylene, m.p. 142° (lit. 151°), reduced (Na, amyl alcohol) to s-*tetra*-p-*tolylethane*, m.p. 278—279°, which is also prepared from 4 : 4′-dimethylbenzhydryl bromide and Mg in Et_2O–C_6H_6; αβββ-*tetra-anisylethyl alcohol*, m.p. 148—150°, yields tetra-anisylethylene; 9-*phenyl*-9-α-*hydroxybenzylfluorene*, m.p. 159—160°, furnishes 9 : 10-diphenylphenanthrene (I); 10 : 10-*diphenyl*-9-*phenanthrol*, m.p. 205—206°, gives (I); 10-*diphenylene*-9-*phenanthrol*, m.p. 177—178°, affords 9 : 10-diphenylenephenanthrene. The alcohols are prepared by reduction of the corresponding pinacolins with $MgPr^{\beta}I$ in Et_2O–C_6H_6. H. B.

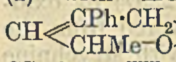
Direct carboxylation of carbon compounds. II. C. R. Kinney and O. W. Ward (J. Amer. Chem. Soc., 1933, 55, 3796—3798; cf. A., 1931, 1053).—Carboxylation of various substances occurs when they are heated with CO_2 under pressure in presence of a catalyst (Zn–Cu–Cr oxide on asbestos); the yields of acids (some of which are very impure) are usually 0·1—0·6%. The following changes are effected: $PhMe \longrightarrow p\text{-}C_6H_4Me·CO_2H$; $CH_2Ph_2 \longrightarrow CHPh_2·CO_2H$; $CHPh_3 \rightarrow CPh_3·CO_2H$; $CHPh:CH_2 \rightarrow CHPh:CH·CO_2H$; $PhOMe \longrightarrow p\text{-}OMe·C_6H_4·CO_2H$; $PhBr \longrightarrow p\text{-}C_6H_4Br·CO_2H$; $NPhMe_2 \longrightarrow p\text{-}NMe_2·C_6H_4·CO_2H$; $PhNO_2 \longrightarrow p\text{-}NO_2·C_6H_4·CO_2H$; $o\text{-}C_6H_4(OH)_2 \longrightarrow 2:3\text{-}(OH)_2C_6H_3·CO_2H$; $p\text{-}C_6H_4(OH)_2 \longrightarrow 2:5\text{-}(OH)_2C_6H_3·CO_2H$; $m\text{-}C_6H_4(OH)_2 \longrightarrow 2:4\text{-}(OH)_2C_6H_3·CO_2H$ (10·6% yield). PhOH gives a trace of an acid. H. B.

Molecular compounds of *p*-nitrophenylacetic acid. A. Dansi (Gazzetta, 1933, 63, 484—489).—NH_4X, where $X = p\text{-}NO_2·C_6H_4·CH_2·CO_2·$, reacts with $CuCl_2$ to form the *Cu* salt, CuX_2. With $HgCl_2$ it yields the *compounds* $HgX_2,HgCl_2$ (I), m.p. 149—150°, and $HgX_2,HgCl_2,(NH_4X)_2$ (II), m.p. 139—140°. HX and $Hg(OAc)_2$ form *HgX_2*, decomp. 170—185°, which combines with $HgCl_2$ to form (II); the latter when heated at 190° condenses to the *compound* $C_{14}H_{10}O_4N_2Cl_2Hg_3$, decomp. 215—220°. The o-*isomeride* of (II) has m.p. 163°. E. W. W.

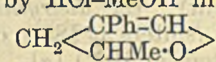
Dehydroperillic acid, an acid from Western red cedar (*Thuja plicata*, Don.). A. B. Anderson and E. C. Sherrard (J. Amer. Chem. Soc., 1933, 55, 3813—3819).—*Dehydroperillic acid* (I), $C_{10}H_{12}O_2$, m.p. 88° (*Me* ester, b.p. 112—113°/14 mm., m.p. 34·5—35°), is isolated (together with a phenolic compound, $C_{10}H_{12}O_2$, m.p. 82°) in 0·03—0·3% yield by steam distillation of sawdust (heartwood). (I) is reduced (H_2, Pd-black, EtOH) to an *acid* (II), $C_{10}H_{18}O_2$, b.p. 150—152°/16 mm., is oxidised (O_3) to CO_2, CH_2O, MeCHO, HCO_2H, AcOH, $H_2C_2O_4$, and (probably) βγ-diketovaleric acid [p-*nitrophenylosazone*, m.p. 294—295° (decomp.); p-*bromophenylosazone*, m.p. 220°], and is isomerised by aq. 3% HCl in AcOH to $p\text{-}C_6H_4Pr^{\beta}·CO_2H$. (I) is probably 4-iso*propenyl*-$\Delta^{1:4}$-cyclo*hexadiene*-1-*carboxylic acid*. (II) is considered to be a form of hexahydrocuminic acid. H. B.

Local anæsthetics. Amino-alcohol ethers with salicylic and other phenolic acids. E. Fourneau and J. Matti (J. Pharm. Chim., 1933, [viii], 18, 247—258).—Acetylsalicyl chloride with β-hydroxy-β-methyl-*n*-butyldimethylamine (I) in dry C_6H_6 yields the *acetylsalicylate hydrochloride* of (I), m.p. 171° (*salicylate hydrochloride*, m.p. 162°). Similarly were prepared the p- and m-*acetoxybenzoate hydrochlorides* of (I), m.p. 167° and 165°, respectively (p- and m-*hydroxybenzoate hydrochlorides*, m.p. 174° and 187°, respectively); 2-*acetoxy*-3-*methoxybenzoate hydrochloride* of (I), m.p. 174° [from 2-*acetoxy*-3-*methoxybenzoic acid*, m.p. 139° (*chloride*, m.p. 69°)] (2-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 158°); 4-*acetoxy*-3-*methoxybenzoate hydrochloride* of (I), m.p. 161° (4-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 178°); 2-*acetoxy*-4-*methylbenzoate hydrochloride* of (I), m.p. 150°; 2-*acetoxy*-3-*methylbenzoate hydrochloride* of (I), m.p. 161°; *acetylsalicylate hydrochloride* of 2-*dimethylaminomethyl*cyclo*hexanol*, m.p. 108°; 2-*hydroxy*-3-*methoxybenzoate hydrochloride* of *diethylaminoethyl alcohol* (II), m.p. 159°; 4-*acetoxy*-3-*methoxybenzoate hydrochloride* of (II), m.p. 140·5° (4-*hydroxy*-3-*methoxybenzoate hydrochloride*, m.p. 160°); 2-*acetoxy*-3-*methylbenzoate hydrochloride* of (II), m.p. 120°. F. O. H.

Course of hydrogenations with amalgam; β-phenylsorbic acid. R. Kuhn and M. Hoffer (Ber., 1933, 66, [*B*], 1263—1273).—Crotonylbenzene, $CH_2Br·CO_2Me$, and Zn in boiling C_6H_6 afford Me β-hydroxy-β-phenyl-Δ^{γ}-hexenoate (I), m.p. 58°, in 70—75% yield, converted by Br in CS_2 through the unstable dibromide into the compound $C_{13}H_{15}O_3Br$, m.p. 179—180° (corr., Berl). (I) is hydrolysed by KOH–MeOH–H_2O to β-*hydroxy*-β-*phenyl*-Δ^{γ}-*hexenoic acid* (II), m.p. 121—122° (corr., Berl), which, with Br in $CHCl_3$, affords the *bromolactone* (III), $C_{12}H_{11}O_2Br$, m.p. 110—110·3° (corr., Berl). Cautious thermal decomp. of (II) leads to β-*phenyl*-$\Delta^{\alpha\gamma}$-*pentadiene*, b.p. 85—86°/15 mm., which readily polymerises when exposed to air. Treatment of (I) with $POCl_3$ gives *Me* β-*phenyl*-$\Delta^{\alpha\gamma}$-*hexadienoate* (IV), b.p. 152—158°/12 mm., hydrolysed by KOH–MeOH to β-*phenyl*-$\Delta^{\alpha\gamma}$-*hexadienoic* (β-*phenylsorbic*) *acid* (V), m.p. 133—134° (corr., Berl). Treatment of (II) or, less advantageously, of (I) with HCl–AcOH yields β-*phenylsorbolactone*,



$CH{<}{\substack{CPh·CH_2 \\ CHMe{-}O}}{>}CO$, m.p. 100°, converted by Br in CS_2 into (III) and by HCl–MeOH into (IV) and β-*phenylsorbolactone*,



$CH_2{<}{\substack{CPh{=}CH \\ CHMe·O}}{>}CO$, m.p. 63°. Reduction of (V) suspended in H_2O with Na–Hg gives a mixture of β-phenyl-Δ^{γ}- and β-phenyl-Δ^{β}-hexenoic acids, the oxidation of which with $KMnO_4$ shows αβ- and αδ-addition to have occurred to the extent of 30% and 70%, respectively. The acids are so stable that a secondary isomerisation to the Δ^{α}-acid is highly improbable. The course of the change does not appear to be influenced appreciably by the purity of the amalgam. It is considered that the primary action is addition of Na or H at a C atom vicinal to a negative group giving a radical-like monohydro-compound in which the double linkings are particularly mobile. The ratio of αβ- to αδ-addition in a diene depends on the relative stability of the tautomeric monohydro-forms. H. W.

Amino-acids. IV. Dihydroxyphenylalanine and related amino-acids. V. Deulofeu and G.

Mendivelzua (Z. physiol. Chem., 1933, **219**, 233—239; cf. A., 1932, 1144).—Protocatechualdehyde (I) and hippuric acid (II) when heated with Ac_2O and NaOAc give an azlactone (Ac_2 derivative, m.p. 137—138°), which on hydrolysis with 3% NaOH affords *benzdihydroxyphenylamidoacrylic acid*, m.p. 224—225° [*Et* ester (III), m.p. 168°]. Reduction of (III) with HI gives 3 : 4-dihydroxyphenylalanine (IV). In presence of Ac_2O and NaOAc, (I) also condenses with diketopiperazine (V) to give *bis*-(3 : 4-*diacetoxybenzylidene)diketopiperazine*, m.p. 291° (decomp.), which is reduced by HI to (IV). With hydantoin (VI) and thiohydantoin, (I) gives 3 : 4-*diacetoxybenzylidene-hydantoin*, m.p. 237—239°, and -2-*thiohydantoin*, m.p. 224—225°, respectively. Veratraldehyde (VII) and (II) afford the *azlactone*, m.p. 152°, which gives on hydrolysis *benz*-3 : 4-*dimethoxyphenylamidoacrylic acid* (VIII), m.p. 211—212°. Reduction of (VIII) with Na–Hg yields N-*benzoyldimethoxyphenylalanine*, m.p. 173—174°, which is hydrolysed by aq. $Ba(OH)_2$ at 100° to 3 : 4-dimethoxyphenylalanine (IX), m.p. 252—253° (*phenylcarbimido*-derivative, m.p. 171°). With (VI), (VII) gives 3 : 4-*dimethoxybenzylidenehydantoin* (X), m.p. 204—206°. Reduction of (X) with Na–Hg affords 3 : 4-*dimethoxybenzylhydantoin*, m.p. 164°, which on hydrolysis with $Ba(OH)_2$ yields (IX). (V) with (VII) gives *bis*-(3 : 4-*dimethoxybenzylidene)diketopiperazine*, m.p. 300—302° (decomp.), reduced by Zn dust and AcOH to the corresponding *benzyl* compound, m.p. 215—216°, which on hydrolysis affords (IX). 3-*Methoxy*-4-*acetoxybenzylidene-hydantoin*, m.p. 262—263°, and -2-*thiohydantoin*, m.p. 246—247°, are described. J. H. B.

Resolution of *cis*- and *trans-dl*-3-carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acids and *trans-dl*-caronic acid. J. Owen and J. L. Simonsen (J.C.S., 1933, 1223—1225).—*cis-dl*-3-Carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acid (A., 1932, 739) is resolved by morphine (half-mol. method) into the d-*acid* (I), m.p. 104—105° (softens at 102°), $[\alpha]_{5461}$ +39° in $CHCl_3$ [*dimorphine* salt ($+H_2O$), m.p. 177—178° (sinters at 168°)], which is identical with the acid obtained (J.C.S., 1922, **121**, 2297) by oxidation of *d*-Δ^4-carene. The acid recovered from the more sol. dimorphine salt is treated with strychnine (= *l*-acid present); the *distrychnine* salt ($+4H_2O$), m.p. 189—190° (sinters at 185°), of the cis-l-*acid*, m.p. 104—105° (softens at 102°), $[\alpha]_{5461}$ −37·8° in $CHCl_3$, is thus obtained. *trans-dl*-3-Carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acid (*loc. cit.*) is resolved by nor-*d*- and -*l*-*ψ*-ephedrines into the l-, m.p. 112°, $[\alpha]_{5461}$ −37·1° in EtOAc [Na salt, $[\alpha]_{5461}$ +11·6° in H_2O; *dinor*-d-*ψ-ephedrine* salt ($+H_2O$), m.p. 192—193° (sinters at 187°)], and d-*acids*, m.p. 112°, $[\alpha]_{5461}$ +37·4° in EtOAc (*dinor*-l-*ψ-ephedrine* salt, m.p. 192—193°). *trans-dl*-Caronic acid is similarly resolved into the d-, m.p. 211—212°, $[\alpha]_{5461}$ +34·8° in EtOH [*nor*-l-*ψ-ephedrine* salt, m.p. 199—200° (sinters at 195°)], and l-*acid* (II), m.p. 211—212°, $[\alpha]_{5461}$ −34·5° in EtOH [*nor*-d-*ψ-ephedrine* salt, m.p. 199—200° (sinters at 195°)]. (II) is identical with the acid obtained (A., 1929, 449, 819) by oxidation of *d*-Δ^3- and -Δ^4-carenes, and chrysanthemum-mono- and -di-carboxylic acids (Staudinger and Ruzicka, A., 1924, i, 510). The 1 : 1-dimethyl-2-*γ*-ketobutyl*cyclo*propane-3-carboxylic acids (*loc. cit.*) are too weakly acidic to form satisfactory salts. H. B.

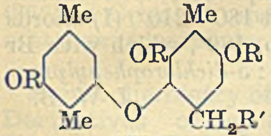
Synthesis of homocaronic acid. J. Owen and J. L. Simonsen (J.C.S., 1933, 1225—1227).—Et Δ^{β}-*iso*hexenoate, $CHN_2{\cdot}CO_2Et$ (I), and Cu-bronze at 45—50° give a mixture of the Et esters of *cyclo*butane-1 : 2 : 3 : 4-tetracarboxylic acid and cis- (II), m.p. 135—136° (sinters at 125°), and trans-, m.p. 190—191°, -*homocaronic acid* (3-*carboxy*-1 : 1-*dimethyl*cyclo*propane-2-acetic acid*). (II) is identical with the acid $C_8H_{12}O_4$, m.p. 136—137° (J.C.S., 1923, **123**, 556), obtained by oxidation of *d*-Δ^3-carene. (II) is attacked by alkaline $KMnO_4$ and is converted by conc. HCl at 100° (sealed tube) into a *lactone*, $C_8H_{12}O_4$, m.p. 101—102°, which could not be reduced [Na–Hg; HI (*d* 1·7) and red P] and is not oxidised by HNO_3 (*d* 1·22). (I) could not be condensed with Et Δ^{α}-*iso*hexenoate. H. B.

Action of sulphuric acid on derivatives of *cyclo*propane. C. F. H. Allen and R. Boyer (Canad. J. Res., 1933, **9**, 159—168).—The residue in the prep. of Ph *γ*-chloropropyl ketone (I) contained PrCl, $Bu^{\alpha}Cl$, PhBr, Ph_2, a *substance*, m.p. 177°, but no benzoyl*cyclo*propane (II). (II) is obtained from (I) with KCN (yield 93%) or CuCN (yield 60%) in MeOH. (II) with H_2SO_4 in AcOH gives *Ph γ-acetoxypropyl ketone*, b.p. 195—200°/40 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 165°), converted by $NHPh{\cdot}NH_2$ into 1 : 2-diphenyldihydropyridazine. Me 2-benzoyl-3-phenyl*cyclo*propane-1 : 1-dicarboxylate (III) with H_2SO_4 in AcOH gives *γ*-hydroxy-*β*-benzoyl-*γ*-phenylpropane-*αα*-dicarboxylic acid (IV), m.p. 118°, which decomposes to give PhCHO and (benzoylmethyl)malonic acid, m.p. 164—165° [also obtained from (III) with conc. H_2SO_4 in 80% yield]. The latter yielded *β*-benzoylpropionic acid at 180°. The yield of (IV) was not sufficient to exclude 2 : 3- as well as 1 : 3-ring scission. 1-Nitro-2-*p*-chlorobenzoyl-3-phenyl*cyclo*propane with the same reagent gives 2-phenyl-5-*p*-chlorophenylfuran (which does not react with maleic anhydride), indicating that the ring has been opened at the 2 : 3-linking. 1-Nitro-2-benzoyl-1-phenyl*cyclo*propane is converted into the isomeride, m.p. 131°. With more conc. solutions N oxides are evolved, the products being indefinite. Both forms of 2 : 3-dibenzoyl-1-phenyl*cyclo*propane are either unattacked or give a bimol. *substance*, m.p. 205°. Me 2-benzoyl-1 : 3-diphenyl*cyclo*propane-1-carboxylate is unattacked by conc. H_2SO_4, whilst *cyclo*propyldiphenylcarbinol yields indefinite products. Et 1-cyano*cyclo*propane-1-carboxylate with conc. H_2SO_4 gives the corresponding *Et amide*, m.p. 126°, hydrolysed to the *H amide*, m.p. 190° (and a little of a *substance*, m.p. 127°), and to *cyclo*propane-1 : 1-dicarboxylic acid. Three forms of 1-cyano-2-benzoyl-1 : 3-diphenyl*cyclo*propane (V) similarly all give the same *amide* (VI), m.p. 179°, and a little of an *isomeride* (VII), m.p. 198°. (VI) gives (VII) with Ac_2O, whilst (VII) gives (VI) with MeOH–HCl. (VI) with PCl_5 in xylene gives (V). It is concluded that H_2SO_4 opens the *cyclo*propane ring in a similar manner to HBr. An explanation is suggested for the anomalous behaviour of 1-phenyl-2-hydroxyphenylmethyl*cyclo*-

propane-1-carboxylic acid with H_2SO_4 in AcOH (A., 1924, i, 1205). A. A. L.

Lichen substances. XXIX. Salazic acid. III. Y. Asahina and J. Asano. **XXX. Cupraric acid.** Y. Asahina and M. Yanagita. **XXXI. Components of certain *Usnea* species, particularly with respect to compounds of the salazic acid group.** Y. Asahina and T. Tukamoto (Ber., 1933, **66**, [*B*], 1215—1217, 1217—1220, 1255—1263; cf. this vol., 823).—XXIX. It is proposed to designate the first (I) and second (II) reduction products of salazic acid ($C_{18}H_{14}O_8$ and $C_{18}H_{14}O_7$, respectively) hyposalazic acid and hyposalazolide. The Me_3 derivative of (I) is therefore Me hyposalazate Me_2 ether, whilst the Me_2 derivative, m.p. 283°, of (II) is hyposalazolide Me_2 ether. The first and second reduction products of stictic acid are hyposalazic acid Me ether and hyposalazolide Me ether, respectively. The name hypoprotocetraric acid is applied to the reduction product $C_{18}H_{16}O_7$ (Me_3 derivative, m.p. 170°) of cetraric acid, also obtained from protocetraric acid.

β-Orcinol Me_2 ether is converted by Br in AcOH at 0° into the *Br*$_1$-derivative, b.p. 165°/25 mm., transformed by the K derivative of β-orcinol Me_1 ether, Cu powder, and $Cu(OAc)_2$ in H_2 into the compound (III) (R=Me; R′=H), m.p. 95°, identical with deoxyhyposalazinol Me_3 ether. Hyposalazinol is therefore (III) (R=R′=H) and its conversion by molten KOH into β-orcinol and 3 : 5-dihydroxy-*p*-toluic acid is due to reductive fission, not to hydrolysis.



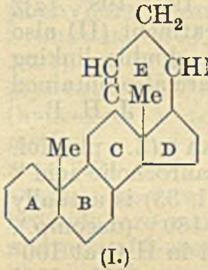
(III.)

XXX. Extraction of Japanese *Parmelia caperata*, Ach., with $COMe_2$, after removal of matter sol. in Et_2O, leads to capraric acid (IV), $C_{18}H_{14}O_9$, decomp. about 250° after becoming discoloured at 220°, identical with the acid obtained by Hesse (A., 1897, i, 631; 1898, i, 680; 1916, i, 264). The application of the name " capraric acid " by Koller *et al.* (A., 1930, 1590) to the *Ac* derivative of (IV) is deprecated. Catalytic hydrogenation of (IV) (Pd–C) yields hypoprotocetraric acid, m.p. 240—243° (decomp.) after softening at 220° (Me_3 ether, m.p. 170°). Protracted treatment of (IV) with boiling EtOH affords cetraric acid, thus further establishing the identity of (IV) with protocetraric acid. (IV) is slowly transformed by boiling AcOH into its Ac_1 derivative, decomp. about 250° after softening at about 220°.

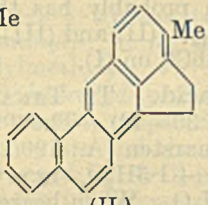
XXXI. The thalli are extracted with boiling Et_2O, the extract is evaporated to dryness, and the residue is treated with boiling C_6H_6, when it generally yields a sol. (*A*) and an insol. portion (*B*). The thalli are next extracted with hot $COMe_2$ and the extract is conc.; if salazic acid (V) is present the matter which separates is thoroughly extracted with Et_2O, leaving an insol. or sparingly sol. product (*C*). (*A*) is usually a mixture of usnic acid (VI) and atranorin (VII), separated into its components by treatment with EtOH–NaOAc, in which (VI) dissolves, whereas (VII) is insol. (*B*) affords protocetraric (? ramulic) acid (VIII), $C_{18}H_{14}O_9$, decomp. about 240° after darkening at about 210° (also $+1H_2O$); the corresponding *anil*, $C_{18}H_{14}O_8$:NPh has m.p. 225° (decomp.). Protracted ebullition with EtOH transforms (VIII) into cetraric acid, whereas MeOH affords protocetraric acid Me ether (probably identical with Hesse's methylprotocetraric acid). Hydrogenation of (VIII) gives hypoprotocetraric acid, $C_{18}H_{16}O_7$, identical with that obtained from cetraric acid. (*C*) from thalli free from (V) yields a neutral product, m.p. about 211°, closely related to or probably identical with Hesse's barbatin (IX). (*C*) from thalli which are coloured red or rust-red with alkali consists of (V) or its *Me*$_1$ *ether* (X), decomp. 210—220°. The formation of hypoprotocetraric in addition to hyposalazic acid by reduction of (V) is confirmed.

The following substances are isolated from individual lichens: (V), (VI), (VII), and (VIII) from *Usnea montis*, Fuji, *Motyka in litt.*; (V), (VI), (VIII), and barbatic acid (XI) from *U. florida*, Hoffm., *v. perplexans*, Wain, from Formosa; (VI), (VIII), and (X) from an *Usnea* from Java; (VI), (IX), and (XI) from *U. longissima*, Ach., from Japan; (VI), (XI), and (IX) from *U. longissima* from Europe; (VI), (XI), (VII), and (IX) from an *Usnea* sp. from Japan; (VI) and evernic acid from an *Usnea* sp. from Sakhalin. H. W.

Constitution of bile acids. LII. Point of attachment of the side-chain. H. Wieland and E. Dane (Z. physiol. Chem., 1933, **219**, 240—244; cf. this vol., 1049).—Dehydrogenation of dehydronorcholene (I) with Se (3 hr. at 150—160° and 25 hr. at 320°) gives *methylcholanthrene* (II), $C_{21}H_{16}$, m.p. 174°. Reduction of (I) with Na in C_5H_{11}·OH gives *hexahydromethylcholanthrene* (III), $C_{21}H_{22}$, m.p. 157°. The unsaturated pentacyclic hydrocarbon $C_{22}H_{34}$ could not be obtained by thermal decomp. of 12-ketonorcholanic acid, as is to be expected from the *trans*-linking of rings C and D. The attachment of the side-chain at C_{17} is thus confirmed. J. H. B.



(I.)



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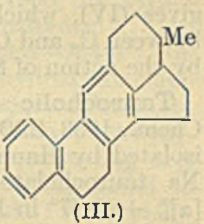
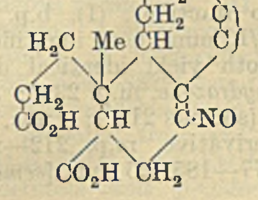
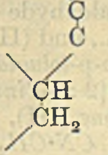


(III.)

Bile acids. XL. M. Schenck (Z. physiol. Chem., 1933, **220**, 61—68; cf. this vol., 713).—Treatment of the gel (I), $C_{24}H_{36}N_2O_9$, with NaOH affords N_2 in nearly quant. yield. Van Slyke analysis of deoxybilianic acid aminocarboxylic acid (II) gives N_2 considerably in excess of theory in 24 hr. (I) and (II) may probably be represented:

(I.)




(II.)

J. H. B.

Conversion of cholesterol into 6-keto*allo*-cholanic acid. O. Stange (Z. physiol. Chem., 1933, **220**, 34—38).—Treatment of 6-hydroxycholestane with PCl_5 in $CHCl_3$ gave 6-*chlorocholestane* (I), m.p. 147°, $[\alpha]_D^{18}$ +45·1° in $CHCl_3$. Oxidation of (I) with CrO_3 in AcOH yielded 6-chloro*allo*cholanic acid, which, on hydrolysis with KOH at 160—170°, afforded 6-*hydroxy*allo*cholanic acid* (II), m.p. 240° (*Me* ester, m.p. 101°). The 6-keto*allo*cholanic acid obtained from (II) by CrO_3 oxidation was identical with Wieland and Dane's product from hyodeoxycholic acid (cf. this vol., 64), although the OH-derivatives differed and are therefore epimeric. This affords a simple proof of the identity of ring II of cholesterol with ring III of the bile acids. J. H. B.

Conversion of a bile acid into a hydrocarbon derived from 1 : 2-benzanthracene. J. W. Cook and G. A. D. Haslewood (Chem. and Ind., 1933, 758—759).—Dehydrogenation (Se) of dehydronorcholene gives " methylcholanthrene " (I), m.p. 171° (cf. Wieland and Dane, this vol., 1161), and a product, m.p. 132—134°, not oxidised to a quinone. (I) is oxidised ($Na_2Cr_2O_7$–AcOH) to an anthraquinonyl acid, m.p. about 270°, which at 400° in CO_2 gives a quinone, m.p. 229°, insol. in alkali. The structure assigned by Wieland to (I) cannot be correct. F. R. S.

Intermediate products in the Hammarsten reaction of cholic acid. K. Yamasaki (Z. physiol. Chem., 1933, **220**, 42—49).—Treatment of cholic acid (I) in AcOH with conc. HCl in absence of air gives *apo*cholic acid (II), dihydroxycholenic acid (III), and iso*dihydroxycholenic acid* (IV), m.p. 197—198°, $[\alpha]_D^{20}$ +5·92° in EtOH. By the same treatment (II) also gives (IV), which probably has the double linking between C_8 and C_{14}. (II) and (III) are also obtained by the action of $SbCl_3$ on (I). J. H. B.

Taurocholic acid. T. Tanaka (Z. physiol. Chem., 1933, **220**, 39—42).—The " taurocholic acid " isolated by Hammarsten (A., 1905, i, 33) is actually Na taurocholate $+1{\cdot}5H_2O$, m.p. 180° (decomp.), $[\alpha]_D^{20}$ +23·87° in H_2O. When heated in H_2O at 100° it gives an *isomeride* ($+2H_2O$), m.p. 230—231° (decomp.), $[\alpha]_D^{20}$ +24·21° in H_2O. J. H. B.

Nutria-bile acid. P. Brigl and O. Benedict (Z. physiol. Chem., 1933, **220**, 106—112).—A " stone " from the stomach of the nutria (*Myocaster coypus*, Mol.) contained *nutria-glycocholic acid* (I), m.p. 226—228° (decomp.), $[\alpha]_D$ +47·8° in MeOH. Hydrolysis with *N*-KOH for 30 hr. gives glycine and *nutria-cholic acid* (II), $C_{24}H_{40}O_5$, m.p. 198°, which gives no Mylius or Hammarsten reactions. (II) loses 0·5 mol. of H_2O at 100° in vac. and 1·5 mols. at 134°. (I) was also obtained from nutria-bile. J. H. B.

Dihydro-*p*-tolualdehyde. C. F. H. Allen, W. L. Ball, and D. M. Young (Canad. J. Res., 1933, **9**, 169—174).—The residual oil in the manufacture of crotonaldehyde gives two fractions, (I), b.p. 68°/10 mm., and (II), b.p. 77°/10 mm., both identified as *dihydro-*p*-tolualdehyde*. Both yield identical derivatives {2 : 4-*dinitrophenylhydrazone*, m.p. 239°; *semicarbazone* (III), m.p. 219° (shrinks 215°); *azine*, m.p. 157°; $CN\cdot CH_2\cdot CO_2H$ derivative, m.p. 212—213°; $COMe_2$ derivative, b.p. 177—185°/25 mm. [*semicarbazone*, m.p. 206—210° (decomp., shrinks 196°)]}. Only (II) is regenerated from (III) or the $NaHSO_3$ compounds. (I) is possibly a mixture of (II) with other substances. Both give *p*-$C_6H_4Me\cdot CO_2H$ (IV) by autoxidation (prevented by quinol) with HNO_3, and with O_3, whilst $KMnO_4$ in $COMe_2$ gives terephthalic acid and a little (IV). The mechanism of formation of the aldehyde is discussed and the $\Delta^{1:4}$-constitution is suggested. A. A. L.

Influences of substitution on velocity of hydrolysis of benzylidene chloride.—See this vol., 1124.

3 : 5-Dichlorobenzaldehyde. F. Asinger and G. Lock (Monatsh., 1933, **62**, 344—348).—3 : 5-*Dichlorobenzaldehyde* (I), m.p. 65°, b.p. 235—240°/748 mm. (*oxime*, m.p. 112°; *phenylhydrazone*, m.p. 106·5°; $NaHSO_3$ additive *compound*), is prepared by side-chain chlorination of 3 : 5-dichlorotoluene (from *o*-$C_6H_4Me\cdot NHAc$) and hydrolysis of the product with 8% oleum at room temp. With PCl_5 (I) gives 3 : 5-*dichlorobenzylidene chloride*, m.p. 36·5°, and with 50% KOH at 100° it gives 3 : 5-dichlorobenzoic acid and 3 : 5-*dichlorobenzyl alcohol*, m.p. 82°, from which 3 : 5-*dichlorobenzyl chloride*, m.p. 36°, is obtained. With NaOAc and Ac_2O in N_2 at 180—210°, (I) affords 3 : 5-*dichlorocinnamic acid*, m.p. 186°, which with Br in $CHCl_3$ gives αβ-*dibromo*-β-3 : 5-*dichlorophenylpropionic acid*, m.p. 209° (corr.). J. W. B.

Action of metals on aldehydes. P. Schorigin, V. Issagulianz, and A. Gusseva (Ber., 1933, **66**, [*B*], 1431—1435).—Treatment of PhCHO (I) in boiling PhMe with activated Mg leads to benzoin (II) in 20% yield when (I) : Mg=1 : 0·5 and $CH_2Ph\cdot OBz$ (III) in 77% yield when (I) : Mg=1 : 0·05. Under the experimental conditions (II) does not arise from (III). Anisaldehyde yields anisil presumably from primarily formed anisoin, whereas piperonal does not react. Al–Hg and (I) yield (II) in about 80% yield, whereas Zn, Al, and Fe are inactive and Cu yields unstable, green crystals. Aliphatic aldehydes with Mg (0·5—0·05 atom) or Al–Hg react: $CH_2R\cdot CHO+CH_2R\cdot CHO \longrightarrow CH_2R\cdot CH{:}CR\cdot CHO+H_2O$. *iso*Valeraldehyde yields γ-methyl-α-*iso*propyl-Δ^{α}-pentenal, whilst *n*-octaldehyde affords α-n-*hexyl*-Δ^{α}-*decenal*, b.p. 148—149°/5 mm. H. W.

Basic properties of hydrazones. VII. G. Ottolino (Gazzetta, 1933, **63**, 513—516).—One of the products from PhCHO, HCl, and $CHPh{:}N\cdot NHPh$ (cf. A., 1932, 51, 609) is αα′-*diphenyl*-pp′-*dihydrazinotriphenylmethane*, $CHPh(C_6H_4\cdot NPh\cdot NH_2)_2$ (I), m.p. 120°. When treated with Ac_2O, HNO_2, and *p*-$NO_2\cdot C_6H_4\cdot CHO$, (I) gives respectively benzaldehydediphenylhydrazone (II), *p*-nitrosodiphenylamine, and *p*-nitrobenzaldehydediphenylhydrazone. The action of PhCHO on (II) gives the *dibenzylidene* derivative of (I), m.p. 226°, or, under different conditions and in presence of a trace of HNO_3, a *compound*, m.p. 165°, probably the corresponding quinonoid quaternary *chloride*, $CHPh{:}N\cdot NPhCl{:}C_6H_4{:}CPh\cdot C_6H_4\cdot NPh\cdot N{:}CHPh$. $CHPh{:}N\cdot NPhMe$, HCl, and PhCHO form a compound, m.p. 155° (cf. A., 1922, i, 475), now formulated $CHPh{:}N\cdot NMe\cdot C_6H_4\cdot CHPh\cdot C_6H_4\cdot NMe\cdot NH_2$, converted by p-NO_2·C_6H_4·CHO in AcOH into pp′-*bis*-(α-*methyl*-β-p″-*nitrobenzylidenehydrazino*)*triphenylmethane*, m.p. 162°, with an *isomeride*, m.p. 138°.

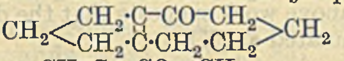
E. W. W.

Tetraconiferylaldehydesulphonic acid (tetraligninsulphonic acid). P. KLASON (Svensk Kem. Tidskr., 1933, 45, 221—226).—A review. R. P. B.

***cyclo*Pentanone and *cyclo*hexanone.** D. VORLÄNDER (Trans. Faraday Soc., 1933, 29, 910—912).—Mechanical double refraction measurements of bisarylidene*cyclo*-pentanones and -hexanones indicates a relation between mol. stability of the direction of movement and liquid-cryst. properties (cf. this vol., 10). E. S. H.

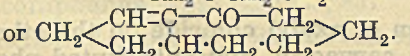
Supposed enolising power of organic magnesium compounds. E. P. KOHLER and D. THOMPSON (J. Amer. Chem. Soc., 1933, 55, 3822—3823).—Contrary to Grignard and Blanchon (A., 1931, 465), *cyclo*hexenyl acetate (I) could not be obtained from $MgPr^{\beta}Br$ (II) and *cyclo*hexanone (III), and hydrolysis of (I) always gave (III). Decomp. of the product from (II) and (III) with aq. NH_4Cl gives *cyclo*hexanol (68%) and *cyclo*hexylidene*cyclo*hexanone (26%). Grignard and Blanchon appear to have mistaken reduction for enolisation. H. B.

Stereochemistry of dicyclic ring systems. IX. Derivatives of *cyclo*pentano*cyclo*heptane. W. HÜCKEL and L. SCHNITZSPAHN (Annalen, 1933, 505, 274—282).—The unsaturated ketone, $C_{10}H_{14}O$, b.p. 123°/12 mm., m.p. < −18° [*semicarbazone*, m.p. 195—200°; *oxime*, m.p. 134° (*Bz* derivative, m.p. 118°)], from *cyclo*decanedione and dil. aq. NaOH (cf. A., 1930, 76; the "α- and β-forms," m.p. 37° and 52°, appear to be impurities), is shown to be homogeneous and to have the structure of a *cyclo*penteno-*cyclo*heptanone,



$$CH_2<\begin{matrix}CH_2\cdot C\!-\!CO\!-\!CH_2\\ \quad\vert \\ CH_2\cdot C\cdot CH_2\cdot CH_2\end{matrix}>CH_2$$

or



$$CH_2<\begin{matrix}CH{=}C\!-\!\!-\!CO\!-\!\!-\!CH_2\\ \vert \\ CH_2\cdot CH\cdot CH_2\cdot CH_2\end{matrix}>CH_2.$$

Hydrogenation (Pd–C) gives a mixture of cis- and trans-cyclo*pentano*cyclo*heptanone*, b.p. 235°/760 mm. [cis-*oxime*, m.p. 119°; trans-*oxime*, m.p. 140° (*Bz* derivative, m.p. 98—99°)], oxidised by aq. $KMnO_4$ to δ-ketosebacic acid. The configurations of the oximes are determined by reduction (Na in EtOH) to two cis- (*Bz* derivatives, m.p. 194° and 154°; *Ac* derivatives, m.p. 161° and 115°, respectively) and one trans-cyclo*pentano*cyclo*heptylamine*, b.p. 97°/10 mm. (*Bz*, m.p. 173—174°, and *Ac*, m.p. 114—115°, derivatives). The *trans*-amine gives the *alcohol* (*H phthalate*, m.p. 132—133°) with HNO_2 and a *trimethylammonium iodide*, m.p. 192° (decomp.), converted by Ag_2SO_4 and $Ba(OH)_2$ into cyclo*pentano*cyclo*heptene*, b.p. 63·5°/8 mm., oxidation of which with O_3 or $KMnO_4$, and distillation of the products with Ac_2O yields (? trans-)*hexahydroindan-4-one* (*semicarbazone*, m.p. 183°), synthesised for comparison by oxidation (CrO_3–AcOH) of 4-hydroxyhexahydroindane.

H. A. P.

Reactions of *aci*-nitro-salts and silver fulminate. H. WIELAND and A. HÖCHTLEN (Annalen, 1933, 505, 237—247).—Interaction of CPh_3Cl with $(CHPh{:}NO_2)_2Hg$ gives α-*nitro*-αβββ-*tetraphenylethane*, m.p. 169—170° (decomp.) (aci-*K* salt). BzBr and CN·CPh:NO_2Ag (I) give *Ph* ω-*nitro*-ω-*cyanobenzyl ketone*, m.p. 118° (decomp.). With $CHPh_2Br$ (I) gives α-*nitro*-αββ-*triphenylpropionitrile*, m.p. 146—147° (decomp.), which with hot 10% KOH in MeOH gives *triphenylacrylonitrile*, m.p. 166—167°, and KNO_2, and with $SnCl_2$–HCl in hot AcOH gives the α-NH_2 (?) compound, m.p. 177°. In presence of air CPh_3Cl and (I) give triphenylmethyl peroxide, and in its absence CPh_3·NCO, CO_2, N_2, *phenyltriphenylmethyldiazomethane*, $CPh(N_2)\cdot CPh_3$, m.p. 145° (decomp.) (identified by thermal fission to tolane, CPh_3, and N_2), and a *compound*, $C_{14}H_{11}ON_3$, m.p. 156—158° (decomp.), isomerised by KOH in EtOH to an *acid*, m.p. 182°. The ·CPh_3 group could not be introduced into CHBr:NO_2Ag on account of its ready decomp. into AgBr, HCO_2H, and N_2. BzBr and C:NOAg (II) give *dibenzoylcarbamide*, m.p. 208—209°, presumably through intermediate formation of Bz·NCO. With $CHPh_2Br$ (II) gives *benzhydryl cyanate*, b.p. 160—164°/11 mm. (dibenzhydrylcarbamide, m.p. 269—270°; *Et benzhydrylcarbamate*, m.p. 129°), as also does AgNCO. CPhCl:NOH reacts only very slowly with (II) in C_6H_6, and in C_5H_5N forms *benzhydroxamylpyridinium chloride*, m.p. 117°; in presence of a little $NPhMe_2$, however, a *compound*, $C_8H_6O_2N_2$ (? phenylfuroxan), m.p. 96—97°, is formed. H. A. P.

Pinacol–pinacolin rearrangement. IV. Rearrangement of pinacols containing the diphenylene group. W. E. BACHMANN and H. R. STERNBERGER (J. Amer. Chem. Soc., 1933, 55, 3819—3821).—9-Hydroxy-9-α-hydroxybenzhydryl-, -9-(*hydroxydi*-m-*tolylmethyl*)-, m.p. 143·5—144·5°, -9-(hydroxydi-*p*-tolylmethyl)-, -9-(hydroxydianisylmethyl)-, and -9-(*hydroxydi*-p-*ethoxyphenylmethyl*)-, m.p. 147—150°, -*fluorenes*, prepared from Me 9-hydroxyfluorene-9-carboxylate and the requisite Mg aryl bromide, are rearranged by AcCl in C_6H_6–AcOH to mixtures of 9-aroyl-9-arylfluorenes and 9 : 9-diaryl-10-phenanthrones, and not single compounds (cf. Meerwein, A., 1913, i, 485; Bergmann and Schuchardt, A., 1931, 1059). 9 : 9-*Di*-m-*tolyl*-, m.p. 198—198·5°, and 9 : 9-*di*-p-*ethoxyphenyl*-, m.p. 135—135·5°, -10-*phenanthrones* are new. 2-*Di*-p-*methyl*-, m.p. 193—194°, and 2-*di*-p-*methoxy*-, m.p. 136—137°, -*benzhydryldiphenyl*-2′-*carboxylic acids* are prepared from the corresponding phenanthrones and EtOH–KOH. The relative migration aptitudes of the groups are Ph 1, *m*-tolyl 0·33, diphenylene 0·31, *p*-tolyl 0·046, *p*-OEt·C_6H_4· 0·012, anisyl 0·006; the order is the reverse of that for *s*-pinacols (cf. A., 1932, 515).

H. B.

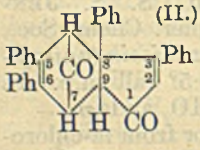
Electrolytic reduction of aromatic ketones in glacial acetic acid.—See this vol., 1127.

Benzoin reduction. II. Mechanism of ketone formation. *m*-Chlorobenzanisoin. S. S. JENKINS and E. M. RICHARDSON (J. Amer. Chem. Soc., 1933, 55, 3874—3879).—m-*Chlorobenzanisoin* (*anisoyl*-m-*chlorophenylcarbinol*) (I), m.p. 86·5° (all m.p. are corr.), prepared from *m*-C_6H_4Cl·CHO and *p*-OMe·C_6H_4·CHO in aq. EtOH–KCN or from *m*-chloromandelamide and *p*-OMe·C_6H_4·MgBr, is oxidised

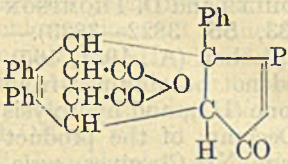
(Fehling's solution) to 3-*chloro*-4′-*methoxybenzil*, m.p. 88°, and is reduced (4% Na–Hg, EtOH) to α-m-*chlorophenyl*-β-*anisylethylene glycol*, m.p. 101·5—102·5°. Dehydration of this with AcOH–conc. H_2SO_4 gives m-*chlorophenyl* p-*methoxybenzyl ketone*, m.p. 73—74° (anti-*oxime*, m.p. 74—75°, rearranged by PCl_5 in Et_2O to p-*methoxyphenylacet*-m-*chloroanilide*, m.p. 86·5°), also prepared from *p*-methoxyphenylacetamide and *m*-$C_6H_4Cl·MgI$ in Et_2O and H_2, and by reduction of (I) with Sn and conc. HCl in EtOH containing a little $CuSO_4$. *Anisyl* m-*chlorobenzyl ketone*, m.p. 70—71° (anti-*oxime*, m.p. 106·5—107·5°, rearranged to m-*chlorophenylacet*-p-*anisidide*, m.p. 148·5°), is also formed in the reduction (Sn) of (I) and is synthesised from *m*-$C_6H_4Cl·CH_2·MgBr$ (II) and anisamide. These results substantiate the mechanism of reduction of *as*-benzoins previously advanced (A., 1932, 516). (II) and *p*-$OMe·C_6H_4·CHO$ give β-m-*chlorophenyl*-α-*anisylethyl alcohol*, m.p. 42—43°, dehydrated (AcOH–conc. HCl) to 3-*chloro*-4′-*methoxystilbene*, m.p. 96°. *Anis*-m-*chlorobenzylamide* and m-*chlorobenz*-p-*methoxybenzylamide* have m.p. 161° and 92·5°, respectively. H. B.

β-Phenyl-β-anthronylpropionic acid. 3-Anthronylindan-1-one. L. Gravel (Natural. Canad., 1933, **57**, 221—255).—β-Phenyl-β-anthronylpropionic acid (cf. Meerwein, A., 1919, i, 25) [*chloride* (I), m.p. 115—116°; *Me*, m.p. 111—112°, and *Et* ester, m.p. 88—89°; *amide*, m.p. 181—182°; *anilide*, m.p. 168—169°; *Ag* salt] is dehydrated by conc. H_2SO_4 at 103—110° to 3-*anthronylindan*-1-*one* (II), m.p. 161—162° [2-*Br*-derivative (III), m.p. 170—171°; *hydrazone* (+1H_2O), m.p. 176°; *phenylhydrazone*, m.p. 224—225° (+1PhMe); *oxime* (+1PhMe), m.p. 181—184°], identified by oxidation (HNO_3, *d* 1·2) to anthraquinone and *o*-$C_6H_4(CO_2H)_2$. (I) with $AlCl_3$ in C_6H_6 or (better) CS_2 gives (II) and in addition an *isomeride*, m.p. 188°, which on account of its conversion into (III) with Br is regarded as the enolic form of (II); in C_6H_6 Ph β-phenyl-β-anthronylethyl ketone, m.p. 115—116° (*loc. cit.*), is also obtained. The following are also described: *Me_2*, m.p. 58—59°, b.p. 175°/3 mm., and *Et_2* o-*chlorobenzylidenemalonate*, m.p. 30°, b.p. 182—183°/5 mm.; *Me_2*, m.p. 148—149°, and *Et_2* β-o-*chlorophenyl*-β-*anthronyl*iso*succinate*, m.p. 119—120°; *Et_2* β-*phenyl*-β-*anthronyl*iso*succinate*, m.p. 104—105°; and β-o-*chlorophenyl*-β-*anthronylpropionic acid*, m.p. 159—161°. H. A. R.

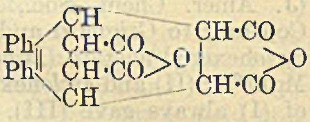
Reactions of anhydroacetonebenzil. II. C. F. H. Allen and E. W. Spanagel (J. Amer. Chem. Soc., 1933, **55**, 3773—3780).—Anhydroacetonebenzil (4-hydroxy-3 : 4-diphenyl-Δ^2-*cyclo*pentenone) (I) and AcOH–conc. H_2SO_4 give 4 : 7-endo*keto*-3 : 5 : 6 : 8-*tetraphenyl*-4 : 7 : 8 : 9-*tetrahydroindenone* (II) [the compound, $C_{34}H_{24}O_2$, of Japp and Burton (J.C.S., 1887, **51**, 426)] (*dioximes*, m.p. 176° and 229°); with Ac_2O–conc. H_2SO_4, (II) and a little of an *acetate*, $C_{19}H_{16}O_3$, m.p. 91° [hydrolysed by dil. aq. NH_3 to (II) and by EtOH–KOH to a *compound*, m.p. 280°], result. Short heating of (II) at 210° gives 3 : 5 : 6 : 8-*tetraphenyl*-8 : 9-*dihydroindenone* (III), m.p. 167° [*oxime*, m.p. 130° (not sharp); *phenylhydrazone*, m.p. 250°, probably identical with (V) (below), since heating in a sealed tube is necessary for its formation], and 2 : 3 : 5 : 6-*tetraphenylhydrindone* (IV), m.p. 176° [*oxime*, m.p. 225°; *phenylhydrazone* (V), m.p. 250° (cf. *loc. cit.*)]; (III) passes into (IV) when heated. (III) and S at 325° give a little PhSH; (IV) is similarly dehydrogenated to 2 : 3 : 5 : 6-*tetraphenylindenone* (VI), m.p. 166° (*oxime*, m.p. 292°; p-*bromophenylhydrazone*, m.p. 226°). (II) heated with maleic anhydride (VII) until evolution of CO ceases gives the *anhydride* (VIII), m.p. 301°, also formed [together with (IV)] from (III) and (VII). (I) and excess of (VII) at 170—230° give CO and the *dianhydride* (IX), shrinks at 334°, becomes liquid at 346°, and decomp. 356° (corresponding *Me_4* ester, m.p. 188°), the formation of which shows that dehydration of (I) affords 3 : 4-diphenyl*cyclo*pentadienone [" dien "-addition of 2 mols. of this yields (II)]. (VI) is oxidised (CrO_3–AcOH) to 2-*phenylglyoxyl*-4 : 5-*diphenylbenzophenone*, m.p. 183° (*quinoxaline*, m.p. 184°), cleaved by cold aq. Na_2O_2 to BzOH and 2-*benzoyl*-4 : 5-*diphenylbenzoic acid*, m.p. 250° (*compound*, $C_{26}H_{17}O_2N$, m.p. 225°, formed with NH_2OH), which with a little $CuCO_3$ at 225° gives a poor yield of 3 : 4-*diphenylbenzophenone*, m.p. 133°. Rearrangement of the *oxime*, m.p. 156°, of this with PCl_5 in Et_2O, hydrolysis of the resultant product to the amine, and deamination of this gives *o*-$C_6H_4Ph_2$.



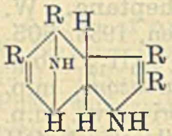
(II.)



(VIII.)



(IX.)



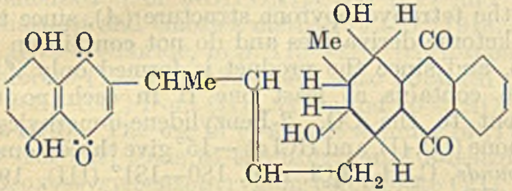
(X.)

The above work suggests that the dipyrroles should be formulated as (X). H. B.

Action of oxalyl chloride on the ethers of the cresols, carvacrol, and substituted phenols. N. Schapiro (Ber., 1933, **66**, [*B*], 1370—1372).—*o*-$C_6H_4Me·OMe$, $AlCl_3$, and $(COCl)_2$ in CS_2 yield 4 : 4′-*dimethoxy*-3 : 3′-*dimethylbenzil*, m.p. 177°, converted by *o*-$C_6H_4(NH_2)_2$ in AcOH into the *quinoxaline* $C_{24}H_{22}O_2N_2$, m.p. 139·5—140°, and oxidised by H_2O_2 in AcOH or, preferably, in C_5H_5N–NaOH to 4-methoxy-3-methylbenzoic acid, m.p. 193° after softening at 192°. *p*- and *m*-$C_6H_4Me·OMe$ yield only resins. *o*-$C_6H_4Me·OEt$ affords 4 : 4′-*diethoxy*-3 : 3-*dimethylbenzil*, m.p. 181—182° (quinoxaline, $C_{26}H_{26}O_2N_2$, m.p. 172—173°), oxidised to 4-ethoxy-3-methylbenzoic acid, m.p. 198—199°. Carvacrol Me ether gives an unidentified oil. *o*-$C_6H_4Cl·OMe$ fairly smoothly yields 3 : 3′-*dichloro*-4 : 4′-*dimethoxybenzil*, m.p. 226·5—227·5°, oxidised to 3-chloro-4-methoxybenzoic acid, m.p. 213°. *o*-$NO_2·C_6H_4·OMe$, under the same reaction conditions, is smoothly hydrolysed to *o*-$NO_2·C_6H_4·OH$. H. W.

Substituted aminoquinones. M. Covello (Gazzetta, 1933, **63**, 517—524).—A mixture of triaminophenol in EtOH+H_2O and maleic anhydride in C_6H_6 treated in N_2 with $NaCO_3$ solution forms 2 : 4 : 6-*trimaleimidophenol*, m.p. 200°, converted by dil. HCl into *phenol-*2 : 4 : 6-*tris*-N-*maleiamidic acid*, decomp. 150° (*Ag* salt), and by HNO_3 (*d* 1·48) into 2 : 6-*di-maleimidobenzoquinone*, decomp. 180° (*phenylhydrazone*, decomp. 100°). E. W. W.

Constituents of alkanet root (*Anchusa tinctoria*, Lam.). I. Constitution of alkannin. M. V. Betrabet and G. C. Chakravarti (J. Indian Inst. Sci., 1933, **16A**, 41—51).—Alkannin (I) (decomp. 220°), prepared from the Ac_4 derivative (II), is $C_{30}H_{26}O_8$ [*Ba* and *Pb* derivatives; *tetrabenzoate*, m.p. > 260° (decomp.)]. (I) with Me_2SO_4 gives *dimethoxyalkannin* (*dibenzoate*), whilst $ClCO_2Et$ gives *dicarbethoxyalkannin*, decomp. > 270°, and bromination affords *di-*, *tetra-*, decomp. 260°, and *hexa-bromoalkannin*, according to conditions. *Tetrabromoalkannin tetra-acetate*, decomp. about 280°, is obtained by treating (II) with Br. (I) is not oxidised by H_2O_2, fuming HNO_3 reacts energetically giving $H_2C_2O_4$, $(\cdot CH_2\cdot CO_2H)_2$, and a NO_2-compound, m.p. 287°, whilst oxidation with dil. HNO_3 produces $H_2C_2O_4$, a neutral *compound*, m.p. 320°, and a NO_2-compound, m.p. 297°. Nitration of (II) gives *dinitroalkannin tetra-acetate*, decomp. 260°. 2-Methylanthracene is produced when (I) is distilled with Zn dust. (I) contains two alcoholic and two phenolic OH groups and is probably



which explains why its absorption spectrum differs so much from that of either naphthazarin or the hydroxyanthraquinones. S. C.

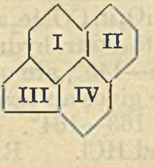
Halogen derivatives of the benzophenone and anthraquinone series.—See B., 1933, 857.

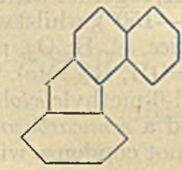
1-Amino-10-anthrones and 1-aminoanthraquinone compounds.—See B., 1933, 857.

Preparation of depsides with the aid of azides. R. O. Pepe (Anal. Asoc. Quím. Argentina, 1933, **21**, 53—60).—An account of work already abstracted (A., 1930, 1039). R. K. C.

Strophanthin. XXVIII. Further degradation of strophanthidin and periplogenin derivatives. W. A. Jacobs and R. C. Elderfield (J. Biol. Chem., 1933, **102**, 237—248; cf. A., 1932, 1138).—The Me_3 ester of the tribasic acid, $C_{21}H_{32}O_6$ (now called dephanthanic acid), from strophanthidin with MgPhBr or MgMeI gives the *hexaphenyl-*, amorphous, or *hexamethyl-tricarbinol*, cryst., respectively, both oxidised by hot CrO_3–AcOH to $COPh_2$ and *dephanthic acid*, $C_{17}H_{26}O_4$, m.p. 243—245° after softening at 200° (*Me*$_2$ ester, m.p. 69—71°), thus proving that the

(*A.*)





(*B.*)

group in position 14 is CH_2. If the accepted structure for ring III of strophanthidin is correct, this substance must contain the C skeletons (*A*) or (*B*), which, however, are not in agreement with the formation of a dimethylphenanthrene as a primary product of Se-dehydrogenation. Alternative structures are discussed on the assumption of the possibility of migration of the ethylenic linking during dehydration of dihydrostrophanthidin. The unsaturated lactone, $C_{24}H_{30}O_8$, from undephanthontriacid Me_2 ester is hydrogenated (PtO_2) in AcOH to a saturated, neutral *lactone*, $C_{24}H_{32}O_8$, m.p. 225—227°, and *undephanthantriacid Me*$_2$ ester, $C_{24}H_{34}O_8$, m.p. 201°; the H ester and $SOCl_2$ give the *chloride*, cryst., whence the *amide Me*$_2$ ester, m.p. 205° after softening at 110—111° (could not be degraded), was obtained. The corresponding *azide*, similarly prepared, gives the urethane, whence 25% KOH–EtOH at 100° forms the very stable *lactam*, $C_{21}H_{29}O_5N$, m.p. 264—266° (*Me* ester, m.p. 226—228°). The unsaturated lactone, $C_{23}H_{30}O_6$, from undeplogondiacid Me ester gives by similar reduction a neutral *substance*, ? $C_{23}H_{32}O_6$, m.p. 189—190° after softening, and a *deoxy-acid*, $C_{23}H_{34}O_6$, m.p. 212°, whence by way of the chloride, azide, and urethane, a small amount of the *amine*, $C_{21}H_{33}O_4N$ (*hydrochloride* of *Et* ester, m.p. 110—120°), was obtained. R. S. C.

Action of heat on resin acids. Fanica (Bull. Inst. Pin, 1933, 151—165, 181—189).—The following are obtained by heating at 230° in CO_2: from Aleppo colophony in one experiment *α-pyroabietic acid* (I), m.p. 172—173°, $[\alpha]_{5790}$ +60° [*NH_4* (unstable), *Ni*, *Co*, *Cu*, *Mn*, *Fe*^{III}, and *Ba* salts; *anilide*, m.p. 148°], but in a second experiment an *acid* (II), m.p. 176—182°, $[\alpha]_{5790}$ −30°; from French colophony an *acid*, m.p. 185—187°, $[\alpha]_{5790}$ −25°; from β-pimaric acid an impure *acid* (III), m.p. 164—165°, $[\alpha]_{5790}$ −38·3°; from α-alepic acid an *acid*, m.p. 172—173°, $[\alpha]$ +70·7°; from abietic acid, m.p. 171—172°, $[\alpha]_{5790}$ −100·2°, *β-pyroabietic acid*, m.p. 185—190°, $[\alpha]_{5790}$ −52·8°, possibly identical with (II), (III), a known colophonic acid (A., 1906, i, 100), and the acid of Fonrobert *et al.* (B., 1929, 403). α-Pimaric acid is only slightly affected by this treatment. The abietic acids from Aleppo and French colophony give the same *nitrosite*, m.p. 150—160° (decomp.) (15 and 25% yields, respectively), and *nitrosochloride*, m.p. 148° (25 and 35% yields, respectively). (I) forms no additive compounds (except with ICl), gives with fuming HNO_3 a *substance*, $C_{40}H_{57}O_4(NO_2)$, m.p. 218—220°, $[\alpha]_{5790}$ +102°, with H_2SO_4 at 0° a *sulphonic acid*, decomp. 213—214°, $[\alpha]_{5790}$ +81·7° in AcOH (*Na H* salt), and with Se at 200—250° a 43·5% yield of retene. R. S. C.

Rhamnol. A. Windaus and M. Deppe (Ber., 1933, **66**, [*B*], 1254—1255).—Rhamnol (I), m.p. 134°, $[\alpha]_D^{18}$ −35·2° in $CHCl_3$, is purified through its 3 : 5-*dinitrobenzoate*, m.p. 202—204°, $[\alpha]_D$ −10·8° in $CHCl_3$. (I) loses its H_2O of crystallisation with great difficulty at 100°/vac., thus causing a low % of C to be observed. Treatment of rhamnol acetate (II) with Br–AcOH yields a small amount of *tetrabromide* of high m.p., but mainly a dibromide which with Zn dust regenerates (II), m.p. 118—119°, $[\alpha]_D^{18}$ −38·2° in $CHCl_3$. In particular, analyses of the ester show the formula $C_{20}H_{32}O$ usually ascribed to (I) to be incorrect.

It probably belongs to the sitosterol group and contains 29 C; this is probably also true of cupreol, cinchol, and quebrachol. H. W.

Cerebronic acid. VIII. P. A. Levene and K. Heymann (J. Biol. Chem., 1933, **102**, 1—6; cf. A., 1929, 1479).—Fractionation of crude phrenosin gives 3% of a product (I), m.p. 200° (decomp.), $[\alpha]^{28}_{D}$ +3·6° in C_5H_5N, whence cerebronic acid (II), m.p. 100—101°, $[\alpha]^{23}_{D}$ +2·9° in C_5H_5N, was obtained. This, when oxidised, gives a mixture including acids (possibly mixtures), $C_{23}H_{46}O_2$, m.p. 76° (Et ester, b.p. 175°/0·4 mm.), and $C_{24}H_{48}O_2$, m.p. 76—78° (Et ester, b.p. 191—194°/0·4 mm.). (II) and (I) are thus mixtures, although the latter forms large crystals. R. S. C.

Tetrahydroxybufostan, a tetrahydric alcohol $C_{27}H_{48}O_4$ from winter-bile of toads. H. Makino (Z. physiol. Chem., 1933, **220**, 49—54).—From the winter-bile of *Bufo vulgaris japonica* there were isolated cholesterol and *tetrahydroxybufostan* (I), $C_{27}H_{48}O_4$, m.p. 230°, $[\alpha]^{20}_{D}$ +37·5° in EtOH (*Ac*$_4$ derivative, m.p. 52—55°). Oxidation of (I) with CrO_3 in AcOH gives a *triketomonocarboxylic acid*, m.p. 221—222°, $[\alpha]^{20}_{D}$ +31° in EtOH [*Et* ester (*trioxime*, m.p. 218°); *Me* ester, m.p. 198—199° (*trioxime*, m.p. 214—215°)]. The primary OH of (I) is probably in the Pr^{β} group. J. H. B.

Fission of wogonin by alkali; formation of iretol. S. Hattori and K. Hayashi (Ber, 1933, **66**, [*B*], 1279—1280).—Iretol, m.p. 186° (decomp.), BzOH, and AcOH are formed when wogonin, m.p. 203° after softening at 200°, is boiled with $KOH-H_2O$ in H_2 (cf. A., 1931, 493). H. W.

Resin acids of American turpentine gum. Preparation of the pimaric acids from *Pinus palustris*. S. Palkin and T. H. Harris (J. Amer. Chem. Soc., 1933, **55**, 3677—3684).—Improved methods of isolation and separation of *d*- (I), m.p. 218—219°, $[\alpha]^{20}_{D}$ +73·3° in EtOH, and *l*-pimaric acid (II), m.p. 150—152°, $[\alpha]^{20}_{D}$ −274·5° in EtOH, from the gum of *P. palustris* are given. (I) differs markedly (in m.p. and rotation) from the *d*-pimaric acid from *P. maritima*, but the properties of the *l*-acid from both sources are almost identical. (I) is reduced (H_2, $Pd-BaSO_4$, EtOAc) to a dihydro-acid, m.p. 249—250° (cf. Ruzicka and Balas, A., 1923, i, 818); (II) similarly gives a mixture from which a dihydro-acid, m.p. 144—146°, is isolated. Crystallographic data for (I) and (II) are given. H. B.

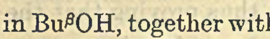
Oxidations by selenium dioxide in the terpene series. G. Dupont, J. Allard, and R. Dulon (Bull. Soc. chim., 1933, [iv], **53**, 599—603).—The oxidation of pinene to verbenone (33% yield) by SeO_2 (modified prep.) (A., 1932, 1253) is confirmed. Nopinene gives similarly (best in ligroin or H_2O) a 25% yield of pinocarvone. CH_2Ph_2 gives $COPh_2$. R. S. C.

Santenone. O. Aschan (Svensk Kem. Tidskr., 1933, **45**, 209—221).—Crude santenone forms two *semicarbazones*, α (m.p. 235—236°) and β (m.p. 221—222°), which give on hydrolysis α-, b.p. 191°, m.p. 55—56°, and *β-santenone*, b.p. 189·5—190·5°, m.p. 46°, respectively. The corresponding *oximes* have m.p. 74° and 50—51°. The α and β forms are regarded as stereoisomerides. R. P. B.

First product of condensation of furfuraldehyde with phenol. A. E. Porai-Kochitz, N. A. Kudrjavtzev, and B. E. Maschkileizon (J. Appl. Chem. Russ., 1933, 6, 685—690).—Furfuraldehyde (I) reacts with PhOH in alkaline media with production of unidentified tarry and resinous substances. In boiling feebly acid solutions 71%, and in alkaline solution in presence of $NaHSO_3$ 5%, yields of o- or p-*hydroxyphenylfurylcarbinol*, m.p. about 150° (*benzyl ether*, m.p. 161—162°; its *Ac* ester, m.p. 285—287°; *Ac*$_2$ ester), are obtained. R. T.

Preparation of tetrahydropyrone. R. Cornubert and P. Robinet (Bull. Soc. chim., 1933, [iv], 53, 565—569).—The prep. of Et_2 acetonedioxalate, chelidonic acid, pyrone, and tetrahydropyrone is modified, the yields obtained being 81, 98, 89, and (?) 100%, respectively. R. S. C.

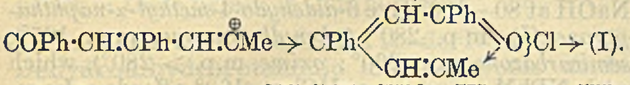
[Confirmation of the constitution of] so-called tetrahydropyrones. R. Cornubert and (in part) P. Robinet (Bull. Soc. chim., 1933, [iv], 53, 610—633).—Partly a detailed account of work previously published (A., 1932, 272). The condensation products of cyclic ketones (1 mol.) and PhCHO (I) (2 mols.) have the tetrahydropyrone structure (*A*), since they form ketonic derivatives and do not contain an OH group, and since the product is formed only if the ketone contains at least one H in each position adjacent to the CO. 2-Benzylidene-6-methyl*cyclo*hexanone (II), (I), and HCl at −15° give three isomeric *compounds*, $C_{28}H_{27}O_2Cl$, m.p. 180—181° (III), 199—200° (IV), and not stated, respectively, probably containing a tetrahydropyrone ring and the grouping CHClPh·C. (II) and HCl in ligroin give the *hydrochloride*, $C_{14}H_{17}OCl$, m.p. 90·5°, which with (I) and HCl gives a compound, m.p. 200—205° after sintering at 192°, probably (IV). The liquid benzylidene compound from 2-methyl*cyclo*hexanone (A., 1932, 58) gives similarly a compound, m.p. 172—173°, probably (III). Hydrogenation (Ni) of 2-benzylidene-6 : 6-dimethyl*cyclo*hexanone gives *2-benzyl-6 : 6-dimethyl*cyclo*hexanone* (V), b.p. 179°/29 mm. (*oxime*, m.p. 145°; *semicarbazone*, m.p. 201—202°). 2 : 6-Dimethyl*cyclo*hexanone and $NaNH_2$ in hot Et_2O give a Na salt, which with CH_2PhBr gives much *2-benzyl*- (VI), b.p. 174°/22 mm. (*oxime*, m.p. 155—156°; *semicarbazone*), and a little *2 : 6-dibenzyl-2 : 6-dimethyl*cyclo*hexanone*, b.p. 240—245°/19 mm., m.p. 78°. The tetrahydropyrone (*A*; R=H, R′=Me) [*semicarbazone*, m.p. 230° (rapid heating)] with Na and EtOH gives a substance, m.p. 127—128° [*loc. cit.* (i), b.p. 127—128°] (also obtained by KOH in $Bu^{\beta}OH$, together with a small amount of a *substance*, m.p. 140—150°), whilst with $KMnO_4$ in $COMe_2$ acids and a *substance*, $C_{21}H_{22}O_3$, possibly the tetrahydropyrone (*A*; R=OH, R′=Me), m.p. 145—146°, are obtained. 2-Benzyl-6-methyl*cyclo*hexanone gives an *oxime*, m.p. 115°, and a *semicarbazone*, m.p. 163—164°. (V) and (VI) do not condense with (I) and HCl. R. S. C.


(*A*.)

(*a*) Case of ketonic activity of acetic anhydride and (*b*) condensation of salicylaldehyde with

benzoylacetone. R. J. W. Le Fèvre and J. Pearson (J.C.S., 1933, 1197—1200).—The compound obtained from COPhMe, Ac_2O, and $FeCl_3$ by Dilthey's method (A., 1916, i, 829) is considered to be 4 : 6-diphenyl-2-methylpyrylium ferrichloride (I) (cf. Schneider and Ross, A., 1922, i, 1171) and not the 2 : 6-diphenyl-4-methyl derivative (II) (cf. Dilthey, *loc. cit.*), since nitration (fuming HNO_3) of the corresponding *perchlorate*, m.p. 265—266° (decomp.), gives a mixture of products which on oxidation ($KMnO_4$; $6N$-H_2SO_4) affords some p-$NO_2\cdot C_6H_4\cdot CO_2H$; (II) should give m-NO_2-derivative almost entirely (cf. this vol., 163). COPhMe, Bz_2O, and $FeCl_3$ at 50° give a little 2 : 4 : 6-triphenylpyrylium ferrichloride. COPhMe and Ac_2O do not react at 100°, whilst treatment of the product from COPhMe, CH_2BzAc (III), and HCl with $FeCl_3$ affords (I). It is unlikely that (III) is an intermediate in Dilthey's method of prep. of (I); the mechanism is considered to be: $2\mathrm{COPhMe} \longrightarrow \mathrm{COPh\cdot CH{:}CPhMe} \xrightarrow{Ac_2O}$

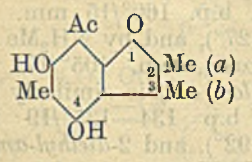
$\mathrm{COPh\cdot CH{:}CPh\cdot CH{:}CMe\cdot OAc} \xrightarrow{HCl} \overset{\ominus}{\mathrm{Cl}}$ +



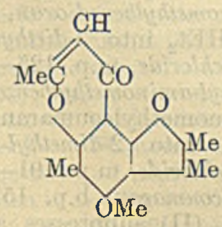
$$\mathrm{COPh\cdot CH{:}CPh\cdot CH{:}\overset{\oplus}{C}Me} \rightarrow \mathrm{CPh}\left<\begin{matrix}\mathrm{CH\cdot CPh}\\ \mathrm{CH{:}CMe}\end{matrix}\right>\mathrm{O\}Cl} \rightarrow \text{(I).}$$

Condensation of o-$OH\cdot C_6H_4\cdot CHO$ (IV) and (III) by Chatterji and Ghosh's method (J.C.S., 1918, **113**, 446) gives a chloride, m.p. 115—120° [corresponding perchlorate (V), m.p. 135—140°, also obtained (with m.p. 103—105°) from (III), (IV), and 70% $HClO_4$ in Et_2O–HCl]. The use of twice the amount of (IV) in Ac_2O (solvent) leads to the isolation of 3-benzoyl-2-*o*-hydroxystyrylbenzopyrylium perchlorate (VI), m.p. 234—235°, which raises the m.p. of (V), and is converted by alkali into the corresponding ψ-base or *spiro*pyran. Reaction proceeds by way of the 3-benzoyl-2-methylbenzopyrylium salt, which then reacts rapidly with (IV) to give (VI). COMeEt, (IV), and 70% $HClO_4$ in Et_2O–HCl give 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate, m.p. 261—262° (lit. 257—258°), even when a large excess of COMeEt is used; the intermediate 2 : 3-dimethylbenzopyrylium salt reacts more rapidly with (IV) than does COMeEt. H. B.

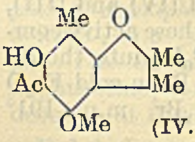
Usnic acid. III. Usnetol, usnetic acid, and pyrousnic acid. F. H. Curd and A. Robertson (J.C.S., 1173—1179; cf. this vol., 831).—Usnetol is shown to be (I) by conversion into (II) and by synthesis of its 4-*Me ether* (III) and of O-*methyl*iso*usnetol* (IV), which resembles (III) in colour and $FeCl_3$ and H_2SO_4 reactions. Arguments are presented that usnetic acid (V) is (I) with a $CH_2\cdot CO_2H$ group for Me in position (*a*) or (*b*), pyrousnic acid (VI) being derived therefrom by loss of the Ac. The formulæ of Schöpf *et al.* (A., 1928, 294) for these and derived substances are refuted. *dl*-Usnic acid (prepared from the *d*-acid by refluxing in xylene) and 50% aq. KOH at 210° in H_2 give $COMe_2$, AcOH, and (VI), m.p. 199—200° (decomp.) after sintering at 195° [also obtained similarly (with AcOH) from (V)]. (VI) and CH_2N_2 in Et_2O give the *Me* ester, m.p. 186° (decomp.), which with MeI–$COMe_2$–K_2CO_3 gives *Me* O-*dimethylpyrousnate*, m.p. 63—64°, obtained similarly from (VI) and hydrolysed to O-*dimethylpyrousnic acid*, m.p. 126—127°. *d*- or *dl*-Usnic acid and 75% aq. KOH give (VI) and *usnetinic acid*, $C_{11}H_{10}O_5$, m.p. 180—181° (decomp.) (cf. Schöpf, *loc. cit.*). Me *O*-methylusnetate, m.p. 117—118° [from (V) and CH_2N_2 in Et_2O], affords O-*methylusnetic acid*, m.p. 164—165°. (I) with MeI–K_2CO_3–$COMe_2$ affords (III), m.p. 127—128°, which with EtOAc and Na at 160° gives 6-*hydroxy*-4-*methoxy*-7-*acetoacetyl*-2 : 3 : 5-*trimethylcoumarone*, m.p. 126—127°, whence by a little HCl in hot AcOH 7-*methoxy*-2 : 8 : 4′ : 5′-*tetramethyl*-5 : 6-*furano*-(2′ : 3′)-*chromone* (II), m.p. 192°, was obtained. Methylphloroglucinol α-Me ether, MeCN, $ZnCl_2$, and HCl in Et_2O lead to 2 : 4-*dihydroxy*-6-*methoxy*-3-*methylacetophenone*, m.p. 224°, whence CHMeAcCl in hot $COMe_2$ forms 6-*hydroxy*-4-*methoxy*-5-*acetyl*-2 : 3 : 7-*trimethylcoumarone* (IV), m.p. 109—110° (*oxime*, m.p. 161—162°). Methylphloroglucinol β-Me ether, m.p. 115—116° (prepared from Me 2 : 6-dihydroxy-4-methoxybenzoate), gives similarly 2 : 6-*dihydroxy*-4-*methoxy*-3-*methylacetophenone*, m.p. 197—198° [giving with MeI–K_2CO_3–$COMe_2$ the 2-OH-4 : 6-$(OMe)_2$-compound], α-3-*hydroxy*-5-*methoxy*-2-*acetyl*-4-*methylphenoxyethyl Me ketone*, m.p. 151—152°, and thence (III). R. S. C.



(I.)



(II.)



(IV.)

Spatial configuration of the valencies in tricovalent carbon compounds. E. S. Wallis and F. H. Adams (J. Amer. Chem. Soc., 1933, **55**, 3838—3851).—Partly an account of work previously reviewed (A., 1932, 611; this vol., 153). 12-Chloro-12-phenyl-β-benzoxanthen hydrochloride (Gomberg and Schoepfle, A., 1917, i, 551) and $SH\cdot CH_2\cdot CO_2H$ in C_6H_6 give dl-12-*phenyl*-12-β-*benzoxanthenylthiolacetic acid* (I), m.p. 187—188°, which is resolved by brucine into *l*- (II), m.p. 183—184°, $[\alpha]^{20}_{D}$ −48·5° in $COMe_2$, and impure *d*-, m.p. 179°, $[\alpha]^{20}_{D}$ +28·9° in $COMe_2$, forms. (II) racemises slowly when kept alone or in $COMe_2$ at 20° and rapidly in boiling C_6H_6. (I) and Na in liquid NH_3 in absence of air give (after decomp. with dry NH_4Br) 12-*phenyl*-β-*benzoxanthen*, m.p. 153° [the substance, m.p. 171°, described as this by Kauffmann and Egner (A., 1914, i, 39) is probably a fluorene derivative]. (II) similarly affords products of $[\alpha]^{20}_{D}$ −2·3° (in C_6H_6) to −11·7° (in $COMe_2$), showing that $[CAr_3]^-$ can exist in an optically active state and that the three covalencies and the central C atom are not co-planar. The anion racemises fairly readily; when the solution is kept for some time before decomp. with NH_4Br, an inactive product results. dl-α-*Phenyl*-α-*methylpropylthiolacetic acid*, m.p. 137—138°, obtained in poor yield from CPhMeEtCl and $SH\cdot CH_2\cdot CO_2H$ in PhMe, could not be resolved; its alkaloid salts show a tendency to decompose into unsaturated hydrocarbons and alkaloid thiolacetates.

(II) and $AgNO_3$ in aq. $COMe_2$ give *dl*-12-phenyl-12-

β-xanthenol, m.p. 170—171° [the *Me*, m.p. 148°, and *Et*, m.p. 118°, *ethers* are prepared from (II) and MeOH– and EtOH–$AgNO_3$, respectively], indicating the optical instability of $[CAr_3]^+$. A cation of this type can, however, maintain an asymmetric configuration, since *d*-, m.p. 160°, $[\alpha]_{5463}^{20}$ +7·2° in CCl_4, and *l*-, m.p. 161—162°, $[\alpha]_{5463}^{20}$ −7·6° in CCl_4, -phenyldiphenylyl-α-naphthylcarbinols are obtained by the action of aq. $COMe_2$–$AgNO_3$ on *l*- (III) and *d*- (IV) -phenyldiphenylyl-α-naphthylthiolacetic acid, respectively; the *d*-, m.p. 125—126°, and *l*-, m.p. 125·5—126°, -Et ethers are prepared from EtOH–$AgNO_3$ and (IV) and (III), respectively (cf. A., 1932, 611). All these active compounds are converted by $SOCl_2$ in C_6H_6 into the *dl*-carbinyl chloride. (III) or (IV) and Br in cold Et_2O give an inactive *compound*, $C_{29}H_{21}Br$, m.p. 191° (decomp.).

The optical instability of neutral free radicals (electron septet) is shown by the formation of an inactive product from (III), CPh_3Cl, and Hg in Et_2O, the production of optically inactive βγ-dimethylhexane from *d*-β-bromobutane and Na in dry Et_2O (and by electrolysis of *d*- and *l*-α-methylbutyric acids), and the prep. of inactive αβγδ-tetraphenylbutane, m.p. 178° (lit. 255°), from l-αβ-*diphenylethyl bromide*, $[\alpha]_{\mathrm{D}}^{22}$ −27·1° in EtOH (from *d*-$CH_2Ph\cdot CHPh\cdot OH$ and HBr in C_6H_6 at 0°), and Na in Et_2O. H. B.

Constituents of the leaves of *Ginkgo biloba*, L. III, IV. S. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 273—277, 278—285; cf. A., 1932, 1138).—III. The diacetate of substance *A* is hydrolysed by H_2SO_4 in aq. EtOH to an *isomeride*, $C_{11}H_{14}O_5$, m.p. 225·5—226·5°, and by aq. KOH to an oil. *A* and Me_2SO_4 yield a *substance*, $C_{11}H_{15}O_5\cdot OMe$, m.p. 100° (decomp.) [*Ag* salt; *Me* ester, m.p. 110° (decomp.)]. *A* is unattacked by HNO_3 in AcOH; alkaline $KMnO_4$ or CrO_3 in AcOH yield oily acids; fusion with KOH yields an *acid*, m.p. 150°. The EtOH mother-liquors of *A* yield a *substance*, $C_{11}H_{14}O_6,H_2O$, m.p. 291—292° (decomp.) [Ac_3 derivative, m.p. 180° (decomp.)].

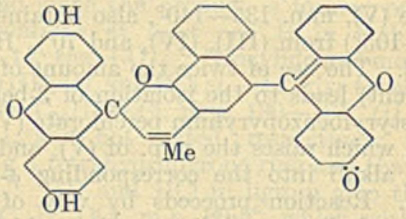
IV. Substance *B* and CH_2N_2 yield a *Me* derivative, m.p. 277—278° (*Ac* derivative, m.p. 218—219°, resolidifies, m.p. 257—259°). Demethyl-*B* yields a Ac_3 derivative, m.p. 237—238°. Treatment of *B* with 40% KOH yields *p*-hydroxyacetophenone, anisic acid, a *substance*, m.p. 266—267°, phloroglucinol, and a little (?) *p*-methoxyacetophenone. *B* is probably 5 : 8-dihydroxy-4′-methoxyflavone, since one OH (at 5) is unattacked by CH_2N_2, the 5 : 7-$(OH)_2$ derivative is acacetin, and the 5 : 6-position in excluded by consideration of the absorption spectrum.

Curves of the absorption spectra of *B* and its derivatives are given and compared with those of acacetin, monoacetylmonomethylacacetin, apigenin acetate, 4′-hydroxy-, 7-hydroxy-, 7-hydroxy-4′-methoxy-, and 6 : 4′-dimethoxy-flavones. 6 : 4′-*Dimethoxyflavone*, m.p. 194·5—195°, is obtained from 2 : 4 : 4′-trimethoxybenzoylacetophenone by treatment with HI. R. K. C.

Yellow colouring matter of Khapli wheat, *Triticum dicoccum*. III. Constitution of tricin. J. A. Anderson (Canad. J. Res., 1933, 9, 80—83).—Tricin (I) (A., 1931, 1426; 1932, 1256) is identical with 5 : 7 : 4′-*trihydroxy*-3′ : 5′-*dimethoxyflavone*, m.p. 288—289° (corr.) [Ac_3 derivative, m.p. 251—254° (corr.)], synthesised by demethylation of 5 : 7-dihydroxy-3′ : 4′ : 5′-trimethoxyflavone with 96—98% H_2SO_4 at 60°. When fused with H_2O–KOH at 200—210°, (I) gives phloroglucinol and syringic acid. J. W. B.

Dye of yellow dahlias. L. Schmid and L. Haschek (Monatsh., 1933, 62, 317—322).—The yellow dye $C_{15}H_{10}O_5$ (I), isomeric with apigenin (II), isolated from the dahlia (A., 1932, 621) affords *p*-hydroxyacetophenone by treatment with 20% KOH. Its Me_2 ether (III) (obtained in 60% yield by use of CH_2N_2) similarly gives *p*-methoxyacetophenone. With Ac_2O and C_5H_5N (I) gives a Ac_3 derivative, m.p. 182°, hydrolysed by 10% HCl in EtOH to a substance chemically and spectroscopically identical with (II), which is also obtained by demethylation of (III) with HI (*d* 1·7). J. W. B.

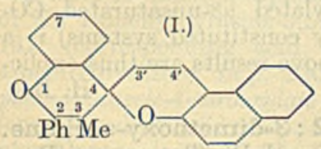
6-Aldehydo-4-methyl-α-naphthapyrone and dyes derived from it. R. N. Sen and G. C. Mukherjee (J. Indian Chem. Soc., 1933, 10, 271—273).—4-Methyl-α-naphthapyrone, EtOH–$CHCl_3$, and aq. NaOH at 80—100° give 6-*aldehydo-4-methyl-α-naphthapyrone* (I), m.p. 280° (*phenylhydrazone*, m.p. 125°; *semicarbazone*, m.p. 260°; *oxime*, m.p. > 280°), which with $NPhMe_2$ and conc. HCl at 100° affords a *leuco-base*, $C_{31}H_{30}O_2N_2$, m.p. > 250° [the oxidised (PbO_2) base dyes silk greenish-blue]. (I), *m*-$C_6H_4(OH)_2$, and conc. H_2SO_4 at 100—130° give the *compound* (II), m.p. > 280°, the Na salt of which dyes silk bright orange. H. B.



(II.)

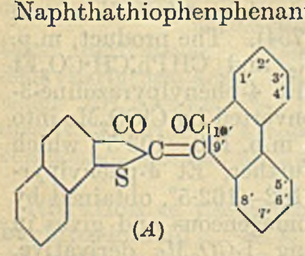
Heterocyclic bases from coumarans and phenyldioxan [benzdioxan]. E. Fourneau, P. Maderni, and (Mme.) Y. de Lestrange (J. Pharm. Chim., 1933, [viii], 18, 185—191).—Br and *o*-allylanisole, in C_6H_6 at 0°, do not yield nuclear Br-derivatives of coumaran (Adams and Rindfusz, A., 1919, i, 340), but α-(o-*anisyl*)-βγ-*dibromopropane*, b.p. 128—131°/0·4—0·5 mm. (I), and a little 2-methylcoumaran. (I) reacts slowly with $NHMe_2$ giving a mixture of bases separable into the *hydrochlorides*, m.p. 134° and 153°, of the stereoisomeric α-(o-*anisyl*)-γ-*dimethylamino*-Δ^{α}-*propenes*, and α-(o-*anisyl*)-βγ-*bis-dimethylaminopropane dihydrochloride*, m.p. 226—227°. $SOCl_2$ and 3-hydroxymethylbenzdioxan yield 3-*chloromethylbenzdioxan*, b.p. 132°/14 mm., converted by $NHEt_2$ into 3-*diethyl*-, b.p. 160°/15 mm. (II) (*hydrochloride*, m.p. 125—127°), and by NH_2Me into 3-*methyl-aminomethylbenzdioxan*, b.p. 105°/17 mm. 2-Bromomethylcoumaran (*loc. cit.*) is similarly converted into 2-*dimethyl*-, b.p 134—135°/19 mm. (*hydrochloride*, m.p. 191—192°), and 2-*diethyl-aminomethylcoumaran*, b.p. 151·5°/15 mm. (*oxalate*, m.p. 123°). (II) suppresses and reverses the vaso-constrictive action of adrenaline, and causes marked lowering of temp. in rabbits. A. C.

Styrylpyrylium salts. XV. Correction. Production of α-benzopyrones by the Kostanecki reaction. I. M. HEILBRON, R. N. HESLOP, and G. F. HOWARD (J.C.S., 1933, 1263—1264; cf. this vol., 614).—The course of the Kostanecki reaction is governed by factors which are not yet understood. The substances called 2-ethyl- and 7-methoxy-2-ethyl-chromone are proved by mixed m.p. and degradation to be 3 : 4-dimethyl- and 7-methoxy-3 : 4-dimethyl-coumarin, respectively, whence the following revised structures are assigned (the new name is given second): 4-phenyl-2-ethylbenzopyrylium perchlorate and its 7-OMe derivative, 2-phenyl-3 : 4-dimethylbenzopyrylium perchlorate and its 7-OMe derivative; 4-phenyl-3′-methylbenzo-β-naphtha*spiro*pyran and its 7-OMe derivative, 2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro*pyran* (I) and its 7-*OMe* derivative. The ionising power of these pyrans is thus normal. R. S. C.



Synthesis of rotenone and its derivatives. IV. Dehydrodihydrorotenonic and tephrosic acids. A. ROBERTSON (J.C.S., 1933, 1163—1165; cf. this vol., 712).—The structures of dehydrodihydrorotenonic acid (I) (and thus of dehydrorotenone) and of tephrosic acid (II) (this vol., 397) are confirmed by synthesis. 4 : 5-*Dimethoxyphenoxyacetic*-2-*pyruvic acid oxime*, $+H_2O$, double m.p. 80° and 160—165° (prepared in 10% aq. NaOH at 50°), and Ac_2O at 100° give 4 : 5-*dimethoxyphenoxyacetic acid*-2-*acetonitrile*, m.p. 174° [*Me* ester (III), m.p. 92°]. 2 : 6-Dimethoxybenzonitrile and $MgBu^{\beta}Br$ (less well $MgBu^{\beta}I$), first in hot Et_2O and then in xylene at 100°, give 2 : 6-*dimethoxy*isov*alerophenone*, b.p. 178°/15 mm. (*semicarbazone*, m.p. 207°), reduced (Clemmensen) to tetrahydrotubanol Me_2 ether, b.p. 142—145°/15 mm., demethylated by $HI-Ac_2O$ at 140—145°. (III), tetrahydrotubanol, $ZnCl_2$, and HCl in Et_2O afford a ketimine, hydrolysed to *Me tetrahydroderrisate*, m.p. 185°, and a little tetrahydroderrisic acid. This acid with hot $Ac_2O-AcOH$ yields 7-acetoxy-6′ : 7′-dimethoxy-8-*iso*amylchromeno-(3′ : 4′ : 2 : 3)-chromone, hydrolysed by HCl–AcOH to the corresponding 7-OH compound [=(I)]. (III) and m-$C_6H_4(OH)_2$ give by the Hoesch reaction 4 : 5-dimethoxyphenoxyacetic acid-2-resacetophenone [=(II)] and its Me ester. R. S. C.

Indigoid dyes. II. 1 : 2-Naphthathiophenphenanthreneindigotin. III. P. C. DUTTA (Ber., 1933, **66**, [*B*], 1226—1230, 1230—1232).—II. 1 : 2-Naphthathiophenphenanthreneindigotins (cf. *A*) are darker than the corresponding thionaphthenphenanthreneindigotins (A., 1932, 753); they do not yield even or darker shades on wool. Phenanthrenequinone and 1 : 2-naphthoxythiophen in boiling AcOH afford 1 : 2-*naphthathiophen*-9′-*phenanthreneindigotin*, m.p. 291°. The following derivatives are described: -2′-*nitro*-, m.p. > 300°; -4′-*nitro*-, m.p. 281°; -2′ : 7′-*dinitro*-, m.p. > 295°; 4′ : 5′-*dinitro*-, m.p. > 295°; -2′-*bromo*-, m.p. >295°; -*dibromo*-, m.p. > 295°; -*bromonitro*-, m.p. > 300°; -2′-amino-, m.p. > 295°; -4′-*amino*-, m.p. > 300°; -2′-*hydroxy*-, m.p. > 295°.



(*A*)

III. The following indigoid dyes are derived from 1 : 2-naphthoxythiophen by condensation in AcOH in presence of a little mineral acid: 1 : 2-*naphthathiophen*-3′-*indoleindigotin*, m.p. > 295°, its -5′-*chloro*-, m.p. > 295°, -5′-*bromo*-, m.p. > 295°, and -5′ : 7′-*dibromo*-, m.p. > 300°, derivatives: 1 : 2-*naphthathiophen*-2′-*acenaphthyleneindigotin*, m.p. 282°, and its 5′-*nitro*-, m.p. > 295°, derivative; 1 : 2-*naphthathiophen*-1-*aceanthyleneindigotin*, m.p. > 295°; di-1 : 2-naphthathiophenethyleneindigotin, m.p. > 295° after decomp. at 280°. H. W.

Polyhalogenated ketones. III. Pyrrole. G. SANNA (Gazzetta, 1933, **63**, 479—484; cf. A., 1931, 630).—The Mg derivative of pyrrole with $CHCl_2\cdot COCl$ in Et_2O forms 2-*dichloroacetylpyrrole*, m.p. 90°; this with 5% KOH or aq. NH_3 at 95° gives brown Cl-free condensation products, probably ter- and bi-mol., respectively. Using $CCl_3\cdot COCl$, 2-*trichloroacetylpyrrole*, m.p. 67°, is formed. E. W. W.

Isomerisation products of pyridine salts of unsaturated acids. O. LUTZ, R. KLEIN, and A. JIRGENSON (Annalen, 1933, **505**, 307—310; cf. A., 1910, i, 879).—Titration of a mixture of 1 mol. of acid with 3 mols. of C_5H_5N after keeping at 18° for 20 days indicates that addition of C_5H_5N occurs readily with maleic, fumaric, itaconic, and crotonic acids, very slowly with aconitic, and not at all with citraconic, mesaconic, allylmalonic, and cinnamic acids. The *betaines* of *pyridiniumsuccinic*, m.p. 192° (decomp.), and β-*pyridiniumbutyric acid*, m.p. 79·5—80°, are described. H. A. P.

Fission of pyridinium salts and new mode of formation of α-ketoaldehydes. F. KRÖHNKE (Ber., 1933, **66**, [*B*], 1386—1392; cf. this vol., 501).—*Phenacylpyridinium iodide*, m.p. 214° (decomp.), is obtained from the bromide (I) and aq. KI. (I) affords a *phenylhydrazone*, m.p. 160—165° (decomp.), and p-*nitrophenylhydrazone*, m.p. 125° (gas evolution) and decomp. about 212°. The primary product of the action of $Br-H_2O$ on (I) is the yellow perbromide (II) (*loc. cit.*), isomerised by heating at 80°, by long preservation in presence of traces of moisture, or immediately by seeding to the stable, red *perbromide* B (III), m.p. 92°, also obtained directly from the reagents in dil. solution at 50°. (II) or (III) when warmed with abs. EtOH passes into *perbromide* C, $C_{13}H_{12}ONBr_2$, m.p. 154—157°. Further action of $Br-H_2O$ leads to ω-*bromophenacylpyridinium bromide* (IV), m.p. 220° (decomp.) (isolated from action in AcOH), which yields a *perchlorate*, m.p. 181° after softening, and a *perbromide*, $C_{13}H_{11}ONBr_4$, m.p. 137°. The final product is regarded as $CBr_2Bz\cdot N(C_5H_5)Br$, the ready hydrolysis of which to C_5H_5N salt, BzOH, and HCO_2H is accompanied by slight fission of the C_5H_5N ring. (IV) is very slightly hydrolysed in acid or neutral solution, more readily in alkaline solution to BzOH, CH_2O, and C_5H_5N,HBr. Boiling H_2O converts (IV) into BzCHO, readily oxidised by $Br-H_2O$ through $BzCO_2H$ to BzOH and CO_2. (IV) and p-$NO_2\cdot C_6H_4\cdot NH\cdot NH_2$ in aq. HBr afford phenylglyoxaldi-*p*-nitrophenylhydrazone, decomp. < 312°. *p*-Bromophenacyl bromide and quinoline in Et_2O–EtOH afford p-*bromophenacylquinolinium bromide* (V), m.p. 242° (corresponding *perchlorate*; *perbromide*, m.p. 162·5° after softening at 157°). (V) and hot Br–AcOH yield *p*-bromophenylglyoxal hydrate, m.p. 133—134° after softening. $CHBr_2Bz$ and excess of C_5H_5N in Et_2O slowly give EtOBz and *methylenedipyridinium bromide* (VI), m.p. 255—258° (decomp.) after becoming discoloured (corresponding *perchlorate*, m.p. 236° after softening; *perbromide*; *periodide*). (VI) is not affected by boiling H_2O and mineral acids, but is converted by 0·25*N*-$Ba(OH)_2$ or Ag_2O into CH_2O and C_5H_5N. Catalytic reduction (PtO_2–H_2O) rapidly causes absorption of $7H_2$ and formation of MeOH and piperidinium bromide. (VI) is quantitatively formed from (IV) and warm C_5H_5N, slowly from CH_2Br_2 and C_5H_5N in Et_2O. H. W.

Derivatives of 3 : 3-dimethylindolinone. II. K. Brunner [with M. von Mikoss and J. Riedl] (Monatsh., 1933, 62, 373—404).—3 : 3-Dimethylindolinone (I) in conc. H_2SO_4 at 100° gives its 5-*sulphonic acid*, $+2H_2O$ and anhyd., m.p. 245—247° (decomp.) [*Ca*, *Na* $+2H_2O$ and anhyd., salts; chloride (II), m.p. 197°; *amide*, m.p. 254—255°], isolated as its *Ba* salt $+4H_2O$ and anhyd. Reduction of (II) with Sn+HCl (*d* 1·19) gives 5-*thiol*-3 : 3-*dimethylindolinone*, m.p. 156—157°, which with $CH_2Cl·CO_2H$ and KOH–EtOH affords the corresponding 5-*thioglycollic acid*, m.p. 193·4° (corr.) (*Na* salt) [also obtained from the 5-NH_2 derivative of (I) (A., 1932, 65) by diazotisation, conversion into the *xanthate*, m.p. 200—202°, reduction with NaOH–Zn, and treatment with $CH_2Cl·CO_2H$]. With 32% oleum at 100° (I) gives its 5 : 7-*disulphonic acid*, $+H_2O$ and anhyd. (isolated as its *Ba* $+4H_2O$; Na $+3H_2O$, and *K* salts), in which both SO_3H groups are replaceable by Br–H_2O or NO_2 (fuming HNO_3), but not by H_2O, 9% NH_3, or 20% HCl, and only one by Na–Hg reduction. 1 : 3 : 3-Trimethylindolinone even with 37·7% oleum gives only its 2-*sulphonic acid*, $+2H_2O$ and anhyd., decomp. 220° (*Ba* $+4H_2O$ and anhyd.; *Na* $+0·5H_2O$ and anhyd.; *K* $+1·5H_2O$ and anhyd., salts), the SO_3H group being eliminated by heating with HCl at 180°, Br–H_2O at room temp., or fuming HNO_3 at 80°. Similarly is obtained 3 : 3 : 7-trimethylindolinone-5-sulphonic acid (*Na* salt $+4·5H_2O$) as its *Ba* salt. With P_2S_5 in xylene at 140° (I) gives 3 : 3-*dimethylthioindolinone*, m.p. 108—109° [tautomeric with the 2-thiol form; *Ag* salt; *mercurichloride*, m.p. 227—228°; *Me thioether*, m.p. 65° (MeI on Ag salt at 86°, or by NaOH–MeOH on the *methiodide*, m.p. 165°); *thioglycollic acid*, m.p. 151°; *Ac*, m.p. 39—40°, and *Bz*, m.p. 80°, derivatives]. Similarly are obtained 3 : 3 : 7-, m.p. 153—154° [oxidised by 5% $K_3Fe(CN)_6$ to the *disulphide*, m.p. 127—128°], and the 2-*thioglycollic acid*, m.p. 90°; 3 : 3 : 5-, m.p. 167° (*Ag* salt; *thioglycollic acid*, m.p. 136°; *disulphide*, m.p. 165°), and 3 : 3 : 6-, m.p. 135—136°, -*trimethylthioindolinone*. J. W. B.

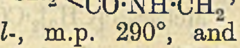
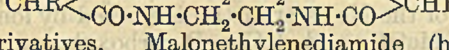
Reversible addition of aromatic compounds to conjugated systems. R. C. Fuson, A. P. Kozacik, and J. T. Eaton (J. Amer. Chem. Soc., 1933, 55, 3799—3803).—2-m-*Bromostyryl*-, m.p. 96° (*dibromide*, m.p. 185—186°), and 2-p-*bromostyryl*- (I), m.p. 137—138° (*dibromide*, m.p. 194—195°), -*quinolines*, prepared from 2-methylquinoline and $C_6H_4Br·CHO$ by the method previously described (this vol., 721) for the *p*-Cl-analogue (II), react with C_6H_6, $AlCl_3$, and HCl (cf. *loc. cit.*) to give 2-ββ-diphenylethylquinoline. PhBr is formed during the reaction with (I), showing that $·C_6H_4Br$ [or $·C_6H_4Cl$ with (II)] is replaced by Ph. *o*- and *p*-Chlorocinnamic acids, C_6H_6, and $AlCl_3$ give $CHPh_2·CH_2·CO_2H$; with PhCl, $AlCl_3$, and HCl, both acids give ββ-*di*-p-*chlorophenylpropionic acid*, m.p. 188—189°, oxidised (aq. $KMnO_4$) to 4 : 4′-dichlorobenzophenone. It is suggested that condensation of PhR with β-arylated αβ-unsaturated CO-compounds (and similarly constituted systems) is a reversible process; the above results are thus explicable. H. B.

2-Methoxy- and (?) 2 : 3-dimethoxy-acridine. W. Borsche, F. Runge, and W. Trautner (Ber., 1933, 66, [*B*], 1315—1318).—*o*-$C_6H_4Cl·CO_2H$ (I), *p*-anisidine, K_2CO_3, and Cu-bronze in tetrahydronaphthalene give 4-*methoxydiphenylamine*-2′-*carboxylic acid*, m.p. 186°, converted by conc. H_2SO_4 at 100° into 2-hydroxyacridone, which with Me_2SO_4 and KOH yields 2-*methoxyacridone* (II), m.p. 263—265°. (II) is reduced by Na and EtOH to 2-*methoxydihydroacridine*, oxidised by $K_2Cr_2O_7$ and H_2SO_4 to 2-*methoxyacridine*, m.p. 103—104° (*chromate*; *hydrochloride*; *sulphate*). (I), 4-aminoveratrole, Cu-bronze, and K_2CO_3 in boiling amyl alcohol yield 3 : 4-*dimethoxydiphenylamine*-2′-*carboxylic acid* (III), m.p. 180—181°, which is not condensed by H_2SO_4. (III) is converted by PCl_5 in boiling CS_2 (cf. Dirscherl *et al.*, this vol., 956) into 2 : 3-*dimethoxyacridone* (IV) (*hydrochloride*) and by a somewhat greater proportion of PCl_5 in boiling C_6H_6 into 9-*chloro*-2 : 3-*dimethoxyacridine*, m.p. 187° [*hydrochloride*, m.p. 226° (decomp.); *picrate*]. Reduction of (IV) leads to *dimethoxydihydroacridine*, m.p. 163—165°, oxidised to 2 : 3-*dimethoxyacridine* ($+1H_2O$) (V), m.p. 107° (*chromate*). Treatment of (V) with AcOH–HI yields 2 : 3-dihydroxyacridine [*hydrochloride* ($+H_2O$), m.p. 235° (decomp.)]. H. W.

Formation and degradation of pyrazoline derivatives. K. von Auwers and O. Ungemach (Ber., 1933, 66, [*B*], 1198—1204; cf. A., 1929, 1080; 1932, 862, 1143).—The action of $CH_2N_2·CO_2Et$ on Et tiglate slowly yields *Et* 4 : 5-*dimethylpyrazoline*-4 : 5-*dicarboxylate*, b.p. 169—176°/10 mm., showing (in conjunction with previous observations) that Δ^1-pyrazolinecarboxylic esters are stable only when they cannot pass into isomerides with conjugated linkings. Doubts are cast on the structures assigned by Müller *et al.* to the compounds obtained from butadiene and diazo-compounds (A., 1932, 754). The product, m.p. 100°, obtained from CH_2N_2 and $CHPh{:}CH·CO_2Et$ appears to be exclusively Et 4-phenylpyrazoline-3-carboxylate (I), since it is converted by $ClCO_2Me$ into a crude 1-CO_2Me derivative, m.p. 103—103·5°, which is almost homogeneous. Further, Et 4-phenylpyrazole-3(5)-carboxylate, m.p. 162—162·5°, obtained by oxidation of (I), appears homogeneous and gives in high yield the corresponding 1-CO_2Me derivative, m.p. 75—76°, and 1-*CO·NHPh* compound, m.p. 105—106°. (I) is transformed by dry distillation into Et *trans*-β-methylcinnamate, b.p. 132—135°/13 mm. (acid, m.p. 96—98°). CH_2N_2 condenses with nitriles to unstable cyanopyrazolines which readily lose HCN to form pyrazoles; thus CHPh:CH·CN and CH_2N_2 ultimately yield 4-phenylpyrazole, m.p. 230°. Treatment of the crude product with Br leads to 3(5)-*cyano-4-phenylpyrazole*, m.p. 149·5—150°, hydrolysed to 4-phenylpyrazole-3(5)-carboxylic acid, m.p. 248—249°. H. W.

Addition of diazomethane to acetylenecarboxylic esters. K. VON AUWERS and O. UNGEMACH (Ber., 1933, 66, [*B*], 1205—1210).—Addition of CH_2N_2 to Me phenylpropiolate in Et_2O gives a mixture of Me 4-phenylpyrazole-3(5)-carboxylate, m.p. 184—187° (corresponding acid, m.p. 233—234°, whence 4-phenylpyrazole, m.p. 230·5—231°), and *Me* 3(5)-*phenylpyrazole*-4-*carboxylate* (I), m.p. 110—111·5° (corresponding acid, m.p. 252—253·5°, whence 3(5)-phenylpyrazole, m.p. 75—77°). Et 3(5)-phenylpyrazole-4-carboxylate, m.p. 85—86°, is converted by boiling $ClCO_2Et$ into *Et_2 3-phenylpyrazole*-1 : 4-*dicarboxylate*, m.p. 57·5—58·5°, and by PhNCO into 4-*carbethoxy*-3-*phenylpyrazole*-1-*carboxyanilide*, m.p. 136—137°. Et tetrolate and CH_2N_2 yield Et 4-methylpyrazole-3(5)-carboxylate, m.p. 156·5—157·5° (corresponding acid, m.p. 217°, whence a methylpyrazole which decolorises only a trace of Br in AcOH and hence is an almost homogeneous 4-derivative), and Et 1 : 4-dimethylpyrazole-5-carboxylate containing a small proportion of Et 1 : 4-dimethylpyrazole-3-carboxylate. The behaviour of Et 4-methylpyrazole-3(5)-carboxylate towards Me_2SO_4 and NaOH is described.

With olefinic and acetylenic carboxylic esters addition of CH_2N_2 occurs to esters $CHR{:}C^*H{\cdot}CO_2Et$ in such a manner that N becomes attached to the C* when R is alkyl or aryl. With esters $CR{:}C^*{\cdot}CO_2R'$ this rule applies only when R=alkyl, whereas when R=aryl addition of N can occur at both C atoms.
H. W.

Homodeoxyveronal [diethylmalonethylenediamide] and its homologues. A. W. DOX (J. Amer. Chem. Soc., 1933, 55, 3871—3873).—$CR_2(CO_2Et)_2$, $({\cdot}CH_2{\cdot}NH_2)_2$, and EtOH–NaOEt at 100—110° give dialkylmalonethylenediamides,  $CR_2<\begin{matrix}CO{\cdot}NH{\cdot}CH_2\\CO{\cdot}NH{\cdot}CH_2\end{matrix}$; the *diethyl*-, m.p. 306°, *dibutyl*-, m.p. 290°, and *hexylmethyl*-, m.p. 188°, -derivatives are described. The properties of *ethyl*-, m.p. 350—355° (decomp.), *propyl*-, m.p. 242—245° (decomp.), and sec.-*butyl*-, m.p. 335—340° (decomp.), -*malonethylenediamides*, prepared similarly from $CHR(CO_2Et)_2$, suggest the structure  $CHR<\begin{matrix}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO\\CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO\end{matrix}>CHR$ for these derivatives. Malonethylenediamide (homodeoxybarbituric acid), m.p. 280° (decomp.), obtained when $CH_2(CO_2Et)_2$ is heated with $({\cdot}CH_2{\cdot}NH_2)_2$, dissolves in H_2O to a colloidal solution. The above compounds possess no hypnotic activity. H. B.

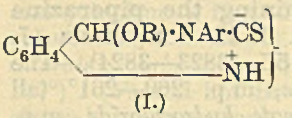
Nitration of phenobarbital [5-phenyl-5-ethylbarbituric acid]. M. M. RISING and A. PIERCE (J. Amer. Chem. Soc., 1933, 55, 3895—3896; cf. this vol., 958).—Nitration of 5-phenyl-5-ethylbarbituric acid gives 5-*m*-nitrophenyl-5-ethylbarbituric acid, m.p. 279—280° (corr.), oxidisable to $m\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2H$. H. B.

Local anæsthetics containing the piperazine ring. J. H. GARDNER and J. H. SCHNEIDER (J. Amer. Chem. Soc., 1933, 55, 3823—3824).—The *phenylcarbamate hydrochloride*, m.p. 260—261° (all m.p. are corr.), and *cinnamate hydrochloride*, m.p. 261—262°, of 1 : 4-di-β-hydroxyethylpiperazine and the *phenylcarbamate hydrochloride*, m.p. 250—251°, *benzoate hydrochloride*, m.p. 251—252°, and *cinnamate hydrochloride*, m.p. 254—255°, of 1 : 4-*di*-γ-*hydroxypropylpiperazine*, m.p. 142—143° [prepared from piperazine and $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ by Pyman's method (J.C.S., 1908, 93, 1802)], all possess local anæsthetic activity; they give highly acid solutions. H. B.

Pyrimidines. CXXXV. Uracil glycol. T. B. JOHNSON and E. DYER. **CXXXVI. Mechanism of formation of tetrahydropyrimidines by the Biginelli reaction.** K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1933, 55, 3781—3783, 3784—3791).—CXXXV. Et uracil-5-carboxylate and Br–H_2O give *Et* 5-*bromo*-6-*hydroxyhydrouracil*-5-*carboxylate*, m.p. 178° (corr.; decomp.), converted by Ag_2CO_3 in H_2O into *Et* 5 : 6-*dihydroxyhydrouracil*-5-*carboxylate* (+H_2O), softens at 72°, melts partly at 110°, and decomp. 125°, m.p. (anhyd.) 135—136° (corr.; decomp.) [*monoacetate*, m.p. 178° (corr.; decomp.)]. This is hydrolysed (under the mildest conditions) to *iso*barbituric acid (I), which is also formed in other processes designed to give uracil glycol (5 : 6-dihydroxyhydrouracil) (II). The instability of (II) is in marked contrast to the comparative stability of its 5-Me derivative (thymine glycol). Attempted addition of HOBr to uracil-5-carboxylic acid gives 5 : 5-dibromo-6-hydroxyuracil. (I) is produced during reduction (H_2, PtO_2) of *iso*dialuric acid (in EtOH) and diacetyl*iso*dialuric acid (in AcOH) [in Ac_2O–AcOH, the Ac derivative of (I) results]. Uracil is not attacked by AcO_2H.

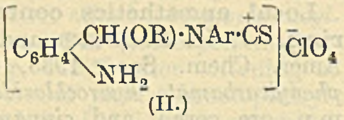
CXXXVI. Condensation of $CO(NH_2)_2$, PhCHO, and $CH_2Ac{\cdot}CO_2Et$ to Et 2-keto-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (III) (Biginelli, A., 1893, i, 645) is catalysed by I, conc. HCl, or conc. H_2SO_4, and the yield of (III) is proportional to the amount of catalyst used. Reaction proceeds through the intermediate $CHPh(NH{\cdot}CO{\cdot}NH_2)_2$ or $NH_2{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et$ (IV), which then reacts with $CH_2Ac{\cdot}CO_2Et$ or PhCHO to give (III). (IV) is also hydrolysed to $CO(NH_2)_2$ and $CH_2Ac{\cdot}CO_2Et$ under the conditions used. It is improbable that $CHPh{:}CAc{\cdot}CO_2Et$ is an intermediate. The isomerides (A., 1932, 1144) obtained from citral (V) are both reduced (H_2, Pt, AcOH) to *Et* 2-*keto*-6-*methyl*-4-βε-*dimethylheptyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate*, m.p. 131—134°; the (V) used contained at least two isomerides. H. B.

Ionic dissociation of 2-thion-1 : 2 : 3 : 4-tetrahydroquinazolines. C. V. GHEORGHIU (Compt. rend., 1933, 197, 622—624).—The colourless 4-hydroxy(or ethoxy)-3-aryl-2-thion-1 : 2 : 3 : 4-tetrahydroquinazolines (A., 1931, 842) give violet to red solutions, insensitive to O_2, in warm C_6H_6, PhMe, xylene, and C_5H_5N, the depth of colour varying with temp. and concn. The solids become red near their m.p. and give intensely red solutions in acids. These phenomena are attributed to ionic dissociation (I) and carbonium salt formation (II) (cf. A., 1926, 1163). In alcohols and ketones (except COPhMe) colourless solutions are formed, probably owing to addition of the solvent. H. A. P.



$$C_6H_4\left<\begin{matrix}CH(OR)\cdot NAr\cdot\overset{-}{C}S\\ \overset{+}{N}H\end{matrix}\right.$$

(I.)

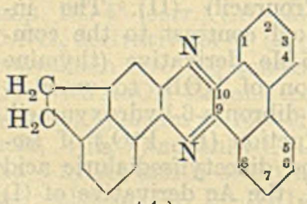


$$\left[C_6H_4\left<\begin{matrix}CH(OR)\cdot NAr\cdot\overset{+}{C}S\\ NH_2\end{matrix}\right.\right]\overset{-}{Cl}O_4$$

(II.)

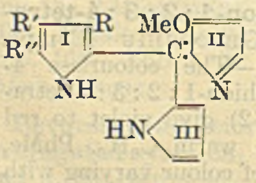
Benzo- and naphtho-pyrazolyl-*o*-benzoic acids. A. Corbellini and A. Cecchi (Gazzetta, 1933, 63, 489—494).—*o*-(2′-Aminobenzoyl)benzoic acid (*Et* ester, m.p. 71—72°) on diazotisation and $SnCl_2$ reduction condenses to o-3-*indazolylbenzoic acid*, m.p. 184—186·5°. o-(2-*Amino*-3-*naphthoyl*)*benzoic acid*, m.p. 279—279·5° (uncorr.), prepared by hydrolysis of its *lactam*, m.p. 277·5° (uncorr.), which is derived by the action of $AlCl_3$ on β-naphthylphthalimide, is similarly converted into o-(3-ββ-*naphthindazolyl*)*benzoic acid*, m.p. 238—238·5°, not identical with the product, m.p. 269—271°, from 2 : 2′-diamino-1 : 1′-dinaphthyl (A., 1932, 524). E. W. W.

Dye derived from phenanthraquinone; acenaphthenophenanthrazines. P. C. Dutta (Ber., 1933, 66, [*B*], 1220—1223).—The following *acenaphthenophenanthrazines* (cf. *A*) are obtained by condensation of phenanthraquinone derivatives with 4 : 5-diaminoacenaphthene, generally in boiling AcOH or EtOH; -2-*nitro*-, m.p. 274°; -4-*nitro*-, m.p. 257—258°; -2 : 7-*dinitro*-, m.p. > 310°; -4 : 5-*dinitro*-, m.p. > 300°; -2 : 7-*diamino*-, m.p. >300°; -4 : 5-*diamino*-, m.p. >300°; -2-*amino*-, m.p. 269—270°; -4-*amino*-, m.p. 204°; -2 : 7-*dihydroxy*-, m.p. > 300°; -2-*hydroxy*-, m.p. > 300°; -4-*hydroxy*-, m.p. > 300°; -2-*bromo*-, m.p. 273°; -dibromo-, m.p. > 300°; -*dibromonitro*-, m.p. 272°; -*bromodinitro*-, m.p. > 300°. The dyes are lighter than fluorenophenanthrazines (A., 1932, 1043), but darker than the corresponding phenanthraphenazines and phenanthranaphthazines (this vol., 167). H. W.



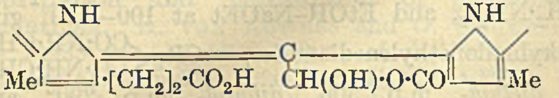
(*A*.)

Prodigiosin, the red pigment of *Bacillus prodigiosus*. IV. F. Wrede and A. Rothhaas (Z. physiol. Chem., 1933, 219, 267—274; cf. this vol., 516).—On catalytic hydrogenation (Pd–C in AcOH) prodigiosin (I) takes up 14 H. Alkaline $KMnO_4$ oxidation of the product gave oxamic acid (II) and an *oil*, $C_{11\,(or\ 12)}H_{20\,(or\ 22)}O_4$, b.p. 125°/1 mm. Acid $KMnO_4$ oxidation yielded the pyrrolidine $C_{10}H_{21}N$ (from ring I) (II), succinic acid (III), and a substance resembling proline, not containing OMe, and therefore not derived from ring II. (III) is readily obtained from pyrrolidine, therefore ring III is an unsubstituted pyrrole. αββ′-Triethylpyrrolidine (*chloroaurate*, an oil; *chloroplatinate*, m.p. 206°, decomp. 224°) differs from the corresponding (I) product (*chloroaurate*, m.p. 105°; chloroplatinate, m.p. 212°), hence ring I is not a 2 : 3 : 4-triethylpyrrole (cf. Raudnitz, this vol., 958). The probable constitution of (I) is as annexed, where R+R′+R″=C_6H_{15}. The position of MeO in ring II is not yet decided. J. H. B.



Tetrazine. D. Wood, jun., and F. W. Bergstrom (J. Amer. Chem. Soc., 1933, 55, 3648—3652).—Tetrazine (I) reduces aq. $AgNO_3$, $HgCl_2$, $AuCl_3$, or H_2PtCl_6 sometimes to the metal; salts (cf. Müller, A., 1915, i, 509) or additive compounds of (I) are not produced. (I) can be recovered from its solution in liquid NH_3 provided this is kept at $\ngtr -40°$; above this temp. decomp. occurs. (I) and KNH_2 in liquid NH_3 at −40° give a red *salt*, $K_2C_2N_4$ (?), which explodes violently when exposed to MeI vapour and from which (I) is regenerated by treatment with NH_4Br. Traces of dihydrotetrazine are formed from NH:CH·OEt,HCl and N_2H_4,H_2O in aq. KOH or N_2H_4 in liquid NH_3. H. B.

Chlorophyll. XXXIV. Chemistry of the chloroporphyrins. Chloroporphyrin e_7 lactone, phæoporphyrin a_7, and their decarboxylation to hydroxymethylrhodoporphyrin lactone and chloroporphyrin e_5. H. Fischer, J. Heckmaier, and W. Hagert (Annalen, 1933, 505, 209—237; cf. this vol., 959).—Chloroporphyrin e_5 (I) is formed in good yield by decarboxylation of phæoporphyrin a_7 (II) with 60% H_2SO_4 at 100°. Its Me_2 ester (III) (CH_2N_2 in Et_2O) readily gives an *oxime*, also obtained from the Me ester (IV) and NH_2OH, and subsequent treatment with CH_2N_2; it also shows evidence of reaction with N_2H_4, but not $NH_2\cdot CS\cdot NH\cdot NH_2$. The Me_2 ester (V) (MeOH–HCl) does not react with ketonic reagents. Esterification of (IV) with CH_2N_2 in MeOH gives (V) [not (II)], and its Bz derivative is unaffected by CH_2N_2. (I) is decarboxylated by heating with Ph_2 and 60% H_2SO_4 to rhodoporphyrin; in AcOH or C_5H_5N there is little or no change. The following lactone formula is therefore assigned to (I), (IV), and (V), the ester (II) having the corresponding open-chain formula.



Chloroporphyrin e_7 lactone (VI) [*Me* ester, m.p. 285° (CH_2N_2 or MeOH–HCl)], previously obtained by oxidation of chloroporphyrin e_6 (VII) with $K_3Fe(CN)_6$ and considered to be an isomeride of (II) (cf. this vol., 724), is obtained from (VII) in 90% yield by action of I in AcOH. It gives (II) with O_2 in C_5H_5N, and a little of the Me ester of (II) is formed by long boiling with MeOH and HCl. Decarboxylation by 60% H_2SO_4 gives *hydroxymethylrhodoporphyrin lactone* (*Me* ester, m.p. 254°) [(I): CH_2 in place of CH·OH], reduced by HI to chloroporphyrin e_4 (VII), and readily oxidised to (I). (VI) is only slightly attacked by HI.

(VII) is formed in quant. yield by heating chloroporphyrin e_6 Me_3 ester with AcOH; with HCO_2H some phæoporphyrin a_5 is also formed. The reverse change is brought about by CH_2N_2 in MeOH. The change of (VII) into (I) is effected by O_2 in KOH–

MeOH or quantitatively by the action of I in AcOH on the Me_2 ester. Interaction of rhodoporphyrin Me_2 ester with MgMeI gives the corresponding *carbinol*, $C_{35}H_{42}O_3N_4$, m.p. 294°. The corresponding tert.-*alcohol*, $C_{36}H_{44}O_3N_4$, m.p. 324° (block), is similarly prepared from the Me_2 ester of (VII). Decarboxylation of chlorin *e* at 100°/high vac. gives a residue that with HI gives (VII) and phylloporphyrin, indicating partial removal of the 6-CO_2H in addition to the $\cdot CH_2\cdot CO_2H$ residue. Chlorin e_4 absorbs 0·5H_2O on keeping in air. H. A. P.

Chlorophyll. XXXVI. Verdoporphyrin and degradation of chlorophyll by alkali. A. Treibs and F. Herrlein. **XXXVII. Chlorophyll *b*. III. Proof of the isocyclic ring in chlorophyll *b*.** H. Fischer, A. Hendschel, and L. Nüssler (Annalen, 1933, **506**, 1—19, 83—106).—XXXVI. Reduction (H_2, PtO_2, Et_2O) of verdoporphyrin (I), probably $C_{32}H_{32}O_4N_4$ (cf. A., 1929, 941) (prep. from phæophytin and MeOH–KOH described) [K_2 salt; *dihydrochloride*; *diacetate*; *Me* ester; Me_2 ester, m.p. 280° (corr.) (*hæmin*, sinters at 261°), which has two active H atoms (Zerevitinov)], and oxidation (air) of the resulting leuco-compound gives rhodoporphyrin (II). ψ-Verdoporphyrin (III) (A., 1931, 1431) [Me_2 ester, probably $C_{34}H_{36}O_4N_4$, m.p. 276° (corr.)] is often obtained instead of (I) in the above prep.; in two cases, (I) and the unstable allo*porphyrin* (IV), $C_{33}H_{34}O_5N_4$ (?) [Me_2 ester (V), m.p. 269° (corr.)], were isolated. (IV) when heated with C_5H_5N or alkali gives (II). (V) passes gradually into chloroporphyrin e_5. The spontaneous rearrangement of (I) into (II) is not an isomerisation (cf. *loc. cit.*) but a reduction process; (I) often rearranges into (III). (I), (II), and pyrro- and phyllo-porphyrins have been isolated from the products of the alkaline degradation of methylchlorophyllide. Structures are suggested for (I) and chlorin *e*.

XXXVII. Phæophorbide *b* (I) and CH_2N_2 in MeOH–C_5H_5N and N_2 or O_2 give rhodin *g* Me_3 ester (II) (about 50%) and some *chlorin* ester (III), m.p. 191° (contains 3 OMe groups). (III) is also formed to some extent from rhodin *g* (which could not be decarboxylated in C_5H_5N) and MeOH–CH_2N_2. (III) is hydrolysed (22% HCl) to a *chlorin* (IV), $C_{36}H_{38}O_8N_4$, m.p. 209°, which contains 1 OMe and is degraded by boiling $(\cdot CH_2\cdot OH)_2$ to a product resembling chloroporphyrin e_4. Fusion of the Fe salt of (IV) with *m*-$C_6H_4(OH)_2$ gives a substance resembling chloroporphyrin e_6 (V), whilst reduction (HI–AcOH at 60°) of (III) affords a porphyrin, the *Me* ester, $C_{37}H_{42}O_7N_4$, m.p. 240°, of which is spectroscopically identical with (V). (I) and EtOH–diazoethane in N_2 give about 70% of *rhodin* g *Et_3* ester (+$COMe_2$), m.p. 223°. Phæoporphyrin b_6 (VI) [oxime (+H_2O) (*Me* ester, m.p. 229°, by the action of CH_2N_2); *oxime*, m.p. 230°, of Me ester, m.p. 256° (this vol., 839; prepared using MeOH–HCl); *Me* ester, m.p. 277°, using Et_2O–CH_2N_2] and MeOH–CH_2N_2 in N_2 for 24 hr. afford a *porphyrin*, $C_{36}H_{36}O_{6(7)}N_4$, m.p. 273° [also formed by the reduction of the cyanohydrin of (I) with HI (*d* 1·96) at 45°], which is spectroscopically identical with phæoporphyrin a_5; the use of conc. Et_2O–MeOH–CH_2N_2 for 5 days gives a porphyrin, m.p. 237°, spectroscopically identical with (V). (VI) and MeOH–KOH in N_2 afford [after esterification (CH_2N_2)] *rhodinporphyrin* g_7 *Me_3* ester (VII), $C_{37}H_{40}O_7N_4$, m.p. 265° (*oxime*, m.p. 277°), also formed by mild reduction (HI–AcOH at 55°) of (II). Successive treatment of (VI) with HBr–AcOH and MeOH–HCl gives a *Me* ester, $C_{36}H_{38}O_6N_4$, m.p. 259°. The *oxime* of phæoporphyrin b_5 ester has m.p. 230°. The conversion of (VII) into (VI) (as ester, m.p. 277°) by C_5H_5N–Na_2CO_3 and the formation of (II) from (I) show definitely that chlorophyll *b* contains the isocyclic ring (cf. Stoll and Wiedemann, A., 1932, 1266). H. B.

Chemistry of chlorophyll. K. F. Armstrong (Chem. and Ind., 1933, 809—816).—A review.

Fluorescence of the porphyrins. II. H. Fink and W. Hoerburger (Z. physiol. Chem., 1933, **220**, 123—136; cf. this vol., 959).—$p_{\rm H}$–Fluorescence curves were determined for ætioporphyrin I, eight mono- and ten di-carboxylic acids derived from the ætioporphyrins. It is concluded that the porphyrins exist as ampholytes in aq. solution. The fluorescence is due chiefly to dissociated pigment. J. H. B.

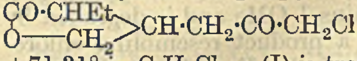
Calorimetric determinations with polynuclear pyrrole derivatives. I. Experimental data for porphyrins, chlorins, phæophorbides, and purpurins. A. Stern and G. Klebs (Annalen, 1933, **505**, 295—306).—Determination of the heat of combustion is a valuable adjunct to elementary analysis in the chlorophyll series, as it indicates the stage of oxidation. The following vals. of Q_v (in kg.-cal.) are recorded: ætioporphyrin I and II, 4304·0, 4310·2; octaethylporphyrin, 4915·0; γ-phylloporphyrin Me ester, 4314·4; pyrroporphyrin XV Me ester, 4150·0; rhodoporphyrin XV and XXI Me_2 esters, 4373·2, 4371·5; verdoporphyrin Me_2 ester, 4283·2, 4298·4; protoporphyrin, 4238·7 (Me_2 ester, 4561·4); mesoporphyrin IX Me_2 ester, 4623·6; coproporphyrin Me_4 ester, 4987·5; *iso*uroporphyrin Me_8 ester, 5741·6; chlorin e_6 Me_3 ester, 4693·3, e_4 Me_2 ester, 4513·0; chloroporphyrin e_6 Me_2 ester, 4684·3, e_5 Me_2 ester, 4411·7 (CH_2N_2), 4486·6 (MeOH–HCl), e_4 *Me_2* ester, 4506·3; chlorin p_6 Me_3 ester, 4461·3; methylphæophorbide *a*, 4524·5; phæoporphyrin a_5 Me_2 ester, 4579·6; pyrrophæophorbide *a* Me ester, 4342·0; phylloerythrin Me ester, 4343·7; deoxophylloerythrin Me ester, 4455·7; methylphæophorbide *b*, 4415·4; dimethylphæopurpurin-7, 4601·0; and phæopurpurin-18 Me ester, 4197·5. H. A. P.

Blue sodium salt of rhodamine-*B* and related substances. W. R. Brown and F. A. Mason (J.C.S., 1933, 1264—1269).—Attempted alkylation or acylation of the blue Na_2 salt of rhodamine-*B* (I) [the salt could only be obtained by Wacker's method (Z. Farbenind., 1907, 201)] resulted in the immediate regeneration of (I). Blue alkali salts could not be prepared from other rhodamines. 4′-Diethylamino-2′-hydroxy-*o*-benzoylbenzoic acid (II) (improved prep. given) [*Me* ester, m.p. 124°; the Me ether could not be prepared either by direct alkylation or from *m*-$NEt_2\cdot C_6H_4\cdot OMe$ (III), *o*-$C_6H_4(CO)_2O$, and $AlCl_3$] condenses with $NPhMe_2$, $NPhEt_2$ (III), m-*ethoxydiethylaniline* (IV), b.p. 148°/15 mm. (from *m*-$NEt_2\cdot C_6H_4\cdot OH$ and *p*-$C_6H_4Me\cdot SO_3Et$ in aq. NaOH), and benzylethylanilinesulphonic acid in presence of $POCl_3$ and C_6H_6 or PhMe to give pairs of P-containing substances; one type dissolves in alkali to a green solution, whilst the other gives a violet solution. Acidification of the alkaline solutions of the products from (III) and (IV) gives (I). Condensation of (II) and $NPhEt_2$, $NPhMe_2$, and α-$C_{10}H_7{\cdot}NMe_2$ with Ac_2O affords 4′ : 4″-*tetraethyldiamino-*, m.p. 136—137°, and 4″-*dimethylamino-*4′-*diethylamino-*, m.p. 130—131°, -2′-*acetoxydiphenylphthalides* and 4″-*dimethylamino-*4′-*diethylamino-*2′-*acetoxyphenyl-α-naphthylphthalide*, m.p. 122—123°, respectively; these are hydrolysed (cold EtOH–KOH) to the 2′-OH-derivatives, which are stable and act as indicators of the *ortho*phthalein type. 4′ : 4″-*Tetraethyldiamino-*2′-*acetoxy-*2″-*methoxy-*, m.p. 176—177°, and -2″-*ethoxy-*, m.p. 206—208°, -*diphenylphthalides*, similarly prepared from (II) and (III) and (IV), respectively, are deacetylated and dealkylated by warm EtOH–KOH with the formation of the rhodamine; with cold dil. MeOH–$Ba(OH)_2$, a purple solution is formed (this changes slowly at room temp. and rapidly on warming, to the typical rhodamine red solution). The last observation suggests that von Baeyer's formula for the above blue salt is correct. (II) could not be condensed with *N*-ethylcarbazole, *m*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$, NHPhAc, *o*-$C_6H_4Me{\cdot}NHEt$, and *o*-$C_6H_4Me{\cdot}NEt_2$. H. B.

Azine dyes derived from α- and β-naphthathiofuran-1 : 2-diones. P. C. DUTTA (Ber., 1933, **66**, [*B*], 1223—1226).—The following *dyes* are prepared by the condensation of α- and β-naphthathiofuran-1 : 2-diones with various *o*-diamines: β-, m.p. 205°, and α-, m.p. 226°, -*naphthathiofuranophenazine*; β-, m.p. 247° after softening at 226°, and α-, m.p. 237°, -*naphthathiofuranonaphthazine*; β-, m.p. 248°, and α-, m.p. 272°, -*naphthathiofuranoacenaphthazine*; β-, m.p. 271°, and α-, m.p. 266°, -*naphthathiofurano*-6-*chloro*-1-*methylphenazine*; β-, m.p. > 295°, and α-, m.p. > 295°, -*naphthathiofuranoquinoxalineazine*; β-, m.p. > 295°, and α-, m.p. > 295°, -*naphthathiofuranophenazineazine*. The size of the mol. has little influence on the depth of colour of these compounds, which is greatly intensified by the introduction of chromophores. The tinctorial properties of the α- are less marked than those of the β-compounds. Although auxochromic groups are absent, they dye wool from an acid bath. H. W.

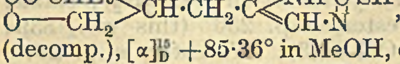
Alkyl derivatives of mono-substituted thiazolidones. I. F. B. DAINS and F. EBERLY (J. Amer. Chem. Soc., 1933, **55**, 3859—3862).—*N*-Chloroacet-*p*-bromoanilide (from *p*-$C_6H_4Br{\cdot}NH_2$ and $CH_2Cl{\cdot}COCl$ in $COMe_2$–C_5H_5N) and KCNS in EtOH give 2-p-*bromoanilino-4-thiazolidone* (I), m.p. 224° (5-*benzylidene* derivative, m.p. > 310°), the Na salt of which with EtI in EtOH affords a mixture of 2-p-*bromoanilo-3-ethyl-4-thiazolidone* (II), m.p. 91° [5-*benzylidene* derivative, hydrolysed (acid) to *p*-$C_6H_4Br{\cdot}NH_2$ and 2 : 4-*diketo-5-benzylidene-3-ethyltetrahydrothiazole*, m.p. 95·5°], and 2-N-*ethyl*-p-*bromoanilino-4-thiazolidone* (III), m.p. 121° [5-*benzylidene* derivative, m.p. 225°, hydrolysed to 2 : 4-diketo-5-benzylidenetetrahydrothiazole (IV); 5-o-*chlorobenzylidene* derivative, m.p. 192°, hydrolysed to 2 : 4-*diketo-5-o-chlorobenzylidenetetrahydrothiazole*, m.p. 172°]. (II) is hydrolysed (H_2SO_4) to *p*-$C_6H_4Br{\cdot}NH_2$ and NH_2Et and is synthesised from *p*-$C_6H_4Br{\cdot}NH{\cdot}CS{\cdot}NHEt$ and $CH_2Cl{\cdot}COCl$ in $COMe_2$–C_5H_5N. (III) is hydrolysed by 50% H_2SO_4 to *p*-$C_6H_4Br{\cdot}NHEt$ (V) (N-*Bz*, m.p. 88°, and *phenylcarbamyl*, m.p. 108°, derivatives), and by 20% NaOH to p-*bromophenylethylcyanamide*, *p*-$C_6H_4Br{\cdot}NEt{\cdot}CN$, m.p. 78°, which is prepared from (V), Br, and KCN. The Na salt of (I) and MeI or Me_2SO_4 give 2-p-*bromoanilo-3-methyl-4-thiazolidone*, m.p. 111° (5-*benzylidene* derivative, m.p. 166°, hydrolysed to 2 : 4-*diketo-5-benzylidene-3-methyltetrahydrothiazole*, m.p. 133°), and 2-N-*methyl*-p-*bromoanilino-4-thiazolidone*, m.p. 197° [5-*benzylidene* derivative, m.p. 256°, hydrolysed to (IV)]; the latter is hydrolysed (50% H_2SO_4) to *p*-$C_6H_4Br{\cdot}NHMe$ (N-*Bz*, m.p. 77°, and *phenylcarbamyl* derivative, m.p. 137°). The Na salt of (I) and CH_2PhCl give only 2-N-*benzyl*-p-*bromoanilino-4-thiazolidone*, m.p. 153° (5-*benzylidene* derivative, m.p. 192°), which is hydrolysed to N-*benzyl*-p-*bromoaniline*, m.p. 55° (also prepared from *p*-$C_6H_4Br{\cdot}NH_2$ and CH_2PhCl). 2-N-*Benzyl*-p-*chloroanilino-4-thiazolidone*, m.p. 129°, is similarly obtained from 2-*p*-chloroanilino-4-thiazolidone. The N-*chloroacetyl* derivative, m.p. 184°, of dibromo-*p*-toluidine and KCNS afford 2-(*dibromo*-p-*toluidino*)-4-*thiazolidone*, m.p. 250°, the Na salt of which with MeI gives approx. equal amounts of 2-(*dibromo*-p-*tolylimino*)-3-*methyl*-4-*thiazolidone*, m.p. 132°, and 2-(N-*methyldibromo*-p-*toluidino*)-4-*thiazolidone*, m.p. 194°. The thiazolidones studied correspond with the stable 2-arylamino-derivatives of Wheeler and Johnson (A., 1902, i, 758). The results of the alkylations disprove the formulation of Beckurts and Frerich (A., 1916, i, 744). H. B.

Structure and synthesis of *iso*pilocarpine. II. N. A. PREOBRASHENSKI, A. F. VOMPE, and V. A. PREOBRASHENSKI (Ber., 1933, **66**, [*B*], 1187—1193).—*d*-Homo*iso*pilopic acid, b.p. 160·8°/0·01 mm., $[\alpha]_D^{15}$ +50·98°, is converted by $SOCl_2$ at 50—60° into the corresponding chloride, which, by successive action of CH_2N_2 and HCl in Et_2O, is transformed into d-*chloromethyl homo*iso*pilopyl ketone* (I),



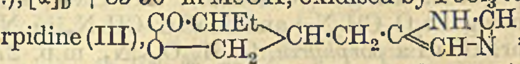
$\begin{array}{l}\mathrm{CO{\cdot}CHEt}\\ \mathrm{O{-}{-}{-}CH_2}\end{array}\!\!>\mathrm{CH{\cdot}CH_2{\cdot}CO{\cdot}CH_2Cl}$

, m.p. 72·5—73·5°, $[\alpha]_D^{16·75}$ +71·31° in $C_2H_2Cl_4$. (I) is transformed by K phthalimide in boiling EtOH into d-*phthalimidomethyl homo*iso*pilopyl ketone*, m.p. 121·5—122·5°, $[\alpha]_D^{16}$ +36·87° in $C_2H_2Cl_4$, hydrolysed by boiling 20% HCl to d-*aminomethyl homo*iso*pilopyl ketone hydrochloride* (II), m.p. 158—160°, $[\alpha]_D^{12·5}$ +57·58° in H_2O. (II) and KCNS in H_2O yield 2-*thiol*-4(5)-d-*homo*iso*pilopyliminazole* (*thiol*iso*pilocarpidine*),



$\begin{array}{l}\mathrm{CO{\cdot}CHEt}\\ \mathrm{O{-}{-}{-}CH_2}\end{array}\!\!>\mathrm{CH{\cdot}CH_2{\cdot}C}\!<\!\!\begin{array}{l}\mathrm{NH{\cdot}C{\cdot}SH}\\ \mathrm{CH{\cdot}N}\end{array}$

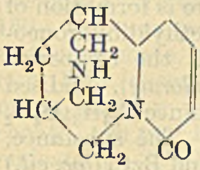
, m.p. 206·5—208° (decomp.), $[\alpha]_D^{15}$ +85·36° in MeOH, oxidised by $FeCl_3$ to *iso*pilocarpidine (III),



$\begin{array}{l}\mathrm{CO{\cdot}CHEt}\\ \mathrm{O{-}{-}{-}CH_2}\end{array}\!\!>\mathrm{CH{\cdot}CH_2{\cdot}C}\!<\!\!\begin{array}{l}\mathrm{NH{\cdot}CH}\\ \mathrm{CH{-}N}\end{array}$

, isolated as the nitrate, m.p. 112—113·5° (decomp.), $[\alpha]_D^{17}$ +27·63° in H_2O, identical with that obtained by Späth *et al.* (A., 1925, i, 575) from the natural alkaloid. Methylation of (III) leads to *iso*pilocarpine (nitrate, m.p. 158—158·5°, $[\alpha]_D^{14}$ +55·62° in H_2O). H. W.

Constitution of cytisine. E. Späth and F. Galinovsky (Ber., 1933, 66, [*B*], 1338—1344; cf. A., 1932, 1146; Ing, this vol., 77).—Cytisine (I) is converted by successive electrolytic reduction and acetylation into N-*acetyltetrahydrodeoxycytisine*, m.p. 70—71°, transformed by MeI at 100° into the *methiodide*, m.p. 249—250° (vac.; decomp.). The corresponding quaternary base is subjected to the Hofmann degradation and the product is reduced; repetition of the degradation and reduction followed by a further degradation leads to NMe_3 and a product reduced to 1-*acetyl*-3-*methyl*-5-n-*amylpiperidine* (II). (II) is hydrolysed by fuming HCl at 150° and the product is dehydrogenated (Pd sponge at 180—190°) to 3-*methyl*-5-n-*amylpyridine* (III) (*picrate*, m.p. 145°). Oxidation of (III) with $KMnO_4$ gives 3-methylpyridine-5-carboxylic acid, m.p. 214—216°, with a small amount of pyridine-3 : 5-dicarboxylic acid, m.p. < 300° (decomp.). The *sec.* N of (I) is therefore present in a piperidine ring. Since oxidation of (I) does not afford methylsuccinic or α-methylglutaric acid, whereas in defined circumstances $(\cdot CH_2\cdot CO_2H)_2$ is produced, (I) is regarded as (*A*). H. W.

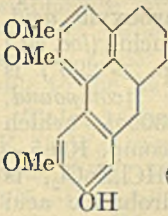


(*A*.)

Hydroxy- and amino-esters of yohimbic acid. D. E. Worrall (J. Amer. Chem. Soc., 1933, 55, 3715—3718).—β-*Chloroethyl* (I), m.p. 119—120°, β-*hydroxyethyl*, m.p. 132—135° [O-*sulphate* (II), m.p. 288—289°], γ-*hydroxypropyl*, m.p. 135—138° (*methiodide*), and βγ-*dihydroxypropyl*, m.p. 111—112° (*methiodide*), *yohimbates*, prepared from yohimbic acid (III), the appropriate alcohol, and HCl, are derivatives of the hydrated form of (III); they lose 1 H_2O (in vac. over P_2O_5) which is regained on exposure to air. (II) is hydrolysed (dil. alkali) to the unsaturated β-*hydroxyethyl* apo*yohimbate*, $C_{22}H_{28}O_4N_2$, m.p. 117—118° (*hydrochloride*, m.p. 292—294°). (I) and the appropriate amine give β-*diethylaminoethyl*, m.p. 76—78° (IV) [*dimethiodide*, m.p. 217—218°; *dihydrochloride*, m.p. 198—200° (decomp.)], β-*allylaminoethyl*, m.p. 124—126° [*methiodide*; *dihydrochloride*, m.p. 263—264° (decomp.)], and β-*piperidinoethyl*, m.p. 129—131° [*dimethiodide*, m.p. 218—219°; *dihydrochloride*, m.p. 212—214° (decomp.)], *yohimbates*. Hydrolysis (2% EtOH–KOH) of the product from (IV) and conc. H_2SO_4 gives β-*diethylaminoethyl* apo*yohimbate*, m.p. 80—82° (*dimethiodide*, m.p. 179—180°). H. B.

Structure of cuscohygrine. Synthesis of ethyl homohygrinate. W. E. Sohl and R. L. Shriner (J. Amer. Chem. Soc., 1933, 55, 3828—3833).—1-Methylpyrrole, $CHN_2\cdot CO_2Et$, and Cu-bronze give Et 1-methyl-2-pyrrylacetate, b.p. 115—118°/10 mm., which is reduced (H_2, PtO_2, EtOH–AcOH) to *Et 1-methyl-2-pyrrolidylacetate*, b.p. 88—89°/10 mm., 78°/6 mm. [*picrate*, m.p. 112—113°; *methiodide*, m.p. 121—122°; *chloroaurate* (+$2H_2O$), m.p. 133—134°]. The latter is identical with Et homohygrinate prepared by esterification (EtOH–HCl) of the acid obtained from cuscohygrine (I), NO, and EtOH–NaOEt using Hess and Fink's method (A., 1920, i, 497). The methylenedi*iso*nitroamine isolated by Hess and Fink (*loc. cit.*) does not arise from (I) but from the EtOH. (I) and Br in Ac_2O–AcOH give a *compound*, $C_{13}H_{25}ON_2Br_3$, converted by $COMe_2$ into the dihydrobromide, m.p. 239° (decomp.), of (I). (I) does not give the CHI_3 reaction (*Me β-diethylaminoethyl ketone*, b.p. 84°/30 mm., 53°/4 mm., from $NHEt_2$,HCl, aq. CH_2O, and $COMe_2$, gives CHI_3 with NaOI), and does not condense with PhCHO, indicating that it is di-(1-methyl-2-pyrrolidylmethyl) ketone (Liebermann and Cybulski, A., 1895, i, 310) and not Me di-(1-methyl-2-pyrrolidyl)methyl ketone (Hess). H. B.

***N*-Methyl-laurotetanine, a new alkaloid from *Litsea citrata*.** E. Späth and E. E. Suominen (Ber., 1933, 66, [*B*], 1344—1348).—The crude bases obtained by extraction of the powdered bark of *Litsea citrata*, Bl., with NH_3–Et_2O are treated with Ac_2O, thus leading to separation of the *sec.* and *tert.* (I) bases. Treatment of (I) with KOH removes *O*-Ac, rendering possible the separation of phenolic (II) from non-phenolic *tert.* bases. Fractional treatment of (II) with HCl leads to separation of a portion (III), b.p. 205—215°/0·01 mm., transformed by CH_2N_2 in MeOH into glaucine in good yield. (III) is treated successively with $CHMeN_2$ and MeI and then subjected to the Hofmann degradation; the resinous methine base thus produced affords a methiodide (IV), m.p. 272—274° (decomp.), identical with that derived from laurotetanine. Degradation of (IV) leads smoothly to 3 : 4 : 6-trimethoxy-7-ethoxy-1-vinylphenanthrene, m.p. 140—141°, oxidised to 3 : 4 : 6-trimethoxy-7-ethoxyphenanthrene-1-carboxylic acid, m.p. 236—237°, which is decarboxylated by Cu powder in quinoline to 3 : 4 : 6-trimethoxy-7-ethoxyphenanthrene, m.p. 114—115°. (III) is therefore mainly *A*. H. W.

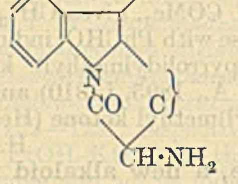


(*A*.)

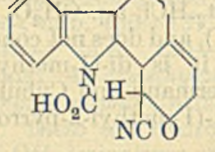
Successive degradation of α-*iso*cinchonine (cinchoniline) to cinchotoxine derivatives. T. Dubas, A. Konopnicki, and J. Suszko (Rocz. Chem., 1933, 13, 464—472).—The anhyd. sulphate of α-*iso*cinchonine (I) (N-*oxide*, m.p. 152—153°), when heated during 5 hr. at 140° under reduced pressure, yields α-*iso*cinchonicine, m.p. 98—100° [N-*Ac*, m.p. 164—165°, N-*NO*-, m.p. 128—130°, *Br*- (II), m.p. 57—58°, and N-*Me* derivative (III), m.p. 81—82° (*hydriodide*, m.p. 218—220°; *methiodide*, m.p. 229°; *Br*-derivative, m.p. 60°)], which on hydrolysis with 5% HCl at 100° during 5 hr. gives α-hydroxydihydrocinchotoxine, the *Br*-, an oil [*hydrobromide*, m.p. 241° (decomp.)], and N-*Me* derivative, an oil (*methiodide*, m.p. 130°; p-*nitrophenylhydrazone*, m.p. 85—90°; *picrate*, m.p. 211°), of which are obtained analogously by hydrolysis of (II) and (III). The chemical behaviour of (I) is analogous to that of α-*iso*quinidine (IV), and the [α] of various derivatives of (I) and (IV) vary similarly, pointing to the similarity in structure of the two compounds. R. T.

***Strychnos* alkaloids. XIII. Degradation of oximinostrychnine.** H. Wieland and K. Kaziro (Annalen, 1933, 506, 60—76).—Oximinostrychnine (I) (A., 1932, 629) (p-*toluenesulphonyl* derivative, decomp. > 290°) is reduced ($SnCl_2$, conc. HCl or Zn, $ZnCl_2$, and dil. HCl) to 12-*aminostrychnine* (as *A*), m.p. 83—86° [*dihydrochloride*, becomes brown at 170° and blackens at 250° (1 : 1-*compound* with $ZnCl_2$, decomp. 305—312°, after darkening from 250°)], which with HNO_2 gives 12-*diazostrychnine*, decomp. 107—108° to 189—190° (according to catalytic effect of impurities). This is converted by warm dil. H_2SO_4 into 12-*hydroxystrychnine* (*A*, $>CH\cdot NH_2 = >CH\cdot OH$), m.p. 205°, reduced ($H_2$, PtO_2, AcOH) to 12-*hydroxydihydrostrychnine*, m.p. 282—284° (decomp.) (*Br*-derivative, m.p. 290—292°), which is oxidised ($KMnO_4$–$COMe_2$) to a small amount of a dicarboxylic *acid*, $C_{21}H_{24}O_5N_2$, decomp. 296°. Oximinobrucine (*loc. cit.*) (p-*toluenesulphonyl* derivative, decomp. > 290°) is similarly reduced to aminobrucine [*compound*, $C_{23}H_{27}O_4N_3,2HCl,ZnCl_2$, decomp. > 300°], which affords the unstable 12-*diazobrucine*, decomp. 100·5—101°. The *compound*, $C_{23}H_{29}O_4N_3,2HCl,ZnCl_2$, is prepared similarly from oximinodihydrobrucic acid nitrosoamine (*loc. cit.*).

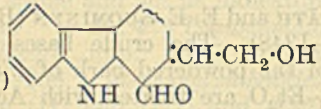
(A.)



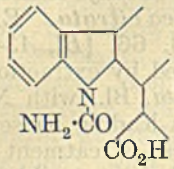
(II.)



(III.)



(IV.)



The hydrochloride of (I) and $SOCl_2$ give (mainly) the *hydrochloride*, decomp. > 300°, of the *carbamic acid* (II), $C_{21}H_{21}O_3N_3$, m.p. 260—263° (decomp.), and the *base*, $C_{20}H_{21}ON_3$ (II, $>N\cdot CO_2H = >NH$), m.p. 258—259°. (II) is hydrolysed [aq. $Ba(OH)_2$] to CO_2, HCN, and the *aldehydo-base* (III), $C_{19}H_{22}O_2N_2$, m.p. 217°, ($+CHCl_3$) decomp. 135—138°, and then re-solidifies [*hydrochloride*, decomp. about 310°; *methiodide*, m.p. > 300°; *oxime*, decomp. 245°; Ac_2 derivative (*hydrochloride*, m.p. > 300°; *oxime*, decomp. 206—207°)]. (I) and $SOCl_2$ give (II) and the *carbamide* (IV), $C_{21}H_{23}O_4N_3$, decomp. 275—276° (*hydrochloride*, decomp. 270—272°), which is hydrolysed (*N*-NaOH) to *norstrychnic acid*, $C_{20}H_{22}O_3N_2$ (II, where $>N\cdot CO_2H = >NH$ and $CN = CO_2H$), m.p. 295—296° (decomp.). H. B.

Strychnos alkaloids. LXXVI. Methoxymethyldihydroneo-brucidine and -strychnidine. Decahydrogenation of strychnidine. H. Leuchs, H. Beyer, and H. S. Overberg (Ber., 1933, 66, [*B*], 1378—1386; cf. this vol., 617).—Hydrogenation (PtO_2) of the ether $C_{25}H_{34}O_4N_2$ (I) (cf. A., 1927, 889) leads only to the H_4-derivative, m.p. 133—135°, $[\alpha]_D^{20}$ −7·6°/*d* in EtOH. The " nitromethoxymethyldihydroneobrucidine " (*loc. cit.*) is N-*methylneobrucidinium nitrate*. Oxidation of (I) with CrO_3 (=15 O) gives methoxymethyldihydroneodiketonucidine (*perchlorate*), whereas oxidation with $KMnO_4$ affords dihydroxymethoxymethyldihydroneobrucidine *Y* form (II), m.p. 184—186°, $[\alpha]_D^{20}$ −20·1°/*d* in EtOH, and *Z* form (III), m.p. 114—117° (decomp.), $[\alpha]_D^{21}$ +54·9°/*d* in EtOH. (III) or (III + II) and CrO_3 give dihydroxymethoxymethylneodihydrodiketonucidine, $C_{19}H_{26}O_6N_2$, m.p. 228—230°, $[\alpha]_D^{22}$ +228·6°/*d* in H_2O [*monoxime*, m.p. 268—271° (decomp.); *monosemicarbazone*, m.p. 272—276° (decomp.), $[\alpha]_D^{25}$ +240°/*d* in H_2O], hydrogenated (PtO_2 or Clemmensen) to the H_2-derivative, m.p. 227—229°, $[\alpha]_D^{22}$ +99·6°/*d* in H_2O; with $Ba(OH)_2$ and H_2O there is formation of CO_2. Hydrogenation of methoxymethyldihydroneostrychnidine (PtO_2–dil. HCl) affords the *compound* $C_{23}H_{38}O_2N_2$, m.p. 119—120° (*diperchlorate*), oxidised ($KMnO_4$=4 O in $COMe_2$) to the substance $C_{23}H_{36}O_4N_2$ (*perchlorate*, $[\alpha]_D^{25}$ −59·1°/*d* in H_2O). The substance, m.p. 215—218°, from strychnic acid and BzCl (*loc. cit.*) is not a mixed anhydride, but is *strychnine benzoate*. Hydrogenation of strychnidine (PtO_2–*N*-HCl) gives *decahydrostrychnidine* I, m.p. 264—265°, $[\alpha]_D^{24}$ −62·5°/*d* in $CHCl_3$ [*diperchlorate*, decomp. 285—290°, $[\alpha]_D^{24}$ +27·6°/*d*; *dimethiodide*, $[\alpha]_D^{24}$ +15·3°/*d* in H_2O; O(?)-*Ac* derivative (*diperchlorate*, $[\alpha]_D^{20}$ +63·4°/*d*)], and *decahydrostrychnidine* II, m.p. 269—271° (vac.), $[\alpha]_D^{24}$ +22·6° in $CHCl_3$ (*diperchlorate*, $[\alpha]_D^{22}$ +21·5°/*d*). *Octahydrostrychnidine dimethiodide* has $[\alpha]_D^{24}$ + 11·5°/*d* in H_2O. H. W.

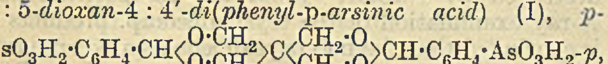
Colour reactions of strychnine and strychnine nitrate. H. Fujiwara (J. Biochem. Japan, 1933, **18**, 153—162).—Colour reactions of strychnine (I) and its nitrate, brucine, and many other alkaloids, etc. with HCl and H_2SO_4 alone and in presence of Na_2MoO_4 or Na phosphomolybdate are described. A reagent of H_2SO_4–Na_2MoO_4 is sp. for (I). F. O. H.

Catalytic hydrogenation of halogenomorphides. Dihydrodeoxymorphine-*D*. L. F. Small, K. C. Yuen, and L. K. Eilers (J. Amer. Chem. Soc., 1933, **55**, 3863—3870).—Reduction (H_2, Pd–$BaSO_4$, MeOH or dil. HCl) of α- (I) and β-chloromorphides and bromomorphide (II) gives (mainly) *dihydrodeoxymorphine*-D (III), m.p. 188—189°, $[\alpha]_D^{26}$ −76·8° in MeOH [*hemihydrate*, m.p. 162—164° (decomp.), $[\alpha]_D^{28}$ −78·6° in EtOAc] [*hydrochloride*; *hydriodide*; *sulphate* ($+2H_2O$); *H oxalate*; *salicylate*; *methiodide*], and smaller amounts of tetrahydrodeoxymorphine and oil (IV). (IV) is the main product from (II) in MeOH (not in dil. HCl). (III) is also prepared by reduction (H_2, PtO_2, AcOH) of deoxymorphine-*C* (this vol., 961) and by demethylation of dihydrodeoxycodeine-*D* (A., 1931, 1077) [which is formed by methylation (CH_2N_2) of (III)]. (III) is unaffected by prolonged electrolytic reduction. Electrolytic reduction of (I) or (II) gives *deoxymorphine*-A (V), m.p. 257—258° (decomp.) [*salicylate*, m.p. 248—250° (decomp.)], whilst reduction with Zn–Hg and 6*N*-HCl affords (V) and β-*iso*morphine. Reduction (Sn, conc. HCl) of (I) gives (cf. Schryver and Lees, J.C.S., 1900, 77, 1024) a small amount of the *hydrochloride*, m.p. 263·5° (decomp.), $[\alpha]_D^{27}$ −78·1° in H_2O, of a non-cryst. base. H. B.

Optical activity of alkaloid salts of geometrically isomeric unsaturated acids. P. Neogi and A. B. Sen-Gupta (J. Indian Chem. Soc., 1933, **10**, 373—381).—Comparison of the sp. rotation (I) (usually in EtOH) of various neutral alkaloid salts of pairs of *cis-* and *trans-*ethylenic acids shows that, with the exceptions observed by Hilditch (J.C.S., 1908, **61**, 704), the salt of the *cis*-form possesses the higher val.; the relationship is reversed for the amyl esters (Walden, A., 1896, ii, 633). The vals. of (I) decrease with dilution; this may be due to compound formation between the solvent and solute. The following *salts* are described: quinine maleate, m.p. 182—183° (decomp.), fumarate, m.p. 187—188° (decomp.), crotonate, m.p. 136°, *iso*crotonate, m.p. 160—162°, mesaconate, m.p. 215—216° (decomp.), and citraconate, m.p. 96—98°; cinchonidine maleate, m.p. 182° (decomp.), fumarate, m.p. 186° (decomp.), mesaconate, m.p. 216—217° (decomp.), and citraconate, m.p. 173—175° (decomp.); strychnine maleate ($+2H_2O$), m.p. 210° (decomp.), fumarate ($+4H_2O$), m.p. 240° (decomp.), crotonate, m.p. 215—217° (decomp.), *iso*crotonate, m.p. 250—252° (decomp.), mesaconate ($+3H_2O$), m.p. 230° (decomp.), and citraconate ($+2H_2O$), m.p. 185°; quinidine maleate, m.p. 98—99° (decomp.), and fumarate, m.p. 154° (decomp.); brucine mesaconate ($+5H_2O$), m.p. 205—207° (decomp.), and citraconate ($+4H_2O$), m.p. 209—210° (decomp.). H. B.

Arsenated derivatives of phenobarbital [5-phenyl-5-ethylbarbituric acid]. M. T. Bush and J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3894—3895).—5-*m*-Nitrophenyl-5-ethylbarbituric acid (I), m.p. 279—280° (all m.p. are corr.) [the position of the NO_2-group (cf. Bousquet and Adams, A., 1930, 351) is shown by the changes (I) $\longrightarrow$ *m*-nitrophenylethylmalonic acid $\longrightarrow$ α-*m*-nitrophenylbutyric acid, m.p. 115·5—116·3°, $\longrightarrow$ *m*-$NO_2·C_6H_4·CO_2H$], is reduced to the 5-*m*-aminophenyl derivative (II), which is converted by the method of Bousquet and Adams (*loc. cit.*) into a 5-(nitro-*m*-aminophenyl)-5-ethylbarbituric acid (III), decomp. 330—340°. Elimination of NH_2 from (III) gives a new 5-nitrophenyl-5-ethylbarbituric acid, decomp. 327—330°. (II) and (III) have been converted into the corresponding arsinic acids and thence into the arseno-compounds. H. B.

Optically active arsinic acid possessing molecular dissymmetry. Resolution of *dl-spiro*bis-3 : 5-dioxan-4 : 4′-di(phenyl-*p*-arsinic acid). C. S. Gibson and B. Levin (Proc. Roy. Soc., 1933, **A**, **141**, 494—501).—*p*-$CHO·C_6H_4·AsO_3H_2$, $C(CH_2·OH)_4$, and 30% H_2SO_4 at 100° (bath) give dl-spiro*bis*-3 : 5-*dioxan*-4 : 4′-*di*(*phenyl*-p-*arsinic acid*) (I), *p*-



$$AsO_3H_2·C_6H_4·CH\left\langle\begin{matrix}O·CH_2\\O·CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}CH_2·O\\CH_2·O\end{matrix}\right\rangle CH·C_6H_4·AsO_3H_2\text{-}p,$$

undecomposed at 290°, purified through its dl-α-*phenylethylamine* salt, decomp. 204° (previous softening). (I) is resolved using nor-*d*- and -*l*-ψ-ephedrine into the l- (II), undecomp. at 300° (slight previous sintering) (*nor*-d-ψ-*ephedrine* salt, decomp. 225°, $[\alpha]_{5461}^{20}$ −24·67° in H_2O), and d-*acids* (*nor*-l-ψ-*ephedrine* salt, decomp. 225°, $[\alpha]_{5461}^{20}$ +23·69° in H_2O), the Na_4 salts of which have $[\alpha]_{5461}^{20}$ −70·6° and +69·74° in H_2O, respectively. (II) is not racemised by boiling with an excess of aq. NaOH, but with SO_2, EtOH–conc. HCl, and a little I gives dl-spiro*bis*-3 : 5-*dioxan*-4 : 4′-*di*(*phenyl*-p-*dichloroarsine*) (III), m.p. 163°, which is oxidised (H_2O_2, aq. NaOH) to (I). It is suggested that the production of (III) may involve the opening (and subsequent re-closure) of the dioxan rings, thus accounting for the racemisation. H. B.

Hydroxy-derivatives of 10-alkyl(aryl)-9 : 10-dihydrophenarsazine. G. A. Razuvaiev and V. S. Malinovski (J. Appl. Chem. Russ., 1933, **6**, 669—676).—The following compounds have been prepared from the dihydroxides (I) of 10-alkyl- and from the oxide (II) of 10-phenyl-9 : 10-dihydrophenarsazine: *tribromo-*, m.p. 271—272°, and 3-*nitro*-10-*methyl-*, m.p. 154—155° (decomp.); *tetrabromo-*, m.p. 219—221°, and *nitro*-10-*phenyl-*, m.p. 139—141° (decomp.); *nitro*-10-*ethyl-*, m.p. 134—136° (decomp.), -10-*propyl-*, m.p. 147° (decomp.), and -10-iso*amyl*-9 : 10-*dihydrophenarsazine*, m.p. 146—147°. The above NO_2-derivatives regenerate (I) or (II) on reduction with $Fe(OH)_2$, Fe and $FeCl_3$, or $NaHSO_3$, and on treatment with alkalis. (I) and (II), on reduction with SO_2, yield the corresponding 10-alkyl(phenyl)-9 : 10-dihydrophenarsazines, together with $NHPh_2$ and the appropriate alkyl- or phenyl-arsine oxides. R. T.

Evidence for an asymmetrical tervalent arsenic atom. C. F. H. Allen and F. B. Wells (J. Amer. Chem. Soc., 1933, **55**, 3894).—7-Chloro-7 : 12-dihydrobenzophenarsazine and Ag *d*-bromocamphorsulphonate give two "dimerides," [α] +35·11° and +59·52°, whence [α] (calc. for As radical) −24·68° and +22·65°, respectively. The activity may be due to the As atom. H. B.

Tolyl derivatives of germanium. J. K. Simons, E. C. Wagner, and J. H. Müller (J. Amer. Chem. Soc., 1933, **55**, 3705—3712).—*Ge tetra*-o- (I), m.p. 175—176° (all m.p. are corr.), -m- (II), m.p. 146°, and -p- (III), m.p. 227° (229° on the Dennis m.p. bar), -*tolyls* are prepared from $GeCl_4$ and the product from $C_6H_4Me·MgBr$ and $ZnCl_2$ in PhMe or xylene (cf. Kraus and Foster, A., 1927, 268). *Ge triphenyl* m-*tolyl*, m.p. 136·5—138·5°, is similarly obtained from $GePh_3Br$ and *m*-$C_6H_4Me·MgBr$. $GeCl_4$ and *p*-$C_4H_4Me·MgBr$ give Ge tri-*p*-tolyl bromide (IV), m.p. 130°, and a little (III). *Ge tri*-m-*tolyl chloride*, m.p. 84—85°, is isolated in a slightly impure state from the mother-liquors from the prep. of (II); the *bromide*, b.p. 222—223°/1 mm., m.p. 78—78·9°, is prepared from (II) and Br in CCl_4. (I) and Br in CCl_4 give Ge tri-*o*-tolyl bromide, b.p. 205—210°/1 mm.; the crude *chloride*, b.p. 216—222°/1 mm. [from the mother-liquors from the prep. of (I)], and an excess of EtOH–$AgNO_3$ afford *Ge tri*-o-*tolyl hydroxide*, b.p. 212—214°/1 mm. *Ge tri*-m- and -p-*tolyl oxides* have m.p. 125—125·2° and 147—148°, respectively. Excess of HBr passed through $GePh_4$ in $CHCl_3$ at room temp. gives $GePh_3Br$; (IV) is obtained similarly from (III). H. B.

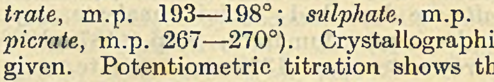
Mono- and di-substituted organo-mercury derivatives of acetylene. R. J. Spahr, R. R. Vogt, and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 3728—3731).—*Di*-(*alkyl*- and -*aryl-mercuri*)-*acetylides*, $(\vdots C·Hg·R)_2$, where R is Pr^{β}, m.p. 110·5—111·5°, sec.-*Bu*, m.p. 105·5—106°, iso*amyl*, m.p. 106—107°, cyclo*hexyl*, m.p. 172—173°, β-*methoxyethyl*, m.p. 129·5—130·5° (decomp.), p-*aminophenyl*, m.p. 188—190° (decomp.), and o-*nitrophenyl*, explodes > 300°, are prepared by the method previously described (this vol., 815) using 10% EtOH–KOH instead of aq. KOH. The alkali acts as a catalyst. The extent of the reaction $(\vdots C\cdot Hg\cdot R)_2$ (I) $+C_2H_2 \longrightarrow 2CH\vdots C\cdot Hg\cdot R$ depends primarily on the solubility of the (I). Δ^{α}-Heptinene and $HgPr^{\beta}Br$ in 10% EtOH–KOH give α-iso*propylmercuri*-Δ^{α}-*heptinene*. Di-(*o*-hydroxyphenylmercuri)acetylide could not be prepared. H. B.

Preparation of aryl derivatives of mercuric oxide by means of aromatic iodo-compounds. A. N. Nesmejanov and L. G. Makarov (J. Gen. Chem. Russ., 1933, **3**, 257—261).—The possibility of preparing aromatic Hg derivatives by the action of aromatic I-derivatives on HgO in presence of alkali hydroxides or freshly pptd. Ag_2O according to a reaction analogous to Meyer's synthesis of iodonium bases was investigated. PhI, *p*-C_6H_4MeI, *o*-, *m*-, and *p*-C_6H_4ClI, *o*-, *m*-, and *p*-$NO_2\cdot C_6H_4I$, were used and in each case the corresponding Hg derivatives obtained. The advantage of this method lies in the ease with which any salt of the derivatives can be prepared by simple pptn. with the corresponding anion. M. Z.

Catalytic decomposition of organo-metallic compounds. II. G. A. Razuvaiev and M. M. Koton. **III. Catalytic decomposition of organic compounds of lead and tin.** M. M. Koton (Ber., 1933, 66, [*B*], 1210—1213, 1213—1215; cf. this vol., 730).—II. Study of the catalytic decomp. of *p*-substituted derivatives of $HgPh_2$ in presence of Pd leads to the sequence, $1\text{-}C_{10}H_7 < C_6H_4Me < C_6H_4Br < C_6H_4\cdot OEt < C_6H_4\cdot OMe < Ph < CH_2Ph$, which differs from that of Kharasch (A., 1932, 409) for the action of HCl on *as.* Hg derivatives. The products are Hg and the Ph_2 derivatives except in the case of $Hg(C_{10}H_7\text{-}1)_2$ (I), which yields $C_{10}H_8$, H being derived from a second $C_{10}H_7$. The order of catalytic activity towards $HgPh_2$ is Pd>Ni>Au>Ag>Cu in EtOH and Pd>Au>Ag>Ni>Cu in tetrahydronaphthalene (II). In EtOH the products are of the type R·R except in the case of (I), whereas in (II) they are of the type RH.

III. The temp. of decomp. of $PbPh_4$ with and without H_2 pressure is lowered by metals in the sequences Pd>Ni>Au>Ag>Cu and Pd>Au>Ag>Ni, respectively. The similar series for $SnPh_4$ are Pd>Ni>Ag>Au>Cu and Pd>Ag>Au>Ni. Decomp. occurs according to $RPh_4+2H_2=4C_6H_6+R$ (I) and $RPh_4=2Ph_2+R$ (II). Under H_2 pressure in presence of Ni and Pd, respectively, reaction occurs exclusively in accordance with (I) and (II). In absence of H_2 reaction (II) takes place solely. In EtOH reaction (II) is catalysed by metals in the sequences Pd>Au>Ag>Ni for $PbPh_4$ and Pd>Ag>Ni>Au for $SnPh_4$. H. W.

Free phenyl radicals in the gas phase. M. F. Dull and J. H. Simons (J. Amer. Chem. Soc., 1933, **55**, 3898).—When $PbPh_4$ is heated at 215—220°/0·01 mm. using the method previously described (this vol., 930), a little $HgPh_2$ is produced presumably owing to the formation of free Ph radicals. H. B.

Monoarylguanidines. IV. Benzoselenazolylguanidine. G. B. L. Smith, J. P. Miale, and C. W. Mason (J. Amer. Chem. Soc., 1933, **55**, 3759—3762).—*o*-$NH_2\cdot C_6H_4\cdot SeH$ [as Zn salt, prepared by reduction (Zn, AcOH) of $(o\text{-}NO_2\cdot C_6H_4\cdot Se\cdot)_2$] and dicyanodiamidine in aq. HCl give the *hydrochloride*, m.p. 247—249°, of *benzoselenazolylguanidine* (I), *o*-  $C_6H_4<\substack{Se\\N}>C\cdot NH\cdot C(\colon NH)\cdot NH_2$, m.p. 198—200° (*nitrate*, m.p. 193—198°; *sulphate*, m.p. 287—289°; *picrate*, m.p. 267—270°). Crystallographic data are given. Potentiometric titration shows that (I) is a weak base and thus resembles its analogues (A., 1929, 1186; 1932, 176). H. B.

Synthesis of metallo-organic compounds of titanium. G. A. Razuvaiev and I. F. Bogdanov (J. Gen. Chem. Russ., 1933, **3**, 367—368).—Unsuccessful attempts were made to synthesise the organo-metallic derivatives of Ti by the action of $TiCl_4$ on $HgPh_2$, on a mixture of Na and PhCl, and on Grignard's reagent in the absence of a solvent. M. Z.

Constitution of casein. M. L. Demanez (Compt. rend. Soc. Biol., 1933, **112**, 1561—1562).—The two casein fractions separated by differential solubility in acid–EtOH behaved similarly in the precipitin test. Nutr. Abs. (*b*)

Proteins. X. Silk fibroin. II. Action of hypobromite on silk. S. Goldschmidt, K. Martin, and W. Heidinger. **III. Action of hydrochloric acid on silk.** S. Goldschmidt, G. Freyss, and K. Strauss (Annalen, 1933, **505**, 255—261, 262—273; cf. A., 1930, 940).—II. The action of alkaline KOBr on silk does not vary with its origin except in the case of Tussah, which differs in composition from true silk. Attack is very rapid at first, but soon lessens; after 8—10 min. the composition of the insol. cryst. decomp. product remains unchanged, and glycine (I) and alanine (II) in the const. mol. ratio 1 : 1·7—1·75 are then the sole hydrolysis products. The presence of polycarboxyamino-acids was not detected.

III. With 5*N*-HCl silk gives a cryst. decomp. product of const. composition, giving on hydrolysis (I), (II), and tyrosine (III) in the mol. ratio 1 : 1·7 : 0·13. This is further decomposed by trypsin to (III) and an amorphous substance of high mol. wt., insol. in H_2O, dil. acids, and alkalis, but sol. in conc. HCl. The KOBr product is also decomposed by trypsin, but silk is unaffected. (III) and its Bz derivatives are destroyed by NaOBr. From the composition and *X*-ray examination of the cryst. decomp. products it is concluded that the polypeptide chains are composed of individual NH_2-acids. H. A. P.

Water content and rate of heat denaturation of crystallisable ovalbumin. H. A. Barker (J. Gen. Physiol., 1933, **17**, 21—34).—Ovalbumin (I) dried over P_2O_5 is equilibrated with saturated salt solutions of different v.p. The temp. of denaturation of (I) is approx. a linear function of the relative humidity (II). The log. of relative velocity of denaturation varies linearly with (II). Heat-denatured (I) takes up approx. 80% as much H_2O at a given v.p. as native crystallisable (I). H. D.

Labile sulphur in proteins. H. Zahnd and H. T. Clarke (J. Biol. Chem., 1933, **102**, 171—186;

cf. A., 1931, 26).—Determination of cystine- (I) -labile S by reduction with $SnCl_2$ to cysteine (II), oxidation with Br and HCl, and subsequent determination of SO_4'' as $BaSO_4$ gave vals. lying between 97 and 107% of the calc. amounts. Vals. obtained for casein, gelatin, cottonseed globulin, zein, edestin, ovalbumin (III), fibrin, and horse hæmoglobin were compared with those in lit. In (III) the labile S val. is considerably > the cystine-S val. by the Folin–Looney (A., 1922, ii, 539) procedure and somewhat > by Sullivan's (A., 1930, 1604). (I) is extracted to a small extent by BuOH from HCl but not from H_2SO_4. (II) is extracted to 50%. Colorimetric determination of (II) in the aq. and BuOH solutions fails to give complete recovery. With (I) this applies to the Sullivan procedure only. On prolonged extraction of a neutral hydrolysate of (III) with BuOH, >70% of the total S passes into the BuOH. From labile S and colorimetric (I) determinations it is shown that all the labile S (15% of the total) is in the (I) form. The aq. solution contains 22% of the original S. Approx. 66% of this is labile, of which only 25% is in the (I) form. 25% of the S in the $COMe_2$-insol. fraction of the benzoylated hydrolysate of (III) was labile, but reacted negatively to the Folin test, showing the absence of ·S·S· or ·SH. H. D.

Nucleoproteins. III. Methods. S. J. von Przylecki (Biochem. Z., 1933, **264**, 334—347).—The methods in general use for investigation of nucleoproteins are discussed and the difficulties encountered in carrying them out are emphasised in a series of experiments dealing with the influence of salts on the solubility of nucleoglobin at p_H > isoelectric point, the influence of the protein component on the solubility of nuclein in presence of acids and salts, the changes induced by repeated dissolution and pptn., the production of mixed ppts., etc. P. W. C.

Nucleic acid in saké press cake and in beer yeast. M. Kimura (J. Soc. Chem. Ind. Japan, 1933, **36**, 50—51b).—Nucleic acid from saké press cake contains 12·77% N, 4·82% P; that from yeast has 12·40% N, 5·6% P. Both contain pentose groups. The former on hydrolysis gives guanine, adenine, cytosine, and uracil, and is essentially the same as that from yeast. H. A. P.

Microbomb for determination of organic halogens. F. E. Beamish (Ind. Eng. Chem. [Anal.], 1933, **5**, 348—349). E. C. S.

Cause of error in the determination of iodine in organic substances poor in carbon by fusion with potassium hydroxide. A. Guerbet (J. Pharm. Chim., 1933, [viii], **18**, 262—263).—The fusion of org. substances such as $CHI_2·SO_3Na$ with KOH produces KIO_3 which, if present in excessive amounts (*i.e.*, with an I equiv. > one sixth of the total I), partly escapes the action of HNO_2. If acidification of the aq. extract of the melt yields free I, Na_2SO_3 must be added until free I is no longer present. F. O. H.

Determination of phosphorus and arsenic in organic compounds by means of the bomb calorimeter. F. Garelli (Chim. et Ind., 1933, **29**, Spec. no., 262—263).—For determination of P, a small quantity of the substance is placed, with 0·2—0·4 c.c. of PhMe or decahydronaphthalene, in a stainless steel bomb containing 10 c.c. of H_2O; after combustion the P is pptd. as $MgNH_4PO_4$. In the case of As, dil. aq. NH_3 is used in the calorimeter, and the bomb is washed several times with $2N$-NaOH and with H_2O after combustion; the As is determined as $Mg_2As_2O_7$. J. W. S.

Condensation of furan compounds. II. Coloured derivatives of the furylidene series, and a method of determining small quantities of acetone based on them. V. V. Tschelincev and E. K. Nikitin (J. Gen. Chem. Russ., 1933, **3**, 319—328).—A new and accurate colorimetric method of determining $COMe_2$, in concns. as low as 0·0001%, is described. $COMe_2$ when treated with a 2½—3-fold excess of furfuraldehyde gives difurfurylideneacetone, m.p. 61°, which develops a characteristic reddish-violet colour in H_2SO_4 solution. This reaction is sp. and is not given by any other aldehyde or keto-compound. M. Z.

Micro-determination of acetyl, benzoyl, and *C*-methyl groups. R. Kuhn and H. Roth (Ber., 1933, **66**, [*B*], 1274—1278).—An apparatus is described for the determination of *O*- or *N*-Ac or -*Bz* by alkaline or acid hydrolysis or of *C*-Me by oxidation with CrO_3 (cf. Kuhn *et al.*, A., 1931, 1437) AcOH or BzOH formed is distilled under atm. pressure and titrated with $0·01N$-NaOH is presence of phenolphthalein. H. W.

Application of the method of Hagedorn and Jensen to the determination of other sugars. W. Weise and T. von Brand (Biochem. Z., 1933, **264**, 357—360).—Extension of the Hagedorn–Jensen method to determinations of *l*-arabinose, *l*-xylose, *d*-galactose, *l*-mannose, *d*-fructose, maltose, and lactose is described. P. W. C.

Application of volumetric methods to the study of non-aqueous cystine solutions. T. F. Lavine and G. Toennies (Amer. J. Med. Sci., 1933, **185**, 302).—NaOMe is used as the base, thymol-blue as indicator, and $CHCl_3$ as diluent for MeCN solutions of cystine perchlorate. Ch. Abs.

Gravimetric determination of phenols as "aristols." M. François and (Mlle.) L. Seguin (Bull. Soc. chim., 1933, [iv], **53**, 711—723; cf. A., 1931, 1438).—Treatment of guaiacol (I) (in glycerol and aq. NaOH) with an excess of I (in aq. KI and Na_2SO_4) gives an "aristol" of the (probable) composition $[C_6H_2I(OH)(OMe)]_2,C_6H_4(OMe)·OH$; isolation of this affords a method for the determination of (I). α- and β-$C_{10}H_7·OH$ similarly give "aristols" of the (probable) composition $(C_{10}H_6OI)_2,C_{10}H_8O$. Determination of guaiacol carbonate is effected by treatment with conc. aq. NH_3 in EtOH [whereby (I) and $CO(NH_2)_2$ result] and evaporation of the excess of NH_3; the (I) is then treated as above. β-$C_{10}H_7·OBz$ and β-$C_{10}H_7$ salicylate are first hydrolysed by NaOH. Full details are given. H. B.

Colorimetric determination of acetylsalicylic acid. G. Denigès (Bull. Trav. Soc. Pharm. Bordeaux, 1932, **70**, 182—183; Chem. Zentr., 1933, i, 1661).—Acetylsalicylic acid (approx. 5 mg.) is treated with aq. NH_3 (3—4 drops), H_2O (5 c.c.), 1% aq. $CuSO_4,5H_2O$ (2 drops), and then 3% H_2O_2 (3—4 drops); an orange-red colour is produced. After boiling and adding 4 drops of 3% H_2O_2 a more intense dark brown colour appears. Either can be used for the colorimetric determination. As a control the sample is boiled for ≮ 30 sec. with modified Millon's reagent, formation of a ppt. being avoided by addition of 0·25 vol. of AcOH. A. A. E.

Microchemical detection of coumarin. M. Wagenaar (Pharm. Weekblad, 1933, **70**, 1007—1011).—Coumarin may be detected microchemically by sublimation, pptn. by acid from a solution in alkali (1 : 500), or better (sensitivity 1 : 1000), as the dichroic "periodide" (I in KI) or the anisotropic mercurichloride. The formation of an insol. Tl salt is not a satisfactory microchemical method. S. C.

Determination of pyridine bases in the presence of ammonia. F. H. Rhodes and K. R. Younger (Ind. Eng. Chem. [Anal.], 1933, **5**, 302—304).—C_5H_5N and quinoline, but not their homologues, can be titrated potentiometrically in presence of NH_4 salts (I). To remove (I), the material, made alkaline with NaOH, is extracted five times with xylene, which is then extracted six times with 10% HCl, and the small quantity of NH_3 in the extract is oxidised with NaOBr and NaOH. The bases are distilled into 2*N*-HCl, and determined by potentiometric titration. The bases extracted from a sample of bath liquor of a by-product coke-oven plant contained approx. 50% of C_5H_5N, and approx. 25% of picolines. E. C. S.

Determination of hordenine as silicotungstate. M. M. Janot and P. Faudemay (Bull. Sci. pharmacol., 1932, **39**, 288—293; Chem. Zentr., 1933, i, 1486—1487).—The compound $4C_{10}H_5ON,12WO_3,Si(OH)_4,2H_2O$, is pptd. in the cold in presence of Na_2SO_4. The accuracy is ±1%. A. A. E.

Identification of cocaine and novocaine. C. C. Fulton (Amer. J. Pharm., 1933, **105**, 326—339, 374—380).—The sensitivity of the pptn. tests for these substances, the nature of the ppt. obtained (when cryst.), tests for their identification in presence of each other, and methods of separation are described. R. S. C.

Detection of phosphatides. W. Diemair, A. Schloemer, and K. Täufel (Z. physiol. Chem., 1933, **220**, 86—88).—Various so-called tests are not sp. for phosphatides. J. H. B.

Biochemistry.

Apparatus for graphical recording of oxygen consumption and carbon dioxide elimination. G. Mansfeld (Klin. Woch., 1933, **12**, 668—671; cf. A., 1932, 955).—Modified apparatus is described. Nutr. Abs.

Nature of oxygen linking in oxyhæmoglobin. R. D. Barnard (Proc. Soc. Exp. Biol. Med., 1932, **20**, 43—44).—Tests for H_2O_2 give negative results. The peroxide formula is rejected in favour of an ozonic linking. Ch. Abs.

Crystallised synthetic carboxyhæmoglobin. A. Herzog (Biochem. Z., 1933, **264**, 431—433).—The method of crystallising is described. P. W. C.

Prosthetic group of blood-pigment, its isolation in crystalline form, and its conversion with native globin into hæmoglobin. A. Herzog (Biochem. Z., 1933, **264**, 412—430).—The prep. of *hæmoprosthetin*, $C_{33}H_{31}O_4N_4Fe$ (I), from hæmin, oxy- and carboxy-hæmoglobin is described. (I) by treatment with NaCl, AcOH, and MeOH gives Teichmann's crystals and by coupling with native globin gives various modifications of hæmoglobin, the absorption curves of which correspond with those of the natural modifications. (I), and not hæmatin, $C_{34}H_{33}O_5N_4Fe$, is the prosthetic group of blood-pigment, the thirty-fourth C of the latter being introduced during its prep. It follows that hæmin has 34, hæmato-, meso-, proto-, and hæmo-porphyrins and the corresponding hæms have 33, whilst ætioporphyrin and ætiohæm have 31 C atoms per mol. (cf. this vol., 622). P. W. C.

Sensitising action of synthetic porphyrins. W. Hausmann and F. M. Kuen (Biochem. Z., 1933, **265**, 105—109; cf. A., 1911, ii, 138; 1917, i, 69; 1932, 1284).—Since synthetic meso- (I), *iso*uro- (II), and copro-porphyrin (III) act photodynamically on blood-agar the action is to be ascribed to the substances themselves, and not to impurities. In the ultra-violet the action of (I) is very pronounced. (II) and (III) have a feeble effect in the region near λ 365 mμ and only an extremely slight effect in visible light. The sensitising effect of hæmatoporphyrin in visible light is destroyed by serum. W. McC.

Physico-chemical properties of hæmocyanins. J. Roche and P. Dubouloz (Bull. Soc. Chim. biol., 1933, **15**, 954—968).—The absorption curves of the oxyhæmocyanins from the octopus (I), the snail (II), and the crab (III) are similar, but unlike oxyhæmoglobulin, each show two bands having max. at 3450 and 2780 Å. Reduction causes a marked decrease in the absorption between 4000 and 3000 Å. The absorption spectra of the Cu complexes [hæmocuprin (IV)] from (I), (II), and (III) separated by the method of Schnitz (A., 1931, 753) are identical. The hæmocyanins are considered as being composed of (IV) (which is responsible for the absorption between 4000 and 3000 Å.) combined with a protein the constitution of which varies according to the hæmocyanin. A. L.

Histone of bird erythrocytes. T. Leipert and E. Leberl (Biochem. Z., 1933, **265**, 115—123).—In the histone hydrochloride obtained from the picrate 45·1% of the total N is basic and is distributed thus: arginine (guanidine group free) 25·02; histidine (NH free) 3·03; lysine (one NH_2 free) 17·05%. Of every 100 N atoms 4·28 are present as $CO{\cdot}NH_2$, whilst 8·37 react with HNO_2. Titration by the methods of Sørensen and Willstätter indicates 10·05—10·15 basic groups (I), but the Cl content indicates 17·37 preformed (I). Methylation products contain 0·27—1·7% OMe and 3·66—5·27% NMe. W. McC.

Determination of amino-acids and peptones in blood-serum. E. Cherbuliez and I. Trusfus (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 154—155).—NH_2-acids and peptones in blood-serum are determined by addition of solid and saturated aq. $(NH_4)_2SO_4$, filtration from pptd. proteins, addition of a 1% solution of triketohydrindene, boiling, extraction of the ppt. with amyl alcohol, removal of extraneous colouring matter by 0·5% NaOH, and colour-matching of the resulting alcoholic solution against a standard glycine solution. R. S. C.

Colorimetric determination of plasma-proteins. M. Andersch and R. B. Gibson (J. Lab. Clin. Med., 1933, 18, 816—820).—The colour produced by Folin and Wu's phenol reagent is intensified if the solutions are first heated for 0·5 hr. at 100°. Ch. Abs.

Determination of protein in serum. R. S. Hubbard and G. E. Sly (J. Lab. Clin. Med., 1933, 18, 946—949).—A further modification of the author's micro-Kjeldahl method for determining proteins in blood-serum, based on the separation of albumin and globulin as recommended by Howe. The solutions containing the proteins are oxidised with the acid oxidising reagent of Folin and Wu and the NH_3 is nesslerised in the presence of K Na tartrate. The error is ±1·6%. Nutr. Abs. (*m*)

Biological effects of high pressures. Effects of very high pressures on proteins. J. Basset, M. Machebœuf, and G. Sandor (Compt. rend., 1933, 197, 796—798).—When blood-serum (horse) is submitted to increasing high pressure for 30 min., opalescence is observed at 5000, increased viscosity at 9000, and complete coagulation at 13,000 atm. Separate examination at p_H 7·2 of isotonic solutions of the serum-globulins and -albumins shows that only the former are coagulated by pressure. Electrometric titration shows that the buffering power of the globulins is unchanged by pressure, whence it is suggested that the observed effects are physical and are due to an irreversible dehydration or modification of the spatial arrangement of the peptide chains. J. W. B.

Simplified colorimetric determination of blood-urea clearance. D. D. Van Slyke and C. L. Cope (Proc. Soc. Exp. Biol. Med., 1932, 29, 1169—1174).—The urea in blood and dil. urine is converted into NH_3 with urease; proteins and other interfering substances are removed, and the NH_3 is determined colorimetrically. Ch. Abs.

Simultaneous determination of blood-carbon dioxide capacity and -urea-nitrogen. W. Z. Fradkin and J. Siegel (J. Lab. Clin. Med., 1933, 18, 949—954).—After liberation of CO_2 from serum by acid phosphate urease is added. An apparatus is described. Ch. Abs.

Blood-uric acid and uric acid excretion on different diets. W. von Moraczewski, S. Grzycki, H. Jankowski, and R. Sliwinski (Klin. Woch., 1933, 12, 738—741; cf. A., 1932, 772).—Blood-Ca is lowered by nuclein (I) when given with a protein- or fat-rich diet. Ingestion of caseinogen increased uric acid (II) production with retention or increased tolerance; this increase was reduced by (I). Diets high in carbohydrate or fat showed the lowest vals. for blood-(II). (I) with these diets increased both blood- and urine-(II). Nutr. Abs.

Lipins of normal [human] plasma. G. G. Villela and C. Silva (Mem. Inst. Oswaldo Cruz, 1933, 27, 1—15).—Vals. are (mg. per 100 c.c.): lecithin 182; fatty acids (men) 314, (women) 350; cholesterol 151, 194. Ch. Abs.

Comparison of the methods of Kanner and Grigaut for determination of free cholesterol of serum. O. Kanner and M. Chancogne (Compt. rend. Soc. Biol., 1933, 113, 57—59).—Grigaut's criticisms are rebutted and errors in his method, leading to too high results, are pointed out. Nutr. Abs. (*m*)

Micro-extractor for determination of cholesterol in blood. G. G. Villela (Mem. Inst. Oswaldo Cruz, 1933, 27, 17—20).—A modified apparatus for Meyer's method is described. Nutr. Abs. (*m*)

Hyperglycæmia in the normal dog. Free sugar. Protein-bound sugar. F. Rathery and I. Cosmulesco (Compt. rend. Soc. Biol., 1933, 113, 248—250, 250—253).—The hyperglycæmic response of different dogs to the administration of similar amounts of glucose is very variable; there is little correlation between the changes in free and "protein-bound" sugar. Nutr. Abs. (*m*)

Use of Somogyi's filtrate to increase the specificity of the gasometric blood-sugar method. D. D. Van Slyke and V. H. Kugel (J. Biol. Chem., 1933, 102, 51—55).—When the gasometric method is applied to Somogyi's $ZnSO_4$ blood-filtrate (A., 1930, 801), it yields results of the same type as the Benedict (A., 1925, i, 994) and Folin (A., 1928, 786) methods. H. G. R.

Determination of lactic and pyruvic acids [in blood]. W. B. Wendel (J. Biol. Chem., 1933, 102, 47—50).—The method of Friedemann *et al.* (A., 1927, 800) has been modified for use with small quantities of blood. H. G. R.

Variations in certain constituents of the blood of relatively normal individuals. E. M. Greisheimer and F. P. Arny (J. Lab. Clin. Med., 1933, 18, 680—683).—Average fasting vals. are (mg. per 100 c.c.): glucose 84·01±0·33, serum-Ca 10·591±0·016, inorg. PO_4 3·419±0·020, serum-Cl 577·06±0·72, urea-N 13·53±0·13, total non-protein-N (men) 34·87±0·23, (women) 32·90±0·26, uric acid (men) 3·417±0·034, (women) 3·070±0·029. Ch. Abs.

Colorimetric determination of the hydrogen-ion concentration of the blood. V. C. Meyers, E. Muntwyler, D. Binns, and W. H. Danielson (J. Biol. Chem., 1933, 102, 19—28).—With increasing CO_2 tension and with decreasing protein concn., the p_{Hc} 20—38° correction (I) decreases. Colorimetric (I) for human plasma has an average of 0·30 p_H. H. G. R.

Determination of the uncombined water in blood-corpuscles. M. A. Slawinski (Bull. Soc. Chim. biol., 1933, 15, 982—991).—The author's method of determining suspension concns. (A., 1929,

1142) is applied to blood, and the vol. of free H_2O in the corpuscles of horse blood is found to be 51%. A. L.

Determination of total base of serum. W. S. Hoffman (Proc. Soc. Exp. Biol. Med., 1933, 30, 834—838).—The author's method for urine is modified so that the total base in 1 c.c. of serum can be determined. Nutr. Abs. (*m.*)

Iron in human blood. A. Sachs, V. E. Levine, and A. Appelsis (Arch. Int. Med., 1933, **52**, 366—377).—The Fe content of whole blood is $50{\cdot}01\pm2{\cdot}56$ and $42{\cdot}67\pm2{\cdot}13$ mg. per 100 c.c. for men and women, respectively. The error in calculating the hæmoglobin from blood-Fe is negligible and both the Fe- and the Fe-colour-indices are preferable to the colour- and the hæmoglobin-colour-indices. H. G. R.

Seasonal variations in the serum-calcium of rabbits. S. Hermann and M. Zentner (Arch. exp. Path. Pharm., 1933, **172**, 5—9; cf. A., 1932, 81).—The ratio of total to free Ca (Ca quotient) in rabbit's serum has a max. val. in winter and a min. val. in spring. The total Ca follows a parallel course. F. O. H.

Determination of chlorides in blood. J. W. Cavett and C. E. Holdridge (J. Lab. Clin. Med., 1933, **18**, 944—946).—Cl' in blood and plasma is determined by direct titration with $Hg(NO_3)_2$ of the Folin–Wu filtrate, using Na nitroprusside as indicator. Nutr. Abs. (*m.*)

Electrometric determination of halogens [in serum].—See this vol., 1132.

Non-solvent space of serum and bound chlorine of serum-protein. A. Hayasida (J. Biochem. Japan, 1933, **18**, 107—124).—Determinations of the [Cl'] and total Cl content of serum (I) indicate that the non-solvent space (II) (cf. A., 1920, ii, 603) of (I) is approx. 20% by vol. and that the protein-bound Cl concn. is $0{\cdot}006M$, *i.e.*, approx. 6% of the total Cl. Dilution of serum with H_2O increases (II), but with aq. KCl the increase in (II) diminishes with increasing [KCl]. F. O. H.

Pharmacodynamic analysis of blood transfusion and hæmotherapy. E. Pribram (Arch. exp. Path. Pharm., 1933, **172**, 444—458).—The physico-chemical characteristics of blood and its constituents are investigated with reference to the interaction on mixing during transfusion. The action of the surface-active substances, assisted by the hydrophilic elements, is important. Thus the action of K–lecithin in presence of hæmoglobin and loosely combined CO_2 of the donor's blood is correlated with the influence of tissue respiration and the action of the heart muscle on the initiation of corpuscular degeneration. Increases in the dispersivity of the plasma and in the turgor of the tissues produce an increased absorption leading to better nutrition, hæmatopoiesis, and oxidation. The rate of decomp. of leucocytes also affects the oxidation–reduction processes leading to an increase in cell respiration. F. O. H.

Theory of blood clotting. II. Syneresis of blood in presence of acids and alkalis. S. Prakash (Kolloid-Z., 1933, 65, 88—92; cf. A., 1932, 870).—The syneresis (I) of clotted blood is increased by the presence of small amounts of AcOH or glycine, by adsorption of $H^{\cdot}$, but at higher concn. the anion is adsorbed preferentially and (I) is normal or reduced. HCl, urea, glucose, and glycerol decrease the amount of (I). Rise of temp. reduces the time of clotting and increases the amount of (I). When clotting is slower the particles develop surface hydration and (I) is less. E. S. H.

Effect of iodoacetic acid on coagulating systems and fermentative processes. Blood-glycolysis and -coagulation. B. Stuber and K. Lang (Pflüger's Archiv, 1932, 230, 465—474; Chem. Zentr., 1933, i, 2130).—$< 0{\cdot}1M$-$CH_2I{\cdot}CO_2Na$ (I) retards blood-coagulation (II); $> 0{\cdot}1M$-(I) arrests it. $0{\cdot}005$—$0{\cdot}05M$-(I) promotes (II). Other coagulation processes are similarly affected. (II) depends on the intensity of glycolysis and the physico-chemical condition of the fibrinogen. Halogenoacetic acids, by arresting glycolysis and increasing the lability of the fibrinogen, have two mutually opposed effects. Tryptic cleavage of proteins, but not lipolysis, is similarly affected by (I). A. A. E.

Reaction between inhibitors of blood-coagulation and calcium ions in aqueous solution. I. K. Mulli, T. Pillewizer, and W. Laves (Arch. exp. Path. Pharm., 1933, **172**, 384—388).—Colorimetric and electrical conductivity measurements indicate that in aq. media "germanin," "liquoid" (cf. A., 1932, 293), "novirudin," and Na citrate form complexes with $Ca^{\cdot\cdot}$, a reaction to which they probably owe their inhibitory activity. F. O. H.

Inhibition of blood-clotting by bile acids *in vitro*. II. H. Elbel (Biochem. Z., 1933, **265**, 36—40; cf. this vol., 296).—The increase in the amount of ultra-filterable Ca in serum produced by adding bile acids (I) may be due to the stimulating effect of (I) on the combination of lecithin and protein. The inhibition of clotting by (I) is possibly related to this effect. W. McC.

Formation of globulin from albumin by heparin. H. A. Oelkers (Klin. Woch., 1933, **12**, 191; Chem. Zentr., 1933, i, 2427).—Contrary to Fischer, an increase in the globulin fraction by the action of heparin on blood-protein was not observed. The colloid-osmotic pressure of serum is unchanged by heparin. A. A. E.

Felton antibody: its distribution and purity as determined by salting-out methods. A. M. Brown (J. Hyg., 1933, **33**, 252—258). Ch. Abs.

Nature of antibodies. A. Eastwood (J. Hyg., 1933, **33**, 259—281).—A discussion. Ch. Abs.

Protein–crystalloid complex as an antigenic unit. A. C. Kurtz, H. C. Sox, and W. H. Manwaring (Proc. Soc. Exp. Biol. Med., 1932, 30, 138—140).—Experiments support the theory that each protein–crystalloid complex functions as a single antigenic unit, and not that according to which the protein is the mechanical carrier of independent superficial unit "determinants." Ch. Abs.

Influence of formaldehyde on various antibody functions. H. Braun (Z. Immunität., 1933, 78, 46—61; Chem. Zentr., 1933, i, 2131).—Various antisera lose by treatment with CH_2O the property of complement formation and hæmolysis, but retain that of coagulation and agglutination. A. A. E.

Reactivity of synthetic lecithin and its antisera. H. Maier (Z. Immunität., 1933, **78**, 1—21; Chem. Zentr., 1933, i, 2130).—Experiments with lecithin and distearyl-lecithin are described. A. A. E.

Cholesterol content of fish muscle. S. Namiki (J. Biochem. Japan, 1933, **18**, 163—171).—Ordinary muscle from *Teleostei* contains 0·035—0·077% of cholesterol, whilst the red muscle contains 0·103—0·146%. The total P content is approx. the same (0·22—0·34%) for the two types of muscle. F. O. H.

Preparation of intact total phosphatide-cerebroside. H. H. Escher (Helv. Chim. Acta, 1933, **16**, 943—958).—Brain or spinal marrow is coarsely subdivided and dehydrated by successive treatments with EtOH or $COMe_2$. The product is extracted at 37° with mixtures of 95% EtOH and light petroleum, b.p. 35—70° (1 : 1, 1 : 3, and 1 : 10 successively). By means of H_2O, EtOH is removed from the extract, which is conc. at 37°/vac., and pptd. with $COMe_2$. The solid is triturated with successive quantities of $COMe_2$, whereby fats, cholesterol and its esters, and lipochromes are removed without considerable loss of total phosphatide-cerebroside, which forms additive compounds with $COMe_2$. The material is pressed into thin sheets from which $COMe_2$ is removed at 37°/1—2 mm., after which it can be preserved indefinitely in CO_2. H. W.

Micro-determination of phosphatides in tissues and blood. B. Norberg and T. Teorell (Biochem. Z., 1933, **264**, 310—315).—A method for the determination of phosphatide in 0·1 g. of tissue or 0·5 c.c. of blood depending on the pptn. of phosphatide + protein with $CCl_3·CO_2H$ and extraction of the ppt. with EtOH–Et_2O is described. P. W. C.

Fatty acids from the larva-fat of the beetle *Pachymerus dactris*, L. G. Collin (Biochem. J., 1933, **27**, 1373—1374).—Fat extracted from the larvæ found in the nuts of *Manicaria saccifera* gave on saponification the following fatty acids: lauric (24%), myristic (21%), palmitic (8%), oleic (32%), linoleic (3%), stearic, oleic, or linoleic (present in residual fractions) (12%). As compared with the kernel-fat of the nuts, the lower fatty acids are diminished, whilst oleic and linoleic acid are increased. W. O. K.

Component fatty acids of rat-body fats. A. Banks, T. P. Hilditch, and E. C. Jones (Biochem. J., 1933, **27**, 1375—1382).—The fatty acids include palmitic (I) (25—30%), myristic (II) (4—5%), stearic (III) (2—3%), and unsaturated (65—70%) acids (oleic with a small quantity of probably palmitoleic acid). Linoleic acid (IV) is almost entirely absent. When the diet contains cod-liver oil, highly unsaturated C_{20} and C_{22} acids may occur and the proportion of (IV) is only slightly increased. The fatty acids of the perinephric fat of the wild rabbit include (I) (23%), (II) (4·5%), (III) (4%), and unsaturated (68·5%) acids [chiefly (IV) with some linolenic acid]. Fully saturated components (almost wholly tripalmitin) occurred in the body-fat of the rat (2—3%) and in the perinephric fat of the rabbit (6—7%). W. O. K.

New group of animal pigments (lyochromes). III. P. Ellinger and W. Koschara (Ber., 1933, **66**, [*B*], 1411—1414; cf. this vol., 847).—Nascent PbS is a very suitable adsorbent for lyochromes. Lactoflavin *b* passes when heated at 60° into an almost colourless compound of purine character and a pigment with lyochrome properties. Purification of the mother-liquors from the crude crystallisates of lactoflavin *a—c* followed by pptn. with $AuCl_3$ leads to *lactoflavin* d (I), $C_{16}H_{20}O_6N_4$ or $C_{17}H_{20}O_7N_4$, m.p. 270—273° (decomp.), oxidation of which with CrO_3 affords $8CO_2$ and $0·5NH_3$ per mol. of (I). The murexide test is negative. A cryst. *pigment* (24% N) is obtained as by-product. Pigment concentrates as present in conc. C_5H_5N eluates when made alkaline to litmus with NaOH and exposed to sunlight yield a *pigment* $C_{14}H_{14}O_2N_4$, m.p. 315—317° (decomp.). H. W.

Flavins as biological hydrogen acceptors. T. Wagner-Jauregg and H. Ruska (Ber., 1933, **66**, [*B*], 1298—1302).—Flavin (I) solutions become decolorised when preserved in vac. in contact with yeast, finely-divided muscle, or powdered liver, kidney, heart, or brain, particularly in presence of $AcCO_2H$, lactic, succinic, or citric acid, or aldehydes. The colour returns on exposure to air. The hydrogenating enzyme can be dissolved by H_2O from ox-liver and purified by addition of acid glycine buffer (p_H 3·7) or saturated $(NH_4)_2SO_4$ and dialysis. Impure but not pure (I) solutions are decolorised by this prep. in vac. Yeast extracts, autolysates, and juices prepared with phosphate buffer (p_H 7·4) do not decolorise (I) solutions even in presence of lactic acid, whereas the yeast residues show the reaction. Reduction is restricted by HCN but not by CO. H. W.

Colouring matter of *Halla parthenopæa*, Costa. F. P. Mazza and G. Stolfi (Arch. Sci. biol., 1931, **16**, 183—197; Chem. Zentr., 1933, i, 1462).—The red colouring matter of the epidermis is the 5 : 6-quinone of 2 : 3-dihydroindole-2-carboxylic acid, $C_9H_7O_4N$. Oxidation with H_2O_2 affords pyrroletricarboxylic acid; *p*-bromophenylhydrazine in AcOH gives $C_{15}H_{12}O_3N_3Br$. Aq. SO_2 gives 5 : 6-dimethoxyindole and its -2-carboxylic acid, m.p. 202° (decomp.). A. A. E.

Biological reversible oxidation–reduction system: the pigment of *Arion rufus*. E. A. H. Friedheim (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 162—164).—A pigment is extracted which forms a reversible oxidation–reduction system, E_0 at p_H 7·0 being −27 mv. R. S. C.

Astacene in Crustacea. R. Fabre and E. Lederer (Compt. rend. Soc. Biol., 1933, **113**, 344—346).—Astacene, m.p. 243°, obtained from different varieties of lobsters, is the only known carotenoid pigment which occurs solely in animals. Nutr. Abs. (*b*)

Presence of carotene in the frog. F. G. Dietel (Klin. Woch., 1933, **12**, 601—602).—A yellow pigment, extracted with $COMe_2$ and Et_2O from the ovaries, skin, and liver of two species of frog (*Rana* *temporaria* and *esculenta*), was identified spectroscopically as carotene. NUTR. ABS. (*b*)

Carotene in the retina and the probable relationship between carotenoid deficiency and night blindness. H. VON EULER and H. HELLSTRÖM (Svensk Kem. Tidskr., 1933, **45**, 203—205).—Ox retina, extracted in Na light, yields an EtOH+$CHCl_3$ extract which exhibits absorption in the blue region of the spectrum with max. at 450 and 484 mμ and in the ultra-violet (255—527 mμ) with a max. at 265 mμ; when freed from EtOH it gives a positive response with $SbCl_3$-$CHCl_3$. Extraction with H_2O+$CHCl_3$ gives a dark red aq. layer having absorption bands at 586—572, 505—478, and 467—440, with max. at 489 and 455 mμ. Hence it appears that the night blindness associated with xerophthalmia is not essentially a consequence of *A*-avitaminosis, but depends on a deficiency of carotenoids in the retina. The relation between carotenoids and the visual purple is discussed. F. O. H.

Quantitative extraction of histamine from tissues by electrodialysis. R. G. MACGREGOR and W. V. THORPE (Biochem. J., 1933, **27**, 1394—1399).—The minced tissue is electrodialysed and the histamine passing into the cathode chamber is determined physiologically. The results are in agreement with those obtained by the EtOH-extraction method (Best *et al.*, A., 1927, 371) and added histamine is quantitatively recovered. W. O. K.

Choline in opotherapeutic powders. M. R. DU NOYER and E. KAHANE (Bull. Soc. Chim. biol., 1933, **15**, 938—943).—The Florence reaction for choline (I) is given by all opotherapeutic powders and cannot therefore be used in the identification of testicle powder. (I) is probably formed by enzymic hydrolysis of lecithin. A. L.

Determination of glutathione in tissues. Y. OKUDA and M. OGAWA (J. Biochem. Japan, 1933, **18**, 75—86).—The tissue is extracted with 0·5*N*-sulphosalicylic acid and the extract is filtered. Reduced and total glutathione are determined in the filtrate by titrating with 0·0001*N*-KIO_3 in presence of KI before and after reduction by Zn dust. The difference between the two results gives the content of the oxidised form. F. O. H.

Determination of gelatin. G. FARKAS (Biochem. Z., 1933, **264**, 361—366).—Gelatin dissolves in picric acid on warming and may then be separated from other proteins. It re-separates on cooling to 8° and is then determined in terms of the N content. P. W. C.

Determination of the gelatin content of different kinds of flesh. F. THAN (Biochem. Z., 1933, **264**, 367—370).—Using the method of the preceding abstract, the % of the total N as gelatin is for three types of ox and calf flesh 9—10, 12—13, and 20—21%, for tendons 80%, and for pig's flesh is rather less. P. W. C.

Isolated cell- and tissue-constituents. M. BEHRENS. **II. Hæmosiderin of horse-spleen.** T. ASHER (Z. physiol. Chem., 1933, **220**, 97—105; cf. A., 1932, 957).—Hæmosiderin in the form of granules containing Fe may, owing to its high sp. gr. (1·6—2·6), be isolated mechanically from powdered spleen. The granules have a varying composition and consist of a protein stroma containing $Fe(OH)_3$ and some $CaHPO_4$. J. H. B.

Distribution of iron in animal tissues. S. KATSUNUMA and H. NAKAMURA (Nagoya J. Med. Sci., 1932, **6**, 101—106).—Various animal tissues were examined by a colorimetric method, using a methylene-blue standard. CH. ABS.

Iron distribution in the earlier stages of growth of soya-bean and chick embryo. S. KATSUNUMA and H. NAKAMURA (Nagoya J. Med. Sci., 1932, **6**, 107—112).—The tegument and embryo of soya-bean contained much, and the cotyledon little, Fe. During sprouting the largest amount of Fe was found in the root, most being in the lower and least in the middle portion. During the development of hen's eggs the Fe content of the embryo increases 20 times at the expense of Fe in other portions. CH. ABS.

Classification of the biological elements; biochemistry of beryllium. W. R. FEARON (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 531—535).—The periodic table can be divided for the upper section only to contain thirty-four biological elements. Be has been detected in the lichens *Parmelia saxatilis* and *Xanthoria parietina*. H. G. R.

Magnesium and other inorganic constituents of some marine invertebrates. R. A. MCCANCE and H. L. SHIPP (J. Marine Biol. Assoc., 1933, **19**, 293—296).—Analyses for H_2O, Na, K, Ca, Mg, and Fe are given. C. W. G.

Fluorine content of bones and teeth. R. KLEMENT (Naturwiss., 1933, **21**, 662—663).—The bones and teeth of land mammalia contain $<$ 0·1% F (0·030—0·065%), whilst those of sea animals contain more (0·57—1·62%). Fossilised bones are especially rich in F (2·36—2·73%). The significance of hydroxy- and fluor-apatite in bone tissue is discussed (cf. this vol., 296). F. O. H.

Determination of chloride in tissues. F. W. SUNDERMAN and P. WILLIAMS (J. Biol. Chim., 1933, **102**, 279—285).—The tissue is digested in *N*-KOH and HNO_3 added to the turning point of Me-orange; excess of $AgNO_3$ is added and titrated with NH_4CNS. H. D.

Fixed mineral matter of seminal elements during spermatogenesis. A. POLICARD (Compt. rend., 1933, **197**, 710—711).—The mineral content (I) of the nuclei of the seminal elements of the rat is high (no Fe) until mitosis causes a low (I) in the resulting spermatids. During development of the latter, (I) increases progressively and its distribution tends towards that in the spermatozoa. A. C.

Eggs of gastropods. T. KUMON (J. Biochem. Japan, 1933, **18**, 145—151).—Analytical data (total N, distribution of N, H_2O content, mineral constituents, etc.) of the vitellin, mucous layer, and capsule protein of the eggs of *Hemifusus tuba*, Gmel., and of the eggs at various stages of development are given. F. O. H.

Chemical composition of the human fœtus. M. H. GIVENS and I. G. MACEY (J. Biol. Chem., 1933,

102, 7—17).—Up to 4 months the fœtus requires total ash (I) 0·55 g., Ca 0·1 g., and Mg 0·028 g., increasing to 54—112 g., 13—33 g., and 0·277—0·78 g., respectively, at maturity. (I) varies between 4 and 21% of the dry body-wt., and contains 6—30% Ca and 0·6—0·9% Mg. H. G. R.

Composition of the new-born rat during early development. A. Roche and I. Garcia (Compt. rend. Soc. Biol., 1933, **112**, 1686—1688).—There is a steady increase with age from 0 to 25 days in the wt. of the rat and in the % of N in the fresh material. During the first 4 days the N and P content of the dry material falls and subsequently rises irregularly. At birth the rats contained on an average 85·3% H_2O, 1·54% N, and 0·37% P. Nutr. Abs. (*b*)

Composition of muscle, liver, and blood of the dog. T. Cahn and J. Houget (Compt. rend. Soc. Biol., 1933, **112**, 1319—1321).—The most const. constituents are H_2O, lipin-P, acid-sol. P, total P, and total fat (I). (I) is more const. in liver and blood than in muscle. Despite variations, the composition of each tissue is characteristic. Nutr. Abs. (*m*)

Methods for standardisation of biological stains. III. Nitro- and azo-dyes. A. R. Peterson, H. J. Conn, and C. G. Melin (Stain Tech., 1933, **8**, 121—130).—Methods for analysis and biological testing are given for the following dyes: Martius-yellow, orange G, Janus-green B, Me-orange, orange II, Sudan III and IV, Bismarck-brown Y and R, Congo-red, and Erie-garnet B. H. W. D.

Block staining of nervous tissue with silver. III. Pericellular end-bulbs or boutons. H. A. Davenport (Stain Tech., 1933, **8**, 143—147).—Fixation in 20—40% C_5H_5N or in 10% chloral hydrate followed by 10—40% C_5H_5N gave the most consistent staining of pericellular structures in the cat's spinal cord. H. W. D.

Phloxine with orange-G as a differential counterstain. L. A. Margolena (Stain Tech., 1933, **8**, 157).—Phloxine and orange-G, following hæmatoxylin, may be used for differential staining of plant or animal tissues. H. W. D.

Determination of small amounts of unsaturated fatty acids in biological fluids. R. Willheim and F. Scholl (Biochem. Z., 1933, **264**, 302—309).—A colorimetric method is described for the determination of oleic acid in 0·2 c.c. of serum using the red colour obtained when oleic acid is treated with a solution of cellulose in conc. H_2SO_4. P. W. C.

Source of lipins in thoracic-duct lymph in fasting. Endogenous lipin secretion and reabsorption in bowel. H. R. Rony, B. Mortimer, A. C. Ivy (J. Biol. Chem., 1933, **102**, 161—170, and Proc. Soc. Exp. Biol. Med., 1933, **30**, 827—828; cf. A., 1932, 878).—The average content in total fatty acids of the thoracic-duct lymph of dogs fasted 2—14 days is 0·63%. Pilocarpine (I) and secretin markedly increase the lipin content, whereas thyroxine, pituitrin, and glucose are without effect. When the bile is excluded from the intestine the lipin content of the lymph is low and does not rise on injection of (I). The lymph fat cannot be increased by (I) in enterectomised animals. It is concluded that during fasting the intestinal mucosa secretes fats which are absorbed after hydrolysis, resynthesised, and passed into the lacteals. H. D.

Gastric juice. I. Proteins of human gastric juice. II. Urea-splitting enzyme and pepsin in relation to proteins. L. Martin (J. Biol. Chem., 1933, **102**, 113—130, 131—136; cf. this vol., 750).—I. A small quantity of sugar-containing protein is pptd. from the gastric juice (I) at p_H 6·8—7. By $\frac{1}{2}$ saturation of the filtrate with $MgSO_4$ or addition of AcOH and $COMe_2$ to 2 and 33·3%, respectively, at p_H 3·5 a heat-coagulable protein, named gastroglobulin (II), is pptd. It is crystallised by the brucine–C_5H_5N method, at its isoelectric point, and from EtOH. Pptn. of a protein substance which reduces $CuSO_4$ after hydrolysis occurs on addition of H_2WO_4 to the filtrate or dialysate from (II). The compounds obtained by treating the hydrolytic products with $NHPh{\cdot}NH_2$ are described.

II. The urea-splitting (III) and peptic (IV) activities of the ppts. and filtrates from $\frac{1}{2}$ saturation of (I) with $MgSO_4$ at different p_H, both dialysed and undialysed, were determined. The non-dialysed (III) was found in connexion with (II), the NH_3 and non-protein-N formed being directly proportional to the quantity of (II). Dialysis tends to increase the activity. (IV) was found only in connexion with (II). H. D.

Neurolytic properties of cerebrospinal fluid. R. Greco (Ann. Inst. Pasteur, 1933, **51**, 265—275).—Nerve substance is destroyed *in vitro* by cerebrospinal fluid within 40 hr. This action, which is probably enzymic, does not take place after warming to 60—70° or in the presence of $CHCl_3$, but is unaffected by thymol or pilocarpine. P. G. M.

Inorganic constituents of mixed and parotid gland saliva activated by reflex stimulation in the dog. H. Baxter (J. Biol. Chem., 1933, **102**, 203—217).—The [Cl′] and [Ca••] and the alkalinity of the saliva from the mixed glands of dogs were < those for the parotid alone. No difference in [K•] was observed. 5% NaCl, 0·125% HCl, and bread and meat powder introduced into the mouth can produce the same vol. of excreted saliva in the same dog, with different concns. of inorg. constituents. Decreasing concns. of NaCl and HCl produce decreasing vols. of parotid and mixed salivas containing decreasing [Cl′] and alkalinity, whilst the [P], [K•], and [Ca••] remain approx. the same. Parotid saliva, excreted in consequence of pilocarpine injections, is less conc. in Cl′, Ca••, and K• than is that produced at the same rate by meat extract, whilst the alkalinities are the same. H. D.

Effect of pilocarpine and "Neu-Cesol" on the amylase content of human saliva. A. Gernhardt (Z. klin. Med., 1933, **123**, 16—22; Chem. Zentr., 1933, i, 2120).—Pilocarpine and "Neu-Cesol" (Merck), injected subcutaneously, increase both the quantity and the ptyalin content of human saliva. A. A. E.

Saponin nature of snake venom. G. Bayer and H. Elbel (Z. Immunität., 1933, **78**, 82—85; Chem. Zentr., 1933, i, 2427).—Experiments on the resistance of hedgehogs to intravenous injections indicate that snake venom is not of saponin nature.

A. A. E.

Formation of bile acids. VI. Rice embryo and bile acid excretion. K. Tanaka and T. Tanaka (J. Biochem. Japan, 1933, 18, 15—22).—Oral administration of irradiated ergosterol (I)-containing sterol mixture (II) from rice embryo (III) to dogs with biliary fistulæ produces a temporary increase (21—24%) in the bile-acid secretion. The increase is more marked (13—43%) with the unsaponifiable fraction of the oil of (III), but does not occur with (II) freed from (I). Hence (I) and vitamin-*D* are concerned with the formation of bile acids.

F. O. H.

Possibility of experimentally changing the concentration of alkali metals in bile. E. Neubauer (Arch. exp. Path. Pharm., 1933, 172, 393—401).—For short periods (4—5 hr.) the concns. of K, Ca, and Mg and the ratio of their concns. in the bile of rabbits remain approx. const. Administration of Na dehydrocholate (I) lowers [Ca] and [Mg], that of the Mg salt lowers [Ca] and, after a preliminary diminution, increases [Mg], whilst that of the K salt lowers the Ca and Mg contents. Inorg. K, Ca, and Mg salts have no effect on the content of these cations in the bile, and hence an anion such as (I) is necessary for their passage through the liver into the bile.

F. O. H.

Concentration and precipitation of bilirubin in the gall-bladder and bile ducts. N. W. Elton and E. Deutsch (Arch. Pathol., 1933, 15, 818—827).—Comparison of the icteric index, *n*, the direct Van den Bergh reaction, and the total bilirubin (I) % of biles (cat, dog) shows that a crit. concn. exists at which bilirubin tends to ppt. in the bile. Further removal of H_2O from the bile is accompanied by progressive passage of (I) (and possibly cholesterol) into the form of a suspensoid colloid or minute crystals.

Nutr. Abs. (*m*)

Biological value of milk of normal and thyroidectomised goats irradiated by the mercury lamp. C. Kucera and M. Soos (Compt. rend. Soc. Biol., 1933, 113, 619—621).—Irradiation of the milk of normal (but not of thyroidectomised) goats produces favourable effects on development and metamorphosis of tadpoles.

Nutr. Abs. (*m*)

Effect on peptic digestibility *in vitro* of artificial feeding as used for American infants. A. Lautz (Amer. J. Dis. Children, 1933, 45, 985—995).—The peptic digestibility of cow's milk is unaffected by dilution, heating, or addition of acids in the usual amounts. It is increased by increasing the caseinogen : lactalbumin ratio and is reduced by addition of gelatin, cereals, or sugar or by increasing the fat content.

Ch. Abs.

Possibility of increasing the milk secretion of cows by feeding with irradiated feeding stuffs. F. Bílek and L. Hynek (Zemed. Archiv., 1931, 22, 449—454; Bied. Zentr., 1933, A, 3, 427).—Addition of irradiated yeast to the winter rations of cows increased the secretion of milk without affecting its fat content. The somewhat better results obtained with irradiated linseed cake are attributed to the activation of the phytosterol therein. The effect persisted 8 days after feeding. Irradiated foods had no beneficial action on cows receiving ample supplies of fresh green fodder.

A. G. P.

Specificity of caseinogens. M. L. Demanez (Compt. rend. Soc. Biol., 1933, 112, 1560—1561).—Whilst the caseinogens of the cow, ewe, and goat are quasi-identical with respect to their antigenic properties, those of the woman and the mare are distinct.

Nutr. Abs. (*b*)

Milk of cows inoculated with anthrax serum. F. I. Denisov (Trans. Omsk Inst. Dairying, 1931, 1, No. 3, 3—33).—The fall in yield is accompanied by an increase in fat, lactose, Cl, albumin, acidity, and total solids, and a decrease in caseinogen.

Ch. Abs.

Influence of certain agents on the lability of the "reducing factor" (vitamin-*C* ?) in milk. A. T. R. Mattick and S. K. Kon (Nature, 1933, 132, 446—447).—Exposure to light rapidly destroys the labile, reducing factor in milk. This is significant in view of the marked fluctuations in reducing power previously observed (this vol., 969).

L. S. T.

Iodometric determination of sugars in human milk. M. Polonovski and A. Lespagnol (Compt. rend. Soc. Biol., 1932, 107, 301—303; Chem. Zentr., 1933, i, 1486).—Gynolactose (I) combines with about 33% of the amount of I corresponding with an equal wt. of lactose or the third sugar of human milk; the Cu-reducing power is, however, the same. The (I) content of milk sera is determined by hydrolysis and iodometry.

A. A. E.

Physiological variations in the concentration of various sugars in human milk. M. Polonovski, A. Lespagnol, and H. Warembourg (Compt. rend. Soc. Biol., 1932, 107, 303—305; Chem. Zentr., 1933, i, 1473).—Variations in concn. of the three forms of lactose are at first inconsiderable; after several months that of gynolactose and the sugar sol. in MeOH appears to fall.

A. A. E.

Effect of increased blood-glucose on milk-sugar. C. H. Whitnah, W. H. Riddell, and R. E. Hodgson (J. Dairy Sci., 1933, 16, 347—353).—Administration of glucose increased the blood-sugar in lactating cows. Milk drawn at the period of greatest increase had a higher lactose (I) content than that on preceding or following days. The (I) increase in milk was not proportional to the blood-sugar increase, and the latter is not a factor controlling the (I) content.

A. G. P.

Monthly variation in the fat content of milk from Welsh farms. P. M. Hickson and S. B. Thomas (Welsh J. Agric., 1933, 9, 240—248).—Analyses for fat of 7372 random samples from the bulk milk of > 1000 herds show that afternoon milk (I) generally has a higher fat content (II) than morning milk (III). There is very little seasonal fluctuation in the (II) of (I), whereas marked seasonal fluctuations occur in the (II) of (III).

Nutr. Abs. (*m*)

[Changes in] amount and properties of fat globules in Siberian cow's milk during the lactation period. A. Zhuravskaya (Trans. Omsk Inst. Dairying, 1931, 1, No. 3, 34—60).—With advance of the lactation period *d* (milk) and the Reichert–Meissl val. (butter) decrease, whilst *n* (butter) slightly increases. Ch. Abs.

Quantity and fat content of milk during milking in women. C. Vincent and J. Vial (Compt. rend. Soc. Biol., 1933, **112**, 1422—1424).—During simultaneous milking of the two breasts the variations in the amount (I) of milk and the % (II) of fat are bilateral and simultaneous. At first (I), (II), and the wt. (III) of fat increase in parallel. Then there is a check in the rate (IV) of milk secretion and in the rise in (II), following which there is a steep rise in (I) and (II). Towards the end of milking (IV) and (III) decrease, whilst (II) attains its max. Nutr. Abs. (*m*)

Composition of human milk. Influence of the method of extraction on the fat percentage. S. T. Widdows and M. F. Lowenfeld (Biochem. J., 1933, **27**, 1400—1410).—The concn. of fat in human milk depends on the method of extraction, being smallest in the case of dripped milk, higher in milk extracted by gentle suction with the pump, and still higher in milk obtained by digital pressure. It varies inversely with the quantity of milk in the breast and depends also on other factors. W. O. K.

Colloidal calcium phosphate of milk. G. T. Pyne and J. J. Ryan (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 471—476).—The colloidal PO_4''' (I) appears to be mainly $Ca_3(PO_4)_2$. The acidity obtained for fresh milk to which a sol. oxalate has been added depends largely on (I). H. G. R.

Micro-determination of calcium in milk. M. Sato and K. Murata (J. Agric. Chem. Soc. Japan, 1933, **9**, 334—336).—Milk (1 c.c.) is heated with conc. H_2SO_4–HNO_3 (1 : 1, 3—4 c.c.); when HNO_3 is removed, H_2O_2 is added dropwise. The solution is heated for 2—3 min., diluted to 50 c.c., made slightly alkaline with 10% aq. NH_3, acidified with AcOH, and boiled. CaC_2O_4 is then pptd. with boiling aq. $(NH_4)_2C_2O_4$, treated with H_2SO_4, and titrated with $0{\cdot}01N$-$KMnO_4$. Ch. Abs.

Calcium and inorganic phosphorus in human and cow's milk. A. F. Hess and H. R. Benjamin (Proc. Soc. Exp. Biol. Med., 1933, **30**, 1358—1361).—Four fractions (I) were determined both for Ca and P in milk : a filterable absorbable fraction, a filterable remainder, a non-filterable absorbable fraction, and a non-filterable remainder. The Ca (I) of human milk, unlike those of cow's milk, are very similar to those of human and bovine sera. The differences in the Ca partitions of the milks cannot account directly for the difference in antirachitic potency. Nutr. Abs. (*m*)

Phosphorus compounds of milk. C. Bomskov (Z. Kinderheilk., 1933, **54**, 779—780).—Hochheimer's technique (this vol., 300) is criticised. His figure for org. P in cow's milk is too low. Nutr. Abs. (*m*)

Organic phosphorus compounds in goat's and mare's milk. C. Bomskov and J. Nissen (Z. Kinderheilk., 1933, **54**, 775—778).—The mean vals. for 14 samples of goat's milk were : total P 97·87, total acid-sol. P 85·53, inorg. + labile P 60·70, pyro-P 4·67, hexose phosphate P 0, residual P 19·85 mg. per 100 c.c. Two samples of mare's milk gave, respectively, total P 87·56, 60·39, total acid-sol. P 74·31, 46·78, inorg. + labile P 53·55, 33·85, pyro-P 13·30, 7·58, hexose phosphate P 2·08, 3·01, residual P 5·69, 1·85 mg. Nutr. Abs. (*b*)

Spectrographic examination of urine in ultraviolet light. G. Huwer (Strahlenther., 1933, **46**, 393—396; Chem. Zentr., 1933, i, 2425).—Prolan fractions (Zondek) gave typical absorption curves, with max. at 290, min. at 265 mμ. The EtOH fraction of urine gave the same absorption. Deproteinised serum gave similar curves. The substance causing the absorption has not been identified. A. A. E.

Determination of porphyrin in urine. H. T. Schreus and C. Carrié (Klin. Woch., 1933, **12**, 146—148; Chem. Zentr., 1933, i, 1660).—A spectroscopic method depends on the fact that the intensity of the absorption bands of porphyrin solutions is proportional to the porphyrin content. A. A. E.

Physiology and pathology of porphyrin excretion. H. T. Schreus and C. Carrié (Klin. Woch., 1933, **12**, 745—748).—Vals. $< 0{\cdot}1$ mg. per day of coproporphyrin in the urine of normal subjects fed on a mixed diet are physiological. Fever from any cause increases porphyrinuria; salvarsan has a similar effect. In the first days of infancy also the urinary porphyrin is high. In all these conditions increased breakdown of blood corpuscles takes place and is assumed to be the cause of increased porphyrinuria. The hæmatin is probably transformed in the liver into coproporphyrin III, the intermediate stage being protoporphyrin. Nutr. Abs. (*b*)

Determination of urinary indican by means of the Pulfrich photometer. M. K. Zacherl (Z. physiol. Chem., 1933, **220**, 113—122).—The indican is converted by means of $FeCl_3$ in conc. HCl into indigotin, which is extracted by $CHCl_3$ and determined by step-photometer. J. H. B.

Ergothioneine in urine. M. X. Sullivan and W. C. Hess (J. Biol. Chem., 1933, **102**, 67—72).—Ergothioneine has been isolated from normal urine. Colorimetrically 90 mg. per litre were found, but $\not>$ 5—6 mg. could be isolated. H. G. R.

Determination of urinary protein. G. Czoniczer (Biochem. Z., 1933, **264**, 348—351).—The protein of 5 c.c. urine is pptd. and separated in a centrifuge tube and its amount calc. from the total N (Kjeldahl). P. W. C.

Blood- and urine-ammonia. Formation of ammonia in the kidney. M. Polonovski, P. Boulanger, and G. Bizard (Bull. Soc. Chim. biol., 1933, **15**, 863—917).—Endogenous NH_3, like exogenous NH_3, is converted into a substance which acts as a " buffer " in the control of the urinary NH_3 level (I) and as a defence against NH_3 toxicity. The renal formation of NH_3 for the elimination of acidosis and the appearance of NH_3 which enters the blood and is not excreted into the urine (" ammoniophaneresis ") are distinct phenomena, the latter being neither increased by a lowering of the blood-p_H nor diminished by alkalosis. Whilst insulin and adrenaline are antagonistic in their action on the blood-sugar of dogs, both produce an increase in (I) probably due to increased utilisation of glucose. Injection of phloridzin or salipurposide (A., 1931, 1199) induces glycosuria, but not an increase in (I). The increase in (I) due to the injection of NH_4 salts is proportional to the degree of elevation of blood-NH_3, but not to the elimination of acid. These and other findings lead to the differentiation of excretory and secretory functions of the kidney. The liberation of NH_3 is enzymic in each case, whilst the secretory function also occurs in the pancreas. F. O. H.

Diathermy test for sugar and albumin in urine. H. E. Kimble (Arch. Phys. Ther., 1933, **14**, 237).—The presence of albumin is indicated by coagulation giving a white line between the plates inserted in urine acidified with AcOH; alkaline $BiONO_3$ is then added, and when the liquid between the plates boils sugar is indicated by the formation of a black ring. Ch. Abs.

Sumner's method for [determining] sugar in urine. J. J. Short (J. Lab. Clin. Med., 1933, **18**, 641—643).—The presence of sugar in strongly acid urine or samples containing $>$ 0·6% is not always detected; the alkalinity of the reagent should be increased by 50%. Ch. Abs.

Mercury-reducing substances of normal urine. B. Gwozdz (Bull. Soc. Chim. biol., 1933, **15**, 969—981).—The reducing power (I) of the oxyproteic acid fraction (II) of urine expressed as the difference between that due to the pigment [pptd. by $Cu(OAc)_2$ from (III)] and that of the $Hg(OAc)_2$ ppt. (III) from the solution obtained after $Ba(OH)_2$ treatment (cf. Giedroyc, A., 1926, 636) is 17·36% of the total (I) when a meat diet (IV) is given and 8·6% when a milk diet (V) is followed. (II) contains 83·4% of the total neutral S on (IV) and 45·7% on (V). A. L.

Evaluation of the Rupp–Schied–Thiel method as a test for thiocyanate in urine. M. X. Sullivan and W. C. Hess (J. Washington Acad. Sci., 1933, **23**, 419—425).—CNS′ is separated from urine as Ba salt in hot EtOH, thereby eliminating ergothioneine-like material and oxyproteic acids which interfere with the method. H. G. R.

Colorimetric determination of chlorides in blood and urine. B. B. Westfall (Amer. J. Med. Sci., 1933, **185**, 148).—Ag_2CrO_4 is added, the mixture is filtered, and CrO_4'' is determined colorimetrically in the filtrate with *s*-diphenylcarbazide. 0·0004 mg. of NaCl can be determined to ±3%. Ch. Abs.

Relation of dietary fat and fat derivatives in the fæces of young dairy calves. C. Y. Cannon, D. L. Espe, and J. B. Waide, jun. (Proc. Amer. Soc. Animal Produc., 1932, 85—90).—The dry fæces of calves fed with skim milk contained 5·3% of fat (daily excretion 2·3 g.); fæces of those fed with milk (fat 4%) contained 22·5% of fat (daily excretion 13·5 g.). The most const. fraction of fæcal fat was the free fatty acids and the most variable was the soaps. Ch. Abs.

Effect of acidosis and alkalosis on the total base, chloride, and carbon dioxide contents of muscle. E. F. Yang and H. Wu (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1165—1167).—In the rabbit the muscle-base and -Cl varied with plasma vals. and not with p_H changes. Ch. Abs.

Carbohydrate metabolism in Addison's disease. O. Porges and D. Adlersberg (Arch. exp. Path. Pharm., 1933, **172**, 433—443).—Addison's disease is frequently accompanied by a mild hypoglycæmia (I) which tends to be emphasised by a deficiency of carbohydrate (II) in the diet. Oral administration of glucose produces a hyperglycæmia followed by a marked (I), especially when the subject has been previously fed on a (II)-free diet. Adrenal cortex preps. restore the (II) metabolism to normal. With morbid cases the acetonuria due to a (II)-free diet resembles that occurring with normal men. F. O. H.

Composition of foodstuffs in relation to nutritional anæmia in cattle. W. M. Neal and R. B. Becker (J. Agric. Res., 1933, **47**, 249—255).—With increase of growth of wire-grass, Ca, Mg, P, Fe, and protein decrease. In areas where nutritional anæmia occurs, forages contain less of the above elements. H. G. R.

Blood-diastase in cancer. L. L. Tureen (Arch. Path., 1933, **15**, 834—842).—Individuals exhibit marked fluctuations. As a diagnostic test for cancer the determination of blood-diastase is not significant. Ch. Abs.

Arginase and arginine in the metabolism of tumours. G. Klein and W. Ziese (Z. Krebsforsch., 1932, **37**, 323—346; Chem. Zentr., 1933, i, 2277).—Edlbacher's observation, that in animals with implanted malignant tumour the muscle-arginase is increased, is confirmed. The total arginine of the tumour tissue is normal, but the free arginine in tumour and muscle of cancerous animals is thrice as high as in normal muscle. A. A. E.

Reducing substance in tumours. L. J. Harris (Nature, 1933, **132**, 605).—The indications (this vol., 872) that the high reducing capacity of tumours in the dichlorophenol-indophenol test is due mainly to a substance other than vitamin-*C* have been confirmed. The powerful reducing substance present in high concn. in the growing cell of the tumour tissue (Jensen rat sarcoma in guinea-pigs) is named "reducytin." L. S. T.

Influence of cations on the fermentation power of tumour cells. III. Action of potassium. IV. Action of lithium. A. Lasnitzki (Biochem. Z., 1933, **264**, 285—291, 292—301).—III. Addition to K- and Ca-free medium of 0·0025 mol. of KCl per litre causes an increase in fermentation intensity with Jensen sarcoma of 70%, and addition of the same amount of KCl together with 0·0018 mol. of $CaCl_2$ per litre, an increase of 115%.

IV. Li cannot replace K with respect to the above activity. P. W. C.

Effect of irradiated ergosterol on the mineral constituents of cancerous tissue. F. Brikker and J. Lasaris (Z. Krebsforsch., 1932, **37**, 423—431; Chem. Zentr., 1933, i, 2276).—In mouse carcinoma the K : Ca ratio was 0·78 in animals treated with vigantol, and 2·72 in untreated animals. Vigantol administration also appears to retard the growth of implanted tumours. A. A. E.

Action of iodo- and bromo-acetic acid on tumours. I. A. A. Krontovski, M. K. Jazimirska-Krontovska, and H. P. Savitzka (Z. Krebsforsch., 1932, 37, 457—491; Chem. Zentr., 1933, i, 2277).—$CH_2I·CO_2H$ and $CH_2Br·CO_2H$ diminish the sugar requirement and the formation of lactic acid in tissue cultures of sarcoma and carcinoma.
A. A. E.

Effect of radiation on blood. G. W. Phillips (Lancet, 1933, 225, 745—747).—No characteristic changes are produced in blood by radiation treatment of malignant disease with Ra or with *X*-rays.
L. S. T.

Alleged cancer-producing qualities of tomatoes. M. J. A. des Ligneris (Lancet, 1933, 225, 698—699).—Askanazy and Bellow's production of peritoneal sarcoma in rats by means of tomato juice could not be repeated. Injections of tomato juice, in combination with tar painting, did not accelerate the formation of skin tumours. L. S. T.

Detection of oxalic acid in urinary calculi. H. Schmalfuss, H. Werner, and R. Kraul (Klin. Woch., 1932, 11, 791; Chem. Zentr., 1933, i, 1486).—A small quantity of powdered material is dissolved in 10% HCl and the filtrate is shaken with Et_2O, the residue from which (0·1—1 mg.) is fused on white porcelain with resorcinol (0·4—2 mg.). After cooling, the residue is treated with conc. H_2SO_4 (10 mg.) and heated several times for 3 sec. with 20-sec. intervals. In presence of $H_2C_2O_4$ a deep blue, and then a green, colour appears. For the separation of $H_2C_2O_4$ and H_3PO_4 the solution is strongly acidified to Congo-red and the $H_2C_2O_4$ extracted with Et_2O. A. A. E.

Biological degradation products of chlorophyll in animal concrements. A. Treibs (Z. physiol. Chem., 1933, 220, 89—96).—Intestinal "stones" contained 75% of lithofellic acid and 0·02% of phylloerythrin (I). A hair-ball contained (I). A horse intestinal stone consisted chiefly of NH_4MgPO_4 with protophorbide *a*, *lithoporphyrin* [which readily yields (I)], and *lithocholin*. Horse fæces contained (I) and probably methylphæophorbide *a*. J. H. B.

Etiology of gallstones. E. L. Walsh (Arch. Path., 1933, 15, 698—713).—Dissolution of human mixed cholesterol gallstones in dog's bile probably depends on the difference in the ratio of non-saponifiable to saponifiable substances in the bile.
Ch. Abs.

Azotæmia and dental affections. E. A. Zawels and H. W. Reilly (Semana méd., 1933, i, 1924—1927).—Dental infections are often accompanied by high blood-non-protein-N. Ch. Abs.

Chemical factors of saliva related to immunity and susceptibility to dental caries. W. A. Price (J. Dent. Res., 1933, 13, 195).—Before treatment of caries by supplement of vitamin and mineral-rich foods, addition of powdered bone to the saliva increased the inorg. P content by 3·07%. After treatment there was a decrease. Nutr. Abs. (*b*)

Variation in salivary proteins. F. Krasnow and E. B. Oblatt (J. Dent. Res., 1933, 13, 239).—A higher salivary protein (I) occurred more often in caries-immune (II) than in caries-susceptible (III) individuals. (I) of (III) was more const. and more (I) was sedimented from saliva of (III), which suggests that (I) of (II) is possibly more stable. In (III) there was a high correlation between (I), P, p_H, and titratable alkalinity of the saliva. Nutr. Abs. (*b*)

Some chemical factors of saliva apparently related to alveolar decalcification and pyorrhœa alveolaris. W. A. Price (J. Dent. Res., 1933, 13, 195—196).—A case of pyorrhœa alveolaris was treated with a diet rich in vitamins and minerals. Before treatment filtered saliva treated with powdered bone gained 33·57% Ca and 2·18% P. After treatment salivary Ca decreased 68·13% and P 19·4%.
Nutr. Abs. (*b*)

Blood-phosphorus insufficiency in pyorrhœa. C. J. Grove and C. T. Grove (J. Dent. Res., 1933, 13, 191—192).—The P content of blood-serum in pyorrhœa (I) (2·2—3·4 mg. per 100 c.c.) was much $<$ normal (3·45 mg.); the average Ca content (10·99 mg. per 100 c.c.) was $>$ normal (9—10 mg.). Deficiency of blood-P may influence bone degeneration as in (I). The intestinal contents should be kept acid (by medicament) to improve absorption of Ca and P.
Nutr. Abs. (*b*)

Diabetic coma refractory towards insulin. S. J. Thannhauser and H. Fuld (Klin. Woch., 1933, 12, 252—258; Chem. Zentr., 1933, i, 2128).—A case of diabetic coma uninfluenced by large doses of insulin is described. Insulin intervenes in carbohydrate metabolism only in presence of an enzyme-like substance in the liver which produces glycogen from sugar. A. A. E.

Diabetic lipæmia. Rôle of fats in diabetes mellitus. Hæmolipocrit method for the determination of fat in blood-serum. D. H. Collins (Quart. J. Med., 1933, 2, 267—279).—The hæmolipocrit method for the volumetric determination of fat in blood-serum is described, vals. for diabetic and non-diabetic sera being recorded. Increase of serum-fat is associated with glycosuria, acetonuria, and the severer cases of diabetes, but no definite relationship appears between serum-fat and either blood-sugar or body-wt. Nutr. Abs. (*m*)

Effect of pancreatectomy in the dog on blood-lipase content. N. Fiessinger, M. Albeaux-Fernet, and A. Gajdos (Compt. rend. Soc. biol., 1933, 112, 549—550).—The blood of depancreatised and normal dogs contains an atoxyl-resistant and quinine-sensitive lipase, not necessarily of pancreatic origin.
Nutr. Abs. (*m*)

Experimental adrenaline epilepsy in guinea-pigs treated with yohimbine, ergotamine, or peptone. J. Tinel and G. Ungar (Compt. rend. Soc. Biol., 1933, 112, 542—543; Chem. Zentr., 1933, i, 2167). A. A. E.

Toxic substance from protein degradation. H. Lieb and E. Schadendorff (Arch. exp. Path. Pharm., 1933, 172, 343—358).—The urine of epileptics and men suffering from scalds contains a thermostable substance (I) which produces necrosis on subcutaneous injection and is also present in peptone in an inactive form, being liberated by heating at 100° with H_2O. (I), which is enzyme-free, non-dialysable, sol. in 70% EtOH, and pptd. by Hg acetate or 50—60% $(NH_4)_2SO_4$, is a polypeptide or peptone. It is hydrolysed by trypsin-free erepsin (when the toxicity is lost) and contains dialysable Ca, the toxicity being proportional to the $Ca^{\cdot\cdot}$ combined with (I). $Mg^{\cdot\cdot}$ has no influence on the necrosis produced. When preceded by adrenaline injection, Ca-free (I) is toxic, due to the retardation of absorption and subsequent combination with tissue-Ca. F. O. H.

Experimental fever in man. II. Energy exchange in fever : thermogenesis and metabolism. E. Delcourt-Bernard (Rev. belge Sci. méd., 1933, 5, 229—292).—In cases (I) exhibiting rigor, the metabolism tends to diminish beforehand, rises markedly (112%) during rigor, and remains approx. 30% high afterwards until the temp. begins to fall. In cases (II) without rigor the mean rise is 16%. On deducting the extra metabolism due to shivering, the increase in (I) is similar to that of (II). Fat combustion increases, especially in the middle and later periods of experiment, in (I) or (II). Carbohydrate combustion increases in (I), in which it is proportional to intensity of shivering, but diminishes in (II). Protein metabolism varies. Nutr. Abs. (*m*)

Iodine and goitre in the Far East. J. F. McClendon (J. Biol. Chem., 1933, **102**, 91—99).—Japan is the only non-goitrous country, owing to the large amount of I ingested in the diet as seaweed. The I content of 79 species of seaweed is given. H. G. R.

Catechin (inhibitory substance) of the thyroid gland and its therapeutic use in exophthalmic goitre. E. Herzfeld and A. Frieder (Deut. med. Woch., 1933, 59, 84—86; Chem. Zentr., 1933, i, 2127).—The properties and use of " tyronorman " are discussed. A. A. E.

Influence of Lugol's solution on the effect of adrenaline in exophthalmic goitre and beri-beri. W. C. Aalsmeer (Klin. Woch., 1932, **11**, 2111—2113; Chem. Zentr., 1933, i, 2167).—The effect on blood-pressure is neutralised by Lugol's solution. Beri-beri is probably a dysfunction of the thyroid gland. A. A. E.

Human iodine metabolism. II. Blood- and urinary iodine after a single intravenous injection of inorganic iodine in hypothyreosis. A. W. Elmer (Deut. Arch. klin. Med., 1933, **174**, 449—455; Chem. Zentr., 1933, i, 2127).—Variations in I excretion show that in thyroid insufficiency the I is utilised much less and more slowly than normally. A. A. E.

Post-operative amino-acid excretion in Graves' disease. W. Krech (Arch. klin. Chirurg., 1933, **174**, 662—666).—After operations on the thyroid (I) in Graves' disease, the urinary output of NH_2-N increased; in other (I) conditions there was a post-operative fall in NH_2-N. The urinary NH_2-N curve seemed to bear no relation to changes in temp. The differences between Graves' disease and other (I) conditions are attributed to the defect in the former of protein synthesis and the effect of pre-operative I medication on the storage of protein in the (I). Nutr. Abs. (*b*)

Post-operative changes in blood-fat. F. Frochnow and L. Findeisen (Arch. klin. Chirurg., 1933, **175**, 121—137).—The total blood-fat (I) in operative as distinct from metabolic diseases varies in the fasting condition from 230 to 310 mg. per 100 c.c. In cholelithiasis and cholecystitis (I) varies from 214 to 354 mg. per 100 c.c. The lowest vals. are 200 mg. (tubercular peritonitis) and the highest 530 mg. (xanthomatosis). The normal individual variations are 13% (fasting), and 20—22% (fed). No significant change of (I) occurs with Et_2O narcosis alone, but hyperlipæmia arises as soon as operative work begins. Variation of (I) as a result of operations under local anæsthesia is very small and post-operative hypolipæmia is rarely observed. Nutr. Abs. (*m*)

Rose-Bengal test of hepatic function. Spectroscopic method. T. L. Althausen, G. R. Biskind, and W. J. Kerr (J. Lab. Clin. Med., 1933, **18**, 954—958).—The dye present in the blood-plasma is determined spectroscopically. Ch. Abs.

Carbohydrate metabolism in obstructive jaundice. S. Nishigaki (J. Chosen Med. Assoc., 1933, **23**, 34—36).—In rabbits and chickens, experimental obstructive jaundice produced by ligature of the common duct to prevent passage of bile into the duodenum causes immediate hyperglycæmia followed by a prolonged hypoglycæmia (I). The effects of administering insulin to the jaundiced animals indicate that a hypersecretion of pancreas hormone, secondary to the disturbed liver function, is the main factor in causing (I). Nutr. Abs. (*m*)

Copper in the normal and pathological liver. A. Policard (Compt. rend. Soc. Biol., 1933, **112**, 1418—1419).—In atrophic cirrhosis (man) Cu (determined histospectrographically) is much more abundant than in normal liver, being particularly localised in the fibrous tissue septa, although irregularly distributed. In pigmentary cirrhosis the Cu content is also above normal. The livers of white rats contain only minute traces of Cu. Nutr. Abs. (*m*)

Pharmacology of inflammation. IX. Action of water- and salt-mobilising agents on the inflammatory reaction. W. Lipschitz and E. Reuter (Arch. exp. Path. Pharm., 1933, **171**, 650—667).—Intravenous injection into rabbits of NaCl solution (3·7%) decreases the inflammatory reaction produced by the application of mustard oil to the skin 1 hr. or 16 hr. later. Injection of glucose solution (25%) has a similar action even after a 16-hr. interval when the blood chemistry has become approx. normal. Administration of salyrgan, which results in a marked increase in H_2O and NaCl excretion, has only an uncertain effect in decreasing inflammation. W. O. K.

Experimental leucocytosis and blood-sugar regulation. P. Lorthioir (Compt. rend. Soc. Biol., 1933, **113**, 401—403).—Experimental leucocytosis in rabbits evoked by injection of colchicine causes the blood-sugar to increase and the glucose tolerance to decrease. Nutr. Abs. (*m*)

Change produced in the fat tissue by insulin in malnutrition. H. Blotner (J. Amer. Med. Assoc., 1933, **100**, 1235—1237).—In a case of non-diabetic malnutrition during a period of gain in wt. (21 lb.) induced by insulin administration, the depth of the subcutaneous fat increased from 3 to 16 mm. and the average diameter of each fat cell from 35 to 79·8 μ, but there was no change in the glycogen content of the skin. Nutr. Abs. (*m*)

Standards of basal metabolism for children of retarded growth. A. Topper (Amer. J. Dis. Child., 1933, **45**, 1203—1210).—In children with retarded growth the basal rate exceeds the normal when referred to standards of total height, sitting height, wt., and surface area, but agrees with standards according to age. Nutr. Abs. (*m*)

Metabolism studies with glycine in progressive muscular dystrophy. S. Kostakow and A. Slauck (Deut. Arch. klin. Med., 1933, **175**, 302—310).—In progressive muscular dystrophy, treatment with glycine, which is sometimes beneficial, is followed by increase in creatinuria. Nutr. Abs. (*m*)

Effect of adrenaline in certain muscular disorders. J. St. C. Elkington and M. W. Goldblatt (Lancet, 1933, **225**, 693—694).—The injection of adrenaline produced a rise in blood-lactate (I) in all the various myopathies examined. Resting lactic acid in the blood remained within normal limits. Differences obtained in (I) increments and in the hyperglycæmias for various kinds of muscular disorder are recorded. L. S. T.

Blood-non-protein-nitrogen and -creatinine in nephritis and prostatic obstruction. A. Cantarow and R. C. Davis (J. Lab. Clin. Med., 1933, **18**, 502—506).—In individuals with obstructive urinary lesions the blood-creatinine is increased to approx. the same extent as in renal disease. Ch. Abs.

Andrewes' diazo-reaction and Becher's xanthoproteic reaction in the blood. C. P. Waldorp (Semana méd., 1933, i, 1817—1826).—Blood (5 c.c.) is mixed with $CCl_3{\cdot}CO_2H$ (5 c.c.) and Becher's reaction applied to the filtrate; a Sahli colorimeter and 0·03874% $K_2Cr_2O_7$ solution are employed. Becher's reaction is positive in normal blood, and increased in nephritis. Andrewes' reaction is negative in normal blood, but positive in renal insufficiency. Ch. Abs.

Unsaturated fatty acids in experimental renal damage and oxygen deficiency. J. Rof and A. Thurnherr (Z. ges. exp. Med., 1933, 88, 693—704).—The I val. (I) of the renal fat of rabbits increases after poisoning with $HgCl_2$ or large doses of salyrgan, but decreases after cantharidin poisoning. Rats and rabbits exposed to decreased atm. pressure (O_2 lack) show a rise in the (I) of the fat of all the organs when the decrease in pressure is moderate, a fall when the decrease is more marked; the total fat content of the kidneys is halved. Rats on fat-free diet are more susceptible to O_2 lack and show a more rapid and marked fall in (I) of the fat than rats on stock diet. Nutr. Abs. (*m*)

Inorganic sulphur of blood in azotæmia. C. B. Udaondo, M. Scheingart, and D. Zanalda (Compt. rend. Soc. Biol., 1933, **113**, 462—463).—The normal inorg. S of human blood varies between 0·8 and 1·4 mg. per 100 c.c. In patients with N retention, the inorg. S of the blood lies between 2·0 and 8·0 mg. per 100 c.c. There is no direct relation between the blood-urea and blood-S. Nutr. Abs. (*m*)

Clinical manifestations of variations in blood-magnesium. A. D. Hirschfelder (Proc. Soc. Exp. Biol. Med., 1933, **30**, 996—997).—Oral administration (I) of 20—30 g. of $MgSO_4$ does not significantly raise the blood-Mg of normal individuals. About 40% is excreted in the urine in 24 hr. In nephritis similar doses raise the serum-Mg from near normal to very high levels (9·8—11·3 mg. per 100 c.c.). The low serum-Mg vals. (0·9—1·37 mg. per 100 c.c.) found in nephritis, epilepsy, and parathyroid tetany are raised by (I) of $MgSO_4$. Nutr. Abs. (*m*)

Adrenaline content of the adrenal gland during upper intestinal obstruction. V. Miura (J. Chosen Med. Assoc., 1933, 23, 133—156).—A decrease is not due to starvation; it can be partly prevented by intraperitoneal, but not by intravenous, injection of adrenaline. Ch. Abs.

So-called "pellagra-producing" diet. T. D. Spies and J. Grant (Amer. J. Physiol., 1933, **104**, 18—22).—A diet low in minerals, protein, and vitamins-*C*, -*D*, and -B_2 (I), beneficial to pellagra patients, was fed to rats 7 weeks old. Symptoms of (I) deficiency developed. The identity of (I) with the pellagra-preventive factor was thus contradicted. The symptoms were prevented or cured by doses of yeast or ventriculin, but not by caseinogen. It is suggested that (I) is the anti-anæmic factor. Nutr. Abs. (*b*)

Cereal food poisoning and its relation to the etiology of pellagra. R. Stockman and J. M. Johnston (J. Hyg., 1933, **33**, 204—223).—Monkeys fed on maize meal, with butter, milk, and fruit, developed, in some cases, paresis, depression, and nervous degeneration as observed in human pellagra. The symptoms could be induced by feeding or injecting the Na salt of an acid separated from the maize. Rabbits and guinea-pigs were slightly susceptible and frogs were killed by injection of the salt. Only one sample of rice had the same deleterious effect; rye, wheat, and oats were toxic. The theory that pellagra is caused by toxic factors present in cereals is confirmed. Nutr. Abs. (*b*)

Acid-base equilibrium and pregnancy. H. Vignes and M. Lévy (Compt. rend., 1933, **197**, 794—796).—Determinations of the p_H val. of the plasma and the Cl ratio (Cl_P/Cl_C) in the plasma and red corpuscles in 14 cases of pregnancy indicate that the acid-base equilibrium is displaced in the direction of alkalosis, the p_H val. increasing and the Cl_P/Cl_C ratio decreasing. J. W. B.

Hyperventilation and acid-base equilibrium in pregnancy. I. Berconsky and J. J. Rossignoli (Rev. asoc. med. Argentina, 1932, **45**, 103).—During pregnancy pulmonary ventilation is increased 53%; CO_2 tension is decreased and O_2 tension increased in the alveolar air, the alkaline reserve of the plasma is diminished, and p_H is normal. In some cases of pelvic disease changes in the same direction were observed. Causes of hyperventilation are discussed. Ch. Abs.

Contents of parovarian cysts. K. Dierks and M. Becker (Arch. Gyn., 1933, **152**, 679—689; Chem. Zentr., 1933, i, 2833).—H_2O, Cl, Ca, PO_4, sugar, and N distribution have been determined. Amylase was present in traces; lipase, ovarian hormone, and gonadotropic hormone were absent. A. A. E.

Renal hypertrophy in rats fed on a high-protein diet. H. E. C. Wilson (Biochem. J., 1933, **27**, 1348—1356).—Gelatin fed to rats produces a greater increase in the kidney wt. than does either caseinogen or liver. Glycine, glutamic acid, and wheat-gluten all cause an increase which is approx. proportional to the additional N consumed. The hypertrophy may be associated with some intermediate process in protein catabolism, possibly deamination by the kidney. A. W.

Evaluation of the phosphorus deficiency of the rickets-producing diet. A. T. Shohl, H. B. Brown, E. C. Chapman, C. S. Rose, and E. M. Saurwein (J. Nutrition, 1933, **6**, 271—284).—On a high-Ca, low-P diet adequately supplemented with vitamin-*A* and -*D* the growth of rats was retarded. Over a long period retention of Ca was high and of P low. The fat-free bones contained normal proportions of Ca and P. P deficiency was the limiting factor causing delayed growth. A. G. P.

Phosphorus and rickets. II. Rôle of the phosphate ion in the antirachitic activity of inorganic phosphorus compounds. R. Lecoq and H. Villette (J. Pharm. Chim., 1933, [viii], **18**, 192—197; cf. A., 1932, 642).—Na_2HPO_3 (up to 3% of diet) has no antirachitic activity in rats. The activity of salts derived from P_2O_5 increases with the no. of mols. of H_2O combined with P_2O_5 in the corresponding acid. Thus the active doses of P are 0·1, 0·2, and 0·3% of diet when given in the forms of Na_2HPO_4, $Na_4P_2O_7$, and $NaPO_3$, respectively. The calcifying action of Na, K, and NH_4 phosphates increases with the acidity of the salt. The activity, referred to P content, of NH_4 phosphates is slightly $<$, of K phosphates almost equal to, that of the corresponding Na salt. A. C.

Plasma-phosphatase in rickets and other disorders of growth. J. Smith (Arch. Dis. Child., 1933, **8**, 215—220).—The average plasma-phosphatase val. (I) of normal breast-fed, healthy infants is 0·248 unit (range 0·20—0·30). Infants suffering from rickets, and others on rachitogenic diets (II), have increased (I). Addition of vitamins-*A* and -*D* to the (II) causes the val. to fall to normal. Conditions characterised by cessation of growth are associated with abnormally low (I). Nutr. Abs. (*m*)

Hydrogen-ion concentration in the organs and body-fluids of scorbutic guinea-pigs. R. McCarrison and G. Sankaran (Indian J. Med. Res., 1933, **20**, 971—974).—In the scorbutic group fed on autoclaved milk and crushed oats, the urine was more acid and the blood, bile, testes, and thyroid tended to have a diminished alkalinity, whilst the spleen, heart, and liver tended to be less acid than corresponding organs of the normally fed group. Nutr. Abs. (*b*)

Blood picture of guinea-pigs during scurvy and recovery. B. Diblicek and C. Kucera (Compt. rend. Soc. Biol., 1933, **113**, 632—634).—Scurvy is accompanied by a 32% reduction in the red blood-corpuscles (I), and an increase of blood-platelets and poikilocytosis, this being most marked during the scorbutic crisis. Recovery results from feeding germinated pulses, decitrated lemon-juice, or green food and is accompanied by an increase in (I), up to 17% above the original. The white-cell count follows the (I) count, falling to 32% of the normal; recovery is accompanied by an increase of eosinophile leucocytes at the expense of lymphocytes; the basophile leucocytes do not vary. Excess (II) of vitamin-*C* causes a transitory acute leucocytosis.

Hæmoglobin (III) is lowered by 3—10% during scurvy. (II) causes a 10—20% increase in (III) and as much as 25% during pregnancy. Although pulses germinated for 5—9 days are the most potent in curing macroscopic symptoms, those germinated for 10—15 days have the most marked effect on the blood picture. Nutr. Abs. (*m*)

Minerals in silicotic lungs. W. R. Jones (J. Hygiene, 1933, **33**, 307—329).—The bulk of the mineral residue (I) from silicotic lungs consists of minute fibres of sericite (II) which is present in the inhaled dust. Quartz (III) is also present in (I), but is not the chief cause of silicosis (IV). Fibrous minerals such as (II), sillimanite, or tremolite etc. which are liberated in air during drilling and blasting and not the relatively large particles of (III) are of prime importance in producing (IV). L. S. T.

Excretion of antigenic substances with the urine in infectious diseases, particularly tuberculosis and syphilis. F. Klopstock (Klin. Woch., 1933, **12**, 249—252; Chem. Zentr., 1933, i, 2269).—A method of extraction is described, and the results of complement-combination tests are recorded. A. A. E.

Amine theory of infantile toxæmia. S. Rosenbaum and A. Chassel (Jahrb. Kinderheilk., 1933, **139**, 131—142).—In the intestine or blood of dogs suffering from intoxication (I) due to exsiccation and injection of *coli* endotoxin there is no increase in amines, but increase occurs always in the intestine (but only occasionally in the blood) of infants with symptoms of (I). The urine or cerebrospinal fluid of such infants contains no amines. The amine theory of toxæmia in infancy hence receives no support. Nutr. Abs. (*m*)

Diagnostic utilisability of peptolytic enzymes in trans- and ex-udates. J. Ammerschläger (Deut. Arch. klin. Med., 1933, **175**, 124—128; Chem. Zentr., 1933, i, 2708).—In pathological exudates of the chest and stomach a " peptolytic " enzyme which decomposes glycyltryptophan is present. Its differential diagnostic val. is limited. A. A. E.

Energy of activation and temperature coefficient of a biological reaction (respiration of the larvæ of *Diphyllobothrium latum*). E. A. H. Friedheim, B. Susz, and J. G. Bær (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 177—182).—The energy of activation for this process between 20° and 37° is 25,000 g.-cal., and the temp. coeff. 3·8 for 10°. The reaction involved is, therefore, not simple addition of O_2, but resembles a catalytic reaction. Above 37° the velocity of respiration decreases rapidly. R. S. C.

Standard metabolism of Australian aborigines. C. S. Hicks and R. F. Matters (Austral. J. Exp. Biol., 1933, **11**, 177—183).

Basal metabolism in different races of fowls. G. Iftimesco, G. Nichita, I. Popesco, and N. Tuschak (Compt. rend. Soc. Biol., 1933, **113**, 492—494).—The data (six different breeds) confirm the increase of metabolism per unit wt. with diminishing size, and its constancy when expressed per unit of surface area. Nutr. Abs. (*m*)

Basal metabolism of small birds. F. G. Benedict and E. L. Fox (Pflüger's Archiv, 1933, **232**, 357—388).—The average metabolic rate (I) of canaries (II) and parrots (III) at 28° at night at least 10 hr. after the last feed is 718 g.-cal. per sq. m. per 24 hr.: under similar conditions that of sparrows is 656 g.-cal.; at 16° the average val. for (II) and (III) is 1077 g.-cal. and for sparrows (IV) 914 g.-cal. The rectal temp. averages about 42°. (I) is slightly higher in males and is considerably higher during the day, even although the birds are kept in the dark. Muscular activity has a great effect on (I). The reaction to reduced temp. is much more marked in (II) and (III) than in (IV). The (I) of small birds (average about 700 g.-cal.) is low when the high cell temp. is taken into account, and compares with the val. for the mouse (640 g.-cal.). Nutr. Abs. (*m*)

Simple eudiometer. L. Plantefol (Bull. Soc. Chim. biol., 1933, **15**, 992—1012).—With the apparatus described R.Q. may be determined with an accuracy of 0·03. A. L.

Tendency of different animal species to ketonuria and ammonuria. H. Trimbach (Compt. rend., 1933, **197**, 708—710).—The degree of ketonuria (I) appears to vary inversely as the size of the animal. In the rat (I) is ten and six times as great as in the calf and pig, respectively, on a cow's milk diet and about twice as great as in the pig on a purely carbohydrate diet, *i.e.*, at the level of sp. min. N output. The variations of urinary NH_3 in different species on the same diet are also considerable, but not parallel to those of (I). A. C.

Ketogenic diet in normal individuals. F. L. Apperly and J. H. Norris (Amer. J. Med. Sci., 1933, **185**, 802—810).—The blood changes produced by ketogenic diets in three normal subjects showed that, despite a profound ketosis, alkalæmia (I) was almost constantly present, accompanied by a fall in plasma- and red-cell-CO_2. (I) may be the result of a hyperpnœa produced by the direct stimulation of the respiratory centre by certain ketone derivatives, and this may outweigh the tendency to acidosis produced by the keto-acids. Nutr. Abs. (*m*)

Effect of cholesterol ingestion on tissue-lipins of rats. A. Chanutin and S. Ludewig (J. Biol. Chem., 1933, **102**, 57—65).—With a diet containing 2·5% of cholesterol (I), (I) ester and total lipin (II) were increased in the liver, reaching a max. after 25 days with production of fatty livers; free (I) increased after the third week, but other organs showed no change. Fats inhibit and carbohydrates accelerate deposition of (I) in the liver and markedly increase (II). H. G. R.

Metabolism during secretion in liver, kidney, and salivary glands. R. Ferrari and R. Höber (Pflüger's Archiv, 1933, **232**, 299—321).—The ability of the frog's liver which is being perfused with Ringer's solution to concentrate and excrete colouring material (eriocyanin-*A* 0·0005%) in the bile is temporarily inhibited by addition of $CH_2I{\cdot}CO_2H$ (I). The stellate cells which possibly take part in the secretion of bile and leucocytes are immune to the presence of CN′, but are prevented by (I) from storing trypan-blue. The formation of urine by renal glomeruli, re-absorption of Cl by the tubules, and secretion of phenol-red are all inhibited by both CN′ and (I). Addition of 0·001*N*-KCN to the perfusing fluid of the submaxillary salivary gland of the cat leads to increased production of lactic acid and H_3PO_4. (I) causes decrease in lactic acid and increase in H_3PO_4 production. CN′ and (I) lead to increased content of Cl and K. The secreting and storing of substances by liver, kidney, and glandular cells depend on the utilisation of carbohydrate and the catabolism of an org. P compound. Nutr. Abs. (*m*)

Composition of different regions of mounds of *Eutermes exitiosus*, Hill. F. G. Holdaway (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 160—165).—The proportion of excreted lignin was highest in the central (nursery) section of the mound and lowest in the external wall. The ratio cellulose : lignin decreased somewhat towards the centre, the average val. being 1 : 4. A. G. P.

Analysis of termite (*Eutermes exitiosus*) mound material. W. E. Cohen (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 166—169).—In the digestion of wood by termites lignin remains practically unchanged. Considerable decomp. of cellulose is shown by the increased alkali-sol. fraction. A. G. P.

Glycogen formation from lower fatty acids with an even number of carbon atoms. II. Glycogen formation from *n*-butyric acid. R. Stöhr (Z. physiol. Chem., 1933, **220**, 27—33; cf. this vol., 855).—Female rats receiving $PrCO_2H$ and glucose show a considerably higher liver-glycogen content than controls with glucose only. This indicates a synthesis of carbohydrate from the acid. J. H. B.

Absorption of glucose from the intestine. I. S. Ravdin, C. G. Johnston, and P. J. Morrison (Amer. J. Physiol., 1933, **104**, 700—709).—In unanæsthetised dogs increase in the concn. and in the vol. of the same concn. of glucose results in increase in the amount (I) of glucose absorbed from jejeunal Thiry loops. No linear relationship exists between (I) and the time, (I), in increasing periods, being dependent on the concn. and vol. of the solution present during any given period. Nutr. Abs. (*m*)

Bile acids and carbohydrate metabolism. XXVI. Production of glycogen in the livers of splenectomised rabbits receiving adrenaline, cholic acid, and spleen extract. K. Fuziwara. **XXVII. Production from bile acids of glycogen in the livers of castrated and ovariotomised rabbits.** H. Takata (Biochem. Z., 1933, **265**, 76—79, 80—84; cf. this vol., 528).—XXVI. In splenectomised rabbits (I) injection of a small amount of adrenaline causes increase (II) in the production (III) of glycogen in the liver from glucose simultaneously administered, but (II) is counteracted by injecting cholic acid (IV) at the same time. Oral administration of ox-spleen extract also causes (II).

XXVII. Although (IV), orally administered, increases (III) in the livers of castrated and ovariotomised rabbits, castration and, still more, ovariotomy decrease (III) and diminish the stimulating effect (V) of (IV). (V) is related to the function of the generative glands. W. McC.

Bile acids and carbohydrate metabolism. XXVIII. Ergosterol glycocholia and the sympathetic nervous system. T. Tanaka (J. Biochem. Japan, 1933, 18, 33—43).—The bile-acid secretion of dogs with biliary fistulæ is increased by unilateral splanchnicotomy (I), whilst subsequent feeding with ergosterol (II), but not with its benzoate, further enhances the effect. (II) also diminishes the glycocholia due to administration of sugar (cf. this vol., 419), whilst subsequent (I) increases it again. F. O. H.

Excretion of citric acid by the rabbit kidney. H. Langecker (Arch. exp. Path. Pharm., 1933, **171**, 744—755).—The daily excretion of citric acid (I) in the urine of rabbits is: fasting 1·8—3·5 mg.; on oats, 1—7 mg.; and on green food, 13—50 mg.; *i.e.*, 0·5%, 1%, and 1·4—2%, respectively, of the total org. acid. Administration of $NaHCO_3$ with the acid-producing oats increases the excretion of (I), whilst HCl with the basic green food has the opposite effect. (I) or Na citrate administered by mouth does not increase the (I) excretion in the urine. W. O. K.

Comparative effect of tomato and orange juices on urinary acidity. L. G. Saywell and E. W. Lane (J. Nutrition, 1933, 6, 263—270; cf. A., 1932, 1056).—Daily addition of 1 litre of juice to the human diet caused an increase in urinary p_H (average 1·2 units) and corresponding reduction in total acidity and NH_3 excretion. Higher proportions of org. acids were excreted and there was an increased alkaline reserve. Increased alkalinity of urine is associated with a higher ratio of sol. to insol. alkalinity in the ash. A. G. P.

Relation between change in volume and the chemical processes of contraction in muscle. O. Meyerhof and H. Hartmann (Naturwiss., 1933, 21, 661).—The disagreement between the data from dilatometer experiments using enzyme preps. of muscle (I) (cf. this vol., 856) and those from the living (I) is due to a secondary swelling of (I) which accompanies contraction. When, however, the Ringer's solution in the measuring vessel is replaced by paraffin this swelling is eliminated and a good agreement is obtained with both normal and iodoacetate-poisoned (I). Hence the normal contraction of (I) is fully explained by changes in vol. due to changes in the constituents. F. O. H.

[Anaërobic formation and disappearance of pyruvic acid in muscle.] A. Hahn (Z. Biol., 1933, **94**, 97—98).—Polemical (cf. this vol., 742). E. S. H.

Acetylation. Fate of *p*-aminobenzoic acid in the rabbit. B. Harrow, A. Mazur, and C. P. Sherwin (J. Biol. Chem., 1933, **102**, 35—38).—p-$NH_2 \cdot C_6H_4 \cdot CO_2H$ is acetylated to the extent of 25% and this is increased by injection of insulin. The effect of the latter is inhibited by injection of reduced glutathione. H. G. R.

Action of surviving tissue on amino-acids. E. C. Glover (Compt. rend. Soc. Biol., 1932, **107**, 1603—1605).—Tissues with anaërobic glycolysis (brain, embryo, tumour) have no action on NH_2-acids; liver and kidney tissue produce NH_3 or urea. A. A. E.

Synthesis of creatine from tissue-protein. G. Pariset (Compt. rend., 1933, **197**, 704—706).—The sum of the creatine- (I) and creatinine-N (II) excreted by rabbits during starvation and of their bodies after death is considerably > their total (I) + (II) content at the beginning of starvation. This demonstrates creatinoid synthesis from tissue-protein. A. C.

Effect of diet on egg composition. II. Mortality of embryos in eggs from hens on diet containing protein supplements of different origin. T. C. Byerly, H. W. Titus, and N. R. Ellis. **III. Relation of diet to the vitamin-B_1 and -B_2 content of eggs: vitamin-*A* content.** N. R. Ellis, D. Miller, H. W. Titus, and T. C. Byerly (J. Nutrition, 1933, 6, 225—242, 243—262; cf. this vol., 631).—II. Rations containing certain cereal products and protein concentrates, supplemented with lucerne, minerals, and cod-liver oil, were deficient in some substance (possibly vitamin-B_2) necessary to produce eggs capable of supporting embryonic life during the second week of incubation.

III. The effect of variations in the proportion of vitamins-B_1 and -B_2 in the diet on the vitamin content of eggs is examined. No relationship was apparent between vitamin status and hatchability. A. G. P.

Chemical mass-action and protein degradation in the living body. O. Krummacher (Z. Biol., 1933, **94**, 119—134).—A discussion, partly mathematical, of the relations between concn. of protein, rate of hydrolysis, and rate of resorption in the alimentary tract. W. O. K.

Distinctive characters of specific minimum nitrogen output and of exogenous protein metabolism. E. F. Terroine and G. Boy (Compt. rend., 1933, **197**, 702—704).—N metabolism is classified as (*a*) sp. min. N output determined on a carbohydrate diet (I), and (*b*) contingent N output which is exogenous on a protein-rich diet (II) and is determined by difference between (I) and (II). Creatinine (III) is found only in (*a*), creatine (IV) in (*b*). The distribution of excreted N in (*a*) varies considerably with the species of animal, but is approx. const. in (*b*) for the pig, rabbit, and rat. Similarly the coeffs. of protein and purine oxidation vary in (*a*) but not in (*b*), where the vals. are higher. Whilst the abs. val. of NH_3 production is higher in (*b*) than in (*a*), it is lower in relation to the sum of urea-, NH_3-, and NH_2-N. Whilst (III) excretion is const., that of (IV) increases with the dietary protein, indicating different processes for their production. A. C.

Comparative biological value of proteins in different animal species. A. Rajzmann (Compt. rend., 1933, **197**, 706—707).—The mean biological vals. of the total proteins of cow's milk, beef muscle, pease-meal, and of caseinogen, expressed in the Terroine form of Martin and Robison's formula, are 92, 100, 61, and 77, respectively, for the rat; 100, 95, 58, and 81 for the rabbit; and 94, 99, 65, and 78 for the pig. The vals. for each protein vary considerably within each species. A. C.

Milk-energy formulæ for various breeds of cattle. O. R. Overman and W. L. Gaines (J. Agric. Res., 1933, **46**, 1109—1120).—Milk-energy vals. (g.-cal. per g.) determined were: fat $9\cdot253\pm0\cdot065$; protein $5\cdot853\pm0\cdot127$; lactose $3\cdot693\pm0\cdot059$. Formulæ for calculating milk energy based on the % fat showed small differences for different breeds, but the single formula expressed in terms of 4% milk, $0\cdot4M+15F$ (M=wt. of milk, F=wt. of fat), may be used for all breeds. Variations in protein-energy ratio with changes in % fat showed more definite differences with breed. Vals. for crossbred cows were intermediate between those of the parent breeds. The utilisation of the above vals. in determining food requirements for milk production is examined. A. G. P.

Form and function of synovial cells in tissue cultures. II. Production of mucin. E. Vaubel (J. Exp. Med., 1933, **58**, 85—95).—Max. mucin production occurs in media containing a min. of growth-stimulating substances. Liquefaction of plasma is attributed to a proteolytic enzyme. Ch. Abs.

Human purine metabolism. F. Chrometzka (Z. ges. exp. Med., 1933, **86**, 483—528; Chem. Zentr., 1933, i, 2271).—A scheme indicating the mode of degradation of uric acid etc. is advanced. In gout this degradation is retarded; in diabetes insipidus the oxidisability of the purine bases may be inhibited. A. A. E.

Purine metabolism. II. Fate of guanine in the dog. F. W. Allen and L. R. Cerecedo (J. Biol. Chem., 1933, **102**, 313—316; cf. A., 1932, 84).—Guanine is partly converted into allantoin and partly broken down to yield urea. Adenine is toxic in doses > 1·3 g. H. D.

Effect of alkaline water on purine metabolism. E. Hesse and K. Nawrath (Klin. Woch., 1932, **11**, 1538—1540; Chem. Zentr., 1933, i, 2271).—H_2O from Salzbrunn (Kronenquelle) contains HCO_3', CO_2, and cations which separately do not affect the purine metabolism of the dog, but together they cause increased elimination of allantoin and uric acid. A. A. E.

Neuromuscular excitability in relation to the biochemistry of minerals. III. Mineral composition of blood-serum and muscle press-juice or their ultrafiltrates in relation to neuromuscular excitability. Influence of parathyroidectomy on the Ca/Mg ratio of blood-serum. B. Sjollema and L. Seekles (Biochem. Z., 1933, **204**, 316—333).—The authors' previous work (this vol., 532, 979), in which changes of neuromuscular excitability (I) were correlated with changes in the mineral content (II) of the diet, is extended, the (II) of the blood-serum (III), muscle press-juice (IV), and of their ultrafiltrates being investigated. Abnormal Na/K ratios of (III) are associated with only irregular changes of (I). The Ca/Mg ratio of (III) shows irregular fluctuations with increasing (I), whereas the Ca/P ratio is invariably decreased. In parathyroidectomised dogs the Ca/Mg and the Ca/P ratios of (III) decrease. The Ca/Mg ratio is changed in different directions in different forms of tetany and does not always run parallel with changes of (I). In (IV) the total Ca content with diets of abnormal Ca/P and Na/K content increases with increasing (I), the results being the reverse of those in (III). The total Mg content was not directly related to the excitability. P. W. C.

Function of calcium deposits as buffer reserves in acid–base regulation. Chalk glands of the earthworm. H. Dotterweich (Pflüger's Archiv, 1933, **232**, 263—286).—The chalk glands (I) of *Lumbricus terrestris* have considerable buffering capacity against acids. After removal of (I) the p_H of the cœlomic fluid remains normal while the worms are kept in air, but falls much > that of normal worms when the atm. contains 5% CO_2. An atm. containing 8—10% of CO_2 raises the Ca content of the tissues of undissected worms from 10·34 to 17·27 mg. per 100 g., but causes only a slight increase in excretion of Ca. (I) contain a buffer reserve of solid $CaCO_3$ which becomes $CaH_2(CO_3)_2$ as the p_H falls, the process being reversible. Allied phenomena in other invertebrates and other functions of (I) are discussed. Nutr. Abs. (*m*)

Calcium and phosphorus metabolism. XIX. Effect of diet on urinary acid and ammonia excretion in man. W. T. Salter, R. F. Farquharson, and D. M. Tibbetts (J. Lab. Clin. Med., 1933, **18**, 669—679).—The daily urinary excretion of NH_3 by adults receiving potentially neutral diets is equiv. to 21 c.c. of N-acid. With acid-producing foods it rarely exceeds 80 c.c. A high-protein diet does not cause increased NH_3 excretion if sufficient alkali is added to neutralise the acid catabolites. Ch. Abs.

Calcium retention on a diet containing leaf lettuce. M. G. Mallon, L. M. Johnson, and C. R. Darby (J. Nutrition, 1933, **6**, 303—311).—In the metabolism of women subjects, utilisation of the Ca of fresh leaf lettuce was > that of pasteurised whole milk. A. G. P.

Excretion of calcium and phosphorus on maize diet. I. I. Nitzescu, G. Popoviciu, and R. Oprean (Compt. rend. Soc. Biol., 1933, **113**, 326—328).—In children a maize diet decreases the urinary Ca and P and increases the fæcal elimination, with consequent constipation and with an average negative balance of 32·1% for Ca and 17·5% for P. Meat and wheat (I) diet results in an average negative Ca balance of 6·2% and a positive P balance of 11·6%, whilst less Ca is lost by the fæces. Treatment with ultra-violet light reduces the fæcal Ca and P. The best retention of Ca occurs on a diet (II) of maize, milk, and cheese. The retention is fair on (I) if milk is given, but poor on (II) if beans are added. The Ca : P ratio in the excreta on (I) is 0·6 and on the maize and beans diet 1·1. Maize is rachitogenic, especially when associated with beans, but this effect is compensated by treatment with ultra-violet light and perhaps by the addition of cheese and milk to the diet. NUTR. ABS. (*m*)

Influence of bile acids on calcium metabolism. VII. Calcium and phosphorus balance in dogs receiving bile acids. I. OKII (J. Biochem. Japan, 1933, **18**, 45—61).—Intravenous injection of cholic acid or subcutaneous injection of ultra-violet-irradiated Me cholate (A., 1932, 615) into dogs produces an increased assimilation of both P and Ca. F. O. H.

Importance of mineral supplements and iodine for milch cows. G. VON WENDT and W. MULLER-LENHARTZ (Z. Fleisch. Milchhyg., 1932, **42**, 221; Bied. Zentr., 1933, **A**, **3**, 424).—The significance of Ca, Fe, and I in mineral supplements for heavily milking cows is discussed. A. G. P.

Feeding of iodine to poultry. J. SCHMIDT (Berlin. Tierärztl. Woch., 1932, **48**, 161; Bied. Zentr., 1933, **A**, **3**, 425).—Hens are less sensitive to I injury than are mammals. Supplementary feeding with 0·3—0·5 g. KI reduced the size of eggs, and larger doses (to 1·5 g.) interrupted the laying period. With 1·5 g. KI the male reproductive system was not affected. Eggs from hens receiving KI had higher I contents and better keeping qualities. A. G. P.

Amount of iodine in the thyroid glands of Australian merino sheep. M. C. DAWBARN and F. C. FARR (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 179—180).—In the area examined, the use of iodised salt licks did not increase the I content of the thyroid glands. A. G. P.

Effect of an iodised lick on the growth and wool of Australian merino sheep. E. W. L. LINES [with R. G. THOMAS] (J. Counc. Sci. Ind. Res. Australia, 1933, **6**, 181—188).—Ingestion of 185×10^{-6} g. I daily by means of iodised salt licks did not affect growth or wool production in sheep. A. G. P.

Ferri-globulin compound of intermediate iron metabolism. E. STARKENSTEIN and Z. HARVALIK (Arch. exp. Path. Pharm., 1933, **172**, 75—92).—The significance of Fe^{III}–protein compounds (A., 1930, 952) in the metabolism of Fe is discussed. The oxidative power (I) of the blood (defined as mg. of $FeCl_2$ oxidised by 100 c.c. in 5 min.) is approx. 500, being high in rabbits (490—550) and low in men (454). No difference occurs between defibrinated and oxalated blood. Erythrocytes suspended in 0·9% NaCl have a (I) of approx. 50, that of serum is nil, whilst that of washed corpuscles re-suspended in serum is markedly < that of the whole blood. Hence during the separation (I) is partly destroyed. (I) is related to hæmoglobin, whilst the protein of the Fe^{III} complex formed appears to be serum-globulin, the bound Fe being anionic. The complex can be separated by half-saturation with $(NH_4)_2SO_4$ or by dialysis; in the latter instance it is insol. in H_2O, whereas serum-albumin pptd. by $FeCl_3$ is sol. Blood treated with sufficient $FeCl_2$ yields an Fe–protein complex with a N : Fe ratio of 4 : 1. F. O. H.

Oxidation of iron in the blood. F. HENDRYCH and S. MORI (Arch. exp. Path. Pharm., 1933, **172**, 1—4).—The oxidation of Fe^{II} salts and the concomitant formation of a Fe^{III}–globulin complex (cf. preceding abstract) does not occur in completely reduced or CO-saturated blood. Gradual saturation or replacement with O_2 in the two types of blood does not yield oxidising activities proportional to the O_2 content; the vals. are < those expected, indicating that the affinity of O_2 for reduced hæmoglobin is > that for Fe^{II} salts. The oxidation of Fe^{II} by oxyhæmoglobin is not inhibited by HCN or quinine. F. O. H.

Periodic variation of bone-marrow activity and blood formation. E. STARKENSTEIN (Arch. exp. Path. Pharm., 1933, **172**, 36—54).—Partial destruction of the bone-marrow of rabbits and dogs produces an anæmia which spontaneously disappears within a few weeks. The effect is far more marked in autumn and winter (I) than in spring and summer (II). During (II) the hæmoglobin, erythrocyte count, and colour index are lowest, probably due to the gradual utilisation of reserve material during (II) and the resulting lack of stimulation of organ function during (I). Parallel variations are shown in metabolic rate, in the excitability of the sympathetic nervous system, in the sensitivity to poisons, and in the reproductive processes. F. O. H.

Oxidation and reduction of iron in organs. E. STARKENSTEIN and F. JOHNE (Arch. exp. Path. Pharm., 1933, **172**, 93—103).—The reducing substances of liver (I) extractable with conc. HCl at 100° consist partly of those extracted with H_2O at 100°. Practically all the Fe in rabbit's (I) is H_2O-insol. and is extracted only by hot 5*N*-HCl. The Fe^{III} of Na Fe citrate is rapidly reduced by (I) to Fe^{II}, which is only partly H_2O-sol. The reducing action of (I) is mainly due to enzyme action; heat or treatment with 2*N*-HCl greatly reduces, whilst absence of O_2 accelerates the action. That of blood is small, whilst its oxidising action on $FeCl_2$, unlike that of (I), is marked and yields a H_2O-sol. form of Fe^{III}, which after a time becomes partly H_2O-insol. Both (I) and blood also reduce $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$; the reverse process of oxidation does not occur. The non-reducible, complex Fe^{III} of (I) probably originates from Fe^{II} oxidised in other organs before being transported to (I). F. O. H.

Autoxidation of ferrous salts and stability of their solutions. E. STARKENSTEIN and R. NEIGER (Arch. exp. Path. Pharm., 1933, **172**, 104—118).—Neutral aq. Fe^{II} salts are not stable in presence of O_2, whilst acid solutions have a stability (I) dependent not only on the p_H, but also on the anion. With simple inorg. Fe^{II} salts, the (I) of the neutral solution depends on the readiness of hydrolysis of the Fe^{III} salt formed by oxidation (II); thus in decreasing order of (I) are obtained: Cl′, SO_4'', AcO′, HCO_3'. The Fe^{II} salts of complex-forming org. acids (citrate, gluconate, lactate) are even less stable. In neutral solution formation of Fe^{III} [which inhibits (II)] is followed by its removal as $Fe(OH)_3$. The course of (II) depends on the concn. of Fe^{II} salt and on the temp. With simple inorg. salts it is independent of light, whilst with Fe^{II} citrate (II) is irregular, due to the reducing action of light. F. O. H.

Rôle of zinc in nutrition. J. M. NEWELL and E. V. MCCOLLUM (J. Nutrition, 1933, **6**, 289—302).—

It is improbable that Zn is an essential nutritional factor in the growth of rats, although in its absence reproduction was adversely affected. The total Zn content of the bodies of rats was influenced by that of the diet. A. G. P.

Carotid-sinus polyuria. S. JANSSEN and J. SCHMIDT (Arch. exp. Path. Pharm., 1933, **171**, 672—690).—In anæsthetised dogs and rabbits, clamping of the two carotids leads after a short latent period (1—2 hr.) to an abnormally high content of NaCl (up to 1·5%) in the urine usually associated with polyuria. The effect is due to a nervous reflex originating at the carotid sinus. W. O. K.

Biological action of intermediate products of tissue decomposition. I. Influence of pancreatolysate on blood-sugar. S. G. GENESS and S. P. EPSTEIN (Arch. exp. Path. Pharm., 1933, **171**, 733—743).—Digests of pancreas administered to rabbits usually reduce the blood-sugar. The effect is especially marked with a fraction free from protein but containing the larger fission products. W. O. K.

Influence of vagotomy on the blood-sugar. F. HÖGLER (Arch. exp. Path. Pharm., 1933, **172**, 325—342).—Unilateral or double vagotomy (I) has no marked influence on the blood-sugar (II) of rabbits, whilst with unilateral (I) ergotamine completely inhibits the alimentary hyperglycæmia (III) following ingestion of glucose or galactose. Thus whilst the vagi play no part in the maintenance of the fasting (II) they are concerned with the function of the liver in the removal of (III). F. O. H.

Suitability of infusions and tinctures of *Digitalis* as medicaments. S. ROSENKRANZ (Arch. exp. Path. Pharm., 1933, **172**, 26—35).—Aq. extraction of the leaves affords a complete extraction even of the normally insol. glucosides. Such extracts are, however, somewhat less active than aq. EtOH extracts (probably due to destruction of glucosides by the high temp. used), whilst their stability is low. An optimum extraction is given by 50—70% EtOH. Higher concns. of EtOH yield more active but less stable preps. Extraction with 70% EtOH and storage in the dark at low temp. ensures retention of activity for at least 3 months. F. O. H.

Physiological action of the principles isolated from the secretion of *Bufo arenarum*. K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 1—13).—From the secretion have been isolated cholesterol (I), *arenobufagin* (II), $C_{25}H_{34}O_6$, m.p. 220°, *arenobufotoxin* (III), $C_{25}H_{34}O_6,C_{14}H_{26}O_5N_4$, m.p. 194—195°, probably a compound of (II) with suberylarginine; *arenobufotenine A* (IV) (*flavianate*, $C_{12}H_{20}O_3N_2,C_{10}H_6O_8N_2S$, m.p. 130—131°), *arenobufotenine B* (V) (*flavianate*, $C_{14}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 265°). (II) and (III) have digitalis-like actions, whilst (IV) and (V) are indole derivatives, which stimulate the guinea-pig's isolated uterus, but differ pharmacologically in certain other respects. The presence of adrenaline in the secretion is indicated. W. O. K.

Physiological action of the principles isolated from the secretion of the European green toad (*Bufo viridis viridis*). K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 14—25).—From the parotid secretion have been separated cholesterol (I) containing approx. 0·3% of ergosterol; *viridobufagin* (II), $C_{23}H_{34}O_5$, m.p. 255—255·5°; *viridobufotoxin* (III), $C_{23}H_{34}O_5,C_{14}H_{26}O_5N_4$ (?), m.p. 199°, possibly a compound of (II) with suberylarginine; *viridobufotenine A* (IV) (*flavianate*, $C_{12}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 170°); *viridobufotenine B* (V) (*flavianate*, $C_{12}H_{20}O_3N_2,C_{10}H_6O_8N_2S$, m.p. 131—132°). (II) and (III) have digitalis-like actions, whilst (IV) and (V) are indole derivatives and act on smooth muscle. (V) is probably identical with arenobufotenine A (see preceding abstract). (IV) was isolated from a 1930 batch of frogs, whilst in a 1931 batch (V) was obtained instead. W. O. K.

Physiological action of the principles isolated from the secretion of the Japanese toad (*Bufo formosus*). K. K. CHEN, H. JENSEN, and A. L. CHEN (J. Pharm. Exp. Ther., 1933, **49**, 26—35).—From the parotid secretion of *B. formosus*, the following compounds have been isolated, cholesterol (I); *gamabufagin* (II), $C_{27}H_{38}O_6$, m.p. 253—254°; *gamabufotoxin* (III), $C_{27}H_{38}O_6,C_{14}H_{26}O_5N_4$, sinters 146°, possibly a compound of (II) and suberylarginine; *gamabufotenine* (IV) (*flavianate*, $C_{12}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 186—187°). (II) and (III) have digitalis-like actions, whilst (IV) is an indole derivative and has pressor activity. Adrenaline has been detected in the secretion (cf. Kotake, A., 1928, 1138; Wieland and Vocke, A., 1930, 1466). W. O. K.

Determination of veratrine. C. H. HUMMELSHEIM (Arch. exp. Path. Pharm., 1933, **172**, 227—244).—The pharmacological properties of veratrine (I) were compared with those of aconitine (II), quinine (III), and colchicine (IV). Both (I) and (II) in a concn. of $1:10^{-5}$ have an optimum effect on the frog's gastrocnemius after 10 min., but with (II) a second poisoning of the muscle does not occur. (III) is effective in concns. of 0·033—0·05%, whilst 0·2% of (IV) is without action. Aq. (I) is stable at room temp. A local anæsthesia is produced by 1% solutions of (II) but not of (I). The content of (I) in *Sabadilla* extracts can be determined by comparison of their action on the dorsal muscle of leech with that of standard solutions of (I). F. O. H.

Pharmacological action of amines related to ephedrine and tryptamine. K. K. CHEN and A. L. CHEN (J. Amer. Pharm. Assoc., 1933, **22**, 813—819).—The following compounds have been examined (cf. Chen *et al.*, A., 1929, 1105): *p*-methyl-, *p*-methoxy-, and 3:4-dihydroxy-norephedrine, 3:4-dihydroxy-ephedrine, tryptamine, *N*-methyl- and *N*-dimethyltryptamine, *N*-trimethyltryptamine methiodide, hypaphorine, and cinobufotenine flavianate, $C_{13}H_{20}O_2N_2,C_{10}H_6O_8N_2S$ (cf. Jensen and Chen, A., 1932, 1142). W. S.

Catalytic influence of iron salts on the decomposition of nicotine during smoking. E. STARKENSTEIN and W. STEJSKAL (Arch. exp. Path. Pharm., 1933, **172**, 119—136).—Treatment of cigars with a solution containing $Fe(NH_4)_2(SO_4)_2$ and other Fe salts (Bonicot solution) reduces the nicotine (I) in the

smoke by approx. 25%. This is due to catalytic acceleration of the decomp. of (I) on the interface of the C–Fe system formed during combustion.
F. O. H.

(I.) Influence of morphine on the premedication value of tribromoethanol (avertin) in relation to nitrous oxide anæsthesia in the rat. (II.) Influence of morphine on the premedication values of ethyl α-methylbutylbarbiturate (pentobarbital) and ethyl*iso*amylbarbituric acid (amytal). O. W. Barlow and J. T. Duncan (J. Pharm. Exp. Ther., 1933, 49, 50—59, 60—66).—(I) In white rats the premedication efficiency of combined doses of avertin and morphine is > the sum of the effects of the two agents administered separately. Respiratory depression and toxicity with combined medication were also marked.

(II.) Somewhat similar results are obtained when morphine is combined with amytal or pentobarbital.
W. O. K.

Comparison of the effects of morphine, pantopon, codeine, narcotine, and papaverine on the respiration of rats and rabbits. O. W. Barlow (J. Lab. Clin. Med., 1933, 18, 785—795).—The respiratory changes produced by the administration of various opium alkaloids differ only quantitatively from those produced by morphine. Ch. Abs.

Relation between the chemical structure of the opium alkaloids and their effect on the movement of the intestines of rabbits *in situ*. K. Kin (Keijo J. Med., 1932, 3, 501—529).—Alkaloids containing *iso*quinoline nuclei tend to stimulate, whilst those containing phenanthrene or C_6H_6 nuclei tend to inhibit, the peristaltic action of rabbits' intestines. Side-chain Ac, alcoholic OH, OMe, and $O{\cdot}CH_2{\cdot}O$ diminish, whilst phenolic OH increases, the effect of the nucleus. Stimulation decreases in the order: *apo*morphine, narceine, narcotine, heroine, codeine, morphine, papaverine, thebaine. Ch. Abs.

Physiological identification of strychnine in forensic toxicology. A. S. Negrão (Arch. Med. Legal, 1932, 5, 45—50).—White mice 14—16 days old are preferable to frogs for identification of strychnine. Injection of a min. of 0·001 mg. of the nitrate or sulphate induces tetany accompanied by a characteristic tremor in the tail. R. K. C.

Reduction in the toxicity of alkaloids by hexamethylenetetramine. J. Gautrelet (Bull. Acad. Méd., 1932, 108, 1678—1681; Chem. Zentr., 1933, i, 2136).—Pretreatment of guinea-pigs with $(CH_2)_6N_4$ (I) protects them against an otherwise lethal dose of nicotine (II). The (I)–(II) mixture is inactivated by previous heating at body temp. The (II)-poisoned dog's heart *in situ* is revived by CH_2O or (I) methiodide. A. A. E.

Detection and determination of aloes in post-mortem cases. G. F. Hall and W. M. Keightley (Analyst, 1933, 58, 518—523).—The dried viscera are extracted with Et_2O and the aloes extracted by boiling with successive quantities of 60% EtOH. Proteins are removed with slightly acid $Pb(OAc)_2$, and excess of Pb with Na_2SO_4. Bile pigments, if present, are removed by treatment for 5 min. with 0·2*N*-NaOH and 0·5 g. of animal C per 25 c.c. Aloin is then determined by semi-quant. methods based on Schoutelen's (Year Book Pharm., 1893, 166) or a modification of Bornträger's (*ibid.*, 1880, 140) reaction. The former is not sp. in presence of cascara. E. C. S.

Detection of extractable poisons by freezing. O. Schmidt (Deut. Z. ges. gerichtl. Med., 1933. 20, 260—266; Chem. Zentr., 1933, i, 2727—2728).—Organs are kept at −10° to −15°; synthetic and vegetable poisons behave as crystalloidally dissolved substances, passing into solution again on melting.
A. A. E.

Inhalation technique for the comparison of semi-volatile liquids. D. A. Bryce (J. Lab. Clin. Med., 1933, 18, 638—640).—An apparatus for the biological assay of liquids of b.p. 37—100° is described.
Ch. Abs.

Determination of alcohol in blood by Widmark's method. H. Kaiser and E. Wetzel (Angew. Chem., 1933, 46, 622—625).—The method is satisfactory. The EtOH content of the blood for a given consumption of alcoholic liquors under controlled conditions varies considerably with the subject.
S. C.

Determination of alcohol in blood. F. J. Holzer (Deut. Z. ges. gerichtl. Med., 1933, 20, 284—288; Chem. Zentr., 1933, i, 2727).—Widmark's procedure is modified. A. A. E.

Blood-alcohol after administration of alcohol. O. Graf and E. Flake (Arbeitsphysiol., 1932, 6, 141—167; Chem. Zentr., 1933, i, 2268).—Widmark's analytical procedure is modified; his results are confirmed. A. A. E.

Relation between blood-alcohol and the psychological effect of alcohol. O. Graf (Arbeitsphysiol., 1932, 6, 169—213; Chem. Zentr., 1933, i, 2268).—Determination of blood-EtOH indicates the degree of psychological disturbance only within wide limits. A. A. E.

Toxicological detection of veronal, luminal, and phanodorm. J. Peltzer (Chem.-Ztg., 1933, 57, 816).—The method is a combination of those previously described (A., 1927, 1219; 1931, 981, 1328) in which proteins are coagulated with $CCl_3{\cdot}CO_2H$ and the hypnotics are characterised with $CoCl_2+$ MeOH–BaO and determined by means of the C_5H_5N–Cu derivatives. E. H. S.

Presence and detection of diethylbarbituric acid in cerebrospinal fluid. G. Vitte (Bull. Trav. Soc. Pharm. Bordeaux, 1932, 70, 255—256; Chem. Zentr., 1933, i, 1661).—In a case of veronal poisoning the substance was found in the cerebrospinal fluid; the procedure of separation is described. A. A. E.

Determination, identification, and elimination of barbituric acid derivatives in urine. Paget and Desodt (J., Pharm. Chim., 1933, [viii], 18, 207—214).—Urine is treated with $K_4Fe(CN)_6$ and $Zn(OAc)_2$, filtered, acidified, and barbituric acid derivatives are extracted with Et_2O. The microchemical reactions of Denigès are recommended for their identification. The mean urinary eliminations of veronal (250 mg. per day), rutonal (200 mg.), dial (100 mg.), and gardenal (200 mg.) by mental patients are 65, 49, 30, and 25% of the ingested amounts, respectively. This order is not affected by the observed daily variations for each drug. A. C.

Behaviour of cyanamide in the animal body. F. Horn (Z. Biol., 1933, 94, 159—170).—$NH\dot{:}C(NH_2)_2$ (I) could not be detected in the urine of rabbits or of dogs poisoned with $CN{\cdot}NH_2$ (II). Both (I) and (II) cause somewhat similar blood-sugar changes, but the course of the temp. and the other clinical symptoms are different. It is probable therefore that the toxicity of (II) is not due to the formation from it of (I) in the animal body. The toxic symptoms of $NH_2{\cdot}C(\dot{:}NH){\cdot}NH{\cdot}CO{\cdot}NH_2$ also differ from those of (II) poisoning. W. O. K.

Pharmacological action of the phosphorous acid esters of the phenols. M. I. Smith, R. D. Lillie, E. Elvove, and E. F. Stohlman (J. Pharm. Exp. Ther., 1933, 49, 78—99).—The pharmacological action of Ph_3, *m*- and *p*-$(C_6H_4Me)_3$ phosphites qualitatively resemble those of the *o*-ester, but differ quantitatively. Part of the action is probably due to phenol liberated by hydrolysis of the unstable ester, and part to the direct effect of the ester itself or some derivative on the nervous system. W. O. K.

Spontaneous motion of spermatozoa and hydrogen-ion concentration. W. Schlenk, jun. (Biochem. Z., 1933, 265, 29—35).—The spontaneous motion of spermatozoa (I) of the rainbow trout in natural waters is controlled exclusively by $[H^{\cdot}]$. At $p_H \ngtr 7{\cdot}8$ no movement occurs, but at p_H 8 there is normal movement. The undiluted (I) have p_H about 7·3 and so begin to move immediately in spring H_2O (p_H about 8·0). W. McC.

Formation of lipin-soluble salts in chloride-sulphate solutions. E. Starkenstein and G. Hahnel (Arch. exp. Path. Pharm., 1933, 172, 55—74).—When aq. solutions of two inorg. salts are mixed and treated with a large excess of $EtOH–Et_2O$ (2 : 1), the amount of material remaining in solution affords a criterion of the lipin-solubility (I) of the salt system. Addition of increasing amounts of NaCl or Na_2SO_4 to aq. $MgCl_2$ produces an increase in the (I) of $Mg^{\cdot\cdot}$, which, however, is not linearly related to the amount of Cl' or SO_4'' added. Addition of *N*- or 2*N*-HCl to $MgSO_4$ results in only a small increase in the (I) of $Mg^{\cdot\cdot}$; with 0·1*N*-HCl, however, the (I) of the $Mg^{\cdot\cdot}$ of a *N*/16 solution is complete. The results of the above and other systems are discussed with reference to their therapeutic action and to their occurrence in mineral H_2O. F. O. H.

Action of curative waters on the composition of the blood. I. Influence of Karlsbad water on serum-calcium. E. Stransky (Arch. exp. Path. Pharm., 1933, 172, 149—160).—Rabbits, on a standard diet and drinking Karlsbad mineral H_2O for a period of 25 days, experience an increase in body-wt., in dry wt. of the serum, and in serum-Ca when compared with controls on pure H_2O. The level of ionised Ca and the ratio of total to free Ca in the serum are not significantly changed. F. O. H.

Arsenic in the ash of cadavers. H. Jesser and A. Schrempf (Deut. Z. ges. gerichtl. Med., 1933, 20, 278—283; Chem. Zentr., 1933, i, 2728).—Ramberg's method for the detection of As is satisfactory. A. A. E.

Resorption of aluminium in the animal organism. Aluminium content of animal tissues. J. Wührer (Biochem. Z., 1933, 265, 169—180).—The organs and body-fluids of dogs contain only traces of Al and no increase occurs following long-continued administration of Al [$AlCl_3$, $Al(OH)_3$]. In man orally administered Al is excreted almost quantitatively in the fæces. Only when large amounts of or readily sol. salts of Al are given is there any detrimental effect on health. W. McC.

Mineral metabolism and salyrgan diuresis. M. Nothmann (Arch. exp. Path. Pharm., 1933, 172, 402—406).—Injection of salyrgan (I) into men produces a marked increase in the blood-K, a max. being attained after 24 hr., whilst the urinary excretion of K is also increased. The blood- and urine-P are unchanged. The increase in electrical excitability, the tetanus occurring during injection of (I), and the changes in the alkali reserve of the blood are probably due to the increased blood-K. F. O. H.

Influence of thallium salts and thyroid preparations on the plumage of ducks. R. Prawochenski and J. Slizynski (Nature, 1933, 132, 482).—Neither thyroid preps. nor TlOAc produce moulting in ducks. L. S. T.

Penetration through tissue of iodine in different solvents. M. S. Biskind (Proc. Soc. Exp. Biol. Med., 1932, 30, 35—37).—Aq. solutions had a greater speed of penetration through ventral frog skin than tinctures containing 3·8 times as much I. Ch. Abs.

Effect of iodine in different solvents on the permeability of frog skin to Ringer solution. M. S. Biskind (Proc. Soc. Exp. Biol. Med., 1932, 30, 37—38).—Permeability was greatly increased by 95% EtOH, unaffected by 2% aq. mercurochrome, and greatly and equally reduced by aq. I and 7% U.S.P. tincture of I. Ch. Abs.

Effect of potassium iodide on basal metabolism and respiratory quotient in thyroidectomised guinea-pigs. W. J. Siebert (Proc. Soc. Exp. Biol. Med., 1932, 29, 1146—1148).—KI (0·05 g. daily) lowered the metabolism and raised the R.Q. of the thyroidectomised guinea-pig. Ch. Abs.

Toxicity of organic fluorides. W. P. Yant (Amer. J. Pub. Health, 1933, 23, 930—934).—20% by vol. of CCl_2F_2 (I) in air has no permanent harmful effect on dogs and monkeys exposed for 121 hr. continuously or for 8 hr. on many successive days. 14—15% of $C_2Cl_2F_4$ (II) is without permanent effect after 21 exposures of 8 hr., but exposure to higher concns. or longer exposures daily cause congestion of all organs and are fatal. During exposure to (I) and (II) symptoms similar to alcoholic ataxia are evident, but disappear immediately after removal. The odour and irritant properties of (I) and (II) are sufficiently marked to give distinct warning of their presence in sub-lethal concns. E. C. S.

Spectrographic analysis of teeth of rats on diets containing fluorine. H. Blumberg, H.

KLEIN, and E. V. MCCOLLUM (J. Dent. Res., 1933, **13**, 188—189).—Traces of F were found in the teeth of rats on a control diet and greater concn. on a diet with 0·05% NaF with a deposition also in the skull bones. The production of defective enamel on diets containing F may be due to inclusion of F during dental growth. NUTR. ABS. (*b*)

Action of minute amounts of copper on the organism of mammals. Effect of minute concentrations of heavy metal on the degradation of glycogen *in vitro*. H. HANDOVSKY, D. VON COTZHAUSEN, and R. SCHALLEHN (Biochem. Z., 1933, **265**, 110—114).—Very low concns. (10^{-4} to 10^{-9} mol.) of $CuSO_4$ attack glycogen (I) in aq. solution *in vitro* with production of a reducing substance (II). If KCl (0·9%) is present the degradation increases by 100%, possibly because the degree of dispersion of (I) is increased. It is the $Cu^{\cdot\cdot}$ which is active. $Fe^{\cdot\cdot\cdot}$ is also active, but not $Mn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ag^{\cdot}$, or $Hg^{\cdot\cdot}$. The amount of (II) produced is independent of the concn. of (I) or $Cu^{\cdot\cdot}$. (II) and also added glucose or maltose fix the $Cu^{\cdot\cdot}$ and hence soon inhibit the effect. W. McC.

Interaction of metallic containers and foodstuffs. III. Biological rating of metals. J. SCHWAIBOLD and F. FISCHER (Biochem. Z., 1933, **265**, 124—132; cf. A., 1931, 652).—Small doses (*e.g.*, 2 mg. per litre) of salts (in some cases also of corrosion products) of Zn, Ni, Pb, Ag, and Hg are poisonous to tadpoles. Brass is also poisonous, but Al, Sn, Au, and Pt are only slightly poisonous or harmless to them. Mice are more resistant; they succumb to Pb and Cu, but are not affected by relatively high doses of $HgCl_2$. W. McC.

Normal absorption and excretion of lead. I. In primitive life. II. In modern American life. III. Sources of normal lead absorption. IV. In infants and children. R. A. KEHOE, F. THAMANN, and J. CHOLAK (J. Ind. Hyg., 1933, **15**, 257—272, 273—288, 290—300, 301—305).—I. Pb is a natural constituent of the soil and vegetation of primitive Mexican regions and occurs in the blood (0·0—0·00006%), urine (I) (average 0·0138 mg. per litre), and fæces (II) (average 0·0035% of the ash) of the inhabitants who live on local produce. Analytical methods based on those of Fairhall (A., 1922, ii, 659) and using the colour developed by *s*-diphenylcarbazide for the final determination of Pb are described.

II. The normal daily intake of Pb by adults is approx. 0·16—0·28 mg., whilst the daily excretion is 0·02—0·08 mg. per litre of (I) and 0·03—0·10 mg. per g. of ash of (II). The greater part of the ingested Pb is unabsorbed and is found in (II). Thus daily oral administration of 1 and 5 mg. of $PbCl_2$ produces a daily absorption of 0·5 and 1 mg., respectively. Data for the distribution of Pb in normal human tissues indicate that the greatest content (0·001%) is in bone. The non-occurrence of Pb in normal (I) and (II) is refuted.

III. Small amounts ($<$ 1 mg. per kg.) of Pb are of general occurrence in food. Analytical data and indications of the sources of contamination are given.

IV. The Pb excretion of normal American children [average 0·08 mg. per litre in (I) and 0·08 mg. per g. of ash of (II)] is $>$ that of Mexican children living under primitive conditions (0·015 and 0·04 mg., respectively). Normal human milk contains 0·0—0·05 mg. per litre, whilst human fœtuses contain small but definite amounts (up to 0·41 mg.) of Pb. F. O. H.

(*a*) Lead absorption and excretion in certain lead trades. (*b*) Lead absorption and excretion in relation to the diagnosis of lead poisoning. R. A. KEHOE, F. THAMANN, and J. CHOLAK (J. Ind. Hyg., 1933, **15**, 306—319, 320—340).—(*a*) The excretion of Pb by workmen engaged in Pb trades is markedly $>$ the normal and serves as a criterion of incipient Pb poisoning.

(*b*) Men absorbing abnormal amounts of Pb subsequently display an increased Pb excretion, which diminishes rapidly for a period of several weeks and then slowly until the normal excretory level is attained. F. O. H.

Stimulation of the excretion of lead by irradiation. L. PINCUSSEN (Klin. Woch., 1933, **12**, 275; Chem. Zentr., 1933, i, 2135).—Mice and rats which had received Pb salts orally contained 10—20% less Pb after irradiation with visible and thermal rays than those irradiated with ultra-violet rays or kept in the dark. A. A. E.

Effect of irradiation on the excretion of zinc. K. NAKADATE (Biochem. Z., 1933, **265**, 61—63; cf. Pincussen and Roman, A., 1931, 1330).—In rats to which $Zn(OAc)_2$ is administered irradiation causes decreased excretion of Zn, light of long λ having more pronounced effect than that of short λ. W. McC.

Effect of some forms of radiant energy on the distribution of colloids in the organism. I. T. TEPLOV and E. A. DOBROKHOTOVA (Arch. sci. biol., U.S.S.R., 1932, **32**, 72—79).—In rabbits which had been injected intravenously with trypan-blue and irradiated, the dye was deposited mainly in the irradiated tissues. CH. ABS.

Metabolic changes produced by irradiation. XII. Effect of various types of radiation on the glutathione content of the organs of irradiated animals. L. PINCUSSEN and S. TAKAHASHI (Biochem. Z., 1933, **265**, 64—68; cf. A., 1932, 96).—Results given previously require multiplication by 1·23. Irradiation of rats with various kinds of visible light (I) (Na- and Hg-vapour lamps, Ne lamp) produces no increase (but sometimes a decrease) in the glutathione (II) content of their livers. Neither (I) nor infra-red (III) light has any effect on the (II) of the spleens. Short-wave (I) and ultra-violet light (IV) produce increase in the (II) of the lungs, whilst long-wave (I) and (IV) cause decrease. In the muscle (I) increases (II), but neither (III) nor (IV) has any effect. W. McC.

Influence of diet on the sensitivity of animal tissues to radiation. E. UHLMANN (Strahlenther., 1933, **46**, 550—564).—Rabbits fed on an acid diet (exclusively oats) are more sensitive to irradiation with *X*-rays than those fed on a normal mixed diet (hay, oats, turnips, potatoes). NUTR. ABS. (*m*)

Action of light on the chemistry of the cell. I. Experiments with tissue slices. II. Ex-

periments with red blood-corpuscles. III. Influence of histamine. J. Wohlgemuth and E. Szörényi (Biochem. Z., 1933, **264**, 371—388, 389—405, 406—411).—I. The O_2 utilisation of slices of tissue does not, but after incorporation of dye sensitisers (I) does, increase on irradiation with an electric bulb, but this additional respiration is accelerated by HCN and is as great at 20° as at 37·5°. Anaërobic formation of lactic acid (II) is unaffected by these conditions. Irradiation with visible or ultra-violet light in presence or absence of (I) injures tissue respiration, anaërobic formation of (II) in absence of (I) being increased and in presence of (I) decreased.

II. When red blood-corpuscles (I) are irradiated in presence of hæmatoporphyrin, methæmoglobin is formed, the process being accelerated by HCN, especially in presence of certain sensitisers. Hæmatoporphyrin increases the respiration of (I) in the dark, the increase being greater when the cells have been previously irradiated. If during a respiration experiment irradiation is started, the O_2 utilisation increases by 300—400%, the action being even greater with hæmolysed than with intact cells. This photo-oxidation is independent of the temp. and is not inhibited by HCN. No parallelism exists between photo-oxidative and photodynamic action of sensitisers. Neither normal oxidation nor the photo-oxidation by (I) is effected by glutathione.

III. Histidine causes a very small increase of liver respiration, but does not affect that of kidney and skin. Histamine increases the respiration of liver and skin by 200—300%, of kidney and brain by about 25%, but does not increase the respiration of Jensen sarcoma. P. W. C.

Spectral resolution of the mitogenetic radiation of the stimulated nerve. G. S. Kalendarov (Arch. Sci. biol., U.S.S.R., 1932, **32**, 26—33).—On stimulation by section the sciatic nerve of frogs emits mitogenetic rays in the range 1200—2400 Å. The metabolism of stimulated nerves apparently includes glycolysis and the oxidation of carbohydrates and possibly of proteins. Ch. Abs.

Yeast as a detector of mitogenetic radiation. S. V. Konstansov (Arch. sci. biol., U.S.S.R., 1932, **32**, 34—38).—A criticism of Gurwitsch's original method. Ch. Abs.

[Yeast as a detector of mitogenetic radiation.] A. G. Gurwitsch (Arch. sci. biol., U.S.S.R., 1932, **32**, 39; cf. preceding abstract).—A reply. Ch. Abs.

Enzyme action and enzyme formation in living cells. H. von Euler and G. Günther (Z. physiol. Chem., 1933, **220**, 69—85).—In barley heated at 43° for 30 min. before germination in order to disturb the enzymic equilibrium, certain grains showed delayed germination but no abnormality in enzymic activity. Catalase formation and stability are greatly dependent on conditions of germination. Similar treatment of yeast produced no marked heat-activation of catalase, but ultra-violet irradiation increased the activity by > 700%. J. H. B.

Peroxidase. D. B. Hand (Ergebn. Enzymforsch., 1933, **2**, 272—281; Chem. Zentr., 1933, i, 2562—2563).—A discussion including reference to Fe-porphyrin compounds (I) in yeast and the relation of (I) in general to HCN and CO. A. A. E.

Determination of peroxidase in agricultural products. A. K. Balls and W. S. Hale (J. Assoc. Off. Agric. Chem., 1933, **16**, 445—453).—The rate of decomp. of H_2O_2 by the enzyme is determined in the presence of pyrogallol (I). The enzyme solution is added to 0·625 g. of (I), 4·0 c.c. 0·1N-H_2O_2, 25 c.c. of phosphate buffer (p_H 8·0), and H_2O to make up to 250 c.c., beneath a layer of paraffin. Samples are removed at 0, 2, 5, and 10 min., run into 0·5 g. of (I) in H_2SO_4, KI is added, and liberated I titrated after 12—20 min. The rate of H_2O_2 decomp. may be converted into the "purpurogallin no." of Willstätter and Stoll (A., 1923, i, 262). The presence of catalase does not interfere, (I) absorbing in peroxidic form all liberated O_2. Peroxidase may be extracted from material for analysis by grinding with sand and a phosphate buffer solution of p_H 8. J. S. A.

Influence of short electrical waves on leucocyte oxidases. G. Jorns (Strahlenther., 1933, 46, 384—388; Chem. Zentr., 1933, i, 2563).—No effect on oxidation mechanism was observed. A. A. E.

Oxidase and dehydrogenase systems of the crystalline style. C. Berkeley (Biochem. J., 1933, **27**, 1357—1365; cf. this vol., 297).—The oxidase system (I) of the cryst. style of *Saxidomus giganteus* consists of a peroxidase, present in the style, and an autoxidisable substance associated with the diatoms of the food. (I) acting on glucose produces glucosone but no acid. A dehydrogenase system (II) is also present, consisting of a substance in the style and another in the diatoms. In vac., (II) produces glucosone from glucose in the presence of methylene-blue. It is suggested that (I) acts as H acceptor for (II). A. W.

Mechanism of dehydrogenation. A. Bertho [with V. Schmitt] (Ergebn. Enzymforsch., 1933, **2**, 204—238; Chem. Zentr., 1933, i, 2259—2261).—A discussion, with special reference to the formation of H_2O_2 in biological and other dehydrogenations. A. A. E.

Specificity of hydratases. Action of peas and yeast on crotonic acid. K. P. Jacobsohn and F. B. Pereira (Compt. rend. Soc. Biol., 1933, **108**, 208—210; Chem. Zentr., 1933, i, 2119).—Crotonic acid is unattacked by peas or yeast at p_H 7·0; hence fumarase is considered sp. A. A. E.

Enzyme models. W. Langenbeck (Ergebn. Enzymforsch., 1933, 2, 314—335; Chem. Zentr., 1933, i, 2561—2562).—A discussion of org. catalysts having an enzyme-like action. The active group of carboxylase is probably NH_2; a reaction scheme is outlined. A. A. E.

Separation of enzymes from their mixtures. M. Sreenivasaya and N. K. Iyengar (Nature, 1933, **132**, 604—605).—The method described utilises the difference in mol. wt. of enzymes. The enzyme extract is cooled and centrifuged into three layers at approx. 6000 r.p.m. for 15 min. The top layer of ice-cold H_2O contains the most easily diffused enzymes and the bottom those of higher mol. or micellar wts. The method has been successfully applied to the fractionation of inulinase and invertase; it also gives a comparative idea of relative mol. wts. L. S. T.

Effect of coagulation of accompanying proteins on the activity of amylase. A. Oparin, S. Manskaja, and M. Magaram (Biochem. Z., 1933, **265**, 21—28; cf. this vol., 634).—The resistance of amylase (I) to inactivation by heat (II) is reduced by non-dialysed but increased by dialysed solutions (III) of ovalbumin. Analogous to (I) is inactivation in the cold (IV) by acid. When (III) are boiled and the protein is pptd. with salt no (II) or adsorption of (I) occurs. (I) is protected from inactivation in the cold by addition of peptone, which, however, does not reactivate inactivated (I). 50—60% reactivation after (II) and (IV) is brought about by digesting the protein ppt. with pepsin. W. McC.

Specificity of emulsin. B. Helferich (Ergebn. Enzymforsch., 1933, **2**, 74—89; Chem. Zentr., 1933, i, 2261).—The behaviour of β-*d*-glucosidase in the "emulsin" of sweet almonds towards various glucosides is summarised and discussed. A. A. E.

Constituent enzymes of myrosinase. C. Neuberg and O. von Schoenebeck (Biochem. Z., 1933, **265**, 223—236; cf. A., 1926, 1060; this vol., 863).—By pptn. with $Hg(OAc)_2$, $Pb(OAc)_2$, or Pb phosphate, adsorption on kaolin, Al_2O_3, or $Fe(OH)_3$, and elution with aq. Na and K phosphates and carbonates or aq. NH_3 with or without glycerol, the sulphatase (I) can be almost completely separated from the thioglucosidase (II). (I) and (II) are inactivated by heat, (II) being more resistant than (I). No separation of (I) from (II) can be attained by dialysis. Both are stable in H_2O at p_H 5·5. At $p_H < 3$ (II) is completely and (I) is half inactivated. (II) is unaffected by strong alkalinity, which, however, partly inactivates (I). Units for measuring the action of (I) and (II) are proposed. W. McC.

Glycolysis. H. K. Barrenscheen and H. Beneschovsky (Biochem. Z., 1933, **265**, 159—168; cf. Nilsson, this vol., 425).—Muscle (pulp and extract) and possibly liver (but not blood, brain, or kidney) dephosphorylate synthetic phosphoglyceric acid to $AcCO_2H$, small amounts of lactic acid (I) being produced at the same time. *dl*-Glyceraldehydephosphoric acid (II) is degraded by tissues with production (in some cases at least) of (I), but if glycolysis is inhibited AcCHO is produced, although the degree of dephosphorylation is unchanged. Much of added (II) seems to be converted into a condensation product, possibly hexosediphosphoric acid. These results and theoretical considerations support the views of Nilsson and contradict those of Embden *et al.* (Klin. Woch., 1933, **12**, 213). W. McC.

Rôle of iron in glycolysis of blood and muscle. H. J. Ustvedt (Biochem. Z., 1933, **265**, 154—156; cf. Zuckerkandl and Klebermass-Messiner, this vol., 751).—αα'-Phenanthroline has no effect on the production of lactic acid in muscle and only temporarily (30 min.) inhibits glycolysis in blood (cf. Barrenscheen and Hübner, A., 1931, 378). W. McC.

Inhibition of glycolysis by oxidation. F. Lipmann (Biochem. Z., 1933, **265**, 133—140).—Glycolysis (I) (which is not dependent on the presence of ·SH) in muscle extract (II) is inhibited by oxidising agents (I, benzoquinone) presumably because the glycolytic enzyme (III) is oxidised. If 2 : 6-dichlorophenol-indophenol (IV) is added, (I), which is otherwise independent of the presence of O_2, is inhibited only if O_2 is present, the inhibition being then complete. (IV) is reduced in (II) when it is in N_2, but remains unchanged if (II) is in O_2. The inhibition by (IV) is reversible. In cells saturated with O_2 the inhibition of (I) is caused by reversible inactivation of (III). W. McC.

Action of co-enzyme. VI. Constitution of adenosinetriphosphoric acid. H. K. Barrenscheen, K. Braun, and W. Filz (Biochem. Z., 1933, **265**, 141—147; cf. A., 1932, 1064, 1287, 1288).—Lohmann's objections (A., 1932, 1274) to the authors' formula for adenosinetriphosphoric acid (I) cannot be maintained, since deamination experiments confirm the authors' results and contradict his. His "inosinepyrophosphoric acid" is a mixture of inorg. phosphate, inosic acid, unchanged (I), and (possibly) inorg. pyrophosphate. W. McC.

Co-enzyme of glycolysis from tumours. II. E. Bumm, H. Appel, and P. Couceiro (Z. physiol. Chem., 1933, **220**, 186—191).—Co-enzyme *T* (I) under various experimental conditions exercises quantitatively the same action on glycolysis as $AcCO_2H$ (II). (I) is probably identical with (II). J. H. B.

Isolation of co-enzyme *T* of glycolysis from normal tissue. H. Kraut and F. Borkovsky (Z. physiol. Chem., 1933, **220**, 173—185).—Ox-brain (grey matter) is a convenient source of co-enzyme *T* (I). The organ is dried with $COMe_2$ and extracted with $0·01N$-NH_3 and the product immediately pptd. with EtOH. A glycolysis inhibitor present may be (incompletely) removed with $Al(OH)_3$ *Cγ*. The activity of (I) is determined by measuring manometrically the lactic acid formed from glucose by washed sections of rat's kidney under anaërobic conditions. J. H. B.

Separation of co-enzyme *T* and phosphatase. H. Kraut and F. Borkovsky (Z. physiol. Chem., 1933, **220**, 192—198).—Co-enzyme *T* (I) from grey brain-matter is associated with a phosphatase (II), together with an inhibitor (III) of (II) which masks its presence, but which may be removed by $Al(OH)_3$. (I) from rat sarcoma also contains (III), but in smaller amount. (I) and (II) may be separated by dialysis, or better by adsorption of (I) on $Al(OH)_3$ *Cγ*. J. H. B.

Phosphatases and phosphatase hæmolysis. S. Munemura (J. Biochem. Japan, 1933, **18**, 23—32).—The following mono-derivatives of H_3PO_4 were prepared: β-naphthyl, *tetrabromo*-β-*naphthyl*, m.p. 140°, thymyl, *bromothymyl* (*Na* salt), *dibromothymyl* (*Na* salt). All the above are hydrolysed by monophosphatases from animal tissues, the optimum p_H being approx. 10, excepting the enzyme from blood with an optimum of p_H 5. Dephosphorylation is also accompanied by the acquisition of hæmolytic activity (I), and hence the rate of hydrolysis can be followed in the above systems by the rate of hæmolysis of erythrocytes (goat, rabbit). The (I) of the dephosphorylated com-

pounds forms the series: di- > mono-bromothymol >tetrabromonaphthol>thymol, naphthol.
F. O. H.

Effect of fluoride on the action of phosphatase. E. Auhagen and S. Grzycki (Biochem. Z., 1933, **265**, 217—222).—NaF does not inhibit the action of kidney-phosphatase on Na β-glycerophosphate or Na diphosphoglycerate, but at p_H 5 (although not at p_H 9) it partly inhibits the action of takaphosphatase (I), possibly because (I) contains two phosphatases, one sensitive to NaF and one not. W. McC.

Enzymic hydrolysis of hexoside phosphate. S. Ohmiya (J. Biochem. Japan, 1933, **18**, 125—143).—Taka-, rice bran-, kidney-, and intestine-monophosphatase hydrolyse Na glycerophosphate, Ca sucrose phosphate (I) (A., 1910, i, 157), and Ca glucose phosphate (II). Taka- and yeast-invertase hydrolyse sucrose and (I), no dephosphorylation occurring with the latter. Taka- and yeast-maltase hydrolyse maltose (III) and, without dephosphorylation, Ca (III) phosphate. Yeast α-methylglucosidase hydrolyses α-methylglucoside (IV) and (III), but not (IV) phosphate (V). The hydrolysis of (III) phosphate by maltase is strongly inhibited by (II) but not by (IV) or (V), whilst that of (I) by the invertase preps. is not influenced by (II), (IV), or (V). F. O. H.

Formation of ammonia and pyrophosphate decomposition in muscle. II. W. Mozołowski and B. Sobczuk (Biochem. Z., 1933, **265**, 41—49; cf. A., 1932, 875).—In pulped frog muscle which has been frozen in liquid air decomp. of creatinephosphoric acid precedes decomp. (I) of pyrophosphate and production (II) of NH_3. (I) then proceeds more rapidly than (II). Poisoning with $CH_2I{\cdot}CO_2H$ does not affect these processes. W. McC.

Transformation of the pyrophosphate fraction in muscle. O. Feinschmidt and M. Dmitrenko (Biochem. Z., 1933, **265**, 69—75; cf. Ferdmann, this vol., 736).—A pentose derivative (I) is produced when frog muscle is ground with H_2O and also, in smaller amount, when $CCl_3{\cdot}CO_2H$ solution replaces H_2O. (I) is partly pptd. by $Ba(OH)_2$. At the same time decomp. (II) of the pyrophosphate [chiefly the free portion (III)] occurs. (II) also occurs during autolysis of the muscle pulp in H_2O at 25°, (III) and the pyrophosphate (IV) combined as adenosinetriphosphoric acid being involved. Other P compounds present are decomposed simultaneously, since the amount of orthophosphate (V) corresponds with more than that produced by (II). On thawing muscle which has been frozen in liquid air (III) and (IV) decompose with simultaneous increase in (V), but the increase is < corresponds with (II). W. McC.

Phosphamidase. M. Ichihara (J. Biochem. Japan, 1933, **18**, 87—106).—$PO(OH)_2{\cdot}NH_2$ (I) and $PO(OH)(NH_2)_2$ (A., 1894, i, 267; ii, 188), but not $PO(OH)(NH_2){\cdot}OPh$ (II), are readily hydrolysed both in acid and alkaline media by kidney, rice-bran, and taka-diastase enzyme preps. $PO(OH)_2{\cdot}NHPh$ and $PO(OH)(OPh){\cdot}NHPh$ are hydrolysed in a manner parallel to (I). $PO(OH)_2{\cdot}NH{\cdot}C_6H_4Cl$ (*p*) is hydrolysed at acid but not at alkaline reactions. (II) at $p_H < 2$ is spontaneously deaminated. Under suitable conditions such a deamination is followed by dephosphorylation due to monophosphatase in the enzyme prep. used. By adsorption methods the phosphamidase can be separated from the phosphatases.
F. O. H.

Transformation of methylglyoxal when added to blood and muscle. E. Auhagen (Biochem. Z., 1933, **265**, 213—216).—The statements of Barrenscheen and co-workers (this vol., 187) regarding the transformation of AcCHO when added to blood (I) could not be confirmed either for (I) or for muscle extract. W. McC.

Milk-coagulating enzymes of gastric mucosa and their zymogens. H. Tauber and I. S. Kleiner (Z. physiol. Chem., 1933, **220**, 205—208).—Propepsin (I), the zymogen of pepsin, differs from prochymosin (II). (I), unlike (II), cannot coagulate milk; (II) has a p_H optimum at 2·8, whilst (I) is active only at p_H 1. EtOH destroys (I) but not pepsin. The mucosa of the adult animal contains no (II), but only (I). Inactive (I) can be prepared in dry form and activated with HCl. J. H. B.

Crystalline ovalbumin. Hydrolysis by pepsin, papain–hydrocyanic acid, and pancreatic proteinase, and the subsequent action of some other enzymes on the hydrolysis products. H. O. Calvery (J. Biol. Chem., 1933, **102**, 73—89).—Pure proteinase (I) of pancreas hydrolyses one third of the calc. no. of peptide linkings, whilst papain–HCN (II) hydrolysed a further one third. Amino- and carboxy-polypeptidase hydrolyse to the same extent as (I), and 60% of total N (III) was liberated as NH_2-N (IV). Dipeptidase (V) liberated a further 10—12%, and after complete enzymic hydrolysis 75% of (III) was present as (IV). Pepsin (VI) liberates 24—26% of (III) as (IV). Protaminase liberates a further 7% and the polypeptidases a further 24—25%; following their action the (V) in erepsin produces a further 24—25%. The total (IV) thus obtained is again 72—75% of (III). The action of (II) is twice as extensive as that of (I) or (VI) and there is no further action by either of these enzymes. H. G. R.

Gelatinase and Gates–Gilman–Cowgill method of pepsin determination. E. R. B. Smith (J. Gen. Physiol., 1933, **17**, 35—40).—The Gates method (A., 1930, 1620) for pepsin determination is uninfluenced by the presence of gelatinase, whilst the Northrop viscosity method (A., 1932, 1166) gives higher vals.
H. D.

Action of pancreatin on gelatin surfaces. II. M. Bergmann and F. Föhr (Biochem. Z., 1933, **264**, 246—250).—Using the method previously outlined (A., 1932, 1064) the rate of dissolution (x) of gelatin by pancreatin in unbuffered solution at p_H 4·8 is given by the equation $x = kt\sqrt{F}$, where F is the enzyme concn. and t the time of digestion. The extent of digestion is greater at p_H 8 and is the same using seven different buffer solutions at p_H 7·8—8·2. P. W. C.

Influence of oxidising and reducing agents on the activity of papain. T. Bersin and W. Logemann (Z. physiol. Chem., 1933, **220**, 209—216).—Papain inactivated by $CH_2I{\cdot}CO_2H$ (I) is not reactivated by reduced glutathione. SeO_3'' also inhibits, particularly in presence of (I). Various oxidising agents, such as H_2O_2, benzoquinone, and I, produce inactivation; reducing agents, as H_2S, SO_3'', and glutathione, but not quinol, reactivate the enzyme. Oxidised papain is also activated by succinodehydrogenase in presence of succinate. J. H. B.

Inactivation of cathepsin and papain by iodoacetic acid and by halogen. E. Maschmann and E. Helmert (Z. physiol. Chem., 1933, **220**, 199—204).—$CH_2I·CO_2H$, but not $CN·CH_2·CO_2H$, inhibits completely the proteolytic action of cathepsin under conditions which preclude oxidation of the thiol activator. The inhibition is reversible and probably due to formation of an additive compound with the enzyme. It differs from inhibition by I and Br, in which the active enzyme group is partly destroyed and partly dehydrogenated. J. H. B.

Pancreatic protease of cat-fish. T. Ôya and S. Yokota (J. Imp. Fish. Inst. Tokyo, 1933, **28**, 97—103).—Pancreatic extract from *Parasilurus asotus*, L., contains a trypsin-like enzyme (I), mostly as zymogen, which is activated by the extract from the intestinal mucosa. The optimum temp. and p_H for the action of the protease are 45° and about 7·7. The action of (I) on caseinogen is unimol. (temp. coeff. 1·5 from 18·5° to 45°). Nutr. Abs. (*m*)

Influence of bile acids on the enzymic hydrolysis of lecithin. H. Takata (J. Biochem. Japan, 1933, **18**, 63—74).—The dephosphorylation of lecithin by $CHCl_3–H_2O$ extracts of rabbit's kidney (I) and liver (II) in borate buffer at p_H 7·5 is somewhat increased by addition of Na cholate (III). With an enzyme prep. from autolysed tissue (A., 1929, 847) the liberation of acid-sol. P (cf. A., 1931, 984) is inhibited by (III), the inhibition with (II) being $>$ that with (I). During autolysis of (II), the presence of (III) accelerates the liberation of inorg. and acid-sol. P. F. O. H.

Lactase in bottom yeast. E. Hofmann (Biochem. Z., 1933, **265**, 209—212).—After preliminary digestion (for $\not>$ 3 days) with lactose a suspension of bottom yeast (from fresh yeast by the action of AcOH or after autolysis in presence of PhMe) hydrolyses lactoseureide (I) (80% in 24 hr.). No fermentation of (I) occurs. Amygdalin, but not salicin, is hydrolysed by the suspension. W. McC.

Enzymes of lactose fermenters. S. Grzycki (Biochem. Z., 1933, **265**, 191—194).—*Saccharomyces fragilis* (I) and another lactose fermenter (II) contain glycolase, glyoxalase, and carboxylase. Under conditions which lead to production of AcCHO with ordinary *Saccharomyces* (I) also produces it and converts it, when added, quantitatively into lactic acid (III). All the (III) then produced by (II) is dextrorotatory. (I) and (II) ferment $AcCO_2H$, 69—75% of the theoretical amount of MeCHO being produced. W. McC.

Phosphorylation produced by lactose fermenters. E. Hofmann (Biochem. Z., 1933, **265**, 203—208).—Fresh *Saccharomyces fragilis* (I) produces fructose 1 : 6-diphosphate and smaller amounts of a hexose monophosphate (II) from lactose in presence of PhMe. (II) is hydrolysed by takaphosphatase, giving H_3PO_4 and sugar, and has about 10% of the reducing power (Fehling's solution) of an equiv. amount of glucose. W. McC.

Maltose as a respiration substrate for non-maltose-fermenting yeasts. A. J. Kluyver and J. C. Hoogerheide (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 605—609).—The rate of respiration (I) of *Saccharomyces cerevisiæ* at p_H 4·7 is practically unchanged by increasing the concn. of glucose (II) from 0·2 to 10·0%. With the non-maltose (III) fermenting yeasts, *S. marxianus*, Hansen, and *S. exiguus*, a 10% concn. of a commercial sample of (III) produces a (I) = or even $>$ that with 10% of (II) when fermented for short periods, whilst fermentation for 4 hr. produces with (III) a steady decline in (I) until the val. for the yeast without sugar is attained. This, together with the finding that the (I) of yeasts in the presence of (III) previously purified by fermentation approximates to that occurring in the absence of (III), refutes the dualistic theory of (I) and fermentation advanced by Trautwein and Weigand (A., 1931, 1457). F. O. H.

Conversion of the alcoholic fermentation of sugar by yeast into a lactic acid fermentation. E. Auhagen and C. Neuberg (Biochem. Z., 1933, **264**, 452—455).—The conditions are outlined under which yeast in presence of glutathione converts Mg hexose diphosphate into lactic acid, yield about 25% of theoretical. P. W. C.

Degradation of lactic acid by yeast enzymes. A. Hahn, E. Fischbach, and H. Niemer (Z. Biol., 1933, **94**, 58—66).—The prep. of yeast extracts containing lactic acid dehydrase is described. In presence of methylene-blue as H-acceptor the dehydrase brings about degradation of lactic acid with formation of $AcCO_2H$ and MeCHO. Degradation also occurs in presence of $o-C_6H_4(NO_2)_2$, but not in absence of H-acceptor. O_2 has practically no influence. E. S. H.

Transformation of acetoacetaldehyde by yeast. S. Grzycki (Biochem. Z., 1933, **265**, 195—198; cf. Claisen and Stylos, A., 1888, 671).—Yeast converts $CH_2Ac·CHO$ into β-butylene glycol, part of which is dextrorotatory. W. McC.

Glyceromonophosphoric acid. III. Simplified preparation of phosphoglyceric acid. C. Neuberg and M. Kobel (Biochem. Z., 1933, **264**, 456—460; cf. this vol., 637, 982).—The method for isolating the *l*-acid as the Ba salt from glucose fermentations by bottom yeast after addition of NaF and MeCHO is described. P. W. C.

Synthesis of alanine by yeast during alcoholic fermentation. C. Fromageot and P. Desnuelles (Bull. Soc. chim., 1933, [iv], **53**, 541—547).—Addition of NH_3, $AcCO_2NH_4$, and NaOH to a mixture of yeast and aq. sucrose at 27—28° gives a 3—65% yield of alanine, according to the variety of yeast used. R. S. C.

Influence of iodoacetic acid on the respiration and fermentation of yeast. A. J. Kluyver and J. C. Hoogerheide (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 596—605).—The O_2 con-

sumption and CO_2 evolution by *Saccharomyces cerevisiæ* in presence of 0·001—0·014% of $CH_2I{\cdot}CO_2H$ (I) indicate that with an increasing concn. of (I) both anaërobic (II) and aërobic fermentation (III) are rapidly inhibited, whilst the respiration (IV) remains unchanged (A., 1930, 954). Above a certain " crit." concn. (approx. 0·0025%) at which both (II) and (III) are reduced to zero, however, (IV) steadily decreases with increasing concn. of (I). This phenomenon is probably due to the inactivation of the oxidation-reduction catalyst by (I) primarily affecting the surplus dissimilation [*i.e.*, (III)], the glycolysis falling below the level necessary for the maintenance of the normal rate of (IV) when the critical concn. of (I) is surpassed. In certain species of yeast, *e.g.*, *S. marxianus*, Hansen, (III) is very low, and in agreement with the above theory, addition of low concns. of (I) immediately causes a reduction in (IV).
F. O. H.

Action of toluene on fermentation by yeast. W. A. Belitzer (Biochem. Z., 1933, **265**, 5—12).—The inhibiting action (I) of PhMe on the fermentation (II) of glucose by yeast is irreversible and is not due to loss by diffusion (caused by increased permeability of the cells) of some substance necessary for (I). (I) is only sometimes due to selective action of PhMe on the phosphatase of the yeast. Harden's views (A., 1912, ii, 284) concerning (I) on the auto-fermentation of yeast are supported and modified to cover (II).
W. McC.

Effect of age on the nitrogen content of yeast. N. Nielsen (Compt. rend. Trav. Lab. Carlsberg, 1933, **19**, No. 16, 11 pp.).—N content and growth (I) of yeast in beer wort give an S-curve. When (I) is small, relatively large amounts of N are absorbed and the decrease with increasing (I) is not due to N storage.
H. G. R.

Endocellular hydrogen donors of yeast and their variation with the age of the culture. F. Chodat and M. Junquera (Arch. Sci. phys. nat., 1933, [v], **15**, Suppl., 199—203).—The amount of endocellular H-donors in yeast increases slightly with the age of the culture for 2—3 days and then decreases rapidly, being nearly 0 after 6 days. R. S. C.

Effect of ultra-violet rays on the fermentation efficiency of yeast in the alcoholic fermentation of molasses. W. L. Owen and R. L. Mobley (Zentr. Bakt. Par., 1933, II, **88**, 273—286).—Exposure of yeast to ultra-violet rays increased the rate of cell development and the fermentative activity. The effect was more marked when yeast on molasses wort or the wort alone was irradiated. The principal benefit of irradiation is the formation of a growth-promoting substance in the substrate which stimulates the yeast. A. G. P.

Lipins of yeast. I. Acetone-soluble fat. II. Phospholipins. M. S. Newman and R. J. Anderson (J. Biol. Chem., 1933, **102**, 219—228, 229—235).—I. The Et_2O solution of the $EtOH$–Et_2O extract of *Saccharomyces cerivisiæ* is separated into a phospholipin fraction (I) by pptn. with $COMe_2$, a $COMe_2$-sol. fraction (II) obtained by removal of the Et_2O, decantation from an oily product, and evaporation to dryness, and a $COMe_2$-insol. fraction (III) by dissolving the oily product in Et_2O, pptn. of (I) with $COMe_2$, and evaporating to dryness. (I) was purified by repeated pptn. from Et_2O with $COMe_2$. The saponified (II) contained a sterol fraction consisting of hydrocarbons $C_{19}H_{35}$—$C_{34}H_{66}$, glycerol, and fatty acids. The saturated fraction of the latter consisted of palmitic (IV) 75% and stearic (V) 25% acids. The unsaturated acids on catalytic reduction gave 25% (IV) and 75% (V).

II. The unsaponifiable matter from (I) was identical with that obtained from (II). The liquid fatty acids on catalytic reduction contained 60% (IV) and 40% (V). The solid acids consisted of equal parts of (IV) and (V). From the ratio of NH_2-N to total N in the aq. hydrolysate it is concluded that lecithin and cephalin are present in (I) in the ratio 4 : 1. Ba glycerophosphate, choline, and $NH_2{\cdot}C_2H_4{\cdot}OH$ were isolated from the aq. hydrolysate. H. D.

Metabolism of fat and lipin in yeast. W. Halden, F. Bilger, and R. Kunze (Naturwiss., 1933, **21**, 660—661).—Lipin formation in yeast is not associated with cellular degeneration, but is a metabolic phase following suppression of fermentation and budding. Thus the reduction of the H_2O content of a yeast suspension to 75—80% and exposure to EtOH vapour increases the ergosterol content from 0·2 to 7—8% in 10—14 days; the fat content increases to a much smaller extent. The EtOH is converted by a dehydrase into MeCHO which does not exert its normal toxic action owing to the rapid conversion into condensation products such as acetoin.
F. O. H.

Schaudinn's fixative for protozoa. D. H. Wenrich and Q. M. Geiman (Stain Tech., 1933, **8**, 158).—A solution half the strength of Schaudinn's, to which 2% of glacial AcOH is added immediately before use, is recommended. H. W. D.

Refractive indices of whole cells. E. S. Castle (J. Gen. Physiol., 1933, **17**, 41—47).—The n of the cell of *Phycomyces* was determined by allowing parallel light to fall on it and measuring the focal distance. The average of six cells was 1·38. H. D.

Physical basis of positive phototropism of *Phycomyces*. E. S. Castle (J. Gen. Physiol., 1933, **17**, 49—62).—By assuming that the primary action of light is on the protoplasm and that the absorbing substance is uniformly distributed within the cell, the possibility of photochemical action in the half of the cell furthest from the source of light being > that in the side nearer is demonstrated. The factors governing the phenomenon are the n and radius of the cell and the absorption coeff. of the intracellular pigment.
H. D.

Growth of *Aspergillus niger* at different hydrogen-ion concentrations, with and without the addition of growth-promoting substance *B*. N. Nielsen and V. Hartelius (Compt. rend. Trav. Lab. Carlsberg, 1933, **19**, No. 15, 23 pp.).—The optimum initial p_H for growth in the presence and absence of the growth-promoting substance (I) is 6—7 and 3, respectively; the highest p_H at which the fungus can germinate is 1·3 and 1·5. The ratio of the amounts of dry matter formed with and without the addition of (I) is 2·12 and 3·48 after 48 hr. with initial p_H 2·6 and 6·3. There is no autolysis in cultures if the initial p_H is $< 2·1$. H. G. R.

Action of certain fungi on solutions of aldoses and other saccharine materials. VIII. A. Angeletti and D. Ponte (Annali Chim. Appl., 1933, **23**, 315—317; cf. this vol., 638).—*Penicillium crustaceum* (L.), Fries, acts on *d*-galactose solutions with formation of small amounts of citric acid, but lactose solutions are attacked only very slightly and without giving acid products, either by this species or by *P. luteum-purpurogenum*. Lactose is attacked directly, without previous hydrolysis. T. H. P.

Formation of fructose and kojic acid by acetic acid bacteria. T. Takahashi and T. Asai (Zentr. Bakt. Par., 1933, II, **88**, 286—295; cf. this vol., 189).—Bacteria isolated from various fruits produced fructose (I) and kojic acid (II) from mannitol (III); in some cases the yield of (I) was 80% of the theoretical. The mechanism of formation of (II) differs from that by *Aspergillus* and probably consists of a progressive oxidation, (III) $\longrightarrow$ (II) $\longrightarrow$ (I). A. G. P.

Production of fructose and kojic acid from mannitol by acetic acid bacteria. II. Effects of p_H of culture solution and addition of calcium carbonate. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1933, **9**, 369—374).—Optimum p_H were 6·95—7·54 and 5·79—6·25, respectively. Fructose (I) was produced in the first, and kojic acid (II) mainly in the latter, stage of fermentation. Production of (II) from (I) was optimal at p_H 6·28—6·46 when $CaCO_3$ was added; succinic acid was then also produced. Ch. Abs.

Relation between enzymic activity, morphology, and resistance to stains of butyric acid bacteria, and the mechanism of residual respiration. M. G. Sevag (Z. Hyg., 1933, **114**, 756—768; Chem. Zentr., 1933, i, 2711—2712).—Butyric acid bacteria, which in the early stage of development are Gram-positive (I), degenerate to the Gram-negative form and lose practically all their enzymes. The enzymic activity and residual respiration are approx. proportional to the no. or wt. of (I) cells. When the enzymic activity of (I) bacilli is extinguished by KCN, the O_2 requirement becomes zero. A. A. E.

Mechanism of the activation of glucose in lactic fermentation. C. Fromageot and J. Roux (Biochem. Z., 1933, **265**, 13—20; cf. A., 1932, 195).—The rate of evolution of CO_2 liberated by the action of *B. bulgaricus* (I) on glucose (II) in absence of O_2 is proportional to the amount of (I) present, whereas changes in the concn. (III) (2·6—0·052%) of (II) have no effect. The period (IV) of induction varies little while (III) remains relatively high, but increases rapidly when it is low. When almost all the (II) is exhausted evolution of CO_2 ceases. The results, considered mathematically, confirm the authors' views concerning the mechanism of the activation of (II). (IV) corresponds with the conversion of (II) into a special form. W. McC.

Respiration and fermentation of lactic acid bacteria. J. G. Davis (Biochem. Z., 1933, **265**, 90—104; cf. Bertho and Glück, A., 1932, 654).—The H_2O_2 produced by *B. Delbrückii* is equiv. in amount to the O_2 consumed in oxidising the substrate and hence the R.Q. is 0·5. The rate of oxidation is accelerated 100—300% by addition of methylene-blue (I) or p-$C_6H_4(NH_2)_2$, the yield of H_2O_2 being reduced 25% (R.Q. 0·7—0·9). The acceleration [which is inhibited by $CH_2I{\cdot}CO_2H$ (II)] is probably due to oxidation of lactate (III), since (II) inhibits neither oxidation of (III) nor increase in respiration by (I) in presence of (III). (II) restricts consumption of glucose after glycolysis whether (I) is present or not. The oxidation of $AcCO_2H$, which is even more rapid, is little affected by HCN and no H_2O_2 is produced. *B. cereale* (IV) produces no H_2O_2; its action is inhibited by HCN and CO, but (I) has no effect. Oxidative fermentation accompanies the action of (IV); the R.Q. is about 2, and $AcCO_2H$ is produced and partly converted into AcOH, acetoin, and EtOH. W. McC.

Gluconic acid fermentation. VII. T. Takahashi and T. Asai (J. Agric. Chem. Soc. Japan, 1933, **9**, 351—360).—Yeast extract containing glucose 10 and $CaCO_3$ 2·5% was fermented with *B. hoshigaki* var. *rosea* at 26—28° for 45 hr. The yields of ε-keto-gluconic (I), gluconic (II), glycollic acids and a uronic acid, $[\alpha]^{25}_{D}$ +67·5°, from 300 g. of glucose were, respectively, 2·5, 1·5, 30, and 59 g. A brown colouring matter was also formed. With other AcOH bacteria, which produced no colouring matter, (I), (II), glycuronic, succinic, lactic, and (?) acetic acids were produced. The yield of (II) is increased by addition of $CaCO_3$. Ch. Abs.

Fermentation of [structurally] *d*- and *l*-arabinose by bacteria. S. A. Koser and F. Saunders (Proc. Soc. Exp. Biol. Med., 1932, **30**, 218—220).—*l*-Arabinose is fermented rapidly by many types of bacteria which ferment the *d*-form with difficulty. Three strains of *Proteus vulgaris* fermented the *d*- and not the *l*-form. *Es. coli* and *Aër. aërogenes* ferment *d*-arabinose with difficulty. Ch. Abs.

Nature of the reaction of *B. coli* on Endo's medium. L. A. Margolena and P. A. Hansen (Stain Tech., 1933, **8**, 131—138).—The typical reaction is caused by MeCHO. H. W. D.

Effects of saliva on growth of *Bacterium coli*. O. W. Clough (J. Dent. Res., 1933, **13**, 183—184).—Fresh, but not treated, filtered saliva partly inhibits growth of *B. coli* and staphylococci, but not of pneumococci. Nutr. Abs. (*m*)

Production of an unsaturated compound by *Es. coli* in a synthetic medium. W. F. Lange (Proc. Soc. Exp. Biol. Med., 1932, **29**, 1134—1137).—In a medium containing dextrin 10, K_2HPO_4 1, KH_2PO_4 1, $MgSO_4$ 0·1, $CaCl_2$ 0·1, $(NH_4)_2C_4H_4O_6$ 10 g., H_2O 1000 c.c., *Es coli* produced acidity not due to lactic, acetic, or acetoacetic acid. An unsaturated acid, corresponding with propiolic acid, was isolated; it is probably an intermediate product in the metabolism of dextrin. Ch. Abs.

Toxic bacterial pigment. A. G. van Veen and W. K. Mertens (Proc. K. Akad. Wetensch. Amster-

dam, 1933, 36, 666—670).—Certain bacteria from coconut food-products, when grown on filter-paper soaked in a glycerol-containing nutrient medium, produce a yellow pigment. On purification by salting out with Na_2SO_4, extraction with $CHCl_3$, EtOAc, etc., this yields a substance, m.p. approx. 200°, the min. lethal dose of which to rats is $< 0{\cdot}005$ mg. when administered intraperitoneally. The poison is rich in N, is amphoteric, and readily dialyses.
F. O. H.

Ultrafiltration in bacteriology. R. Le Guyon (Ann. Inst. Pasteur, 1933, 51, 377—406).—Diphtheria toxin and anatoxin cannot be separated from each other by ultrafiltration, and their mol. size is approx. equal. The exogenous toxin of the tubercle bacillus can be separated by ultrafiltration, whilst bacteriophage cannot be so separated. Pyocyanine is completely ultrafilterable. P. G. M.

Action of formaldehyde on diphtheria toxin. I. Significance of formaldehyde concentration, temperature, and hydrogen-ion concentration in the production of anatoxin. S. Schmidt (Z. Immunität., 1933, 78, 27—45; Chem. Zentr., 1933, i, 2421).

Immunising properties of partial antigens from diphtheria bacilli. III. V. N. Kruizhanovski (Arch. sci. biol., U.S.S.R., 1932, 32, 263—270). Ch. Abs.

Metabolism of purple sulphur bacteria in organic media. F. M. Muller (Arch. Mikrobiol., 1933, 4, 131—166).—In the absence of oxidisable S the bacteria develop in media containing a simple N-free org. substance. Radiant energy is essential for growth. In cultures containing lactate, pyruvate (I), acetate, succinate, malate, or butyrate (II), no metabolic products other than small amounts of CO_2 are formed. In the case of (II) additional CO_2 is taken up. The conversion of org. acid into (I) as a necessary stage in the synthesis of cell material is discussed. The photosynthetic processes involved may be represented as a sp. case of the general equation. A. G. P.

Influence of aërial-earth circuit on biological activity. II. A. Itano (Proc. Imp. Acad. Tokyo, 1933, 9, 309—312).—The potential of *Azotobacter chroococcum* cultures (I) is influenced by the aërial-earth circuit (II), and the differences in the fixation of N by (I) previously reported under varying conditions of (II) may be due to this. A. L.

Dehydrogenases during staphylolysis. Method of evaluating bacterial lysis. F. Chodat and F. Wyss-Chodat (Compt. rend., 1933, 197, 657—660).—Data are recorded from which it is claimed that the dehydrogenase activity of *Staphylococcus aureus*, as measured by reduction of methylene-blue in the presence of Na succinate, progressively decreases during lysis by phage. A. C.

Specific protein of the capsule of the anthrax bacillus. J. Tomcsik and H. Szongott (Z. Immunität., 1933, 78, 86—99; Chem. Zentr., 1933, i, 2124).—Agar cultures were extracted with KOH and pptd. with EtOH, and then by pptn. with $CuSO_4$ a fraction containing 10% N and free from carbohydrate was obtained. The supernatant liquid contained the carbohydrate, probably a polysaccharide. The ppt. gives no biuret, xanthoproteic, or Molisch reaction, but is nevertheless regarded as a protein. A. A. E.

Polysaccharides of lepra bacilli. M. S. Newman and R. J. Anderson (Z. physiol. Chem., 1933, 220, 1—4).—By the acetylation of the crude polysaccharides of the lepra bacillus, cryst. trehalose octa-acetate, and an amorphous *acetate*, $[\alpha]$ +142° in $CHCl_3$, of a *polysaccharide*, decomp. 225°, $[\alpha]_D$ +156° in H_2O, giving the reaction for pentoses, were obtained.
J. H. B.

Solubility of *Pneumococcus* in saponin. III. Sensitisation by ergosterol. S. J. Klein (J. Bact., 1933, 26, 215—219).—Ergosterol (I) and cholesterol sensitise the organism to lysis by saponin. Irradiation of (I) reduces its activity in this respect.
A. G. P.

Chemical and immunological studies of *Pneumococcus*. III. Cellular carbohydrate fractions. A. Wadsworth and R. Brown (J. Immunol., 1933, 24, 349—368).—Type-sp. carbohydrates all contained P and N; they differed from the sol. sp. substances of Heidelberger, Avery, and others, and from Tillett and Francis' C-fraction. Ch. Abs.

Decomposition of specific bacterial polysaccharides by a species of *Myxobacterium*. W. T. J. Morgan and A. C. Thaysen (Nature, 1933, 132, 604).—A micro-organism (I), probably a typical *Myxococcus*, Thaxter, which rapidly decomposes the sp. polysaccharide, $[\alpha]^{18}_{5461}$ +110°, of Shiga's bacillus, has been isolated from decayed vegetable debris. (I) also attacks the sp. polysaccharides of *B. dysenteriæ*, Flexner Y, *Pneumococcus* (Type II), and the tubercle bacillus, and destroys their power to form a sp. ppt. when mixed with the homologous immune serum. L. S. T.

Influence of foodstuffs on the respiratory metabolism and growth of human tubercle bacilli. R. O. Loebel, E. Shorr, and H. B. Richardson (J. Bact., 1933, 26, 139—166).—The O_2 consumption of the organism is increased by glycerol, Na lactate, and Na salts of higher fatty acids, lecithin, milk- and serum-fat. Glucose and glycogen produce smaller effects. The stimulation of respiratory activity is produced by much smaller concns. of the above substances than are required for abundant growth. A. G. P.

Influence of adverse conditions on the respiratory metabolism and growth of human tubercle bacilli. R. O. Loebel, E. Shorr, and H. B. Richardson (J. Bact., 1933, 26, 167—200).—Metabolism of the organisms under conditions of starvation, changing p_H, and anaërobic exposure is examined. A. G. P.

***In vitro* action of tuberculin.** M. Popper, A. Teitel-Bernard, C. Raileanu, and G. T. Dinischiotu (Arch. exp. Path. Pharm., 1933, 172, 429—432).—The O_2 uptake (I) of the blood of normal and tuberculous guinea-pigs and men with and without the addition of tuberculin (II) has been studied in the micro-respirometer. The addition of (II) scarcely affects (I) of normal guinea-pig's, or of new-born human, blood. (II) raises (I) of blood from tuberculous guinea-pigs and man. H. W. D.

p_H value of bacteria. M. GUTSTEIN (Arch. Mikrobiol., 1933, **4**, 241—247; cf. this vol., 427).—The internal reaction of the majority of Gram-positive bacteria is slightly acid and of Gram-negative organisms slightly alkaline. A. G. P.

Gram reaction and the electrical charge of bacteria. V. BURKE and F. O. GIBSON (J. Bact., 1933, **26**, 211—214).—Gram reaction is unrelated to the electrical charge of the cells. A. G. P.

Bacteriophage in relation to nitrogen fixation by red clover. L. ALMON and P. W. WILSON (Arch. Mikrobiol., 1933, **4**, 209—219).—The behaviour of cultures of *Rh. trifolii* towards the action of a sp. bacteriophage *in vitro* has no relationship to its N-fixing ability in association with the host plant. A. G. P.

Inactivation of bacteriophage by mercuric chloride; reactivation of inactivated phage. A. P. KRUEGER and D. M. BALDWIN (J. Gen. Physiol., 1933, **17**, 129—133).—The inactivation of phage (I) by $HgCl_2$ proceeds by a pseudo-unimol. reaction; when $Hg^{\cdot\cdot}$ is pptd. by H_2S an increase in the concn. of (I) occurs, indicating the possibility of a reversal of inactivation. H. D.

Nature of the effect of carbon dioxide under pressure on bacteria. J. S. SWEARINGEN and I. M. LEWIS (J. Bact., 1933, **26**, 201—210).—The lethal action of CO_2 under pressure is ascribed to pptn. of colloidal matter within the cell substance. A. G. P.

Bactericidal power of sodium ricinoleate. H. VIOLLE (Compt. rend., 1933, **197**, 714—716).—High doses of aq. Na ricinoleate are not toxic to laboratory animals. Its bactericidal power varies in different groups of organisms. In general, intestinal bacteria, fungi, and yeasts are not destroyed, whilst bacteria of the respiratory system are very sensitive to its action *in vitro*. A. C.

Action of metals on bacteria at a distance. G. A. NADSON and C. A. STERN (Zentr. Bakt. Par., 1933, II, **88**, 320—334; cf. A., 1932, 778).—The toxic action of plates of Mg, Al, Ni, Cu, Ag, Sn, Pt, Au, and Pb on cultures of yeast and bacteria at a distance of 1—3 mm. increased with the at. wt. of the metal and is ascribed to electronic bombardment. A. G. P.

Oligodynamic action of silver with special reference to in- and re-activation. I. BUHRMANN (Z. Hyg., 1933, **115**, 241—258).—The activity of various species of bacteria was inhibited by oligodynamic Ag solution at rates which increased with the $[Ag^{\cdot}]$. The catalytic acceleration of oxidation of leucomalachite-green base is an approx. measure of the activity of the Ag. The bactericidal action of metallic Ag is destroyed by the removal of sol. Ag salts from the surface by heating or washing with aq. $Na_2S_2O_3$ or by conversion into insol. compounds. Inactivated Ag regains its bactericidal power by treatment with oxidising agents the efficiency of which is in the order $KMnO_4 > H_2O_2 >$ aq. $Cl_2 > NaOCl >$ moist O_3. Org. and inorg. acids (except HCl), $NaBO_3$, and $(NH_4)_2S_2O_8$ are ineffective in this respect. Electrical polarisation of Ag plates activates the anode and inactivates the cathode. Activation of Au results from treatment with aq. Cl_2, and to a small extent with $KMnO_4$, but not with H_2O_2. A. G. P.

Endocrinology; chemistry of hormones. II. H. P. TEUNISSEN (Chem. Weekblad, 1933, **30**, 590—597).—A review. S. C.

Chemical control of the circulation. ANON. (Nature, 1933, **132**, 487—488).—A summary of the British Association discussion. L. S. T.

Appearance of an acetylcholine-like substance in the venous blood of the mammalian heart on stimulation of the vagus. W. FELDBERG and O. KRAYER (Arch. exp. Path. Pharm., 1933, **172**, 170—193).—With dogs and cats in which intravenous injection of physostigmine has inhibited decomp. of acetylcholine (I) in the blood (cf. A., 1930, 800), stimulation (II) of the vagi produces in the coronary venous blood a substance probably identical with (I). The concn. during (II) is $1 : 10^{-7}$ to 10^{-8} and the abs. amount corresponds with 0·0002—0·006 mg. of (I), whilst its action is apparent, although decreasing in intensity, for several min. after (II). F. O. H.

Local hormonal mechanism of parasympathetic excitation. V. E. HENDERSON and M. H. ROEPKE (Arch. exp. Path. Pharm., 1933, **172**, 314—324).—An acetylcholine-like substance is produced (from a labile precursor) in the glands subserved by the chorda tympani even when the excitation is insufficient to produce any apparent secretion. Either the toxicity or contractility of the bladder appears to be based on a similar local hormonal mechanism. F. O. H.

Purification of secretin. IV. E. HAMMARSTEN, E. JORPES, and G. ÅGREN. **V.** E. HAMMARSTEN, G. ÅGREN, H. HAMMARSTEN, and O. WILANDER (Biochem. Z., 1923, **264**, 272—274, 275—284).—IV. The method for the prep. of large amounts of crude secretin for electrodialysis is described.

V. Secretin obtained in acid aq. extracts is purified by electrodialysis and forms with picrolonic acid a cryst. salt which after recrystallisation from anhyd. C_5H_5N shows const. and high activity. The mol. wt. (ultracentrifuge) is about 5000. The presence of peptide linkings is shown by protease digestion. Aromatic NH_2-acids are probably not present. The prep. contains 1 atom S per mol. The ninhydrin reaction is negative, the Ac_2 reaction strong, and arginine is probably present. P. W. C.

Effect of parathyroid hormone and sodium hydrogen phosphate on bones of guinea-pigs. R. C. GRAUER (Proc. Soc. Exp. Biol. Med., 1932, **30**, 57—59). CH. ABS.

Preparation of a blood-calcium-raising substance from placenta. C. BOMSKOV and H. BREMM (Klin. Woch., 1933, **12**, 944—946).—Human placentas, treated by Collip's original method of preparing parathormone (I), yield a substance, possibly identical with (I), which increases the Ca content of blood. NUTR. ABS. (*m*)

Thyroxine and tissue oxidation. U. S. VON EULER (Klin. Woch., 1933, **12**, 671).—Addition of thyroxine in concns. of 10^{-11} to 10^{-7} to tissue preps. slightly increased the rate of reduction of methylene-blue in vac. tubes. The rate of O_2 uptake was also slightly increased when the O_2 pressure was sub-optimal. NUTR. ABS. (*b*)

Hormonal regulation of purine metabolism. O. FLÖSSNER, F. KUTSCHER, and W. WITTNEBEN (Z. physiol. Chem., 1933, **220**, 13—19).—In athyreotic and hypothyreotic conditions the purines (I), particularly adenine, in the urine are greatly increased. Thyroxine treatment restores (I) almost to normal. *d*-Lysine, which is present before treatment, disappears. J. H. B.

Anti-oxidative action of thyroxine and of substances resembling thyroxine.—See this vol., 1126.

Detoxication of the thyroid hormone. E. HESSE and K. R. JACOBI (Klin. Woch., 1932, **11**, 2117; Chem. Zentr., 1933, i, 2167).—Oral or subcutaneous administration of Cu^{II} compounds or $Fe_2(SO_4)_3$ to dogs protects against the toxic effect of thyroid powder by the formation of insol. and physiologically inactive thyroxine complexes. A. A. E.

Effect of thyroid on fat metabolism. F. SILBERSTEIN, F. GOTTDENKER, and A. GLASER (Klin. Woch., 1933, **12**, 788—789).—Intravenous injection of di-iodotyrosine into cats rendered hyperlipæmic by administration of olive oil increases and prolongs the hyperlipæmia. NUTR. ABS. (*m*)

Transmineralisation and liver damage due to thyroid. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1933, **12**, 631—632).—After administration of the thyreotropic hormone of the pituitary or of thyroxine, the liver contains little or no glycogen and the Na content of blood and liver is diminished; K and Cl′ are unchanged. NUTR. ABS. (*m*)

Determination of thyroxine in thyroid. N. F. BLAU (J. Biol. Chem., 1933, **102**, 269—278).—The distribution ratios of thyroxine (I), di-iodotyrosine, and KI in presence of Na_2SO_4 and the products of alkaline hydrolysis of muscle-proteins are determined. For the determination of (I) the NaOH-hydrolysate of the gland is cooled and H_2SO_4 added, while shaking, to p_H 3·5. The flask used for hydrolysis is washed with BuOH and the washings are transferred to the separating funnel. The aq. layer is removed and the BuOH layer extracted twice with 4*N*-NaOH containing 5% Na_2CO_3. The BuOH solution is removed and the BuOH distilled off. The residue is ashed and analysed for I. H. D.

Determination of thyroxine-iodine in thyroid gland powder. L. CUNY and J. ROBERT (J. Pharm. Chim., 1933, [viii], **18**, 233—246).—The method of Harington and Randall (A., 1930, 504) is somewhat superior to that of Leland and Foster (A., 1932, 432). F. O. H.

Influence of insulin, adrenaline, and thyroxine on galactose assimilation. L. POLLAK and G. FEHÉR (Arch. exp. Path. Pharm., 1933, **172**, 407—428).—Insulin promotes the assimilation of both orally and intravenously administered galactose (I). Adrenaline and orally or intravenously administered glucose have a similar action with orally but not with intravenously administered (I); the mechanisms of adrenaline and glucose action are therefore probably identical. Thyroxine inhibits the assimilation of orally administered (I); with intravenously administered (I) its action is not apparent. F. O. H.

Plasma-phosphate and -lactic acid in normal and adrenalectomised animals during changes in carbohydrate metabolism. C. F. CORI and G. T. CORI (Arch. exp. Path. Pharm., 1933, **172**, 249—260).—Intravenous injection of sub-convulsive doses of insulin (I) into rabbits lowers the plasma-inorg. PO_4 (II), the effect being considerably diminished by adrenalectomy (III). Subcutaneous injection of adrenaline (IV) also lowers (II) both before and after (III). During (I)-hypoglycæmia in normal rabbits, the blood-lactic acid (V) is approx. doubled, whereas after (III) the level is unchanged. These facts together with the changes in muscle-hexose phosphate (A., 1932, 199) indicate that in normal fasting animals the fall in (II) and the rise in (V) following injection of (I) are secondary effects of (IV) liberated from the adrenals. Intravenous injection of glucose produces only slight changes in (II). After (III), hypoglycæmia is accompanied by a return to normal vals. of (II), whilst with normal animals it produces a further decrease in (II). The probability of a rapid utilisation of sugar leading to the formation of a hitherto unidentified P compound at the expense of (II) is discussed. F. O. H.

Physiology of insulin. G. H. TUTTLE (Lancet, 1933, **225**, 687—690).—A review. The view that wherever carbohydrate metabolism occurs some kind of insulin, either pancreatic or cellular, must be present is advanced, and evidence for the existence of multiple insulins is discussed. L. S. T.

Hypoglycæmic effect of insulin injected into the portal vein of the dog. E. AUBERTIN and E. TRINQUIER (Compt. rend. Soc. Biol., 1933, **112**, 583—584; Chem. Zentr., 1933, i, 2167).—The usual hypoglycæmic effect, and the initial hyperglycæmia, are observed; hence the liver has no "neutralising" action on insulin. A. A. E.

Influence of insulin on reduced glutathione of blood. E. ZUNZ (Ann. Physiol. Physicochim. biol., 1931, **7**, 314—317; Chem. Zentr., 1933, i, 2128).—Insulin produces a slight increase in the glutathione-SH content of arterial blood; the effect is not related to the corpuscle : plasma ratio. A. A. E.

Antagonism between insulin and pituitrin. P. WERMER and J. MONGUIÓ (Klin. Woch., 1933, **12**, 748—751).—Pituitrin (I) (subcutaneously) had no effect on the action of insulin (II) injected intravenously; when (II) was administered subcutaneously, (I) diminished its effect in some cases. Probably (I) inhibits absorption of (II) from the subcutaneous tissue. NUTR. ABS. (*b*)

Exciting action of the vagus on the secretion of insulin studied by anastomosis of pancreatic and jugular veins and by similar methods. R. GAYET and M. GUILLAUMIE (Compt. rend. Soc. Biol., 1933, **112**, 1327—1331, 1331—1336).—When a pancreatic–jugular vein anastomosis is established between two dogs there is no evidence of increased secretion of insulin when the right vagus nerve of the donor is stimulated, or when its head is perfused with hyperglycæmic blood. Nutr. Abs. (*m*)

Callicrein in the internal and external pancreatic secretions. E. K. Frey and E. Werle (Klin. Woch., 1933, **12**, 600—601).—The callicrein (I) content of the urine of the dog with pancreatic fistula does not diminish, but does so when the whole gland is removed. Diminution also occurs when the blood supply of the pancreas is shut off. Significant quantities of (I) are found in the pancreatic juice of dogs and in human duodenal juice. (I) is not inactivated by trypsin. Nutr. Abs. (*m*)

Reduction of blood-pressure by vagotonin and other pancreatic extracts not containing insulin. D. Santenoise, L. Merklen, E. Morelle, and M. Vidacovitch (Compt. rend. Soc. Biol., 1932, **111**, 912—916; Chem. Zentr., 1933, i, 2426).—The effect is hormonal; that of other pancreatic extracts is pharmacodynamic. A. A. E.

Effect of the parotid gland on carbohydrate metabolism. M. Cahane (Compt. rend. Soc. Biol., 1933, **112**, 1438—1441).—The parotid glands (dog) appear to contain an internal secretion which acts antagonistically to insulin. Nutr. Abs. (*m*)

Adrenalinæmia and adrenalinuria. G. Viale (Rev. sudamer. endocrinol., 1933, **16**, 387—391).—Adrenaline (I) is identified by the production of a red colour after boiling with $HgCl_2$, sulphanilic acid, and KIO_3. (I) is inactivated against this reaction by CH_2O. Dog's blood contains 1 in 4×10^5 and serum 1 in 5×10^5. The blood of adrenalectomised animals is only slightly lower in (I). Healthy individuals excrete (I) in the urine. High vals. are recorded in persons with high blood-pressure. Ch. Abs.

Mechanism of adrenaline hyperglycæmia. R. C. Formiguera and E. Bieto (Compt. rend. Soc. Biol., 1933, **113**, 333—336).—In dogs receiving 0·026 mg. of adrenaline (I) per kg. the sugar content of arterial and venous blood is identical after saphenous injection, but is higher in arterial than in venous blood after injection into the mesenteric vein. When (I) acts peripherally it does not cause retention of glucose in the tissues, but when it acts principally, if not exclusively, on the liver, it produces a hyperglycæmia by acting on liver-glycogen, part of the liberated glucose being immediately retained by the tissues. This action on the liver is partly independent of the action of (I) in stimulating the metabolism of sugar in the peripheral tissues. Nutr. Abs. (*m*)

Adrenal cortex. II. Metabolism, circulation, and blood concentration during adrenal insufficiency in the dog. G. A. Harrop, A. Weinstein, L. J. Soffer, and J. H. Trescher. **III. Plasma electrolytes and electrolyte excretion during adrenal insufficiency in the dog.** G. A. Harrop, L. J. Soffer, R. Ellsworth, and J. H. Trescher (J. Exp. Med., 1933, 58, 1—16, 17—38).—II. The assumption that the adrenal cortex or its hormone has a detoxifying action on some product of metabolism is unnecessary.

III. One function of cortical extract injected into the adrenalectomised dog is participation in the regulation of Na and Cl metabolism. Ch. Abs.

Anterior pituitary hormone with specific effect on carbohydrate metabolism, antagonistic to that of insulin. H. Lucke, E. R. Heydemann, and R. Hechler (Z. ges. exp. Med., 1933, **88**, 65—77).—In pregnant bitches which are excreting prolan there is no disturbance of carbohydrate metabolism (II) despite hypertrophy of the anterior pituitary (I), so that the sex hormone of (I) is apparently not concerned with (II). Injection of präphyson (III) (anterior pituitary extract not containing prolan) produces a rise of blood-sugar in rabbits, dogs, and man. The hypoglycæmic effects of insulin are reduced or abolished by simultaneous administration of (III) in normal dogs and in those with (I) removed. The disturbances in (II), especially the increased reaction to insulin, occurring in dogs in which (I) has been removed, can be greatly reduced by administration of (III). Nutr. Abs. (*m*)

Fat metabolism hormone of the anterior pituitary lobe. H. Magistris (Endokrinol., 1932, **11**, 176—191; Chem. Zentr., 1933, i, 1464).—A rabbit unit is the smallest quantity of the hormone (I) which, 2 hr. after injection, doubles the total ketonic substances in the blood. The $OH\cdot CHEt\cdot CO_2H$ is particularly increased. Normal vals. are reattained after 24 hr. The prep. is completely or largely inactivated by *N*-NaOH; hence the active substance is not histamine and it is not identical with known anterior pituitary hormones. The sp. dynamic action and effect on the basal metabolism are described. (I) is found in the urine; only the gonadotropic hormone is adsorbed by animal C. The two hormones are closely similar in properties. (I) is not combined with protein, and probably has a relatively small mol. wt. A solution free from protein (ultrafiltration) gives the biuret reaction, but no turbidity with sulphosalicylic acid. (I) is adsorbed by kieselguhr, but not by bone-C, kaolin, or talc. A. A. E.

Glycosuria in rabbits following injections of saline extract of anterior pituitary. E. J. Baumann and D. Marine (Proc. Soc. Exp. Biol. Med., 1932, 29, 1202—1223).—Hyperglycæmia, lipæmia, glycosuria, and polyuria were produced by injection of ox pituitary gland extract. "Phyone" caused severe glycosuria in only one of four rabbits. Ch. Abs.

Anterior pituitary hormone in saliva. B. Ofstad (Klin. Woch., 1932, **11**, 1761; Chem. Zentr., 1933, i, 2833).—Saliva of pregnancy, when injected by Aschheim and Zondek's method into mice, did not give a positive pregnancy reaction, but hyperæmia of the ovary and uterus indicated the presence of the anterior pituitary hormone in small concn. A. A. E.

Influence of the gonads on protein metabolism. III. (*a*) Effect of injections of anterior pituitary extracts on urinary creatinine in normal and castrated rabbits. (*b*) Tolerance of normal and castrated animals to injected creatine. I. Schrire and H. Zwarenstein (Biochem. J., 1933, 27, 1337—1341).—Normal but not castrated rabbits show an increased excretion of creatinine (I) in the urine following the subcutaneous injection of antuitrin or extracts of the anterior lobe (II) of the pituitary. The results support the view that there is a direct relationship between (II) and (I) metabolism. Normal rabbits excrete less, and thus retain more, creatine than do castrated rabbits when large amounts are injected subcutaneously. A. W.

Melanophore hormone. A. Jores (Klin. Woch., 1932, **11**, 2116; Chem. Zentr., 1933, i, 2425).—Polemical (cf. Zondek and Krohn, A., 1932, 432; this vol., 98, 319). A. A. E.

Oxytocic hormone of the posterior lobe of the pituitary gland. IV. Action of animal proteolytic enzymes: nature of the hormone. J. M. Gulland and T. F. Macrae (Biochem. J., 1933, **27**, 1383—1393).—One commercial trypsin (I) prep. rapidly inactivated the oxytocic hormone (optimum inactivation at p_H 8·8), whereas another was only slightly effective. Enzyme preps. of equal (I) activity had different inactivating powers. The inactivating enzyme is probably therefore not (I) and the hormone may not be proteinoid in nature. The hormone was not attacked by a pepsin prep., or by a bone-phosphatase prep. W. O. K.

Œstrogenic hormones. Anon. (Nature, 1933, **132**, 609—610).—A review. L. S. T.

Extraction of folliculin from the urine of pregnant mares. A. Lipschütz and E. Poch (Compt. rend. Soc. Biol., 1932, **111**, 856—857; Chem. Zentr., 1933, i, 2265).—The urine is acidified with HCl (10—20%), boiled for 5 min., and extracted with Et_2O. A. A. E.

Does menstrual blood contain growth-hormones or auxins as well as the supposed menotoxins? A. Sack (Münch. med. Woch., 1933, **80**, 10—12; Chem. Zentr., 1933, i, 2126).—The presence of auxin has not been detected. The stimulating action on plant growth is attributed to the presence of follicular hormone. A. A. E.

Relation between ovarian function and calcium metabolism. O. Bokelmann (Arch. Gyn., 1933, **152**, 492—500; Chem. Zentr., 1933, i, 2833).—The total and ash-Ca of mice receiving injections of folliculin was $<$ those of controls. The total ash was normal. A. A. E.

Inhibitory factors and the mechanism of the action of sex hormones of the opposite sex on the development of sex glands. W. Schoeller and M. Gehrke (Biochem. Z., 1933, **264**, 352—356).—Inhibition of the development of male sex glands on administration to young male animals of œstrin is confirmed and an explanation attempted. P. W. C.

Sexual hormone in the urine of men of various ages. F. Bühler (Z. ges. exp. Med., 1933, **86**, 650—658; Chem. Zentr., 1933, i, 2126).—At 20—40 years (male) the daily excretion is 1—2 fowl units; in puberty and old age androkinin could not be detected except after administration of "proviron." The thelykinin (I) content is (male): puberty—30 years 25—20, 30—50 years 10—15 mouse units. Before puberty and after 60 years (I) was not detected in the urine. A. A. E.

Male hormone from pigs' testicles. A. Ogata and S. Hirano (Proc. Imp. Acad. Tokyo, 1933, **9**, 345—346).—An improved method for the isolation of the testicular hormone is described. Saponification with 10% KOH in EtOH almost, oxidation with $KMnO_4$ in $COMe_2$ solution completely, destroyed the gonadotropic activity of the preps. A. L.

Action of the testicular hormone on cockscombs and seminal vesicles. K. Matsuzaki (Proc. Imp. Acad. Tokyo, 1933, **9**, 342—344).—Hormone preps. from male urine, active in promoting comb growth (I), showed no activity on the vesicles of rats (II). The testicular hormone (III) from pigs, on the other hand, showed activity in respect of both (I) and (II), although on treatment with $KMnO_4$ in $COMe_2$ solution (II) was no longer apparent. (III) is therefore considered to contain two different hormones. A. L.

Vitamins and hormones. J. Kühnau and W. Stepp (Münch. med. Woch., 1933, **80**, 87—92; Chem. Zentr., 1933, i, 2126).—Chemical relationships are discussed. A. A. E.

Systematisation of avitaminosis and vitamins. W. Kollath (Med. Klinik, 1933, **29**, 143—146; Chem. Zentr., 1933, i, 1470—1471).—A classification based on bodily changes produced in dietary experiments on rats is advanced. A. A. E.

Dietary factor concerned with carbohydrate metabolism. L. G. Wesson and F. C. Murrell (J. Biol. Chem., 1933, **102**, 303—311; cf. this vol., 527).—A liquid-fat fraction (I), obtained from the mother-liquors from crystals of an EtOH solution of lard after the solid fraction has crystallised out, is ten times as active as the solid fraction in restoring the carbohydrate metabolism of rats, fed on a fat-deficient diet (II), to normal. The feeding of Et stearate in (II) reduces the effectiveness of (I). Saponified (I) is active. The abnormal metabolism is ascribed to the absence of a metabolic factor in fat. H. D.

Vitamin-*A* in fish-liver oils. P. N. Chakravorty, H. C. Mookerjee, and B. C. Guha (J. Indian Chem. Soc., 1933, **10**, 361—366).—The Carr–Price blue vals. of the liver oils from *Labes rohita* (*Rohit*) (I), *Cirrhina mrigala* (*Mrigal*), *Catla catla* (*Katla*), *Clupea ilisha* (*Hilsha*), and *Lates calcarifer* (*Vetki*) are 227, 174, 109, 59, and 284, respectively. Considerable seasonal variations may occur with (I). The mesenteric fat of (I) contains no vitamin-*A*. The relation between dilution of the oil and the intensity of the colour in the Carr–Price method (A., 1926, 870) is discussed. H. B.

Vitamin-*A* content of milk irradiated by various carbon arcs. R. C. Bender and G. C. Supplee (Amer. J. Dis. Children, 1933, **45**, 995—998).—The vitamin-*A* content of milk containing 1·2% of fat was not appreciably reduced by irradiation during 8—48 sec. Ch. Abs.

Vitamin content of the Indian mango. B. C. Guha and P. N. Chakravorty (Indian J. Med. Res., 1933, **20**, 1045—1048).—Three varieties of Indian mangoes were fairly good sources of vitamin-*A*, but were relatively poor in the vitamin-*B* complex and in vitamin-*C*. Nutr. Abs. (*b*)

Vitamin-*C* and -*A* in blueberries. C. R. Fellers and P. D. Isham (J. Agric. Res., 1933, **47**, 163—165).—The vitamin-*C* content of *Vaccinium corymbosum* is high and not appreciably affected by freezing or by certain methods of canning. *V. pennsylvanicum* contains less vitamin-*C* and is practically devoid of -*A*. A. G. P.

Rôle of fat-soluble vitamin in the nutrition of growing cattle and pigs, with consideration of certain other vitamin problems. H. Isaachsen, O. Ulvesli, M. Husby, and K. Breirem (Fôringsforsøk. Norges Landbruksh., 1931, No. 30, 27 pp.; Bied. Zentr., 1933, A, 3, 419—420).—Various typical rations and special supplements are examined as sources of vitamin-*A* and -*D*. A. G. P.

Application of the paired feeding method to the determination of the vitamin-*A* content of foods and artificial concentrates. O. F. Garrett and H. H. Mitchell (Amer. J. Physiol., 1933, **104**, 608—614).—4% of butter-fat from stall-fed cows provided sufficient vitamin-*A* (I) for normal growth of newly-weaned rats, the mothers of which were deprived of (I) during lactation but received 1% of cod-liver oil during gestation. Nutr. Abs. (*b*)

Complement content of sera in avitaminosis-*A* and -*C*. P. E. Simola (Acta Soc. med. Fennicae "Duodecim," 1932, A, **16**, No. 1, 12 pp.).—In guinea-pigs (I) suffering from vitamin-*C* deficiency, there is no change in the val. for serum-complement, but it decreases in (I) suffering from vitamin-*A* deficiency. Addition of vitamin-*D* to the diet does not alter the serum complement of (I). Nutr. Abs. (*m*)

Vitamin-*A* deficiency in dogs. A. M. Stimson and O. F. Hedley (Pub. Health Rep., U.S. Treasury Dept., 1933, **48**, 445—449).—The symptoms of the deficiency in dogs are conjunctivitis, corneal opacity, ulceration, perforation (in 6—32 weeks), ophthalmia, nasal hæmorrhage, bronchopneumonia, and malnutrition. Deposit appears on the teeth and deciduous teeth fail to shed. In some cases there is disturbance in locomotion. The spinal cord is also affected. Nutr. Abs. (*m*)

Occurrence of γ-carotene. A. Winterstein (Z. physiol. Chem., 1933, **219**, 249—252).—The new provitamin-*A* found in *Gonocaryum* fruits (I) is a mixture of γ-carotene (II) and *δ-carotene*, absorption bands 526, 490, 457 mμ in CS_2. The rind of (I) is the best source of (II). J. H. B.

Activity of carotene from the suprarenal glands of various animals. L. Randoin and R. Netter (Bull. Soc. Chim. biol., 1933, **15**, 944—953).—The activity of the carotene (I) extracted by the method of Bailly and Netter (A., 1932, 76) from the suprarenal glands (II) of the ox is only slightly $<$ that of purified (I). (I) is also present in the (II) of the horse and the pig, but not in the white rat. A. L.

Biological relation between carotene and vitamin-*A*. J. C. Drummond and R. J. MacWalter (Biochem. J., 1933, **27**, 1342—1347).—The vitamin-*A* (I) content of the liver, determined spectrophotometrically, showed no increase following the injection of carotene (II) into the portal circulation of rabbits until 8 days after the injection. The possibility cannot be excluded that the vitamin produced is utilised or the amounts are too small for determination by this method. Attempts to obtain *in vitro* conversion of (II) into (I) by liver-tissue have failed. A. W.

Metabolism of carotene in different animals. B. Ahmad and K. S. Malik (Indian J. Med. Res., 1933, **20**, 1033—1038).—Rats' livers contained large quantities of vitamin-*A* when carotene had been administered after a vitamin-*A*-deficient diet, but no increase occurred in the case of the cat, whilst the rabbit, pigeon, and chicken showed moderate increases. Nutr. Abs. (*b*)

Influence of the carotenes on growth, xerophthalmia, cornification, and the œstrous cycle. R. Kuhn and H. Brockmann (Klin. Woch., 1933, **12**, 972—973).—For growth promotion and for the cure of xerophthalmia and of persistent vaginal cornification in rats α-, β-, and γ-carotenes were active, but β-carotene, which presumably affords 2 mol. of vitamin-*A* (I), appeared to be twice as active as the α- and γ-forms, which may be supposed to lose half the mol. as inactive material on conversion into (I). For the complete restoration of the œstrous cycle the dose required was 5—8 times the min. dose for growth. Only above this level was (I) stored in the liver, the amount found after β-carotene feeding being double that found after feeding α-carotene. A daily dose of 1·0 mg. of carotene produced no signs of hypervitaminosis-*A*, possibly on account of incomplete absorption. Nutr. Abs. (*b*)

Antirachitic action of β-cholic acid. T. Kikuzawa (Z. physiol. Chem., 1933, **220**, 54—56).—Irradiated Me α-cholate (2 mg. dose) and β-cholate (20 mg. dose) protect rats to a small extent against rickets. J. H. B.

Evaluation of vitamin-*D* preparations. III. M. Schieblich (Biochem. Z., 1933, **265**, 1—4; cf. A., 1931, 531).—When buckwheat (I), which contains less P than wheat (II), is substituted for (II) in McCollum's diet (A., 1921, i, 757) the amount of vitamin-*D* required to prevent rickets in rats receiving the diet is doubled. The modified diet is otherwise as useful as the original. When the vitamin-*D* content of foods is determined, only a half or one third of the (II) should be replaced by (I). W. McC.

Bile in the absorption of vitamin-*D* in the rat. J. D. Greaves and C. L. Schmidt (J. Biol. Chem., 1933, **102**, 101—112).—Bile-fistula rats have negative Ca and P balance. Irradiated ergosterol (I) is absorbed in small amounts only from the intestinal tract, but deoxycholic acid, given orally, can act as a carrier of (I) across the intestinal wall. H. G. R.

Renal lesions in hypervitaminosis-*D*: urinary calcium and phosphorus excretion. J. Gough, J. B. Duguid, and D. R. Davies (Brit. J. Exp. Pathol., 1933, **14**, 137—145).—Calcification and parenchymatous degeneration ("nephrosis"), which frequently co-exist in the kidneys of rats in hypervitaminosis-*D*, are largely independent of one another. Whilst calcification could be correlated with a high renal excretion of Ca, no connexion could be established between nephrosis and any urinary disturbances, although it was influenced by administration of NaH_2PO_4 with excess of vitamin-*D*. The urinary Ca was greatest when the alkaline phosphate was administered with vitamin-*D*, and urinary P when NaH_2PO_4 was given. Calciferol decreased the urinary P when either the acid or alkaline salt was administered. NUTR. ABS. (*b*)

Behaviour of glycogen in the organism in absence of the vitamin-*B* complex (particularly -B_1) from the diet. E. ABDERHALDEN and E. WERTHEIMER (Pflüger's Archiv, 1932, 230, 601—613; Chem. Zentr., 1933, i, 1645).—In pigeons avitaminosis-B_1 is accompanied by marked accumulation of glycogen in the liver and heart muscle; blood-sugar is unchanged. Normal vals. are regained on administration of yeast, but not if the yeast has been heated at 120° for 6 hr. A. A. E.

Application of the paired feeding method to the determination of the relative vitamin-*B* contents of foods and artificial concentrates. H. H. MITCHELL (Amer. J. Physiol., 1933, **104**, 594—607).—The vitamin-B_1 (I) content of a substance was measured by determining the least amount of it which prevented any significant difference in growth between the animal and its paired control on adequate (I) diet. This was 40—45% for maize and 50—55% for wheat, with diets containing 18% of protein. Less (I) appeared to be needed for higher % of protein (caseinogen). 6% of whole dried yeast supplied sufficient of the vitamin-*B* complex for max. growth of young rats. NUTR. ABS. (*b*)

Photochemical activation of adenine. B. C. GUHA and P. N. CHAKRAVORTY (Nature, 1933, 132, 447; cf. A., 1932, 1294).—Further biological experiments indicating the formation of a growth-promoting substance on irradiation of adenine sulphate are described. L. S. T.

Concentration and probable chemical nature of vitamin-B_2. L. E. BOOHER (J. Biol. Chem., 1933, 102, 39—46).—The probable identity of vitamin-B_2 and the fluorescent pigment of whey is suggested. A 2000-fold concn. of fresh milk, of which the lactochrome is the main constituent, active in 1 mg. doses, practically free from vitamin-B_1, is described. H. G. R.

Vitamin-*C*. VI. Identity of ascorbic acid and vitamin-*C*. F. MICHEEL and T. MOLL (Z. physiol. Chem., 1933, 219, 253—256; cf. this vol., 936).—The $COMe_2$ compound of ascorbic acid (I) has less antiscorbutic activity than (I) *per os* and none when parenterally administered. The identity of (I) with vitamin-*C* is thus confirmed. J. H. B.

Potentials of ascorbic acid.—See this vol., 1015.

Vitamosazone. Y. KOTAKE and M. NISHIGAKI (Z. physiol. Chem., 1933, 219, 224—232).—A substance (phenylosazone, m.p. 205—206°; 2 : 4-dinitrophenylosazone, m.p. about 240°) of high reducing power found in many animal organs and fluids and also in a species of orange is probably ascorbic acid. From ox testes and aq. humour a *phenylosazone*, m.p. 158—160°, of a pentose was also obtained. J. H. B.

Ascorbic acid content of corpora lutea. S. HUSZÁK (Z. physiol. Chem., 1933, 219, 275—277).—Corpora lutea contain about the same amount (1 mg. per g. of tissue) as the adrenals, much > any other animal organ. J. H. B.

Determination of vitamin-*C* (antiscorbutin) in milk. B. BLEYER (Münch. med. Woch., 1933, 80, 257—258; Chem. Zentr., 1933, i, 2577).—Titrimetric determinations (Tillmans) gave the highest results with human colostrum; vals. become const. after 1 month. Vals. are approx. double those for cow's milk. On keeping in air at room temp. 50% of the vitamin-*C* content is lost in 4 hr.; at 0° only 3% is lost. Heating at a high temp. for a short time has less destructive effect than pasteurisation. Ni, Cr, and Al have no influence; Cu and Ag are injurious. Goat's milk has approx. the same vitamin-*C* content as cow's milk, ewe's milk one sixth thereof, and ass' milk six times as much as cow's milk. A. A. E.

Biochemistry of carotenoids and of vitamin-*C* (ascorbic acid). H. VON EULER and E. KLUSSMANN (Z. physiol. Chem., 1933, 219, 215—223).—NH_2-acids assist the dissolution of carotene (I) by means of bile-acid salts. (I) is liberated when the p_H of the solution becomes > 7—7·5 or when the bile acids or salts are bound by other substances. Egg-yolk contained 9×10^{-6} g. of vitamin-*A* and 40×10^{-6} g. of (I) per g. In determining the vitamin-*C* (II) content of beans, the extraction should be performed in H_2. The O_2 uptake by guinea-pig's liver is less for scorbutic than for normal or *C*-hypervitaminised animals. Fish-roe contains relatively little (II). J. H. B.

Plant growth-substances. VII. Occurrence of auxins in the human and animal organism. F. KÖGL, A. J. HAAGEN-SMIT, and H. ERXLEBEN. **VIII. Occurrence of auxins and growth-substances of the "bios" group in carcinomata.** F. KÖGL, A. J. HAAGEN-SMIT, and B. TÖNNIS (Z. physiol. Chem., 1933, 220, 137—161, 162—172; cf. this vol., 987).—VII. Excretion of auxin *a* in human urine is independent of age and sex, and is not increased during pregnancy or influenced by menstruation. Carcinomatous and tuberculous patients showed a normal excretion. The max. excretion occurs about 3 hr. after the main meal. The excretion is much increased after ingestion of salad (arachis) oil and butter, but not after hydrogenated coconut oil and other foods devoid of auxin; *i.e.*, foods containing auxin (even although chiefly *b*) increase the output of auxin *a*, no *b* being obtainable from urine. Certain individuals show a high auxin excretion (about four times normal); this is a constitutional idiosyncrasy. Auxin occurs in small amount in many animal organs.

VIII. In human carcinoma plant-growth substances and "bios"-factors occur in higher concn. than in neighbouring normal tissue. Auxin *a* and *b* do not stimulate the growth of heart-fibroblasts in tissue culture, nor of yeast cells. J. H. B.

Presence of growth-promoting substance in animal and plant material. E. MASCHMANN and F. LAIBACH (Naturwiss., 1933, 21, 517).—The growth-promoting substance (cf. A., 1932, 1156) is found in the blood, liver, and kidneys of fasting guinea-pigs and rabbits in smaller quantities than in the case of fed animals. It is also found in rabbit's lung, pig's thyroid, calf's thymus, and ox testicle and pancreas. It exists in various grains, but decreases during germination; it occurs also in peas, beans, lentils, asparagus, tomatoes, oranges, and lemons. W. O. K.

Growth substance (auxin) in plants. F. A. F. C. Went (Nature, 1933, **132**, 452).—A summary. L. S. T.

Plant growth hormone. J. Bonner (J. Gen. Physiol., 1933, **17**, 63—76).—Sections of *Avena* coleoptiles (I) immersed in H_2O cease growth after 7—8 hr. Addition of "growth substance" (II) increases the length by 55% in 24 hr. Top sections of (I) grow more rapidly in the presence of (II) than the lower sections. An optimum concn. of (II) exists in the region of 10 units per c.c. Addition of KCN or phenylurethane, or the absence of O_2, inhibits growth. A correlation exists between growth and respiration. H. D.

Increased respiration coefficient of stimulated seeds. M. Popoff and M. Stefanowa (Biochem. Z., 1933, **264**, 434—436).—Using millet seeds, stimulated (with 3% KBr) embryos always gave a higher R.Q. than non-stimulated. P. W. C.

Mechanism of the activation of oxygen by irradiated pigments. H. Gaffron (Biochem. Z., 1933, **264**, 251—271).—In continuation of the author's work on the photochemical reactions during O transport by chlorophyll (I) and porphyrins (A., 1927, 67, 428, 1225) an attempt is made to follow quantitatively the relationship between O_2 concn. and photochemical action. The pigment does not react itself with mol. O_2 and all the autoxidation processes with (I) depend on reactions with peroxides arising by secondary processes. The oxidising action of irradiated pigment in solutions containing pigment, O_2, and oxidisable substance (acceptor) depends on an activation, not of O_2, but of the acceptor. P. W. C.

Assimilation of sulphates by fungi: euthiotrophy and parathiotrophy. M. Volkonsky (Compt. rend., 1933, **197**, 712—714).—Cultures of 26 varieties of *Saprolegnia* are parathiotrophic, *i.e.*, unable to grow on the basic nutrient medium (this vol., 752) if K_2SO_4 is the source of S. Growth occurs if S is supplied as cysteine (I). Several euthiotropic species are described which assimilate SO_4'' as well as, or better than, S in the form of (I). A. C.

Effects of starvation on distribution of mineral nutrients in French prune trees grown in culture solutions. H. L. Colby (Plant Physiol., 1933, 8, 357—393).—Symptoms of Ca starvation appeared almost entirely in roots, little or no leaf growth occurring. Deficiencies of other elements were apparent primarily in the leaves. Mg starvation resulted in high N and P and low Ca and Mg in leaves, low N and P in the trunk, and high ash contents in all organs except leaves. In the absence of Ca all parts of trees except wood had low N and ash contents. Ca in the trunk prior to starvation was not translocated. K starvation produced leaves high in N, P, Ca, and Mg and low in total ash. Trunk and roots had low N contents. Trees starved of N had low ash contents except in wood and very low N throughout. Young wood had low Ca and Mg and high K. Main roots were very low in N, low in Mg and P, and high in Ca. Leaves of P-starved trees were high in ash and N, very high in Mg and Fe, and low in Ca and P. All other parts were low in N, and roots and trunks were low in Mg. S starvation produced leaves low in N, ash, and SO_4''. Young wood was low and the remainder of the tree high in N. K absorption decreased and that of Ca and Mg increased. The Fe content of young wood and roots was high in trees starved of K, Mg, or S. High Fe in bark occurred only in cases of P and Ca starvation in which young wood and main roots showed low vals. for Fe. Trees grown for 2 years in distilled H_2O made better growth than those in nutrients containing all essential elements except Ca, but were inferior to those in aq. $Ca(OH)_2$ at p_H 7·2. K starvation was more detrimental to growth than complete starvation. Starvation of one element was more effective in changing the p_H of leaf sap than were changes in the p_H of the nutrient solutions. A. G. P.

Bast-sap. H. H. Dixon (Sci. Proc. Roy. Dublin Soc., 1933, **20**, 487—494).—Further evidence is presented for the theory that the bast is the most important channel for the transport of org. substances, which is brought about by a difference in the osmotic pressure between the upper and lower levels. H. G. R.

Factors affecting the electrolytes of starch granules. D. S. Edwards and J. C. Ripperton (J. Agric. Res., 1933, **47**, 179—191).—In sol. canna- but not in potato-starch lowered viscosity is associated with lower K and increased Ca contents. Electrolytes held by starch *in vivo* are influenced by sap composition and growth conditions, but the variations are small compared with corresponding effects on starch *in vitro*. A. G. P.

Hydrolysis of dipeptides in germinating chlorophyll mutants of barley. H. von Euler and B. Sjöman (Biochem. Z., 1933, **264**, 237—245).—A stronger dipeptidase action using *d*-alanylglycine and *l*-leucylglycine is detected both in the scutellum and in the embryo of chlorophyll-defective strains of barley than in chlorophyll-normal mutants. P. W. C.

Apparatus for making autographic records of catalase activity of plant tissues. A. J. Heinicke (J. Agric. Res., 1933, **46**, 1137—1143).—Apparatus is described whereby the O_2 produced forces H_2O into a burette containing a floating indicator pen. Records of twelve simultaneous determinations may be obtained. A. G. P.

Graphic registration of the transpiration of leaves. K. Boresch (Planta [Z. wiss. Biol.], 1933, **20**, 448—469).—The movement of a strip of cellophane lightly attached to the leaf is utilised to obtain a record of transpiration activity. A. G. P.

Changes in leaves during the period preceding frost. F. E. Denny (Contr. Boyce Thompson Inst., 1933, 5, 297—312).—No important changes occurred in the dry matter or total carbohydrate content of leaves of *Viburnum dentatum* or *Syringa vulgaris* during 3—5-day periods before frost. Considerable migration of N from leaves of *Viburnum* but not from *Syringa* are recorded in this period. A. G. P.

Influence of carbohydrates on the daily course of photosynthesis. A. L. Kurssanov (Planta [Z.

wiss. Biol.], 1933, 20, 535—548).—The curve of photosynthesis has two max. with a min. early in the day. Artificially increased carbohydrate in the leaves reduced CO_2 assimilation and *vice versa*. A. G. P.

Seasonal osmotic variations in some evergreen woody plants. M. Steiner (Jahrb. wiss. Bot., 1933, 78, 564—622).—Variation in the osmotic pressure of the expressed sap of *Ilex aquifolium*, *Hedera helix*, and *Pinus sylvestris* is largely controlled by changes in the sugar content, in *Buxus sempervirens* by changes in total H_2O content. Both factors operate in *Taxus baccata*. A. G. P.

Effect of ethylene chlorohydrin vapour on the chemical composition of gladiolus corms. F. E. Denny (Contr. Boyce Thompson Inst., 1933, 5, 435—440).—In comparison with untreated corms, those treated with the $CH_2Cl{\cdot}CH_2{\cdot}OH$ showed marked lowering of reducing sugar and some increase in sucrose contents together with an increase in sol. and a decrease in insol. N constituents. A. G. P.

Effect of potassium thiocyanate and ethylene chlorohydrin on amylase activity. F. E. Denny (Contr. Boyce Thompson Inst., 1933, 5, 441—450).—The action of $CH_2Cl{\cdot}CH_2{\cdot}OH$, KCNS, and $CS(NH_2)_2$ in stimulating the growth of dormant buds is in no way related to the direct effect of these substances on amylase activity. A. G. P.

Carbon dioxide narcosis. III. Salt antagonism. IV. Is lack of oxygen a factor in the narcotic effects of carbon dioxide? V. Water and electrolytes in *Nitella* during exposure to carbon dioxide solutions. D. L. Fox (J. Cell. Comp. Physiol., 1933, 3, 340—354).—The presence of dissolved salts, *e.g.*, KNO_3, in concns. of 0·1—0·4%, with or without traces of $CaSO_4$, $Ca_3(PO_4)_2$, and $FePO_4$, increases the threshold tolerance of *Nitella* (I) for CO_2. Solutions of NaCNS (0·2%) or glucose (0·2%) do not antagonise the effects of CO_2. Dil. salt solutions induce antagonism in (I) towards strong acids, *e.g.*, HCl. Narcotic and lethal effects previously observed are not due to deficiency of O_2 but to sp. action of the CO_2 or H_2CO_3 mol. Excess O_2 is not injurious. A. G. P.

(*a*) Anæsthesia produced by distilled water. (*b*) Anæsthesia in acid and alkaline solutions. (*c*) Reversible loss of potassium effect in distilled water. W. J. V. Osterhout and S. E. Hill (J. Gen. Physiol., 1933, 17, 87—98, 99—103, 105—108).—(*a*) Cells of *Nitella* fail to respond to electrical stimulation after 2 or 3 days in distilled H_2O; the same anæsthesia (I) is produced on restricted areas of a cell. The sensitivity returns after 1—2 days in their normal environment or in dil. solutions of $CaCl_2$. It is concluded that (I) is due to a loss of substances from the cell which is inhibited by $Ca^{\cdot\cdot}$.

(*b*) Cells of *Nitella* in 0·001*M*-NaOH and 0·0001*M*-HCl lose their irritability. In the case of NaOH they fail to regain it on neutralisation, and only partial recovery occurs on treatment with $CaCl_2$. With HCl complete recovery occurs on treatment with $CaCl_2$.

(*c*) The p.d. between one part of *Nitella* in contact with a mixture of electrolytes and another part in contact with NaCl becomes more negative on replacing the NaCl by KCl. This effect disappears reversibly on exposure of the cell to distilled H_2O. The change appears to be confined to the outer surface of the protoplasm. H. D.

Effects of temperature on metabolism in tomato. G. T. Nightingale (Bot. Gaz., 1933, 95, 35—58).—Tomato plants grown in sand cultures for 10-day periods at 13° accumulated relatively large amounts of carbohydrates (I), especially starch. Absorption and translocation of NO_3' was rapid, but protein synthesis was very slow. Reducase activity was small. Leaves were deficient in chlorophyll and stems coloured purple due to the presence of anthocyanins. These conditions were accentuated in N-deficient plants. During exposure to 21° plants having no external N supply showed considerably decreased (I) contents and symptoms of protein deficiency were less marked than at 13°. Added NO_3' was absorbed at once and translocation was more rapid than at 13°. The plants possessed high NO_3'-reducing powers and N assimilation was rapid. (I) accumulation was reduced to a much lower level when N was supplied. At 35° decomp. of (I) was rapid in N-deficient and N-supplied plants and was accompanied by degradation of proteins. The temporarily accelerated growth was quickly followed by the death of the plants. Absorption and translocation of NO_3' was rapid. Reducase activity was high for a short period, but soon declined. At this temp. plants receiving N died sooner than those in N-free media. A. G. P.

Rubber content of various species of goldenrod. L. G. Polhamus (J. Agric. Res., 1933, 47, 149—152).—Of twenty-four species of *Solidago* examined none contained more than traces of rubber in any parts other than leaves. A. G. P.

Aromatic constituent of products from sugar maple [*Acer saccharum*]. J. Risi and E. Bois (Natural. Canad., 1933, 60, 181—193).—The aromatic constituent of maple syrup is readily extracted with Et_2O; it contains phenolic and aldehydic functions in a ratio of approx. 1, and differs from the aromatic principle of fenugreek. H. A. P.

Determination of coumarin and melilotic acid in *Melilotis officinalis*. S. J. Kanevskaja and A. M. Fedorova (Z. anal. Chem., 1933, 93, 176—180).—The substance is extracted with boiling Na_2CO_3 solution. Coumarin dissolves, with the opening of a lactone ring and formation of a salt of coumaric acid. The salt is extracted with Et_2O, and coumarin is regenerated by adding dil. acid. The org. acid present in the original substance is determined by acidifying the Na_2CO_3 solution and extracting with Et_2O. Results of analysis of *M. officinalis* are given. E. S. H.

Latex of the lac tree of Cambodia. G. Bertrand and G. Brooks (Compt. rend., 1933, 197, 661—665).—Moreac, the lac of *Melanorrhœa laccifera*, yields a H_2O-sol., EtOH-insol. gum (2·5%), and Et_2O-sol. *moreacol* (I) (55—60%), $C_{23}H_{36}O_2$, b.p. 242—250°/0·5 mm., m.p. 28°. Like laccol (this vol., 947), (I) contains two phenolic OH groups (*Ac*$_2$ derivative, b.p. 233—240°/0·2—0·3 mm.), and is hydrogenated in presence of Pt-black to *tetrahydromoreacol*, m.p. 95·3°, b.p. 280—290°/12—14 mm. (*Ac_2* derivative, m.p. 70·5°). (I) is either $C_6H_3(OH)_2{\cdot}C_{17}H_{31}$, or more probably $C_6H_2Me(OH)_2{\cdot}C_{16}H_{29}$. A. C.

Oleoresin of *Pinus monticola*, Dougl. P. A. Foote and N. T. Mirov (J. Amer. Pharm. Assoc., 1933, **22**, 828—834).—The oleoresin contains 60% of *d*-α-pinene, 26% of β-pinene, limonene (uncertainly), indeterminate amounts of sesquiterpenes, and 1—2% of *n*-undecane. The significance of the latter constituent is discussed in relation to a possible origin of petroleum. W. S.

Enzymes of lichens and constitution of umbilicaric acid. G. Koller and G. Pfeiffer (Monatsh., 1933, **62**, 359—372).—The extraction of a depsidase from *Umbilicaria pustulata*, *U. deusta*, and *E. prunastri* is described. This effects enzymolysis of lecanoric, gyrophoric, evernic, and diploschistesic acids into orcinol (I) and its mono-ether. A carboxylase, also present, readily attacks orsellinic and evernic acids, but not atranorin, umbilicaric (II), paraorsellinic, β-resorcylic, quinolcarboxylic, or pyrogallolcarboxylic acids. It is suggested that such H_2O-insol. depsides are reserve materials in the lichen and are broken down by the enzymes into H_2O-sol. orcinol derivatives. Alcoholysis of (II) with MeOH at 140° affords (I), Me orsellinate (III), and a *substance* (IV), $C_{18}H_{18}O_7$, m.p. 163—165°, which is a didepside containing the *iso*evernic residue, obtained by fission of (I) and subsequent esterification of the new CO_2H. With EtOH at 160° (IV) gives (III). Longer alcoholysis of (II) gives Me *iso*evernate (Me 5-hydroxy-3-methoxy-*o*-toluate) in addition to (I) and (III). Of the alternative structures previously suggested (this vol., 714), that given as (I) with a CO_2H added between Me and OH in the right-hand nucleus is preferred for (II) on the basis of these results, and (IV) is $C_6H_2Me(OH)(OMe){\cdot}CO{\cdot}O{\cdot}C_6H_2Me(OH){\cdot}CO_2Me$. J. W. B.

Rotenone. XXVIII. Preparation of dihydrorotenone. H. L. Haller and P. S. Schaffer (Ind. Eng. Chem., 1933, **25**, 983).—Hydrogenation of rotenone (I) with a Ni catalyst in neutral solution at 35—40° and atm. pressure gives about 90% of dihydrorotenone. Plant extracts containing (I) may also be used. F. R. S.

Active constituents of *Urtica dioica* and *U. urens*. E. Starkenstein and T. Wasserstrom (Arch. exp. Path. Pharm., 1933, **172**, 137—148).—The pharmacological properties of 50% EtOH extracts (I) of nettles were investigated. From (I) were isolated the following fractions: (*a*) pptd. by Pb acetate and containing HCO_2H, (*b*) pptd. by $HgCl_2$ and free from N, and (*c*) the filtrate from (*b*) containing small amounts of fructose and glucose. None of these fractions contained any glucoside, alkaloid, or protein. (I) contained 0·003—0·005% of HCO_2H. Analytical data for the ash of (I) and of the plant residue are given. F. O. H.

Arrow grass—chemical and physiological considerations. O. A. Beath, J. H. Draize, and H. F. Eppson (Wyoming Agric. Exp. Sta. Bull., 1933, No. 193, 36 pp.).—The poisonous principle of arrow grass is HCN derived from glucosides present mainly in the leaf, which also contains a high proportion of NaCl. HCN is more readily released from dried than from fresh samples. Extraction with H_2O is the most effective method of removing toxic matter. A. G. P.

Pungent principle from the water-pepper, *Polygonum hydropiper*, L. W. R. Witanowski and H. P. Krynska (Arch. exp. Path. Pharm., 1933, **172**, 463—470).—The Et_2O-extracted substance of the dried plant was steam-distilled and the distillate extracted with Et_2O to yield an oil (n_D^{23} 1·4886, d^{23} 0·932, $[\alpha]_D$ $-5{\cdot}4°$, acid val. 39·6, ester val. 81·5, Ac val. 94·5) from which was separated polygonum oil (I) (n_D^{20} 1·5054, d^{20} 0·994) [*thiosemicarbazide*, $C_{20}H_{34}N_6O_2S_2$, m.p. 194—195° (*Ag* derivative)]. Fractional distillation of (I) yielded *polygonone*, $C_{18}H_{26}O_3$, an unsaturated ketone. (I) paralyses the isolated intestine and uterus and, when intravenously injected into cats and rabbits, lowers the blood-pressure. F. O. H.

Indian medicinal plants. I. *Withania somnifera* [winter cherry]. II. *Swertia chireta*. D. N. Majumdar and P. C. Guha (J. Indian Inst. Sci., 1933, **16**, A, 29—33, 34—39).—I. The Bengal variety contains the same constituents as the South African variety, namely, KNO_3, tannin, glucose, phytosterol, hentriacontane, stearic, palmitic, oleic, linoleic, and withanic acids, ipuranol, somnirol, somnitol, and an alkaloid, $C_{12}H_{16}N_2$ (cf. Power and Salway, J.C.S., 1911, **99**, 490), and there are indications of the presence of three other basic constituents.

II. The following have been isolated from an aq.-EtOH extract of the drug: *iso*amyl alcohol, a phenolic *compound* $(C_{13}H_{14}O_5)_x$, m.p. 179—180°, oleic, palmitic, stearic, and (probably) cerotic acids, a *phytosterol*, m.p. 128—130° (*acetate*, m.p. 127—129°), a OH-*acid*, $C_{26}H_{44}(OH){\cdot}CO_2H$, m.p. 295° (*Ac* derivative, m.p. 250—251°), a phenolic *compound*, m.p. 256—257°, ophelic acid (*tetrabromide*, m.p. 114—115·5°), and a neutral *compound*, m.p. 197—198°. Chiratin (Höhn, Jahr. Fort. Chem., 1869, 771) is a mixture and has been resolved into two *compounds*, m.p. 118—119° and 179—180°, respectively, and a viscous resin. The drug contains no alkaloids. S. C.

Volatile oil of *Sarothra gentianoides*, L., and detection therein of *n*-nonane. M. T. Bogert and S. J. Marion (J. Amer. Chem. Soc., 1933, **55**, 4187—4194).—The oil (I), obtained in approx. 0·1—0·2% yield by steam-distillation of the whole green plant, contains C 84·03 and H 14·75% and has d_{20}^{20} 0·7665, n_D^{20} 1·4262, $[\alpha]_D$ $+6{\cdot}39°$, acid val. 0·58, sap. val. 4·43, ester val. 3·85, and sap. val. after acetylation 17·35; 96% of (I) is localised in the tops of the plants. (I) contains *n*-nonane ($\nless 20\%$), an optically active olefine (probably an octene), unidentified terpenes and sesquiterpenes, α-terpineol, geraniol, traces of phenols, aldehydes, and ketones, hexoic acid, and an ester of octoic acid. H. B.

Non-pre-existence of azulene in milfoil. K. Graham (J. Amer. Pharm. Assoc., 1933, **22**, 819—824). W. S.

Kæmpferol rhamnoside from the leaves of *Pueraria hirsuta*, Matumura. I. T. Ohira (J. Agric. Chem. Soc. Japan, 1933, **9**, 337—342).—Extraction with 60% EtOH containing 3% NaOH at 60—70°, neutralisation with HCl, evaporation under diminished pressure, acidification, filtration, neutralisation, and concn. afforded kæmpferol in 0·15% yield; the sugar residue was rhamnose. Ch. Abs.

Occurrence of dulcitol in *Irideæ laminarioides* (*Rhodophyceæ*). W. Z. Hassid (Plant Physiol., 1933, 8, 480—483).—Dulcitol, but not mannitol, is present. A. G. P.

Determination of carbohydrates in leaves. R. H. Dastur and K. M. Samant (Indian J. Agric. Sci., 1933, 3, 460—477).—A modification of the method of Davis, Daish, and Sawyer (B., 1916, 373) is used. Basic Pb acetate is used for clarification of the conc. extract and excess Pb is removed by Na_2HPO_4. Hexoses are determined by a modification of the method of Folin and Wu. For determining sucrose 10% aq. tartaric acid is used in place of citric acid, since Na citrate inhibits the production of the blue colour. Maltose, if present, is determined by measuring the reducing power before and after hydrolysis with H_2SO_4. Starch is determined as glucose after successive hydrolysis with takadiastase and 10% aq. H_2SO_4. Reducing sugars can be determined at a concn. of 1 : 100,000 and sucrose at 1 : 20,000. Nutr. Abs. (*m*)

Micro-analysis of plant juice for reducing sugars and sucrose. F. S. Schlenker (J. Biol. Chem., 1933, 102, 29—34).—Clarification is effected by neutral $Pb(OAc)_2$, which removes colouring matter and proteins. Folin's Cu method (A., 1929, 714) gives most trustworthy results, discrepancies being due not to NH_2-acids, but to some other type of non-glucose reducing substance. H. G. R.

Alkaloids of *Artabotrys*. I. Artabotrin and suaveolin. A. C. Santos and F. R. Reyes (Univ. Philippines Nat. Appl. Sci. Bull., 1932, 2, 407—415).—*A. suaveolens* affords artabotrin, $C_{21}H_{25}O_4N$ (cf. Marañon, A., 1929, 857), m.p. 187°, $[\alpha]_D^{30}$ +198·7° in $CHCl_3$, and *suaveolin*, $C_{16}H_{10}(OH)(OMe)_3{\cdot}NMe$, m.p. 182°, $[\alpha]_D^{30}$ +203—206° in $CHCl_3$ (*chloroaurate*, decomp. 167°). Ch. Abs.

Proteins of mulberry leaves. I. Kinds of protein-nitrogen in mulberry leaves and a comparison of the quantities of protein-nitrogen in different parts of the mulberry tree. III. Quantitative changes of proteins contained in the mulberry leaves during maturation. Y. Kishi (J. Agric. Chem. Soc. Japan, 1933, 9, 397—411, 412—415).—I. Of the protein-N 66% is extracted by 60% EtOH containing 0·3% NaOH. Proteins of the root, seed, sap, and stem consist chiefly of globulin. The extracted protein contains very little P.

II. Mulberry leaf-protein decreases with maturation. Ch. Abs.

Nitrogenous composition of horse beans and peas. K. Yoshimura and T. Iwata (J. Agric. Chem. Soc. Japan, 1933, 9, 375—378).—Horse beans (5 kg.) afforded arginine ($-NO_3$) 0·4, betaine (-HCl) 2·7, trigonelline (-HCl) 0·5, and choline (Au salt) 1·8 g. Peas (5 kg.) afforded adenine, trace, trigonelline (-HCl) 0·5, and choline (Au salt) 0·3 g. Ch. Abs.

Sterols of rice embryo. II. Ergosterol and vitamin-*D*. K. Tanaka (J. Biochem. Japan, 1933, 18, 1—13).—The absorption spectra of irradiated (I) and non-irradiated sterols of rice embryo and the antirachitic activity of (I) indicate the presence of ergosterol. F. O. H.

Kernel-fats of the Palmæ: *Acrocomia sclerocarpa*, Mart. (gru-gru palm), *Manicaria saccifera*, Gaertn., *Astrocaryum tucuma*, Mart., *Maximiliana caribæa*, Griseb., *Attalea excelsa*, Mart. (pallia palm), and *Cocos nucifera*, Linn. (coconut). G. Collin (Biochem. J., 1933, 27, 1366—1372).—Analyses are given for these six seed-fats, the first five of which have not previously been examined completely. The composition of the fatty acid mixtures indicates a tendency for the various species within the palm family to synthesise fats of similar composition. Figures are given for the % of the different fatty acids present in each fat, and the content of saturated and unsaturated glycerides. A. W.

Fat and oil from the seeds of *Actinodaphne Hookeri*, Meissn. Indigenous source of lauric acid. S. V. Puntambekar and S. Krishna (J. Indian Chem. Soc., 1933, 10, 395—400).—The fat and oil from the seeds contain glycerides of lauric acid, oleic acid and its isomerides, and sitosterol; the oil also contains a small amount of resin acids. F. R. S.

Oil from the seeds of *Tectona grandis* (teak). S. V. Puntambekar and S. Krishna (J. Indian Chem. Soc., 1933, 10, 401—403).—The oil contains mainly stearic, palmitic, oleic, and linoleic acids. F. R. S.

Constituents of the wax from alkanet root. M. V. Betrabet and G. C. Chakravarti (J. Indian Inst. Sci., 1933, 16, A, 52—53).—The wax from alkanet root (m.p. 78°, d^{30} 0·9676, n_D^{30} 1·438, sap. val. 69·16, acid val. 12·92, unsaponifiable 58·56%, I val. 12·2, mol. wt. of mixed acids 380) consists essentially of carnaubyl cerotate. A small amount of an *acid*, m.p. 68°, was also isolated. S. C.

Barium as a normal constituent of brazil nuts. W. M. Seaber (Analyst, 1933, 58, 575—579).—Ba found in sweets was traced to the Brazil nuts present, and the white kernels of various samples of such nuts were found to contain 0·02—0·31% (Para nuts, 0·02—0·17%); negligible amounts were found in Brazilian oranges and sugars. Solubility determinations indicate that Ba is present as a salt of an org. acid which is insol. in H_2O, slightly sol. in acids of the concn. of those present in the human stomach, and readily sol. in more conc. acids. J. G.

Relation between chlorophyll and iron in green and chlorotic pear leaves. J. Oserkowsky (Plant Physiol., 1933, 8, 449—468).—CaO-induced chlorosis is not necessarily associated with low total Fe contents in leaves. "Active" Fe [*i.e.*, that effective in chlorophyll (I) formation] is determined by extraction with 1% HCl of dried leaves, in which Fe appears in the ionic form or as compounds readily yielding $Fe^{\cdots}$. The (I) content of leaves is proportional to their "active" Fe contents, but the ratio of (I) to "active" Fe differs considerably in different sets of leaves. A. G. P.

Salicylic acid as a fixative. I. COHEN (Stain Tech., 1933, 8, 153—156).—Two fixatives containing salicylic acid are described; the first is recommended for studying mitosis and chromosomes, and the second for plastids. H. W. D.

Method for staining certain bacteria and antherozoids. W. N. STEIL (Stain Tech., 1933, 8, 139—142).—A modification of Loeffler's method is adopted. It is particularly suitable for the antherozoids of mosses, liverworts, and ferns. H. W. D.

Verification of analytical technique for biological media, by the method of added quantities. H. GRIFFON (J. Pharm. Chim., 1933, [viii], 18, 198—206).—The applicability of the method of added quantities is discussed theoretically. A. C.

Apparatus for study of redox potential in biological systems. J. P. BAUMBERGER (J. Gen. Physiol., 1933, 17, 1—6).—The Thunberg tube is modified, avoiding the use of a greased stopper and being capable of sustaining high vac. The Borsook and Schott tube (A., 1931, 1189) is modified by substituting the evacuation sealing system for ground-glass stoppers by adding a boot (I) at the tip so that satisfactory circulation may be obtained and by introducing the Pt electrode (II) into (I). A simplified reduction burette (Clark, A., 1928, 129) is described. A vac. oxidation–reduction cell adapted to the study of cell suspensions has, besides (I) and (II), a glass electrode, thus dispensing with a salt bridge. H. D.

Liebermann–Burchard colour reaction for cholesterol. I. A. MIRSKY and M. BRUGER (J. Lab. Clin. Med., 1932, 18, 304—306).—Appearance of a brown colour resulting from the action of H_2SO_4 and Ac_2O on $CHCl_3$ extracts containing cholesterol can be avoided by keeping the reaction mixture at 5°. CH. ABS.

Mesobilirubinogen as a standard in the determination of urobilin. M. ROYER (Rev. soc. argentina biol., 1932, 8, 489—490).—Mesobilirubinogen (0·0128 mg.) is dissolved in a little dil. aq. NaOH, a few crystals of $Zn(OAc)_2$ are added, and then a few drops of I solution to effect oxidation to urobilin; the solution is acidified with HCl and diluted to 1 litre. This solution has the same intensity of fluorescence as the trypaflavine solution (0·05 mg. per litre) used for comparison. CH. ABS.

Micro-methods for determining proteins in medicine and biology. A. WASITZKY (Mikrochem., 1933, 14, 85—112).—A review.

Micro-determinations of purine substances in tissues. II. Guanine, adenine, and hydroxypurines. G. SCHMIDT (Z. physiol. Chem., 1933, 219, 191—206; cf. A., 1932, 870).—The acid hydrolysate of 1—3 g. of tissue is pptd. with H_4WO_5 to remove protein degradation products. In one portion of the filtrate (I) aminopurines are pptd. by ammoniacal Ag solution, and the NH_2-N, determined by HNO_2, ×5 gives the total N of aminopurines. Guanine is separately determined by means of guanase, adenine being obtained by difference. The purines in a portion of (I) are pptd. by $CuSO_4$ and $NaHSO_3$. A Kjeldahl determination on the ppt. gives the total purine-N, from which the hydroxypurine-N is found by difference. Other purine derivatives must be absent. J. H. B.

Histochemistry of enzymes. VI. Micro-determination of ammonia. K. LINDERSTRØM-LANG and H. HOLTER (Z. physiol. Chem., 1933, 220, 5—12; cf. this vol., 864).—A micro-technique for NH_3 by distillation at 40° is described. J. H. B.

Gasometric determinations by means of the ureometer. IV. G. D'ESTE (Boll. Chim.-farm., 1933, 72, 601—614).—With the apparatus described (A., 1932, 550), 0·010 g. of urea when treated with alkaline NaOBr yields 3·41 c.c. of N_2 (at 0° and 760 mm.). The greatest accuracy is obtained by parallel determinations with a standard solution of urea. Serum and milk are deproteinised by $CCl_3\cdot CO_2H$ before urea determinations; normal cerebrospinal fluid is used directly. With the same method applied to NH_4 salts, 0·010 g. of NH_3-N yields 7·45 c.c. of N_2. For total N, the material is first treated by the Kjeldahl method. Differentiation of NH_3- and urea-N is achieved by xanthhydrol pptn. of urea. The application of the apparatus to the determination of the alkaline reserve of blood (1 c.c.) is described. F. O. H.

Errors in determination of bound water. H. B. BULL (J. Gen. Physiol., 1933, 17, 83—86).—The results of Greenberg and Greenberg (this vol., 523) show that an adsorption of solute on to the substrate can produce large changes in the calc. bound H_2O. H. D.

Analysis. XVII. Micro-determination of lead and zinc in organic material. L. PINCUSSEN and E. BRÜCK (Biochem. Z., 1933, 265, 58—60).—Pb ($\not<$ 0·1 mg.) is determined by destroying org. matter (I) with H_2SO_4, HNO_3, and H_2O_2, dissolving the pptd. $PbSO_4$ in NH_4OAc, pptg. the Pb with 10% aq. Na_2S in presence of gum arabic, and comparing the colour of the suspension produced with that of a standard. Fe salts, if present, must be removed by boiling after the addition of NH_4OAc. Zn is determined, after destruction of (I) as before, treatment with HCl and H_2S, filtration, and removal of Fe by pptn. with H_2S in dil. AcOH (II), ignition of the ZnS, dissolution of the ash in (II), repptn. with H_2S in presence of HCl, AcOH, and NH_4OAc, and comparison of the turbidity so obtained with that produced in a standard solution. $\not<$ 0·03 mg. in 15 c.c. of solution can be determined. W. McC.

Histochemical detection of gold. F. TIMM (Deut. Z. gerichtl. Med., 1933, 20, 211—214; Chem. Zentr., 1933, i, 2436—2437).—Sanocrysin is decomposed in the body affording Au_2S_3 which is detected ultramicroscopically. A. A. E.

[Determination of uranium] by the magneto-optic method. H. D. JONES and R. GOSLIN (J. Amer. Chem. Soc., 1933, 55, 3500—3501; cf. this vol., 137).—The distribution of U, after injection into the blood of animals, has been determined to within ±10%. J. G. A. G.