BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1932.

General, Physical, and Inorganic Chemistry.

Resonance spectrum of hydrogen. K. R. Rao (Nature, 1932, 129, 869). L. S. T.

Theory of some electron levels in H_2. J. K. L. MacDonald (Proc. Roy. Soc., 1932, A, 136, 528—537).—Mathematical. The electron energies for 2- and 3-quantum levels in H_2 are calc., using the variation method, based on H_2^+ and at. H functions. The sequence of levels is the same as that found experimentally. L. L. B.

Lower limit for the ground state of the helium atom. D. H. Weinstein (Physical Rev., 1932, [ii], 40, 797—799).—Mathematical. The calc. and experimental vals. are $-6{\cdot}2R$ and $-5{\cdot}818R$, respectively. N. M. B.

Second spark spectrum of sodium, Na III, in the extreme ultra-violet. J. Söderqvist (Z. Physik, 1932, 76, 316—318). A. B. D. C.

Plane waves of light. III. Absorption by metals. T. C. Fry (J. Opt. Soc. Amer., 1932, 22, 307—332).—Theoretical. The absorption of light by thin films of alkali metals deposited on glass or Pt is investigated. A. J. M.

Variations in wave-length of copper lines in a very intense arc. J. Gilles (Compt. rend., 1932, 194, 2200—2202).—A steady Cu spectrum in a very intense arc is obtained with brass anode and graphite cathode. Diminutions of wave-length occurred at the cathode and increases at the anode. C. A. S.

Arsenic spectrum. L. Winand (Bull. Acad. roy. Belg., 1932, [v], 18, 422—436).—The extinction coeff. of As vapour has been measured at various temp. and over the wave-length range 3000—3900 Å. The emission spectrum of As vapour shows a group of bands in the region 2700—4200 Å., which are attributable to As_2, whilst several lines in the region 2148—3047 Å. appear to be due to As atoms. No As fluorescence spectrum could be obtained. J. W. S.

Fine structure in the arc spectra of bromine and iodine. S. Tolansky (Proc. Roy. Soc., 1932, A, 136, 585—604).—An examination has been made of 29 Br lines and 16 I lines. The nuclear spin found for Br is 3/2, both the isotopes (79, 81) having the same spin. A simple mass isotope displacement is observed, of the same order as that calc. The nuclear spin for I is 9/2. The fine structure interval factors for 24 terms in Br and 17 in I are calc. L. L. B.

Shift of the transmission band of silver by cold working. H. Margenau (Physical Rev., 1932, [ii], 40, 800—801; cf. A., 1929, 972).—The shift can be explained on Kronig's theory of metallic dispersion due to change in lattice const. N. M. B.

Magnetic quenching of iodine fluorescence and Λ-doubling in $^3\Pi_0$ states. J. H. Van Vleck (Physical Rev., 1932, [ii], 40, 544—568).—Turner's proposal that the magnetic quenching of I fluorescence is a predissociation phenomenon is developed theoretically (cf. A., 1931, 1). N. M. B.

Conditions of origin of forbidden lines in the spectrum of Hg II. S. Sambursky (Z. Physik, 1932, 76, 266—267). A. B. D. C.

Hyperfine structure of mercury. V. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 177—190; cf. this vol., 552).—Data are recorded and interpreted for λλ 5791, 3663, 3662, 3654, 4046, 4077, 4358, 5460, 4339·23, and 3650·15. The components of even isotopes in λ 5461 emit only 74% of their theoretical intensity. N. M. B.

Mean lives of mercury lines λ 2537 and λ 1849. P. H. Garrett (Physical Rev., 1932, [ii], 40, 779—790).—The mean life of λ 2537 measured by a photoelectric method was $1{\cdot}08\times10^{-7}$ sec. accurate to 1%, and that of λ 1849 by an absorption method was $2{\cdot}9\times10^{-10}$ sec. accurate to 25%. N. M. B.

Hyperfine structure of lead. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 191—204).—Data are recorded and interpreted for λλ 3639, 3683, 4019, 4057, 4062, and 4168 of Pb I, and for 3786, 4386, 4244, 4579·15, 5372, 5608, and 6660 of Pb II. The abundance ratios of isotopes are $Pb^{208,\ 207,\ 206} = 47{\cdot}7 : 25{\cdot}9 : 26{\cdot}4$. N. M. B.

Hyperfine structure of lead. J. L. Rose and L. P. Granath (Physical Rev., 1932, [ii], 40, 760—778).—Data for 13 lines of Pb I and 5 lines of Pb II are reported. Isotope displacements of Pb^{206} and Pb^{207} with respect to Pb^{208} were found; vals. for Pb II were much larger than for Pb I. N. M. B.

Plasma vibrations and selective optical reflexion by metals. M. Steenbeck (Z. Physik, 1932, 76, 260—265).—Theoretical. A. B. D. C.

Processes of excitation and ionic motions in the luminous arc. R. Mannkopff (Z. Physik, 1932, 76, 396—406).—A spectroscopic study of the arc current before and after breaking the circuit reveals that 75% of the excitation is thermal. A. B. D. C.

Origin of coronal lines. R. Frerichs (Nature, 1932, 129, 901—902). L. S. T.

Origin of coronal lines. H. Dingle (Nature, 1932, **129**, 902). L. S. T.

Scattering of *X*-rays by monatomic gases. Y. H. Woo (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 135—143).—Wollan's results (A., 1931, 781, 1106) on the intensity of *X*-ray scattering by inert gases are compared with theoretical vals. deduced from a modified Raman–Compton formula. W. R. A.

Absorption and scattering of *X*-rays by argon. S. H. Yü (Sci. Rep. Nat. Tsing Hua Univ., 1932, **A**, **1**, 155—157).—The scattering is calc. from the Compton formula. W. R. A.

Structure of absorption edges of light elements. H. Geiger (Z. Physik, 1932, **76**, 420).—Neufeldt's results (A., 1931, 781, 1206) could not be reproduced. A. B. D. C.

Origin of the *X*-ray non-diagram lines in the *K* series. M. Sawada (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 43—56). A. R. P.

Wave-lengths of the tungsten *K* series spectrum with the double spectrometer. J. H. Williams (Physical Rev., 1932, [ii], **40**, 791—796).—Experimental. N. M. B.

Two-crystal analysis of *L*-absorption limits of mercury. H. L. Hull (Physical Rev., 1932, [ii], **40**, 676—683). N. M. B.

Relative excitation of the three *X*-ray *L* levels with cathode rays of different velocities. D. Coster and J. van Zuylen (Nature, 1932, **129**, 942—943). L. S. T.

Displacement in the *N* lines of tungsten and tantalum. F. C. Chalklin and L. P. Chalklin (Nature, 1932, **129**, 905—906).—Lines at 55·58 and 58·42 Å. have been obtained from W sputtered on to a H_2O-cooled anticathode. With an incandescent anticathode of W sheet the lines are displaced to 55·29 and 58·09, respectively, representing an increase of 1·2 electron volts in the energies for each line. The $O_{\text{II, III}}$ level is concluded to be 1·2 volts deeper within the atom for cold W than for hot, and the shift is attributed to measurements for hot W being due to the metal and for the cold measurements to oxidised W. L. S. T.

Absorption of scattered *X*-rays. S. R. Khastgir (Phil. Mag., 1932, [vii], **14**, 99—112; cf. A., 1931, 1105).—Additional evidence is adduced in support of the existence of the *J* phenomena. H. J. E.

Scattering of cathode rays at crystal surfaces. F. Kirchner and H. Raether (Physikal. Z., 1932, **33**, 510—513). A. J. M.

Compound photo-electric effect of *X*-rays in light elements. G. L. Locher (Physical Rev., 1932, [ii], **40**, 484—495; cf. Compton, A., 1930, 138).—The *K* fluorescence yields of O_2, Ne, and A are 8·2, 8·3, and 14·9%, respectively, for 0·709 Å. *X*-rays. These vals. are related with available data for 47 elements. A new type of double track attributed to metastable Kr atoms, and having components of similar energy but producing unequal ionisation, was observed. 15 parts of Kr in 10^5 of O_2, or 50 parts of Xe in 10^6 of O_2, can be detected by the cloud method. N. M. B.

Anomalies in radiographs produced by means of resistance cells. G. Reboul (Compt. rend., 1932, **194**, 2304—2405; cf. this vol., 446). C. A. S.

Photo-electric microphotometer for *X*-ray work. W. Büssem and B. Lange (Z. Krist., 1932, **82**, 474—476).—The instrument makes use of Lange's new photo-cell (cf. A., 1931, 9). C. A. S.

Multiple interference spectroscope compared with other interference spectroscopes. E. Lau and E. Ritter (Z. Physik, 1932, **76**, 190—200). A. B. D. C.

Measurements with liquid helium. XVIII. Behaviour of superconducting tin on bombardment with slow electrons. W. Meissner and K. Steiner (Z. Physik, 1932, **76**, 201—212).—Electrons of the velocity of conductivity electrons do not pass through Sn foil when this is superconducting. A. B. D. C.

Determination of potential curves for diatomic molecules with the aid of spectral terms. O. Klein (Z. Physik, 1932, 76, 226—235).—Theoretical. A. B. D. C.

Ionisation potential of molecular hydrogen. W. Bleakney (Physical Rev., 1932, [ii], **40**, 496—501; cf. A., 1930, 969).—A mass spectrograph for use with gases at pressures of the order 10^{-6} mm. is described, and gives 15·37±0·03 volts for the ionisation potential of mol. H_2. Previous vals. are critically reviewed. N. M. B.

The Hume-Rothery relationship between ionisation potentials of elements and their atomic number. H. Yagoda (Phil. Mag., 1932, [vii], **13**, 1163—1171; cf. A., 1930, 1233).—A more exact relationship for elements in any one periodic group is $\log n^2V = a \log z + b$. This is also valid for singly-ionised atoms. H. J. E.

Photo-electric effect at surfaces of magnesium. H. Gerding and R. Gerding-Kroon (Rec. trav. chim., 1932, **51**, 612—618; cf. A., 1931, 138).—As with Al, the photo-electric current is increased by scraping in a vac., and diminishes on keeping, more rapidly in presence of air. The photo-electric threshold is displaced by scraping from about 3126 Å. to 4900 Å. The effect of air is due to the retarding action of the contact potential between O_2 and Mg. F. L. U.

Depth of origin of photo-electrons. H. E. Ives and H. B. Briggs (Physical Rev., 1932, [ii], **40**, 802—812).—In the earliest development of Na or Cs films on Ag the photo-emission is characteristic, at first, of the light absorption in Ag, and, as the film builds up, of energy above the Ag, indicating that the photo-electrons originate partly in the Ag and partly in the film, the proportion varying with the film thickness. N. M. B.

Resemblance between longitudinal asymmetry of the classical field of an accelerated electron and distribution of scattered photo-electrons. L. Simons (Phil. Mag., 1932, [vii], **14**, 148—158).—Theoretical. H. J. E.

Influence of salts on minimum potential. W. Gräwe (Physikal. Z., 1932, 33, 483—488).—The min. discharge potential of a negatively-charged wire is lowered by inorg. salts, the effect increasing with increasing quantity of salt and with rising temp. The emission from positively-charged wires is not affected. H_3BO_3 and H_3PO_4 do not lower the min. potential, but their salts do so; electron emission is due, therefore, to the metal ion. E. S. H.

Photo-electric and thermo-electric effect of palladium–silver and palladium–gold alloys charged with hydrogen. J. Schniedermann (Ann. Physik, 1932, [v], 7, 761—779).—The absorption of H_2 by Pd and its alloys with Ag and Au increases linearly with the quantity of Ag or Au added. The photo- and thermo-electric effects are increased by the absorbed H_2. There is a max. for alloys with 40% Ag or Au. A. J. M.

Photo-electric properties of films of beryllium, aluminium, magnesium, and thallium. H. de Laszlo (Phil. Mag., 1932, [vii], 13, 1171—1178).—The photo-electric response for films of these metals has been studied in monochromatic light between 5000 and 2400 Å. Mg is specially suitable for the construction of ultra-violet photo-cells. H. J. E.

Polarisation of electrons by scattering. E. G. Dymond (Proc. Roy. Soc., 1932, **A**, 136, 638—651).—Electrons of max. velocity 70 kv. were scattered successively through 90° by thin Au foils, and a small change in intensity was noted as the azimuth of the second scattered beam was altered. The polarisation effect was found to be $1{\cdot}7 \pm 0{\cdot}3\%$, that predicted by Mott being 10%. L. L. B.

Electron polarisation. G. O. Langstroth (Proc. Roy. Soc., 1932, **A**, 136, 558—568).—Electrons are scattered twice at approx. 90° from thick W targets, and results indicate that the intensities scattered at 0° and 180° of the azimuth do not differ by more than 1%, the experimental error, for primary electron energies up to 10 kv. L. L. B.

Scattering formulæ for electrons of relativity velocities. H. Bethe (Z. Physik, 1932, 76, 293—299).—Theoretical. Energy loss per cm. reaches a min. at 96% the velocity of light. A. B. D. C.

Radius of electrons. E. Guth (Naturwiss., 1932, 20, 470—471. W. R. A.

Electron radius and molecular recoil. E. Guth (Naturwiss., 1932, 20, 490).—Polemical. W. R. A.

Expulsion of electrons from a negative probe by excited atoms or positive ions. F. Lüdi (Z. Physik, 1932, 76, 319—321).—Attention is directed to work of Kobel (Brown-Boveri-Mitt., Feb. 1930). A. B. D. C.

Diffraction of low-speed electrons by single crystals of copper and silver. H. E. Farnsworth (Physical Rev., 1932, [ii], 40, 684—712; cf. A., 1929, 1212).—Data for classes of diffraction beams and related refractive indices are reported. Intensities as a function of angle of incidence, and regular reflexion of electrons from crystal planes were investigated. The change in structure with thickness of a surface gas lattice gives rise to characteristic beams. N. M. B.

Angular distribution of electrons scattered elastically and inelastically in mercury vapour. J. T. Tate and R. R. Palmer (Physical Rev., 1932, [ii], 40, 731—748).—Experimental. N. M. B.

Motion of electrons in the static fields of hydrogen and helium. J. McDougall (Proc. Roy. Soc., 1932, **A**, 136, 549—558).—Mathematical. L. L. B.

Examination of a thin layer of paraffin with electronic radiation. J. Garrido and J. Hengstenburg (Z. Krist., 1932, 82, 477—480).—A stream of electrons passed through a thin film of the paraffin $C_{21}H_{44}$ gives a sharp diffraction diagram. It indicates that the film consists of crystallites the *c* axes of which coincide with the length of the mols. C. A. S.

Ratio *h*/*e* by means of electron diffraction. R. von Meibom and E. Rupp (Ann. Physik, 1932, [v], 13, 725—731).—From direct measurement of electron velocity by the Wiechert–Kirchner method and from the estimated wave-lengths of fast electrons diffracted by Au a val. for $h/e = 1{\cdot}3798 \times 10^{-17}$ was obtained from the de Broglie relation. W. R. A.

Transference of slow positive particles through canal rays. J. Koenigsberger (Ann. Physik, 1932, [v], 7, 780—782).—A discussion. A. J. M.

Formation, detection, and absorption of slow neutral rays. H. Kallmann, V. Lasarev, and B. Rosen (Z. Physik, 1932, 76, 213—225).—Homogeneous neutral rays of 30 to 800 volts were obtained, and their relative intensity was measured by their emission of electrons from metals. Absorption curves are given for neutral rays in other gases. A. B. D. C.

Absolute values of the mobility of gaseous ions in pure gases. N. E. Bradbury (Physical Rev., 1932, [ii], 40, 508—523).—The abs. method of Tyndall and Grindley (cf. A., 1926, 219), with improved resolving power, was used for highly-purified gases. Mobilities in cm./sec. per volt/cm. are, for air, positive ion 1·6, negative ion 2·21; for O_2 from $KClO_3$, negative ion 2·65 (anomalously high); for O_2 from $KMnO_4$ and a commercial source, positive ion 1·58, negative ion 2·18; for N_2 (commercial), no negative ions, positive ion 2·09; for H_2, no negative ions, positive ion 8·2, and indications of 13·1; for He, no negative ions, positive ion 17·0. N. M. B.

Mobility experiments in gaseous mixtures and ageing experiments in pure gases. N. E. Bradbury (Physical Rev., 1932, [ii], 40, 524—528; cf. preceding abstract).—Vals. for the positive ion mobility in H_2–NH_3 and N_2–NH_3 mixtures were 9·4 (at 0·15 mm. partial pressure of NH_3) and 1·83 (in addition to 2·09 for the normal positive ion in pure N_2), respectively. A continuation of experiments on ageing is reported (cf. A., 1931, 889). N. M. B.

High-velocity positive ions. I. Method of obtaining high-velocity positive ions. J. D. Cockcroft and E. T. S. Walton (Proc. Roy. Soc., 1932, **A**, 136, 619—630).—To obtain large steady potentials for the acceleration of protons, a method is developed by which the voltage of a transformer can be rectified and multiplied several times by an arrangement of valves and condensers. L. L. B.

At. wts. of H^2 and Be^9. N. S. Grace (J. Amer. Chem. Soc., 1932, **54**, 2562—2563).—The at. wts. 2·0113±0·0012 and 9·005±0·002 are theoretically deduced for H^2 and Be^9, respectively. The existence of H^2 nuclei and neutrons suggests that all known at. nuclei may originate from protons and electrons by a succession of two-body collisions, *e.g.*, two H^2 nuclei form an α-particle. C. J. W. (*c*)

Hydrogen isotope of mass 2. H. Kallmann and W. Lasarev (Naturwiss., 1932, **20**, 472).—From an examination of distilled H_2 by a mass spectrograph it is concluded that H^2 is present. This isotope seems to be bound in the H_3 ion. W. R. A.

Separation of gaseous isotope mixtures. G. Hertz (Naturwiss., 1932, **20**, 493—494).—A method for separating the isotopes of Ne is described. Ne^{21} and Ne^{23} were found by the mass-spectrograph method, but are not encountered in optical spectra. These isotopes occur in the ratio 1 : 2000 in normal Ne. W. R. A.

Existence of isotopes of selenium and tellurium deduced from the examination of the resonance multiplets of Se_2 and Te_2. P. Swings and Y. Cambresier (Bull. Acad. roy. Belg., 1932, [v], **18**, 419—421).—The rotation quantum nos. of Se_2 and Te_2 mols. in the excited state have both odd and even vals. Consequently these elements must each exist in at least two isotopes (cf. A., 1931, 1348). J. W. S.

Radioactive transformations. L. Wertenstein (Compt. rend., 1932, **194**, 2305—2307).—Theoretical. A discussion of the modifications of the views as to the mechanism of radioactive transformations, and the nature and origin of the radioactive elements consequent on the idea of demihelions (cf. this vol., 556). C. A. S.

Existence of a neutron. J. Chadwick (Proc. Roy. Soc., 1932, **A**, **136**, 692—708).—When Be (or B) is bombarded by α-particles from Po a very penetrating radiation is produced which effects long-range particles from H_2 and many light elements. The results are consistent with the view that the radiation consists of neutrons, a neutron being a proton and an electron in close association, the binding energy being 1 to 2×10^6 electron volts, the mass 1, and the charge 0. Experiments on the passage of neutrons through matter give information on the frequency of their collisions with at. nuclei and electrons. L. L. B.

Attempts to detect the interaction of neutrons with electrons. P. I. Dee (Proc. Roy. Soc., 1932, **A**, **136**, 727—734).—From experiments in a Wilson cloud track chamber it is concluded that the probability of an interaction of a neutron with an electron with production of a recoil electron track is less than 1% of the probability of a similar interaction with a N nucleus. L. L. B.

Collisions of neutrons with nitrogen nuclei. N. Feather (Proc. Roy. Soc., 1922, **A**, **136**, 709—727).—Neutrons obtained from Be, by α-particle bombardment, give rise to tracks in an expansion chamber after collision with N nuclei and are shown to be emitted with energies distributed over a wide range. Two types of inelastic collision resulting in disintegration are found, one in which a neutron is captured and an α-particle liberated, and another in which a neutron is not captured but a proton is probably liberated. L. L. B.

Demihelions. F. Perrin (Compt. rend., 1932, **194**, 2211—2213; cf. this vol., 556).—It is suggested that the single anomalous forked track observed by Blackett (cf. this vol., 672) is due to expulsion of a demihelion, composed of one proton and one neutron, of at. wt. 2·0115±0·0005. C. A. S.

Radiations excited in light atoms by α-particles. (Mme.) I. Curie, F. Joliot, and P. Savel (Compt. rend., 1932, **194**, 2208—2211; cf. this vol., 555, 672).—The neutrons projected from Be by α-particles in the same direction as that of the α-particles eject from paraffin a main group of H-particles of path 28 cm. in air and a small group of max. path about 70 cm. Neutrons projected backward (at 120—180°) eject H-particles of path 23 cm. The velocities of the two main groups are 3·84 and $2\cdot94\times10^9$ cm./sec. respectively; they possibly result from the reactions $Be^9+\alpha=C^{12}+n\nearrow$ and $Be^9+\alpha=C^{12}+n\nearrow+\gamma$, respectively, which gives as at. wt. of Be^9 9·006. Neutrons projected backwards are diffused more by Pb than by Cu. Po+Li radiation is similarly dissymmetric; the ratio of the ionisation produced by the forward radiation to that produced by γ-rays of Po in H_2, N_2, and A is, respectively, 0·55, 0·31, and 0·25; it is absorbed equally by 1 g. per sq. cm. of paraffin or 4 g. of Pb. This radiation is also probably neutrons, due possibly to the reactions $Li^6+\alpha+\text{electron}=Be^9+n\nearrow$ or $Li^7+\alpha=B^{10}+n\nearrow$. C. A. S.

Disintegration constant of uranium by the method of counting α-particles. A. F. Kovarik and N. I. Adams, jun. (Physical Rev., 1932, [ii], **40**, 718—726).—More than 100,000 counts of α-particles emitted from thin films of pure U_3O_8 gave $1\cdot53_2\times10^{-10}$ year^{-1} for the disintegration const., $3\cdot40\times10^{-7}$ for the Ra–U ratio, and 0·96—0·97 for the branching ratio. N. M. B.

Anomalous scattering of α-particles by H_2 and He. H. M. Taylor (Proc. Roy. Soc., 1932, **A**, **136**, 605—618).—Mathematical. In H_2 and He the scattering at small angles of α-particles can be explained by the same field as that for large angles, and the results are independent of the form of the potential energy curve assumed for one particle in the field of the other, as long as the energy is Coulombian for distances greater than 5×10^{-13} cm. L. L. B.

Magnetic spectrum of β-rays of Th-C+C'+C''. S. V. Sze (Compt. rend., 1932, **194**, 2206—2208; cf. this vol., 442, 443).—The intensities, H_ρ, and energies of 56 (18 new) β-rays in this magnetic spectrum, referred to H_ρ 1398 as standard, have been determined. 12 of these rays are considered to be due to γ-rays converted in the atom of Th-C'' (cf. A., 1926, 6). C. A. S.

Close collisions of fast β-particles with electrons, photographed by the expansion method. F. C. Champion (Proc. Roy. Soc., 1932, **A**, **136**, 630—637).—In a no. of collisions of fast β-particles and electrons, in all cases except one momentum and energy were conserved and results predicted by the principle of restricted relativity verified. L. L. B.

Gamma-radiation and its relation to nuclear structure. P. G. Kruger (Physical Rev., 1932, [ii], **40**, 727—730).—The calc. wave-lengths of γ-radiation from the nucleus for 14 radioactive elements are in moderate agreement with observed vals. N. M. B.

Interaction between γ-radiation and the atomic nucleus. L. H. Gray and G. T. P. Tarrant (Proc. Roy. Soc., 1932, **A**, **136**, 662—691).—Elements of high at. no. absorb the hard γ-rays of Th-*C″* and Ra-*C*, and emit a secondary radiation quite unlike that scattered by the electronic system of the outer atom. The absorption curves of the characteristic radiations of Pb, Sn, Fe, and O_2 are very similar. The results indicate that the absorption process is an excitation of the nucleus which subsequently emits characteristic radiations. L. L. B.

δ-Rays and the relation between range and velocity for slow electrons. T. Alper (Z. Physik, 1932, **76**, 172—189).—The lengths of δ-ray tracks were measured at different points along an α-ray track in a Wilson chamber, and a relation was obtained connecting range and velocity of electrons of 200 to 4500 volts. A. B. D. C.

Structure of atomic nuclei. (Proc. Roy. Soc., 1932, **A**, **136**, 735—762.)—(Lord) Rutherford. Progress in certain fields of research bearing on this problem is reviewed, with special reference to optical methods (*e.g.*, the relative intensities of lines in band spectra of light elements), applications of wave-mechanics, Gamow's theory of a high potential barrier surrounding the nucleus, the origin of γ-rays, the conception of energy levels in the nucleus, the excitation of nuclei by γ-rays, the artificial transmutation of the elements, and the scattering of α-particles.

J. Chadwick reviewed the evidence for the existence of the neutron.

C. D. Ellis discussed α- and β-ray spectra.

R. H. Fowler discussed the question of nuclear spin.

J. C. McLennan described the data obtainable from a study of the fine structure of spectral lines, from which can be calc. the mechanical moments and the ratio of magnetic to mechanical moments for a no. of at. nuclei.

F. A. Lindemann indicated difficulties in the conception of free electrons in the nucleus and the idea of the neutron.

N. F. Mott described the application of quantum mechanics to the problem of the anomalous scattering of α-particles. L. L. B.

Wave-mechanical calculation of the polarisibility of the hydrogen molecule. B. Mrowka (Z. Physik, 1932, **76**, 300—308). A. B. D. C.

Pressure effect in radiationless dissociation. K. Wurm (Z. Physik, 1932, **76**, 309—315).—The predissociation system of AlH bands was obtained by temp. emission; the band lines become sharp near 2 mm. pressure. A. B. D. C.

Destruction of matter by ultra-radiation. E. G. Steinke and H. Schindler (Naturwiss., 1932, **20**, 491—493). W. R. A.

Ultra-violet transmission of thin blown glass windows. H. Klumb and T. Haase (Z. Physik, 1932, **76**, 322—327).—A method of making and using windows 10 μ thick is described. A. B. D. C.

Spectroscopic determination of electron affinities of the pseudo-halogens OH and CN. E. Lederle (Z. physikal. Chem., 1932, **B**, **17**, 362—368).—Available data show that for the halides of a given metal the graphs of the electron affinity of the halogen against the heat of dissociation of the halide and against the energy level of the ultra-violet absorption max. are often rectilinear, deviations from this rule being associated with differences in crystal form. By means of this relation the following data have been obtained: electron affinities of OH and CN, 88 ± 1 and 92 ± 2, respectively; heat of dissociation $(CN)_2 \rightleftharpoons 2CN$, 61 ± 3; splitting of aromatic C·Br linking, 75 kg.-cal. R. C.

Determination of electron affinities of halogens from continuous absorption spectra of alkali halide vapours. E. Lederle (Z. physikal. Chem., 1932, **B**, **17**, 353—361).—From the energy levels of the ultra-violet absorption maxima of alkali halide vapours (A., 1925, ii, 1025) and the heats of dissociation (A., 1924, ii, 434) the electron affinities of Cl, Br, and I have been calc. to be 90 ± 1, 82 ± 1, and 73 ± 1 kg.-cal., respectively. By extrapolation the electron affinity of F has been found to be 95 ± 2 and the heat of dissociation 66·8 ± 0·5 kg.-cal. R. C.

Predissociation in the spectrum of iodine chloride. W. G. Brown and G. E. Gibson (Physical Rev., 1932, [ii], **40**, 529—543).—The 17,446, 17,664, and 17,828 cm.$^{-1}$ bands lying just beyond the convergence of the visible absorption bands are analysed, and reveal a case of predissociation due to interaction with a repulsive O^+ state derived from two normal atoms. N. M. B.

Increase of predissociation by collision and Beer's law. V. Kondratéev and L. Polak (Z. Physik, 1932, **76**, 386—389).—Observations of absorption by Br and NO_2 showed that Beer's law does not hold for regions of predissociation, and deviations increase with increasing pressure of the original or foreign gas. A. B. D. C.

Simple relations between molecular spectra and structures. H. Deslandres (Compt. rend., 1932, **194**, 2093—2097; cf. this vol., 444).—Further examples are given. C. A. S.

Theory of the relationships between absorption of light and constitution. A. Burawoy (Ber., 1932, **65**, [*B*], 941—947).—The author's views (A., 1931, 144, 544, 1052) are developed further and the results are applied to the elucidation of the chemical valency problem of unsaturated compounds. It is shown that the unsaturated nature of double linkings is due to equilibria between saturated mols. and those with free valencies. Addition to compounds containing neighbouring double linkings invariably occurs in such a manner that a new conjugated system results. Addition in the 1 : 2 position is ascribed to the presence of mols. in which conjugated systems are not present but which contain their electron-isomeric forms with free valencies in 1 : 2 position. H. W.

Absorption of light and constitution. IV. A. Burawoy (Ber., 1932, **65**, [*B*], 947—949; cf. A., 1931, 144, 544, 1052).—A reply to Dilthey (A., 1931, 955). H. W.

Rotational structure of the ultra-violet absorption bands of formaldehyde. G. H. Dieke and G. B. Kistiakowsky (Proc. Nat. Acad. Sci., 1932, **18**, 367—372).—Rotational fine structure of bands at 3520, 3430, and 3390 Å. was investigated, and moments of inertia in upper and lower states are deduced. A. B. D. C.

Ultra-violet bands of formaldehyde and their presence in the solar spectrum. N. R. Dhar (Z. anorg. Chem., 1932, **206**, 270—272).—Some lines of the absorption spectrum of CH_2O vapour correspond with lines in the solar spectrum of which the source has not hitherto been determined. Especially notable are those bands of which the strongest parts of the central max. are at 3035·8, 3088·7, 3143·4, 3170·4, and 3389·3 Å. M. S. B.

Absorption of ultra-violet light by glyoxaline and some of its derivatives. C. S. Hicks and H. F. Holden (Austral. J. Exp. Biol., 1932, **10**, 49—52).—Glyoxaline-4 : 5-dicarboxylic acid has an absorption band at approx. 251·0 mμ whilst histidine, glyoxaline, methylglyoxaline, and histamine have no bands but only increasing absorption on approaching the region 220 mμ. W. O. K.

Ultra-violet absorption spectrum of histidine. F. Ellinger (Biochem. Z., 1932, **248**, 437—448; cf. A., 1929, 98; 1930, 1048).—An unknown Fe compound (probably of protein) sensitises the absorption by histidine hydrochloride of long ultra-violet rays and promotes the production of a histamine-like substance. $FeCl_3$ acts in the same way but to a smaller extent. The biological significance of the results is discussed. W. M.

Attempt at co-ordinating infra-red absorption bands of some ring hydrocarbons. J. Lecomte (Compt. rend., 1932, **194**, 2037—2040).—The frequencies of the infra-red (λ 6—16 μ) absorption bands of C_6H_6, C_7H_8, C_8H_{10}, and $C_{10}H_8$ are classified into several series expressed by $\nu=a+bn+cn^2$, n being an integer. C. A. S.

Intensity of infra-red absorption bands. L. A. Matheson (Physical Rev., 1932, [ii], **40**, 813—828).—The abs. intensities of infra-red absorption bands in CO and a band analysis were obtained by measuring the absorbed energy directly by the vol. change in the gas due to the heat evolution in it. N. M. B.

Absorption spectrum of water vapour beyond 10 μ. L. R. Weber and H. M. Randall (Physical Rev., 1932, [ii], **40**, 835—847).—Using a new type spectrometer of high dispersion (cf. A., 1931, 1387) the highly complex spectrum in the region 10—25 μ was re-measured. N. M. B.

Cabannes-Daure effect and molecular field. A. Rousset (Compt. rend., 1932, **194**, 2299—2301; cf. A., 1928, 1310; 1929, 752).—It is shown that the intensity of laterally scattered light depends on the anisotropy and refractive index of the liquid concerned, and that dissymmetry in the Cabannes-Daure effect is confined to anisotropic liquids. Experimental results with C_6H_6, AcOH, CCl_4, and EtOH are in agreement. C. A. S.

Intensity measurements in Raman spectra. A. Carrelli and J. J. Went (Z. Physik, 1932, **76**, 236—249).—Quant. measurements of the intensity of Raman displacements must allow for these being bands, not lines, and each Raman band has a characteristic form. The degree of polarisation is not const. throughout the band. CCl_4 showed no continuous spectrum, whilst C_6H_6 did so. A comparison of the intensity of Raman bands and Rayleigh radiation gave the ratio of the scattering moments of the mol. for displaced and undisplaced radiation. A. B. D. C.

Scattering of light by liquid helium. J. C. McLennan, H. D. Smith, and J. O. Wilhelm (Phil. Mag., 1932, [vii], **14**, 161—167).—No Raman lines were observed with liquid He, but certain Hg lines had "wings," interpreted as due to rotational Raman transitions in loosely-bound He mols. in the liquid. Surface tension measurements also indicate association. H. J. E.

NO_3 frequency in organic nitrates. A. S. Ganesan and V. N. Thatte (Nature, 1932, **129**, 905).—The characteristic inactive frequency at 9·5 μ appears as a Raman line in EtOH solutions of org. nitrates. Raman lines for $MeNO_3$ are recorded. L. S. T.

Raman effect of polyatomic molecules. J. Weigle (Arch. Sci. phys. nat., 1932, **14**, 82—95).—A descriptive survey of the principle and some applications of the phenomenon. N. M. B.

Polarisation of Raman lines in crystals. J. Cabannes (Compt. rend., 1932, **194**, 2134—2136; cf. this vol., 212).—It is shown, with a crystal of type C_{2h} as example, that when the vibrations of the incident polarised ray are parallel to an axis of symmetry of the crystal depolarisation of light diffused perpendicularly to the incident ray is zero for rays symmetrical relative to the axis of symmetry, complete for rays antisymmetrical thereto, or degenerate (cf. A., 1930, 397; 1931, 893). C. A. S.

Raman effect and molecular anisotropy. J. Weiler (Physikal. Z., 1932, **33**, 489—498).—A summary of work on the connexion between the width of the primary lines and mol. anisotropy. A. J. M.

Raman bands of water. S. Rafalovski (Bull. Acad. Polonaise, 1931, **A**, 623—628; cf. A., 1931, 1353).—Details are given of results described previously. Support is given to the view that Raman bands for H_2O have a threefold structure. J. W. S.

Raman spectra of a series of octanols. G. Collins (Physical Rev., 1932, [ii], 40, 829—834).—Data are reported for 19 octanols differing only in the relative position of a Me and OH group along a chain of 7 C atoms, using Hg λ 4358 as the exciting line. Results are interpreted by comparison with mol. structure. N. M. B.

Polarisation of Raman lines in liquids. S. Bhagavantam (Indian J. Physics, 1932, 7, 79—86).—Results are reported for C_6H_6, CS_2, HCO_2H, thiophen, CCl_4, $SiCl_4$, $TiCl_4$, and $SnCl_4$. N. M. B.

Raman spectrum of quinoline, and the carbon–nitrogen linking. G. B. Bonino and P. Cella (Atti. R. Accad. Lincei, 1932, [vi], 15, 385—389).—The Raman spectrum is described. A line at 1433 cm.$^{-1}$ is attributed to the C:N linking, since a line of approx. the same frequency occurs also in the spectrum of pyridine and various thiocarbimides. The double nucleus gives rise to a line at 1375 cm.$^{-1}$ H. F. G.

Raman spectra of piperidine, ethyl alcohol, and acetone. S. C. Sirkar (Indian J. Physics, 1932, 7, 61—78).—Full data and comparisons with infrared absorption curves are reported. Piperidine shows 14 new lines; EtOH shows new lines at 2709 and 2743 Å., and the older line 925 of $COMe_2$ is corrected to 2689 cm.$^{-1}$ N. M. B.

Lateral radiation and the nature of the colouring substance in rock-salt. M. Kahanowicz (Z. Physik, 1932, 76, 283—292).—An investigation of the blue and violet fluorescence of rock-salt revealed that the emitted radiation is identical with the fluorescent bands of Na_2, and the source of the rock-salt emission is impurities of small Na crystals; transition from the Na crystals to colloidal Na is accompanied by change from fluorescence to Rayleigh scattering. A. B. D. C.

Extinction curve of scintillation of zinc sulphide. J. Stalony-Dabrowski (Rocz. Chem., 1932, 12, 299—310).—The duration of scintillation of ZnS excited by α-particles is 0·125 sec.; the most intense luminescence is emitted during the first 0·00003 sec., during which 7% of the total energy is dissipated. The light intensity then falls sharply to 19% of the original val., after which it continues to diminish progressively, at first rapidly, and then more slowly. R. T.

Relation between certain types of luminescence. E. L. Nichols and F. G. Wick (J. Opt. Soc. Amer., 1932, 22, 357—368).—Experiments in support of the view that in cando- and cathodo-luminescence there is the same process are described. A. J. M.

Luminescence of glass and fluorite. T. Lyman (Physical Rev., 1932, [ii], 40, 578—582). N. M. B.

Phosphorescent sulphides: extinguishing action of metals of the iron group. M. Curie and J. Saddy (Compt. rend., 1932, 194, 2040—2042; cf. this vol., 560).—The addition, at the time of prep., of small amounts of $CoCl_2$, $FeCl_2$, or $PbCl_2$ to a phosphorescent ZnS causes large (Co), moderate (Fe), or no (Pb) diminution in its conductivity and luminescence. C. A. S.

Electrostatic potential of some cubic crystal lattices. T. S. Wheeler (Phil. Mag., 1932, [vii], 14, 56—66).—A method for calculating the electrostatic potential of a cubic lattice with regard to the central lattice point is developed and applied. H. J. E.

Dependence of ionisation number on field strength and the mean "ionisation field strength" in liquids. A. Nikuradse (Ann. Physik, 1932, [v], 7, 851—873).—Mean "ionisation field strength" depends on the nature of the liquid. A. J. M.

Ionisation phenomena in benzene [vapour]. E. Friedländer and H. Kallmann (Z. physikal. Chem., 1932, B, 17, 265—275; cf. A., 1930, 514).—The principal intensity maxima in the mass spectrograph of C_6H_6 vapour bombarded with electrons of variable velocity correspond with the ions $C_6H_6^+$, $C_6H_4^+$, and $C_2H_2^+$. Other ions are formed either by direct ionisation of the C_6H_6 or from products of its thermal decomp. The ionisation voltages have been determined. By collision with a gas mol. the $C_6H_6^+$ ion may be dissociated into $C_2H_4^+$ and a residue, or $C_4H_2^+$ and a residue. R. C.

Outer photo-electric effect for liquids. Determination of the long-wave limit for water. P. Görlich (Ann. Physik, 1932, [v], 7, 831—850).—The long-wave photo-electric limits for H_2O and conc. solutions of $AgNO_3$, $K_4Fe(CN)_6$, Na_2SO_4, and NaCl were determined. The val. for H_2O is 203—204 mμ. Solutions have the same limit as the solvent. The spectral photo-electric distribution for H_2O was also found. An absorption max. occurs at 185 mμ. A. J. M.

Photo-cells and light elements. F. von Körösy and P. Selényi (Ann. Physik, 1932, [v], 13, 703—724).—Experimental methods are developed for determining the characteristics of the unidirectional layer of a $Cu–Cu_2O$ photo-cell. W. R. A.

Nature of electrical conductivity of cuprous oxide. H. Dünwald and C. Wagner (Z. physikal. Chem., 1932, B, 17, 467—470).—At 800—1000° and under such O_2 pressures that neither Cu nor CuO can be present as a second solid phase the conductivity of Cu_2O plates, κ, is approx. given by $\kappa=p_{O_2}^{1/7}$. const. The thermo-e.m.f. $Pt|Cu_2O$ has been measured at 900—1000°. R. C.

Becquerel effect for cuprous oxide as a boundary layer photo-effect. F. Waibel (Z. Physik, 1932, 76, 281—282). A. B. D. C.

Dielectric behaviour of colloidal particles with an electric double layer. J. B. Miles, jun., and H. P. Robertson (Physical Rev., 1932, [ii], 40, 583—591).—Mathematical. N. M. B.

Dielectric constant of nitrogen up to 150 atmospheres at 25°, 75°, and 125°. A. Michels and C. Michels (Phil. Mag., 1932, [vii], 13, 1192—1196).—The experimental details and results are recorded. H. J. E.

Inorganic halides and their molecular compounds. VI. Dipole moments of titanium and tin tetrachlorides. H. Ulich, E. Hertel, and W. Nespital (Z. physikal. Chem., 1932, B, 17, 369—

379; cf. this vol., 676).—Solid and liquid halides and solutions in CCl_4 have zero dipole moment. In C_6H_6 solution the moment of $SnCl_4$ is 0·80, perhaps due to the formation of a mol. compound. Bergmann and Engel's experimental methods (A., 1931, 999, 1000) are criticised. R. C.

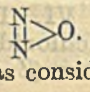
Dielectric constant of liquids. VII. Dielectric constant and electric moment in aqueous solution. G. Devoto (Atti R. Accad. Lincei, 1932, [vi], **15**, 471—473; cf. A., 1930, 1358).—Vals. of the dielectric constant–concn. coeff., *de/dc*, for $NH_2{\cdot}CH_2{\cdot}CO_2H$ and its homologues are given. If the increase in the length of the chain per CH_2 group is 1·3 Å., as with the fatty acids, the calc. increase of *de/dc* per CH_2 group is 11—12 units, in agreement with experiment. O. J. W.

Electric moments of 1-halogeno-2 : 4-dinitrobenzenes. H. Lütgert (Z. physikal. Chem., 1932, **B**, **17**, 460—462).—The moments have been determined by measurements with C_6H_6 solutions and have made it possible to calculate the direction of the moment produced by the two groups in the *o*-position. R. C.

Electric moment and molecular structure. VII. Carbon valency angle. C. P. Smyth and W. S. Walls (J. Amer. Chem. Soc., 1932, **54**, 1854—1862).—Determinations of the moments of several CH_2Ph and *p*-substituted CH_2Ph compounds have given vals. for the C valency angle differing from the theoretical tetrahedral angle by no more than the probable error. H. F. J. (*c*)

Calculation of "angular values" from dipole moments of aromatic compounds. K. L. Wolf (Z. physikal. Chem., 1932, **B**, **17**, 465—466).—Polemical against Bergmann (cf. this vol., 677). R. C.

Molecular area and volume in films: application to determination of molecular mass. D. G. Dervichan (Compt. rend., 1932, **194**, 2294—2296).—Deviations from the thickness of the film at the "vaporisation point" being exactly $V^{1/3}$ are due to the orienting effect of the liquid surface. The mol. mass of the film substance, $M=d(SRT/S'P)^{3/2}/N^{1/2}$, where S is the area of the film at the vaporisation point, S' the corresponding area when the relation $Ps=RT$ holds (s being the surface per g.-mol.), d density, and R, T, N, and P have their usual meanings. The formula, which gives M for oleic acid=190, would be useful in microchemical analysis as 10^{-6} g. gives a measurable film. C. A. S.

Kerr effect, optical anisotropy, and molecular structure. Structure of molecules of stannic chloride, propyl chloride, and nitrous oxide. H. A. Stuart and H. Volkmann (Z. physikal. Chem., 1932, **B**, **17**, 429—456; cf. A., 1929, 872).—The Kerr consts. of the vapours of $SnCl_4$, C_6H_6, $CHCl_3$, $C_2H_4Cl_2$, *cis*- and *trans*-$C_2H_2Cl_2$, PrCl, and COMeEt have been determined and the polarisation ellipsoids calc. The data for $SnCl_4$ agree with a tetrahedral structure of the mol. and not with a pyramidal structure, and the N_2O mol. has the form $N\vdots N{:}O$, not  O. In PrCl the linking holding the Et group has considerable or total freedom of rotation, and the mol. has no fixed plane configuration, such as a zigzag. The optical anisotropy and thence the structure of a mol. may be determined in cases where the Kerr effect and the scattering of light give no assistance by means of an examination of the rotational fine structure of Raman and Rayleigh lines and the polarisation relations of Raman lines (cf. A., 1930, 840; 1931, 893). R. C.

Explanation of a magneto-optic effect. M. Cau (Compt. rend., 1932, **194**, 2042—2045).—The modification of the magnetic rotation caused by a thin layer of Fe due to its being in contact with one of Pt is explicable as due to multiple reflexions at the Fe–Pt surface. C. A. S.

Variation of Faraday effect with concentration. P. K. Pillai (Indian J. Physics, 1932, **7**, 87—90).—The rotation of $Ce(NO_3)_3$ at 10 different concns. plotted against concn. gave a straight line relation. Variations of Verdet's const. for $FeCl_3$ are discussed. N. M. B.

Magnetic rotations of liquid mixtures. R. N. Mathur and A. N. Kapur (Indian J. Physics, 1932, **7**, 15—18).—The max. differences between the experimental and calc. vals. for $CHCl_3$–$COMe_2$, Et_2O–$CHCl_3$, and Et_2O–$COMe_2$ mixtures are of the order 1% (cf. Trew and Spencer, A., 1931, 676). N. M. B.

Thermal variation of magnetic rotatory power of nickel chloride. H. Ollivier, (Mlle.) J. Pernet, and J. Lesne (Compt. rend., 1932, **194**, 2301—2303; cf. A., 1930, 1095).—The sp. magnetic rotation of anhyd. $NiCl_2$, as deduced by the additive law from its aq. solutions, is independent of the concn. It is also independent of temp. for moderately conc. solutions, but for dil. solutions diminishes as temp. rises, but less than required by the Curie–Weiss law. C. A. S.

Influence of temperature on the natural and magnetic rotation of *d*- and *l*-α- and *l*-β-pinene. C. Salceanu (Compt. rend., 1932, 2136—2138; cf. A., 1931, 148).—The ordinary and magnetic rotations of these liquids have been determined at various temp. $\ngtr$ 141·5° for λ 5780, 5460, and 4360, and the dispersion is discussed (cf. A., 1911, ii, 352). C. A. S.

Influence of solvents and other factors on the rotation of optically active compounds. XXIX. Rotation-dispersion of camphor, camphoroxime, *iso*nitrosocamphor, and oxymethylenecamphor. T. S. Patterson, E. F. M. Dunn, C. Buchanan, and J. D. Loudon. **XXX. Rotation-dispersion of various derivatives of camphor.** T. S. Patterson and J. D. Loudon (J.C.S., 1932, 1715—1725, 1725—1744).—XXIX. The rotation of camphor is influenced by the solvent, being a max. in $C_2H_4Br_2$, and a min. in PhOH, among the org. solvents used. Conc. H_2SO_4 depresses the rotation to −75·6°.

XXX. Conc. H_2SO_4 depresses the rotation of a no. of camphor derivatives, particularly camphor-10-sulphonic acid. A method for the esterification of this acid and its α-Cl- and α-Br-derivatives is described. The rotations of these esters and their corresponding amides, except camphor-10-sulphonamide where the anhydramide was used, and of α-chloro- and α-bromo-camphor have been investigated in different solvents.

Camphor-10-sulphonic acid may possibly have a lævo-configuration, and the α-halogen derivatives dextro-configurations. A. J. M.

Molecular structure and physical properties of hydrocyanic acid. I. Refractive dispersion of hydrocyanic acid and its homologues. T. M. LOWRY and S. T. HENDERSON (Proc. Roy. Soc., 1932, A, **136**, 471—487).—With an improved method, mean deviation 5 units in the 5th decimal place, measurements have been made of the vals. of *n* of HCN and the homologous MeCN (I), EtCN (II), MeNC (III), and EtNC (IV) for 26 wave-lengths in the visible spectrum and up to 2473 Å. in the ultra-violet. The results are expressed by equations of the Ketteler–Helmholtz type, the characteristic frequencies being at 978, 994, 994, 1085, and 1067 Å. for HCN, (I), (II), (III), and (IV), respectively. A comparison of the mol. refractions of cyanides and carbylamines with HCN shows that the liquid acid is almost completely HCN. L. L. B.

Attack of oxygen molecules on highly crystalline graphite. E. N. GREER and B. TOPLEY (Nature, 1932, **129**, 904—905).—The brilliant reflexion from the surface of a flake of Ceylon graphite remains unimpaired during oxidation at 900° in O_2 at 1 mm. pressure. The C atoms appear to be removed layer by layer without pitting. The holes which finally appear have a well-defined hexagonal form. L. S. T.

Quantum theory and chemistry. E. A. HYLLERAAS (Tids. Kjemi, 1932, **12**, 89—94).—Theoretical. H. F. H.

Theory of induced polarities in benzene. E. HÜCKEL and W. HÜCKEL (Nature, 1932, **129**, 937—938).—A reply to Lapworth and Robinson (this vol., 324). L. S. T.

Structure of complex salts containing various co-ordinated atoms or groups. I. Complexes of co-ordination number 6: $(NH_4)_3[VF_6]$ and $Tl_2[VF_5(H_2O)]$. II. $(NH_4)_3[CrF_6]$ and $Rb_2[CrF_5(H_2O)]$. L. PASSERINI and R. PIRANI (Gazzetta, 1932, **62**, 279—288, 289—295).—I. $(NH_4)_3[VF_6]$ and $Tl_2[VF_5(H_2O)]$ form cubic crystals. The former has *a* 9·04±0·005 Å., $d_{\text{calc.}}$ 1·97, 4 mols. in unit cell; the latter *a* 8·45±0·005 Å., $d_{\text{calc.}}$ 6·29, 4 mols. in unit cell, and the 5 F′ ions and the H_2O group occupy equiv. positions with regard to the V atom. It is therefore possible for a neutral mol. (H_2O) to replace an ion (F′) without change of structure provided that the two are of similar vol.

II. $(NH_4)_3[CrF_6]$ forms cubic crystals; *a* 9·01±0·005 Å., $d_{\text{calc.}}$ 1·997, 4 mols. in unit cell. $Rb_2[CrF_5(H_2O)]$, prepared by evaporation of a solution containing $RbNO_3$ and CrF_3, forms sparingly sol. light green cubic crystals, *a* 8·38±0·005 Å., $d_{\text{calc.}}$ 3·79, 4 mols. in unit cell; the H_2O group occupies a position equiv. to those of the F ions, in confirmation of the view expressed above. H. F. G.

Magnetic susceptibility of sulphur vapour. L. NÉEL (Compt. rend., 1932, **194**, 2035—2037).—The magnetic susceptibility, χ_{S_2}, of S_2 has been deduced from determinations made on the vapour in sealed quartz tubes, corrected for the diamagnetism of S_6 and S_8 (cf. A., 1909, ii, 977). $\chi_{S_2}\times 10^6$ decreases from 12·2 at 600° to 8·40 at 800°, or thrice as rapidly as required by the Curie law, indicating variable magnetic moment. C. A. S.

Diamagnetic susceptibilities of some beryllium compounds. W. R. ANGUS and J. FARQUHARSON (Proc. Roy Soc., 1932, A, **136**, 579—584).—The diamagnetic susceptibilities of basic Be acetate, propionate, pivalate, and acetylacetonate were measured on a Curie–Chéneveau torsion balance. Pascal's method was used to calculate the susceptibilities of the org. groups; the ions were calc. by the Angus–Slater method. L. L. B.

Ionic diamagnetic susceptibilities. W. R. ANGUS (Proc. Roy. Soc., 1932, A, **136**, 569—578).—The ionic or at. susceptibilities of 76 atoms or ions having completed groups and sub-groups are evaluated by Slater's method and by a modification. Vals. for the ionic susceptibilities of 24 ions with incomplete groups or sub-groups have been calc. by the same methods. L. L. B.

Magnetic behaviour of compounds. V. Ferric dibutyldithiocarbamate. L. CAMBI, L. SZEGÖ, and A. CAGNASSO [with C. JACINI] (Atti R. Accad. Lincei, 1932, [vi], **15**, 329—335).—The following *compounds* are described: $NHBu^{\alpha}Bu^{\beta}$, b.p. 150°; $NHBu^{\alpha}$*sec*.Bu, b.p. 147°; $NHBu^{\beta}$*sec*.Bu, b.p. 137°;

$Fe(NBu^{\alpha}_2{\cdot}CS_2)_3$; $Fe[NBu^{\alpha}Bu^{\beta}{\cdot}CS_2]_3$;

Fe[N*sec*.$Bu_2{\cdot}CS_2]_3$; $Fe[NBu^{\alpha}$*sec*.$Bu{\cdot}CS_2]_3$; and $Fe[NBu^{\beta}$*sec*.$Bu{\cdot}CS_2]_3$. The susceptibilities of the Fe derivatives and of $Fe(NBu^{\beta}_2{\cdot}CS_2)_3$ have been determined at temp. between 84° and 350° abs., and the results are discussed in relation to those previously obtained for the analogous Pr derivatives. H. F. G.

Magnetic properties of iron, nickel, cobalt, and some alloys at high temperatures. H. KÜHLEWEIN (Wiss. Veröff. Siemens-Konz., 1932, **11**, No. 1, 124—140).—Magnetic measurements confirmed Forrer's observation (A., 1930, 529) that some metals and alloys have two Curie points. For Ni with 1% Mn the paramagnetic point, Θ_p, is 436° and the ferromagnetic point, Θ_f, 378° on heating; on cooling, Θ_p occurs at 394° and Θ_f at 340°. For Fe Θ_p is 830° and Θ_f 790°.

In Co–Fe alloys with 20—70% Co the magnetic transformation is identical with the A3 change, and $\Theta_p>\Theta_f$. A. R. P.

Direct measurement of magnetic susceptibility of liquids by the Curie–Chéneveau magnetic balance. C. COURTY and C. CHÉNEVEAU (Compt. rend., 1932, **194**, 2197—2198; cf. this vol., 216).—The balance is further improved by replacing the cylindrical tubes by vessels resembling sp. gr. flasks. The coeffs. of magnetisation and susceptibility (× 10^6) of C_6H_6 are 0·713 and 0·628, respectively; of CCl_4 0·427 and 0·697; $CHCl_3$ 0·488 and 0·742; EtOH 0·744 and 0·595; and of pyridine 0·622 and 0·610. C. A. S.

Diamagnetism and structure of some compounds of ethylene, carbon tetrachloride, and titanium tetrachloride. V. I. VAIDYANATHAN and B. SINGH (Indian J. Physics, 1932, **7**, 19—26).—The magnetic susceptibilities of C_2H_4, $C_2H_4(OH)_2$, $C_2H_4(NH_2)_2$, $C_2H_4Cl_2$, $C_2H_4Br_2$, $C_2H_4I_2$, CCl_4, and

$TiCl_4$ are reported. Deviations from additivity were found; interpretation from the nature of the valency linkings is discussed. N. M. B.

Ethyl palmitate. Its density, surface tension, parachor, and Eötvös–Ramsay–Shields coefficient. C. P. Ellis (J.C.S., 1932, 1697—1699).—The determination of the density and surface tension of Et palmitate over a temp. range of 20—150° gives the parachor as 785·7 and the Eötvös–Ramsay–Shields coeff. −3·45. A. J. M.

"Back-reflecting" [camera to obtain] Laue interference figures. L. Chrobak (Z. Krist., 1932, **82**, 342—347). C. A. S.

Precision comparison of calculated and observed grating constants of crystals. Y. Tu (Physical Rev., 1932, [ii], **40**, 662—675).—Calc. values based on density measurements and observed vals. obtained from the angles of reflexion of the Mo $K\alpha_1$ line by two methods for calcite, rock-salt, artificial KCl, and diamond, using calcite as standard, agree within experimental error. No evidence of Zwicky's "secondary structure" was found (cf. A., 1930, 660). Measurements on two quartz crystals showed variation of internal structure. N. M. B.

Measurement of reflecting power of absorbing crystals, especially of ores. III. Methods of standardising reflecting power. A. Cissarz (Z. Krist., 1932, **82**, 438—450; cf. A., 1931, 587, 703). C. A. S.

***X*-Ray studies of the thermal expansion of bismuth single crystals.** A. Goetz and R. C. Hergenrother (Physical Rev., 1932, [ii], **40**, 643—661; cf. this vol., 681).—The vals. of thermal lattice expansion α, calc. from measurements of the temp. shift of Bragg reflexions between liquid air temp. and the m.p. of the metal show wide divergence from those of macroscopic crystal measurements. The discontinuity in macroscopic expansion at 75° was not found by the *X*-ray shift method. N. M. B.

Crystallisation surface of supercooled liquids. H. E. von Gronow and W. Weyl (Z. anorg. Chem., 1932, **206**, 224—226).—Theoretical. A formula is derived for the vol. of super-cooled liquid cryst. in a given time and a space diagram is constructed showing how time, vol. of crystals formed, and degree of supercooling may be connected. It is calc. from available data (A., 1931, 1360) that isothermal crystallisation of piperine occurs most rapidly for supercooling of 55°. M. S. B.

Very thin crystals with curved boundaries. L. Kowarski (Compt. rend., 1932, **194**, 2126—2129).—The process of the growth and disappearance of crystals of *p*-toluidine about 1 μ thick (cf. A., 1930, 1111, 1336) is described and figured. C. A. S.

Structural relations of silicon compounds on assumption of tetrahedral domains of the atoms. Geometrical derivation of cubic crystals as a guide to structure determination. R. Reinicke (Z. Krist., 1932, **82**, 394—418, 419—437).—The domain of influence of Si is represented as a tetrahedron, similar to that of C, and also, with certain modifications, the domains of O, N, F, and Ne. The structures of SiC and of the various varieties of SiO_2 are deduced, and then, regarding silica as $Si(SiO_4)$, those of the silicates, leading to results differing from Bragg's (cf. A., 1927, 501). Extending the assumption of tetrahedral domains the co-ordinate relations of a cubic body-centred lattice are deduced, and a general method for deducing the positions of the atoms in any cubic substance when the no. of mols. in the unit cube is known. C. A. S.

Stereochemistry of crystal compounds. VIII. Geometrical derivation of structure-types AB_3. W. Nowacki (Z. Krist., 1932, **82**, 355—378; cf. this vol., 682). C. A. S.

***X*-Ray investigations of solid nitrogen and oxygen.** M. Ruhemann (Z. Physik, 1932, **76**, 368—385).—Above 35° abs. β-N_2 forms crystals of hexagonal spherical packing, with 2 mols. per cell and with *a* 4·03 Å., *c*/*a* 1·63. At lower temp. α-N_2 crystallises in cubic form with side 5·67 Å. The modifications of solid O_2 show little difference in their *X*-ray patterns, but these do not agree with the rhombohedral structure of McLennan and Wilhelm (A., 1927, 297). A. B. D. C.

Crystal [structure] of zinc coating [produced by hot-dipping on] the surface of iron plate. Y. Matsunaga (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 263—265).—The deposit consists of single-crystal Zn with the (0001) plane inclined at 18° to the surface of the Fe. A. R. P.

Arrangement of micro-crystals in compressed single-crystal plates of aluminium. IV. Y. Fukami (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 23—30; cf. A., 1931, 1358).—The relation between the initial orientation of the crystallites in Al and the type of fibrous arrangement produced by compression is shown by the aid of the crystallographic globe. A. R. P.

Arrangement of the micro-crystals in the film of molybdenum obtained by deposition [from electronic bombardment of a molybdenum anode]. T. Fujiwara (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 31—33).—In most of the crystals the (110) plane is parallel to the surface of the film and a cube edge is parallel to the longitudinal direction, but the larger crystals are arranged in fibres about the (110) axis which is normal to the flat surface of the film. A. R. P.

Effects of the direction of drawing on the arrangement of the micro-crystals in aluminium wire and on its tensile strength and broken fracture. T. Fujiwara (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 35—42).—In wire drawn continuously in one direction micro-crystals with their (111) axes inclined to the direction of drawing predominate. In wire drawn alternately in reverse directions the (111) axes of the crystals in the outer layers are inclined to the wire axis on both sides. In the first case the wire is harder and more brittle. A. R. P.

Structure of steel explained by the form of the lattice. H. Hanemann (Arch. Eisenhuttenw., 1931—1932, **5**, 621—624).—The microstructure of steel depends on the rate of movement of the C atoms; in the γ-phase movement of C takes place at a high rate by perfusion (cf., A., 1931, 301), and in the α-phase at a much lower rate by true diffusion. The ferrite in steel with a very coarse Widmannstätten structure is distributed as thin plates along octahedron planes and occasionally along cube planes, but never in any other direction. A. R. P.

Lattice distortion and carbide formation in tungsten magnet steels. W. A. Wood and C. Wainwright (Phil. Mag., 1932, [vii], **14**, 191—198).—In a 6% W magnet steel in the spoiled state the W and C have been ejected from the parent lattice to form Fe_4W_2C and WC, thus releasing the lattice strain. In the normal and recovered state W and C dissolve in the lattice producing distortion, with enhanced coercive force and hardness. H. J. E.

Molecular process of crystal growth in hexagonal metals. Deposition upon monocrystalline hemispheres of zinc. P. A. Anderson (Physical Rev., 1932, [ii], **40**, 596—606).—A monocryst. hemisphere formed from a small orifice into a mass of molten Zn is bombarded uniformly by Zn vapour, and the variation of depositional rate with crystal surface structure is studied. The macroscopically observed growth is interpreted in terms of atom-by-atom deposition. N. M. B.

Precision determination of lattice constants of beryllium. M. C. Neuburger (Z. physikal. Chem., 1932, B, **17**, 285—292).—The vals. $2{\cdot}2680 \pm 0{\cdot}0002$ and $3{\cdot}5942 \pm 0{\cdot}0003$ Å. have been obtained for a and c, respectively. R. C.

Crystal structure of gallium. F. Laves (Naturwiss., 1932, **20**, 472).—Ga seems to have a pseudotetragonal crystal structure, space-group V_h^{18}, u 0·159, v 0·080; $a=b=4{\cdot}51$, c 7·64 Å. W. R. A.

γ-η-Martensite as a Widmannstätten structure. H. Hanemann (Arch. Eisenhüttenw., 1931—1932, **5**, 625—626).—Crystallographic measurements of two sections of γ-η-martensite cut at right angles to one another from the same crystal show that the η-needles lie on corresponding octahedron or cube planes and that, therefore, the γ-η-martensite structure is a true Widmannstätten structure. A. R. P.

Crystal structure of nitrogen tetrasulphide and tetrahydronitrogen tetrasulphide. F. M. Jaeger and J. E. Zanstra (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 782—807).—Small orange-yellow dichroic crystals of N_4S_4 were obtained by slow evaporation of a C_6H_6 solution. Calc. axial ratios, $a:b:c=1{\cdot}039:1:0{\cdot}842$, are in good agreement with those derived from X-ray examination, $a:b:c=1{\cdot}0472:1:0{\cdot}8512$. Other crystallographic data are given. Powder spectrograms were made, using Cu-α and -β radiation at 50,000 volts. The principal and accessory spectra from rotation spectrograms about (100), (010), and (001) are given. The val. of $d^{18}_{\text{calc.}}$ is 2·23. The lattice parameters from powder spectrograms are a_0 8·76, b_0 8·44, c_0 7·11 Å., whilst the identity distances calc. from the rotation spectrograms are I_a 8·87, I_b 8·47, I_c 7·21 Å. From the reflexions the space-group is V_h^1. The simple orthorhombic cell contains 16 S and 16 N atoms for which parameters have been assigned so as to give good agreement between calc. and observed intensities. The symmetry of each N_4S_4 mol. is C_{2v}. The arrangement of N_4S_4 mols. within the elementary cell is discussed.

Crystals of $H_4S_4N_4$ are orthorhombic. The axial ratios are $a:b:c=1{\cdot}8202:1:1{\cdot}1723$ whilst the ratios calc. from X-ray measurements are $a:b:c=1{\cdot}7869:1:1{\cdot}1582$. The val. of $d^{20}_{\text{calc.}}$ is 1·88. Principal and accessory spectra of the rotation spectrograms about the (001), (100), and (010) faces give I_a 12·08, I_b 6·76, I_c 7·86 Å., and indicate that there are 4 mols. in the unit cell. The structure has the symmetry C_{2v} of the space-group V_h^1 as for N_4S_4. The powder spectrograms of the two mols. have not much in common. W. R. A.

Density and crystal structure of magnesium nitride. G. Hägg (Z. Krist., 1932, **82**, 470—472).—Magnesium nitride prepared by the action of NH_3 on Mg contains varying amounts of NH_3 only removed by heating to 400°; this explains the varying density of the product, which with greatest content of NH_3, corresponding approx. with $Mg_3N_2,2NH_3$, is 1·75. The pure product prepared thus or by the direct action of N_2 on Mg has d 2·72. This (cf. A., 1931, 549) gives 16 mols. to the unit cell, indicating that the Mg atoms are not all equiv., or that the constituent atoms are ionised. C. A. S.

Transition of silver oxide under pressure. P. W. Bridgman (Rec. trav. chim., 1932, **51**, 627—632).—The change of vol. of Ag_2O when subjected to a pressure of 12,000 kg. per sq. cm., after allowance is made for the true compressibility, shows a residual effect which is attributed to a transition to a new phase. No new lines were observed in an X-ray powder diagram of a specimen which had been maintained at a pressure of 20,000 kg. per sq. cm. for four days. The p–v curves show wide hysteresis loops. F. L. U.

Structure of thin films of certain metallic oxides. W. L. Bragg and J. A. Darbyshire (Trans. Faraday Soc., 1932, **28**, 522—529; cf. A., 1931, 1207).—The electron diffraction spectra of the oxide films formed on the surface of Pb and Sn by heating correspond with the rutile structure for PbO_2 and SnO_2. The film of ZnO formed on molten Zn corresponds with a hitherto unrecorded cubic modification of which the unit cell of side 4·62 Å. contains 4 mols. J. G. A. G.

Needle-shaped crystals of sodium chloride obtained by percrystallisation. H. Tauber and I. S. Kleiner (J. Amer. Chem. Soc., 1932, **54**, 2392—2393; cf. A., 1917, ii, 295).—By evaporation of aq. NaCl in air as it diffuses through a collodion bag, needle-shaped crystals of the regular cubic system are obtained. F. D. S. (*c*)

Structure of dihalides of mercury and of lead. J. M. Bijvoet and H. J. Verweel (Rec. trav. chim., 1932, **51**, 605—611; cf. this vol., 450).—Reasons for the differences between the structure of the chlorides and bromides of Hg^{II} and Pb and that of their fluorides and iodides are discussed. F. L. U.

Crystalline structure of tetramminoplatinous chloride. E. G. Cox (J.C.S., 1932, 1912—1920).—X-Ray investigation shows that the four Pt covalencies in the complex $[Pt(NH_3)_4]$ are coplanar and directed to the corners of a square. The general configuration of complexes of the form $[PtX_2Y_2]$ is discussed. A. J. M.

Lattice dimensions of spinels. G. L. Clark (Z. physikal. Chem., 1932, **B**, **17**, 463—464).—Comments on Hauptmann and Novák's paper (this vol., 326). R. C.

Structure of kernite. J. Garrido (Z. Krist., 1932, **82**, 468—470; cf. A., 1928, 1349).—Kernite, $Na_2B_4O_7,4H_2O$, is only pseudo-rhombic, really monoclinic, with *a* 15·65, *b* 9·07, *c* 7·01 Å., β 108° 52′; the unit cell contains 4 mols.; space-group C^4_{2h}. C. A. S.

Structure of asbestos. B. E. Warren (Ind. Eng. Chem., 1932, **24**, 419—422).—The unit cell of diopside, $CaMg(SiO_3)_2$, contains 4 mols.; each Si atom is surrounded tetrahedrally by 4 O atoms and such tetrahedra are linked in chains. A similar stronger type of Si–O chain is responsible for the fibrous structure of asbestos. The crystal is monoclinic, *a* 9·71, *b* 8·89, *c* 5·24 Å. The structure of mica is "two-dimensional asbestos." C. I.

Rotation of molecules in crystals. J. D. Bernal (Nature, 1932, **129**, 870).—Further cases of rotating and fixed mol. forms in aliphatic compounds are reported. $C_{12}H_{25}\cdot OH$ has a hexagonal rotating form between 16° and 24° with 4·76 Å. between the chains. The low-temp. form differs by being monoclinic with inclined chains corresponding with the high-temp. form of the monobasic acids. The transitions between the forms can be followed in single crystals in the polarising microscope. $C_{18}H_{37}\cdot NH_2,HCl$ has a non-rotating form which is orthorhombic with a base 5·2×5·15 Å. Four layers per cell in alternate pairs inclined at approx. 48° to the *c* plane produce a negative birefringence unlike that of all other long-chain compounds. L. S. T.

Determination of the mol. structure of acetone and formic acid by means of electron diffraction [measurements]. J. Hengstenberg and L. Brú (Anal. Fis. Quím., 1932, **30**, 341—358).—Debye's theory of the diffraction of electrons by gases is outlined, and a form of apparatus is described. Measurements with $COMe_2$ give the distance between the 2 C atoms $1{\cdot}57\pm0{\cdot}04$ Å. Interpretation of the diffraction diagram obtained with HCO_2H requires the assumption that the linkings C·O and C:O are of the same length; the most probable configuration is that in which the O atoms are situated at the corners of a tetrahedron. The calc. distance between the C and O atoms is $1{\cdot}24\pm0{\cdot}04$ Å. H. F. G.

***X*-Ray analysis of crystals of the 1 : 4-*cyclo*hexanediol with the m.p. 139° (*trans*-quinitol).** E. Halmöy and O. Hassel (Z. physikal. Chem., 1932, **B**, **17**, 258—264; cf. A., 1931, 1219).—This compound has the space-group C^5_{2h} and *a* 6·31, *b* 21·00, *c* 7·26, and *d* 9·18 Å. R. C.

***X*-Ray analysis of the structure of diphenyl.** J. Dhar (Indian J. Physics, 1932, **7**, 43—60).—The two Ph rings in each mol. are flat regular hexagons lying in one plane. The distance between the consecutive C atoms in each ring from centre to centre is 1·42 Å.; the length of the C·C linking connecting the two rings is 1·48 Å. N. M. B.

Crystal form of ethyl fluorene-9 : 9-dicarboxylate. G. Schäfer (Z. Krist., 1932, **82**, 472—473; cf. this vol., 614).—This compound is monoclinic, $a : b : c = 0{\cdot}8224 : 1 : 0{\cdot}8346$, β 114·46°; dispersion strong, $\rho > \upsilon$. C. A. S.

Relations between hydrated 10-bromophenanthrene-3(or 6)-sulphonic acid and paracrystalline structures in organisms. F. Rinne (Z. Krist., 1932, **82**, 379—393).—*X*-Rays show anhyd. 10-bromophenanthrene-3(or 6)-sulphonic acid (cf. A., 1916, ii, 556) to be cryst. Addition of a little H_2O transforms it into a paste showing a nematic phase where there is more H_2O, passing into a smectic phase where there is less. The addition of H_2O causes a loosening of the crystal lattice (*d* increasing from 3·40 to 3·47 Å.). Slow drying reverses the change. The phenomena are discussed in their bearing on biological products (cf. A., 1931, 1081). The effect of H_2O is attributed to its high dielectric const. and the presence of the SO_3H group. C. A. S.

***X*-Ray evidence of structure of the furanose and pyranose forms of α-methylmannoside.** E. G. Cox and T. H. Goodwin (J.C.S., 1932, 1844—1855).—The mols. of the two forms in the cryst. state have the constitutions assigned by Haworth (A., 1928, 156; 1930, 748), the form m.p. 193° having a C_5O ring, and that m.p. 118° having a C_4O ring. Hence methylation in this case is not accompanied by changes in ring structure. The side-chain in the furanose mol. lies in approx. the same plane as the ring, and Me groups, when present, are also in this plane. A. J. M.

Polymorphic system of the natural triglycerides. C. Weygand and W. Grüntzig (Z. anorg. Chem., 1932, **206**, 304—312).—The fats tristearin (C_{18}), tripalmitin (C_{16}), trimyristin (C_{14}), and trilaurin (C_{12}) may each be obtained in 7 polymorphic forms with definite m.p. Each group of polymorphs shows a periodicity, since it may be divided into 3 sub-groups of 3, 3, and 1, in which the m.p. varies to a small extent only, beginning with the forms of highest m.p. A similar periodicity was found for *p*′-methylchalkone (A., 1929, 815), but there the grouping was 1, 3, and 3. The m.p. increment for the increase of the mol. by $6CH_2$ diminishes with increasing mol. wt. The m.p. range is as follows: (C_{18}) 71—55°; (C_{16}) 65—45·5°; (C_{14}) 56·5—32°; (C_{12}) 46·5—18°. M. S. B.

Structure of highly-nitrated cellulose nitrate films. Desmaroux and Mathieu (Compt. rend., 1932, **194**, 2053—2054; cf. this vol., 218).—Using cellulose nitrate of N 13·13%, films obtained from $COMe_2$ solutions show structures passing from amorphous in films from dil. (0·5%) solutions to cryst. from conc. solutions. This decrease in crystallinity with increased dispersion indicates progressive separation of the elementary fibres composed of chains of glucose residues. C. A. S.

***X*-Ray diffraction photographs of vegetable and animal fibres.** W. T. Astbury (Phot. J., 1932, **72**, 318—323).—A lecture. A. J. M.

Improvement of the zinc–aluminium alloy, Al_2Zn_3. H. Meyer (Z. Physik, 1932, **76**, 268—280).—A study of the effect on electrical resistance, for d.c. and a.c., of the drop in temp., time of maintenance at the higher temp., and mean temp. of the temp. interval. A. B. D. C.

Dependence of the piezo-electric constant of quartz on temperature. V. Fréedericksz and G. Michailow (Z. Physik, 1932, **76**, 328—336).—The piezo-electric const. of quartz begins to diminish at 500°. A. B. D. C.

Effect of mechanical and electrical fields of force on the double refraction of quartz. N. Günther (Ann. Physik, 1932, [v], **7**, 783—801). A. J. M.

Cohesion limits for synthetic potassium halide crystals. W. Schütze (Z. Physik, 1932, **76**, 135—150). A. B. D. C.

Dependence on orientation of cohesion limits of synthetic potassium chloride crystals. W. Schütze (Z. Physik, 1932, **76**, 151—162). A. B. D. C.

Properties of pure silicon. R. L. Templin (Metals and Alloys, 1932, **3**, 136—137, 150).—Young's modulus for cast Si (99·41%) is 16,350,000 lb. per sq. in. Failure occurs suddenly in the form of general fragmentation at 13,470 lb. per sq. in. E. S. H.

Cathodic evaporation in a magnetic field. O. Goche (Bull. Acad. roy. Belg., 1932, [v], **18**, 412—418; cf. A., 1926, 693; 1927, 118; 1931, 407; this vol., 211).—The cathodic evaporation of hydride-forming elements (Sb, Bi, and Te) is mainly of the "directed" type, but not to the same degree as that of C. The evaporation of Pt is almost entirely directed, so it is concluded that, except in the case of C, chemical reaction between the cathode and gas must play at most only a secondary rôle in the phenomenon. Au, Ag, and Cu show mixed directed and undirected evaporation. J. W. S.

Allotropy in liquids. III. A. Smits and H. Gerding [with F. W. Broekman and W. C. Stapper] (Z. physikal. Chem., 1932, **160**, 231—244; cf. this vol., 683).—Dilatometric measurements with liquid $PhNO_2$ between 6° and 11° and AcOH between 15° and 19° and the heating curve of H_2O between 3° and 5° give no evidence of the existence of transition points (cf. this vol., 329). A thermoregulator by means of which the temp. of a thermostat may be kept const. to within 0·0005° is described. R. C.

Measurements with liquid helium. XVII. Resistance of lead in a magnetic field below the transition temperature. W. Meissner (Ann. Physik, 1932, [v], **13**, 641—648).—The resistance below the transition temp. for pure Pb was determined by extrapolation to zero field. Agreement with the T^5 law was obtained. W. R. A.

Thermal diffusivity of nickel. R. H. Frazier (Physical Rev., 1932, [ii], **40**, 592—595; cf. this vol., 442).—Further results, accurate to 0·06%, are reported. N. M. B.

New optical properties produced in liquids by high-frequency sound waves. R. Lucas and P. Biquard (Compt. rend., 1932, **194**, 2132—2134).—Parallel light passed through H_2O subjected to high-frequency sound waves shows diffraction effects similar to those produced by passing perpendicularly through a grating. C. A. S.

Heat of dissociation of nitrogen. A. K. Datta (Nature, 1932, **129**, 870).—The absorption spectrum of N_2O is continuous with no trace of bands. Absorption begins at 2740 Å. corresponding with 104·4 kg.-cal. Assuming a photochemical decomp. into NO and N, the calc. val. of the heat of dissociation of N_2 is 203 kg.-cal. L. S. T.

Surface energy and heat of vaporisation of liquids. L. S. Kassel and M. Muskat (Physical Rev., 1932, [ii], **40**, 627—632; cf. Margenau, A., 1931, 1114).—An approx. calculation of the total surface energy and heat of vaporisation of He, Ne, A, N_2, Cl_2, and O_2 is made by quantum mechanics. N. M. B.

Alternating m.p. in homologous series. C. Weygand and W. Grüntzig (Z. anorg. Chem., 1932, **206**, 313—316).—By comparing the polymorphic forms of the fats (C_{14}), (C_{16}), and (C_{18}) (cf. this vol. 798) containing even nos. of C atoms with the odd members (C_{15}) and (C_{17}), it is found that no alternation of m.p. is observed, provided corresponding modifications are compared, but only a regular rise in m.p. with increase in mol. wt. (C_{15}) and (C_{17}) have each 4 modifications, of m.p. ranging from 40° to 52° and 49·5° to 57·5°, respectively. M. S. B.

Effect of particle size on m.p. N. Schoorl (Z. physikal. Chem., 1932, **160**, 158—160).—The m.-p. depression exhibited by certain solids when finely powdered (A., 1910, i, 740) seems to be caused by products of devitrification of the walls of the m.-p. tube, or by impurities on the surface of larger crystals. R. C.

Specific heat of gases at high temperatures. W. T. David (Nature, 1932, **129**, 942).—Incomplete combustion at the moment of max. pressure in closed vessel explosions is generally so large that the explosion method as usually employed is untrustworthy for sp. heat determinations. Data for H_2–O_2 and CO–air explosions in large and small vessels support this view. L. S. T.

Permeability of glass and fused quartz to ether, alcohol, and water at high pressure. T. C. Poulter and R. O. Wilson (Physical Rev., 1932, [ii], **40**, 877—880).—Pressures of the order 15,000 atm. for 5—15 min. caused considerable penetration and a weakening effect. With non-penetrating liquids higher pressures could be used. N. M. B.

Physical properties of compressed gases. III. Hydrogen. W. E. Deming and (Miss) L. E. Shupe (Physical Rev., 1932, [ii], **40**, 848—859; cf. A., 1931, 553; this vol., 220).—Complete data for sp. vol., density, temp. and pressure expansion coeffs., fugacity, C_p, $C_p - C_v$, C_v, and μ are obtained from available compressibility data for the temp. range −215° to 500° and up to 1200 atm. pressure. N. M. B.

Entropy, strain, and the Pauli exclusion principle. W. S. Kimball and G. Berry (Phil. Mag., 1932, [vii], **13**, 1131—1143).—Theoretical. H. J. E.

Salts of low m.p. VII. Density, conductivity, and viscosity of molten mixtures of picrates. P. Walden and E. J. Birr (Z. physikal. Chem., 1932, **160**, 161—193; cf. this vol., 685).—The *d*, mol. conductivity, λ, viscosity, η, and val. of $\lambda\eta$ for a molten mixture of tetra-alkylammonium picrates (I) are additively constituted of the vals. for the constituents, but the mol. vol. < the additive val. For mixtures of (I) with di- (II) or mono-alkyl salts (III) the val. of $\lambda\eta$ < the additive val., which is traced to diminution in the degree of dissociation, α, of (III) or (II) by (IV). This diminution, which is the greater the lower is the temp. and the higher is the concn. of (I), is accompanied by a proportionate decrease of η below the additive val., which shows that in molten (III) and (II) the cations have an envelope of undissociated mols., which are released when the ions combine. Such solvation is more marked with (III) than with (II). On mixing (II) with (I) or trialkyl salts (IV) α diminishes for both constituents. No appreciable change in α occurs when (I) and (IV) are mixed. The above observations are supported by mol. vol. data, the contraction in vol. on mixing being abnormally small when repression of ionisation occurs. R. C.

Critical constants and vapour pressure of boron trifluoride. H. S. Booth and J. M. Carter (J. Physical Chem., 1932, **36**, 1359—1363).—The crit. temp. is $-12{\cdot}25\pm0{\cdot}03°$ and the crit. pressure $49{\cdot}2\pm0{\cdot}1$ atm. From 10 to 50 atm. $\log p=5{\cdot}1009-0{\cdot}8896\times1000/T$, where p is the v.p. The mol. heat of vaporisation calc. from p is 4057 g.-cal. At about $-50°$ and 13 atm. the viscosity becomes appreciable, suggesting association. Dry BF_3 does not attack Hg, Cr plating, or glass over long periods even at high pressure. A. L. H. (*c*)

Calculation of the effect of a solid wall on the state of aggregation of a liquid from viscosity determinations. M. Reiner (Physikal. Z., 1932, **33**, 499—502).—Theoretical. A. J. M.

Coefficient of viscosity of liquid sodium amalgams. G. R. Paranjpe (Indian J. Physics, 1932, **7**, 95—97).—The viscosity of liquid Na amalgams decreased continually with time, the initial val. being restored by mechanical agitation. N. M. B.

Critical temperatures and pressures of the three two-component systems composed of carbon dioxide, methyl ether, and propylene. C. A. Winkler and O. Maass (Canad. J. Res., 1932, **6**, 458—470).—The crit. phenomena associated with the three separate pairs of binary mixtures have been examined in detail. Above the "crit. contact temp." liquefaction is impossible, whatever pressure is applied. At temp. below the plait point condensation is regular; between the plait point temp. and the crit. contact temp. the amount of liquid increases as the pressure is increased. A single crit. point cannot be ascribed to a mixture, but the plait point temp. and the crit. contact temp. are regarded as the limits of a crit. region. No evidence of compound formation in any of these systems was obtained. E. S. H.

Viscosity of potassium–sodium alloys in the liquid state. R. Kremann, M. Pestemer, and H. Schreiner (Rec. trav. chim., 1932, **51**, 557—563).—Viscosities of K–Na alloys with 0—100% K have been measured at 125°. The viscosity–composition curve shows a sharp max. at 66·7 at.-% K, indicating the existence of the compound K_2Na in the liquid state. F. L. U.

Theory of formation and state of glass. E. Berger (Kolloid-Beih., 1932, **36**, 1—42).—The formation of glass differs from crystallisation in consisting in the transformation of the viscous, undercooled liquid into the brittle state. At a certain temp. the temp. coeff. of this change increases suddenly, thus providing a transformation point. The transformation is influenced by the thermal history of the material; this effect is not due to mechanical strain, but to a change in state of aggregation, which proceeds more slowly as the transformation point is approached and is completely inhibited at lower temp. Measurements of viscosity and electrical resistance between 1300° and 300° show clearly the difference between the viscous and brittle states, and indicate that below the transformation point glass is not simply an undercooled liquid. The mol. kinetics of the transformation point and the structure of the brittle state are considered theoretically. Regarding the system as composed of secondary aggregates dispersed in a medium consisting of primary particles and single mols., the transformation point is analogous to the sol–gel transformation. E. S. H.

Diffusion of zinc in copper and its alloys. Y. Yamauchi (Mem. Coll. Sci. Kyoto, 1932, **A**, **15**, 67—95).—The rate of absorption of Zn vapour per unit area of Cu (ΔW) in an atm. of H_2 at 400—655° is given by $\Delta W=Ae^{-B/T}$ where A and B are consts. ΔW for rolled Cu is lower than for cast Cu at temp. below the recryst. point. The Zn loss from α-brass on heating varies with the Zn content (C) of the brass according to the equation: $\Delta W=ae^{bC}$ where a and b are consts. Brass containing β or $\alpha+\beta$ loses Zn on heating according to the same law as that which controls absorption of Zn by Cu. Addition of Pb, Fe, Mn, and especially Sn increases the rate of Zn loss from brass on heating, whereas addition of Al appreciably reduces this rate. A. R. P.

Lattice dimensions in copper–silver alloys. (Miss) H. D. Megaw (Phil. Mag., 1932, [vii], **14**, 130—142).—The variation of spacing with composition in Ag-rich and Cu-rich alloys subjected to varied heat-treatment has been examined. The spacings for pure Ag and Cu are 4·0774 and 3·6090 Å. respectively. H. J. E.

Gold–silver alloys as a type of continuous solid solutions. W. Broniewski and E. Wesolowski (Compt. rend., 1932, **194**, 2047—2049; cf. this vol., 566).—Further observations show that the alloys form a typical series of solid solutions free from any discontinuity. C. A. S.

Superconductivity of alloys containing gold and silver. J. C. McLennan, J. F. Allen, and J. O. Wilhelm (Phil. Mag., 1932, [vii], **13**, 1196—1209).—Au and Ag lower the superconducting temp. of Pb and Sn, whereas Bi, Sb, and As raise it. The phase relations in the systems Ag–Sn, Au–Sn, Au–Pb have been studied. H. J. E.

β-Transformations in copper– and silver–zinc alloys. M. Straumanis and J. Weerts (Metall-Wirt., 1931, **10**, 919—922; Chem. Zentr., 1932, i, 629).—Results of *X*-ray study of the crystal structure at 100—300° are described. A. A. E.

Equilibrium diagram of the binary system, nickel–zinc. K. Tamaru (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 90).—Thermal and dilatometric analysis and electrical resistance measurements on Ni–Zn alloys show that the α-phase extends to 61·61% Ni at 1403° and the β-phase to 37·5% Ni at the eutectic point. The eutectoid transformation in β extends from 45·5 to 24·4% Ni and occurs at 700° on heating and at 640° on cooling. The δ-phase is homogeneous between 49 and 45·5% Ni and the compound $NiZn_3$ dissolves up to 1·4% Ni. The reaction $\alpha+\beta \rightleftharpoons \delta$ takes place at 804° and the peritectic reaction near $NiZn_3$ previously reported does not take place. The α-phase is face-centred cubic, the β- and δ-phases are hexagonal, and the γ-phase has an α-Mn structure. A. R. P.

***X*-Ray determination of the solubility of manganese in magnesium.** E. Schmid and G. Siebel (Metall-Wirt., 1931, **10**, 923—925; Chem. Zentr., 1931, ii, 629—630).—Accurate determinations of the lattice consts. by the reflexion method have been used to find the effect of temp. on the saturation concn. of the α-mixed crystals. The solubility falls rapidly from 3·4% at the eutectic temp. (645°) to zero at 200°. L. S. T.

System iron–cobalt–molybdenum. W. Köster and W. Tonn (Arch. Eisenhüttenw., 1931—1932, **5**, 627—630).—The system has been investigated up to a Mo content corresponding with that of the CoMo–Fe_3Mo_2 section using thermal, dilatometric, and micrographical methods. CoMo and Fe_3Mo_2 form a continuous series of δ-solid solutions. The eutectic points in the Fe–Mo and Co–Mo systems and the peritectic point in the Fe–Co system are all lowered by the addition of the third constituent and eventually merge at 1300° into the 4-phase equilibrium: liquid$+\alpha \rightleftharpoons \gamma+\delta$. From this point two lines of 3-phase equilibrium extend, viz., (*a*) liquid$=\gamma+$CoMo and (*b*) $\alpha=\gamma+\delta$. Equilibrium diagrams are given for ternary alloys with 10, 20, 30, and 45% Mo showing particularly the changes which occur in the shape of the α–γ curve. Many of the alloys show pptn.-hardening phenomena with suitable heat-treatment. A preliminary examination of the section Mo–CoMo–Fe_3Mo_2 indicates that FeMo forms solid solutions with CoMo and with Fe_3Mo_2 both of which are of the η type. A. R. P.

Active oxides. L. Change of the catalytic, magnetic, and *X*-ray spectroscopic properties during the formation of spinel in mixtures of zinc oxide and chromic oxide. G. F. Hüttig, H. Radler, and H. Kittel (Z. Elektrochem., 1932, **38**, 442—449).—The catalytic activity, ϕ, in the decomp. of MeOH at 300°, the magnetic susceptibility, ψ, the solubility in 0·28*M*-KOH, and the *X*-ray diagrams of various mixtures of ZnO and Cr_2O_3 of different origins have been determined, and the effect of heating the mixtures up to about 1150° has been studied. Heating at 300—400° does not cause spinel formation, but ϕ increases 7-fold, and ψ also increases; subsequent heating at 400—500° causes a gradual reduction of ϕ and ψ, and at 500° spinel formation commences. A mixture of Cr_2O_3 with ignited ZnO does not catalyse the decomp. of MeOH. The results may be interpreted in part in terms of reaction at the ZnO–Cr_2O_3 interface. H. F. G.

Physical properties of mixtures of acetone and bromoform. V. C. G. Trew (Trans. Faraday Soc., 1932, **28**, 509—514).—The density, viscosity, refractive index, heat of mixing, and sp. heat of $COMe_2$–$CHBr_3$ mixtures show deviations from the simple mixture rule which resemble those found for $COMe_2$–$CHCl_3$ mixtures. Mol. compound formation is indicated. J. G. A. G.

Measurement of small vapour pressures. Pressure of water vapour over various concentrations of sulphuric acid. W. von Meyeren (Z. physikal. Chem., 1932, **160**, 272—278).—The v.p. at 0—40° has been determined with the aid of Gaede's vacuscope. The latter operates on the McLeod gauge principle, and enables v.p. of 0·01—5 mm. to be measured. R. C.

Theory of conjugate solutions. P. Brun (J. Chim. phys., 1932, **29**, 184—191).—The system H_2O–MeOH–*iso*amyl alcohol has been examined with reference to the theory of Antonov (A., 1928, 593). W. R. A.

Critical liquid mixtures as colloidal emulsions. W. Ostwald (Austral. J. Exp. Biol., 1932, **9**, 83—88).—Crit. liquid mixtures (C_6H_{14}–MeOH and $Pr^{\beta}CO_2H$–H_2O) possess structural viscosity, do not obey Poiseuille's law at low pressures, and show large increases in viscosity at low rates of flow. In these respects they resemble gelatin solutions. W. M.

Equilibria in the systems: alcohol–benzene–water and alcohol–toluene–water. D. N. Tarasenkov and E. N. Poloshinceva (J. Gen. Chem. Russ., 1932, **2**, 84—88).—Miscibility data are shown in the form of equilibrium diagrams. R. T.

Isobars of the system *iso*butyl alcohol–water. T. Bylewski (Rocz. Chem., 1932, **12**, 311—326).—The b.p. mixtures have been determined at pressures at which the b.p. of H_2O is 100°, 110°, 120°, and 130°. The v.p.–temp. curves of $Bu^{\beta}OH$ and H_2O do not intersect but approach each other most closely at 117°. At high pressures the mixtures change from the heteroazeotropic to the azeotropic type. R. T.

Solubility of potassium perrhenate in water, and certain physicochemical constants of its solutions. N. A. Pushin and D. Kovatsch (Bull. Soc. Chim. Yougoslav., 1931, **2**, 25—31).—The eutectic point is at −0·060° and 0·343% of $KReO_4$. The solubility rises from 0·35% at 0° to 3·08% at 50° and 9·44% at 100°. The *d* and *n* increase with concn., whilst the viscosity decreases slightly. R. T.

Solubility relations of silver chloride in aqueous solutions of strong electrolytes. E. W. Neuman (J. Amer. Chem. Soc., 1932, **54**, 2195—2207).—The solubility at 25° in aq. solutions of H, K, Ca, Mg, and La sulphates, and K, Ba, and La nitrates has been determined. The solubility in H_2O is $1{\cdot}273\times10^{-5}M$,

and the activity coeff. 0·9985. There are marked deviations from the Debye–Hückel limiting law. The Gronwall and La Mer extensions agree with the data for symmetrical compounds. Neither accounts for the sulphates of unsymmetrical valency type.
G. M. P. (c)

Solubility of thallous chloride in presence of edestin nitrate. C. F. Failey (J. Amer. Chem. Soc., 1932, 54, 2367—2371; cf. this vol., 457).—The negative logarithm of the activity coeff. of TlCl, obtained from solubility determinations in HNO_3 containing 0—5% of edestin, is approx. proportional to the edestin concn. Other data for the activities of salts in protein solutions are collected and compared.
H. A. B. (c)

Dichloroethylene as a solvent. D. Mann (Chem.-Ztg., 1932, 56, 452).—$C_2H_2Cl_2$ is found to be more selective than Et_2O as a solvent for chemically similar substances. J. G.

Increase in the solubility of sparingly soluble materials in the presence of hydrophilic colloids or surface-active materials. H. Brintzinger and H. G. Beier (Naturwiss., 1932, 20, 254—255).—The solubility of many sparingly sol. acids, bases, and salts is increased by the presence of hydrophilic colloids, such as gelatin, albumin, and gum arabic, or of active charcoal, SiO_2 gel, clay, $Al(OH)_3$, hydrated SnO_2, etc. This is due to the adsorption of one of the ions on the added material, causing a disturbance of the ionisation equilibrium and consequently of the equilibrium between solid and dissolved material.
J. W. S.

Mechanism of dissolution of organic substances in non-aqueous solvents. III. Cellulose nitrate in *cyclo*hexanone, *p*-methyl*cyclo*hexanone, fenchone, and *m*-xylene. T. Tomonari, C. Trogus, and K. Hess (Z. physikal. Chem., 1932, B, 17, 241—257; cf. this vol., 568).—The formation of compounds has been demonstrated by the methods previously described. The proportions in which combination occurs with ketones depend on the nature of the ketone, and are changed by even slight variations of the structure of the latter. It is probable that compound formation between cellulose esters and org. substances follows the principles of the co-ordination theory, the C_6 group serving as a centre at which addition occurs in the ratio 1 : 1 or 1 : 3. Cellulose nitrate combines with *m*-xylene only in presence of a ketone, which, however, does not enter into the composition of the compound formed. The "constancy of the fibre period of cellulose in its derivatives" is illusory. R. C.

Formation and properties of precipitates. Theory of co-precipitation. III. I. M. Kolthoff (Chem. Weekblad., 1932, 29, 332—338).—Largely a review of recent work. The Paneth–Fajans adsorption law has been extended by the statement that when a crystal lattice has adsorbed one type of ion, an equiv. quantity of a different ion will be found on the surface ("secondary adsorption"). Preferential adsorption of ions occurs when these secondary ions carry a large charge of sign opposite to that of the ions adsorbed on the lattice, or when they form with the adsorbed ions a sparingly sol. or only slightly dissociated compound.
H. F. G.

Formation and properties of precipitates. Theory of co-precipitation. IV. I. M. Kolthoff (Chem. Weekblad, 1932, 29, 346—348).—Fineness of subdivision increases the solubility of $BaSO_4$ and $CaSO_4$, and the fact that a mixture of fine and coarse particles dissolves to an extent which corresponds with the solubility of the coarse particles is explained by the relatively greater effect of ionic charges in the case of fine particles. The conception of supersaturation in connexion with rate of formation of ppts. has no exact significance. S. I. L.

Formation and properties of precipitates. Theory of co-precipitation. V, VI. I. M. Kolthoff (Chem. Weekblad, 1932, 29, 362—363, 378—380).—V. An explanation of the fact that many finely divided ppts. become more easy to filter after being allowed to remain for a time in contact with the solution.

VI. Weimarn's theory of the formation of ppts. is based on unjustifiable assumptions and the term "amorphous modification" has no real significance. The rate of formation of nuclei is not governed solely by the abs. concn. of the reacting ions, since adsorbed ions may exert considerable influence on the rate of growth of the particles. H. F. G.

Formation and properties of precipitates. Theory of co-precipitation. VII. I. M. Kolthoff (Chem. Weekblad, 1932, 29, 395—400).—The relation between adsorption, crystal growth, and the separation of metastable modifications is discussed. Crystal formation in a ppt. is less complete as co-pptn. of foreign ions increases. S. I. L.

Carrying down of polonium by crystalline oxalates in nitric acid solution. Servigne (Compt. rend., 1932, 195, 41—43).—Observations have been made with La, Sc, Ca, and Sr salts. C. A. S.

Supersaturation. J. R. Partington (J. Physical Chem., 1932, 36, 1853—1854).—A claim for priority over Kolthoff (cf. this vol., 457).
G. M. M. (c)

Some solvent properties of soap solutions. II. E. L. Smith (J. Physical Chem., 1932, 36, 1672—1684; cf. this vol., 687).—The distribution ratio, K, of *p*-dimethylaminoazobenzene (I) between Et_2O and aq. soap solution at room temp. decreases with increasing soap concn. and concn. of excess alkali in the soap solution, whilst with gradual addition of MeOH it passes through a max. If the colloidal soap is regarded as a third phase, the results are in semi-quant. agreement with the theory that I is distributed between the Et_2O and the non-colloidal aq. phase according to the partition law and between the non-colloidal and colloidal aq. phases according to an adsorption law. MeOH greatly increases the solubility of I in the aq. phase, thus increasing K, but diminishes the proportion of soap in the colloidal form, tending to reduce K. In the partition of NH_2Ph between EtOAc and aq. Na oleate at 25° K is decreased considerably by increase in the soap concn. and slightly by addition of NaCl, but is almost independent of the NH_2Ph concn. O. T. Q. (c)

Partition of iodine between carbon disulphide and water. J. LANZA (Anal. Fís. Quím., 1932, 30, 372—376).—Herrero's work (this vol., 118) is criticised. The view is re-affirmed that the I in the H_2O phase is introduced by dissolution of CS_2 in the H_2O. H. F. G.

Sorption of gases by iron. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1932, 54, 1820—1830; cf. this vol., 689).—The sorption of N_2, CO, and H_2 on reduced Fe has been studied at −195° to 400°. At the low temp., sorption consists solely of physical adsorption. Activated adsorption takes place at higher temp., the rate being greatest for CO and least for N_2. With H_2 at 110° and above, dissolution probably occurs. A stepwise increase in the adsorption at low temp. suggests the accumulation of molecular layers. H. F. J. (*c*)

Active charcoal. I. Adsorption isotherms of organic acids on ash-free charcoals. C. OCKRENT (J.C.S., 1932, 1864—1875; cf. this vol., 332).—Adsorption data agreeing with Langmuir's equation, $k\Gamma=C(I-\Gamma/\Gamma_{\text{max.}})$, were obtained with 4 specimens of charcoal, for aq. HCO_2H, AcOH, $CH_2Cl{\cdot}CO_2H$, $CHCl_2{\cdot}CO_2H$, and $CCl_3{\cdot}CO_2H$, salicylic acid, and BzOH. Each acid gives the same *k* for all the charcoals, showing that they have the same structure, in agreement with *X*-ray data (this vol., 16), but differ in $\Gamma_{\text{max.}}$, which also depends on the size of the adsorbed mols. The effects of grinding and activation are explained by the assumption that active charcoal is an assembly of ultrapores of mol. dimensions. Grinding increases $\Gamma_{\text{max.}}$ for large mols. and decreases it for small mols. D. R. D.

Adsorption of weak electrolytes on charcoal. R. A. PETERS and H. J. PHELPS (Nature, 1932, 129, 939).—The adsorption of weak electrolytes by highly purified C is essentially a process different from the adsorption of strong electrolytes under the same conditions. L. S. T.

Surface effect and exchange adsorption of pyrophosphate by charcoal. F. AXMACHER (Kolloid-Z., 1932, 59, 298—305).—$Na_4P_2O_7$ is taken up by pure animal charcoal in accordance with the adsorption isotherm. The amount of PO_4''' given up by blood C of high ash content is greater in $Na_4P_2O_7$ solution than in H_2O; the influence of time, temp., and relative amounts of the adsorbent and electrolytes has been studied. The exchange of PO_4''' is also effected by other anions in the order $P_2O_7>F>C_2O_4>$tartrate$>OAc>SO_4=NO_3>Cl$, but there is no evidence of exchange adsorption of Cl′. E. S. H.

Adsorptive power and graphite structure of carbon. P. M. WOLF and N. RIEHL (Angew. Chem., 1932, 45, 400—401).—Photographic records show that the adsorption of Rn by a large graphite crystal occurs mainly at the prism faces, thus supporting the view that the linkings between the hexagonally-disposed C atoms are essentially different from those between the basal planes (cf. this vol., 16). The result suggests also that the adsorptive power of C depends not only on the particle size of the crystallites of graphite but also on their development of prism faces. E. S. H.

Adsorption of nitrogen peroxide by colloidal silicic acid. II. A. P. OKATOV and I. A. CHAINSKI (J. Gen. Chem. Russ., 1931, 1, 1181—1192).—Colloidal SiO_2 is a satisfactory adsorbent for NO_2 at 20°. The data agree with Freundlich's equation. R. T.

Adsorption of radium emanation by silica gel in relation to state of dehydration. M. FRANCIS (Kolloid-Z., 1932, 59, 292—298).—Measurements of the adsorption of Rn by SiO_2 gel show a max. for specimens dehydrated at 800° (1·2% H_2O) and at 150° (5·5% H_2O), indicating structural differences in the gels. Ageing of the gel has a differential influence on the adsorption of Rn and air. E. S. H.

Displacement of chemical equilibria due to selective adsorption of hydroxides by silica gel. BERTHON (Compt. rend., 1932, 195, 43—45).—SiO_2 gel (Patrick's) adsorbs Na ions only from a solution of NaCl containing NH_3. The order of the effect for the alkali metals as chlorides is the reverse of that for the free bases (cf. A., 1929, 757); for the alkaline-earth metals the order is the same as that of the lyophilic series. Fe^{III} tartrate behaves similarly to NaCl. C. A. S.

Adsorption at the surface of a solution. W. F. K. WYNNE-JONES (Phil. Mag., 1932, [vii], 14, 203—204; cf. this vol., 458).—Polemical. H. J. E.

Height of liquid between parallel plates. S. RAY (Kolloid-Z., 1932, 59, 280—283).—The observation of Schultze (A., 1931, 679) is explained in terms of the colloidal theory of surface tension (A., 1928, 702). E. S. H.

Determination of relative surface tension (capillary activity): use for characterising essential oils and related substances. A. MÜLLER (J. pr. Chem., 1932, [ii], 134, 158—166).—The liquid is allowed to drop from a capillary tube (a series is used for liquids of varying viscosity) on to a sheet of filter-paper placed at a definite distance beneath. The area of the spreading drop is measured at definite intervals. The results are comparable with those given by Traube's stagonometer (B., 1928, 111), and are of val. in the characterisation of essential oils. H. A. P.

Dependence of the angle of contact on the constitution of adsorbed organic compounds. A. B. COX, E. E. WARK, and I. W. WARK (Nature, 1932, 129, 871).—A trace of K Et xanthate in H_2O gives an angle of contact in the system mineral–H_2O–air which is independent of the concn. of the xanthate and the nature of the mineral. Na Et_2 dithiophosphate and other Et compounds containing an SH group give the same angle 60°±2°. Each alkyl or aryl group shows a characteristic angle of contact which is apparently independent of the nature of the polar group of the adsorbed mol. L. S. T.

Conductance of some sodium oleate solutions in relation to interfacial adsorption. R. F. NICKERSON and P. SEREX (J. Physical Chem., 1932, 36, 1585—1593).—The conductivity–concn. relation of Na oleate at 25° changes abruptly at 0·002*N*, which coincides with the min. of surface tension, γ, and loss of foaming power. Between 0·059 and 0·002*N* γ

varies inversely as the hydrolysis. More acid oleate is adsorbed at the oil–solution than at the vapour–solution interface of a Na oleate solution. Foaming is attributed to a hydrolytic equilibrium between a saturated surface and an excess of colloidal and crystalloidal oleate. Oils differ in their adsorbent capacity for acid Na oleate. S. L. (*c*)

Electrokinetic potentials. XI. Effect of soaps on the electric moment of the double layer at an aqueous cellulose interface. H. B. Bull and R. A. Gortner (Physics, 1932, **2**, 21—32).—Aq. Na formate, acetate, propionate, butyrate, octoate, oleate, and oxalate were investigated by a streaming-potential method. The electric moment of the double layer is practically const. after the fourth C atom. Long-chained soaps give a val. independent of the concn. The max. val. is $2\times10^{-4}N$. Ch. Abs.

Electrocapillary effect of capillary-active organic molecules. A. W. Davis (Phil. Mag., 1932, [vii], **13**, 1188—1192).—The max. in the electrocapillary curve for aq. KI is depressed by MeOH. The effect is compared with that for aq. KCl and MeOH. H. J. E.

Capillary activity of normal aliphatic dicarboxylic acids. B. Tamamushi (Bull. Chem. Soc. Japan, 1932, **7**, 168—176).—The depression of the surface tension of aq. solutions of the acids $(CH_2)_n(CO_2H)_2$ (n=0—7) is proportional to the concn., and for solutions of equiv. concn. increases in the order $n=0<2<3<1<4<7<6$. Adsorption by animal charcoal increases in the same order. When n is even, the work needed to bring 1 mol. of acid from the surface into the solution increases by 620 g.-cal. for each CH_2 group. D. R. D.

Wetting and ultra-porosity. Adsorption and stabilisation of hydrophobic and hydrophilic carbons in solutions of dyes. B. V. Iljin and S. G. Pinsker (Kolloid-Z., 1932, **59**, 283—285).—Both hydrophobic and hydrophilic suspensions of C are stabilised by Me-violet, which is adsorbed thereby, in accordance with the view that hydrophilic C is characterised by ultra-porosity. E. S. H.

Heat of wetting of carbon and silica gel in mixtures of water and acetic anhydride. B. V. Iljin, W. A. Oschmann, N. L. Rebenko, and N. K. Archangelskaja (Z. anorg. Chem., 1932, **206**, 174—176).—The heat of wetting of powdered hydrophobic C in mixtures of H_2O and Ac_2O shows a max. for a 50% mixture (glacial AcOH). With powdered hydrophilic C there is inversion, glacial AcOH giving a min. heat of wetting. Similar results are obtained with powdered hydrophilic SiO_2 gel and thus confirm the view that the method may be employed for studying compound formation in solution (cf. A., 1930, 153). M. S. B.

Schaum's phenomenon. H. Reibstein (Kolloid-Z., 1932, **59**, 337—342).—The factors affecting the movements of small crystals at the interface Hg/dil. H_2SO_4 are discussed. E. S. H.

Influence on diffusion of salts through gels and of gases through membranes. H. Eppinger and W. Brandt (Biochem. Z., 1932, **249**, 11—20).—The permeability of gelatin for NaCl is increased by small and decreased by large amounts of caffeine and uric acid, increased by carbamide, strophanthin, digitalis, and saponin, and decreased by EtOH, Et_2O, and deoxycholic acid. The permeability of a soap film for H_2 is increased by addition of lecithin and deoxycholic acid and decreased by addition of strophanthin, caffeine, digitalis, Et_2O, EtOH, $CCl_3\cdot CH(OH)_2$, histamine, cholesterol, saponin, and $CaCl_2$. The last three substances in min. doses cause a small increase of permeability. P. W. C.

Cryoscopic study of ether and acetone in solutions of potassium chloride. F. Bourion and E. Rouyer (Compt. rend., 1932, **194**, 2050—2052; cf. this vol., 570).—Further f.-p. data are recorded. C. A. S.

Ebullioscopic experiments. M. Centnerszwer and M. Łaźniewski (Z. physikal. Chem., 1932, **160**, 257—271).—By means of Swientosławksi's ebullioscope (cf. A., 1931, 1388) the vals. of 26·42° and 38·02° have been obtained for the mol. b.-p. elevations of C_6H_6 and $CHCl_3$, referred to 100 g. of solvent, and the degrees of association of alkylammonium salts in $CHCl_3$ have been determined. R. C.

Variation with concentration of equivalent refraction of dissolved electrolytes. G. Pesce (Z. physikal. Chem., 1932, **160**, 295—300; cf. A., 1931, 1122).—The apparent refraction of aq. $CaCl_2$, $SrCl_2$, and Na_2CO_3 at 25° from about $1M$ to saturation is a linear function of the concn. With $BaCl_2$ it falls more rapidly with increasing concn. than with $SrCl_2$, pointing to a greater tendency to ionic association. With Na_2CO_3 it rises with the concn. R. C.

Effect of concentration and of degree of ionisation on the optical refractivity of solutions of amino-acids, proteins, and other compounds. R. Craig and C. L. A. Schmidt (Austral. J. Exp. Biol., 1932, **9**, 33—67).—The factors which govern the change of n of aq. solutions of NH_2-acids on the addition of strong acid or strong base also operate with gelatin, edestin, and serum-albumin. In gelatin solutions the change from gel to sol causes a change in n. W. M.

Dispersion of air in aqueous solutions. N. A. Alejnikov (Kolloid-Beih., 1932, **36**, 82—122).—The methods available for the prep. of disperse systems of air in aq. solutions are reviewed, particularly in relation to their application to flotation processes. The systems formed by shaking a solution of a surface-active substance sparingly sol. in H_2O tend to a limiting mean degree of dispersion as the concn. of the surface-active substance is increased. The polydisperse system originally formed rapidly separates into two systems, viz., foam and emulsion. The time-stability of the emulsion tends towards a limiting val. with increasing concn. of surface-active substance, whilst that of the foam possesses a max. The pneumatic method of dispersion (leading the air into the solution through a capillary or porous diaphragm) is more suitable for the subsequent examination of the systems. Experiments on the pressure and stability of several such systems are described. E. S. H.

Making gold sol for [cerebro]spinal-fluid tests. B. S. Levine (Amer. J. Syph., 1932, **16**, 103—109).—Carefully distilled H_2O is necessary; cleanliness of reaction vessels and concn. of reagents are important matters. The mixed reagents must not be exposed to the flame. Org. substances should be eliminated and some active O_2 must remain dissolved in the H_2O. Directions for the prep. of Au sol by treating a solution of AuCl and K_2CO_3 with CH_2O and H_2O_2 are given. Ch. Abs.

Diffusion of colloid particles. IV. Influence of charge on diffusion velocity and its alteration during coagulation. H. R. Bruins (Kolloid-Z., 1932, **59**, 263—266).—During the coagulation of amylum sols by electrolytes the rate of diffusion does not decrease, as expected, but increases in accordance with the electrical theory developed (A., 1931, 561). E. S. H.

Reproducibility and rate of coagulation of stearic acid smokes. H. S. Patterson and W. Cawood (Proc. Roy. Soc., 1932, A, **136**, 538—548).—An apparatus for the production of reproducible uniform stearic acid smokes is described. For many smokes of the same wt. concn. the velocity of coagulation is const. within small limits. The measured velocities of coagulation agree with Smoluchowski's theory if account is taken of the fact that smokes originally homogeneous become heterogeneous during coagulation. L. L. B.

Colloidal systems. Peptisation of ferric hydroxide by ferric chloride. A. Dumanski and V. M. Simonova (J. Gen. Chem. Russ., 1931, **1**, 1229—1244).—The process of peptisation of $Fe(OH)_3$ by $FeCl_3$ is represented using triaxial co-ordinates. The coagulative action of anions diminishes in the order $SO_4''>F'>Cl'$ or Br', and of cations in the order $Li^{\cdot}>K^{\cdot}$ or $Na^{\cdot}$, and $Mg^{\cdot\cdot}>Ca^{\cdot\cdot}>Sr^{\cdot\cdot}>Ba^{\cdot\cdot}$. In high concns. sulphates produce complex peptisation, both $FeCl_3$ and SO_4'' being adsorbed by $Fe(OH)_3$; no coagulation of the sols is observed in such cases. The action of $AlCl_3$ is antagonistic to that of $FeCl_3$. R. T.

Acclimatisation and sensitisation of colloidal ferric hydroxide. A. V. Dumanski and A. I. Solin (Kolloid-Z., 1932, **59**, 314—324).—The coagulation of $Fe(OH)_3$ sols, prepared by different methods, by alkali halides with and without the addition of MeOH affords evidence of acclimatisation, particularly in the more dil. sols. In general, the dil. sols are the most stable. A connexion is established between acclimatisation and adsorption. No acclimatisation was observed with K_2SO_4. The sols are sensitised towards coagulation by K_2SO_4 by adding MeOH, but to an extent which depends on the nature of the electrolyte produced simultaneously with the colloid. Sols of $Fe(OH)_3$ containing NaF do not show acclimatisation towards coagulation; the strongly coagulating power of NaF suggests the ion F_2''. E. S. H.

Silver ferrite. V. Ageing process of orthoferric hydroxide and the constitution of goethite (α-FeO_2H). A. Krause and A. Lewandowski (Z. anorg. Chem., 1932, **206**, 328—336).—The ageing process of orthoferric hydroxide may be followed by its decreasing ability to form Ag ferrite (this vol., 481), after an initial rise, and also from the nature of the insol. residue from the Ag ferrite. The rate increases with increasing concn. of OH′. Ageing is the result of the following changes: orthohydroxide $\longrightarrow$ polyorthohydroxide $\longrightarrow$ ferrous acid $\longrightarrow$ goethite. It is also possible for hydrohæmatite to be formed, depending on the OH′ concn. Ag ferrite becomes ferromagnetic after decomp. sets in at 250—280°, but on calcination it loses this property. The relationship between amorphous and cryst. γ-FeO_2H is discussed, and also the constitution and mol. wt. of goethite. M. S. B.

Coagulation of colloids from the point of view of Smoluchowski's theory. III. Coagulation of arsenious sulphide sol by sulphuric acid solutions. S. S. Joshi and G. R. Phansalkar (J. Indian Chem. Soc., 1932, **9**, 157—161).—The results previously obtained (A., 1931, 1124) are amplified and confirmed. Contrary to Linder and Picton (J.C.S., 1905, **87**, 1906), the rate of coagulation is increased by rise in temp. The influence of temp. depends on the colloid concn. when the concn. of coagulator is const. H. B.

Electrolyte coagulation of copper oxide sol in the presence of starch. H. Breindl and K. Söllner (Kolloid-Z., 1932, **59**, 331—335).—The coagulation of CuO sols by K_2SO_4 has been followed by centrifuging the coagulate and determining Cu in the liquid. Small amounts of starch have practically no effect, but when a crit. concn. of starch is reached (increasing with increasing concn. of K_2SO_4) the velocity of coagulation is sharply reduced, further addition of starch causing little more change. The influence of starch is not reversible; subsequent dilution has little influence. E. S. H.

Influence of temperature on the coagulation of colloidal manganese dioxide. S. S. Joshi and T. S. Narayan (Kolloid-Z., 1932, **59**, 335—336).—In this system, with rising temp. the Smoluchowski factor β passes through a min. at 30°, and rises rapidly at 45°, reaching a const. val. at 50°. E. S. H.

Influence of salts on viscosity of hydrophilic colloids. E. H. Buchner (Rec. trav. chim., 1932, **51**, 619—623).—Viscosities of sols of gum arabic, casein, ovalbumin, and glycogen in the presence of neutral Na salts of various acids have been measured at 25°. The viscosity of the two first-named substances is considerably lowered by small concns. of salt, and but little changed above $N/8$, whilst that of the other two is only slightly lowered at first and is subsequently raised until it is equal to or higher than that of the pure sol. The lyotropic effect of the salts used (sulphate, tartrate, bromide, thiocyanate) is much less marked in these experiments than in those on swelling and salting out. F. L. U.

Relation between coagulation and gelation points of sols. S. Prakash (J. Indian Chem. Soc., 1932, **9**, 133—136).—Larger quantities of KCl, KBr, K_2CrO_4, K_2SO_4, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ are required to set a jelly than to coagulate the jelly-forming sol ($Fe^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$ arsenates, Zr molybdate and borate, and titanic acid) in the same time. The ratio (R) of the gelation and coagulation concns. (of K_2SO_4) decreases towards unity with increasing purity of the sol ($Fe^{\cdots}$ arsenate). R is greater for K_2SO_4 than for KCl with $Fe^{\cdots}$ arsenate, Zr molybdate and borate, and titanic acid sols. H. B.

Influence of charge on the sedimentation velocity of colloids, especially in the ultracentrifuge. A. Tiselius (Kolloid-Z., 1932, 59, 306—309).—The sedimentation of colloidal particles is retarded as the charge on the particles is increased. The effect is due to an increase in friction, and becomes noticeable only when the particle size falls below a certain val., but the effect has an influence on the determination of particle size by ultracentrifugal sedimentation analysis. The relation $s'=s(1-t_K)$ is derived, where s' and s are respectively the apparent and true sedimentation velocities, and t_K is the fraction of the total electrical conductivity (colloid+electrolyte) which is carried by the colloid ion. Experiments on the velocity of sedimentation of phycoerythrin have given results in accordance with the theory. E. S. H.

Cataphoretic measurements. A. J. Rabinovitsch and E. B. Fodiman (Kolloid-Z., 1932, 39, 310—314).—The technique of electrophoretic measurements is discussed, whence it appears that abs. quant. vals. cannot be obtained by present methods, particularly in view of the varying influence of the overlayer liquid. These difficulties have been studied experimentally with sols of $Fe(OH)_3$ and As_2S_3. A sharp boundary is obtained only if the conductivity of the overlayer liquid is equal to or slightly $>$ that of the sol. Increasing the conductivity of the overlayer liquid relatively to that of the sol lowers the electrophoretic velocity; lowering the p_H of the overlayer liquid has the opposite effect. E. S. H.

Cataphoretic velocity in a concentrated suspension. S. Komagata (Bull. Chem. Soc. Japan, 1932, 7, 137—143).—The electrode on which the colloid is deposited is suspended from a spring balance. The cataphoretic velocity is calc. from the change in wt. The results for suspensions of clay in aq. NaOH agree well with those obtained by the U-tube method. D. R. D.

Colloidal charcoal. II. Cataphoresis. H. Lachs and K. Gestel (Rocz. Chem., 1932, 12, 327—340).—The velocity of cataphoresis ζ of charcoal sols falls as the concn. of KCl rises to $0{\cdot}04M$. ζ increases as the concn. of $K_4Fe(CN)_6$ rises to $0{\cdot}01M$, above which it falls, at first rapidly and them more slowly. ζ is similarly increased by addition of KOH, and greatly reduced by even very small concns. of $ThCl_4$. The results obtained are discussed in relation to Stern's theory (Z. Elektrochem., 1924, 30, 508). R. T.

Physical properties of colloidal clay. C. La Rotonda (Kolloid-Beih., 1932, 35, 413—440).—Colloidal clay of particle size $<0{\cdot}1\mu$, obtained from acid soils, is converted by electrodialysis into H-clay and by treatment with alkalis into Na-, K-, Mg-, and Ca-clays. Viscosity measurements show a max. in H-clay, decreasing to a min. as the $H^{\cdot}$ is replaced by other cations and afterwards rising to higher vals. as saturation is approached. The electrophoretic velocity and ζ potential increase with the cation saturation of the clay. The "suspension effect" (a difference in p_H of the suspension and the ultrafiltrate) was observed in all the systems except the H-clay. E. S. H.

Behaviour of clay gels under small pressures, and influence of the exchangeable base present. R. M. Woodman and G. W. Chapman (J.S.C.I., 1932, 51, 175—178T).—A simple apparatus for measuring the swelling of clays under small excess pressures is devised. Swelling under pressure depends on (1) the total base-exchange capacity of the clay or the SiO_2/Al_2O_3 ratio, (2) the base saturating the clay, and (3) the age of the clay suspension used. A hysteresis effect in subsequent swelling probably occurs on reduction of the pressure to which a clay has been subjected.

Thixotropy of bentonite suspensions. H. Freundlich, O. Schmidt, and G. Lindau (Kolloid-Beih., 1932, 36, 43—81; cf. A., 1931, 1232).—Suspensions of H-bentonite are not thixotropic, but are made so by adding alkali-metal ions, $Tl^{\cdot}$, and to a smaller extent $Ca^{\cdot\cdot}$ and $Ba^{\cdot\cdot}$. $Al^{\cdots}$, $Th^{\cdot\cdot\cdot\cdot}$, and org. bases do not induce thixotropy. The particles of H-bentonite are negatively charged; small concns. of alkali hydroxides raise the ζ potential, whilst higher concns. lower it; multivalent ions cause a reversal of charge. The phenomena of thixotropy, swelling, and electrophoresis in these systems are consistent with the view that the metal aluminosilicates are dissociated, the degree of dissociation depending on the nature of the metal cation. E. S. H.

Lyophilic colloids. XIII. Measurement of small elastic deformations of hydrophilic gels. Agar gel. H. G. B. de Jong and J. P. Hennemann (Kolloid-Beih., 1932, 35, 441—475).—Apparatus and technique for measuring elastic deformations ($<1\%$ of the length of the specimen) of hydrophilic gels are described. The deformation of agar gel is reversible and consists of two partial deformations occurring with different velocities. These have been analysed and expressed by equations. During slow compression H_2O is expressed and is taken up during slow expansion; the process is strictly reversible, therefore, only when the gel is immersed in a liquid in equilibrium with it. E. S. H.

Formation of inorganic jellies. S. Prakash (Allahabad Univ. Studies, 1932, 8, Sci. Sect., 119—154).—A review of published work on jellies of inorg. oxy-acids, basic hydroxides, arsenates, phosphates, molybdates, tungstates, and borates. E. S. H.

Viscosity anomalies of gelatin solutions. M. Pichot (J. Phys. Radium, 1932, [vii], 3, 205—218).—A theory is developed, which describes the observed phenomena in terms of a viscosity coeff. and a coeff. of structure. Both coeffs. are functions of concn., temp., and treatment of the solution. A gelatin solution of given concn. obeys Poiseuille's law above a certain temp., θ. The decomp. of the solution is accompanied by a decrease in the viscosity coeff. to a limiting val., whilst the structure coeff. gradually falls to zero. At temp. below θ the theory is consistent

with the viscosity anomalies, provided that the solution is sufficiently far from gelation. Apparatus and technique for viscosimetry and the graphical determination of the two coeffs. are described.
E. S. H.

Swelling of gelatin. I. A. Karssen and G. C. Heringa (Rec. trav. chim., 1930, 51, 593—597).—A method of preparing isotropic gelatin is described. The total swelling of the latter in dil. AcOH is limited, proportional to the respective initial dimensions in different directions, and reversible. The rates of increase in the length and breadth of a rectangular strip of uniform thickness are equal until the diffusion boundaries from the two surfaces meet, after which the longer dimension increases more rapidly.
F. L. U.

Antagonistic influence of cations on the diffusion velocity of OH ions in gelatin jellies. V. V. Efimov (Kolloid-Z., 1932, 39, 279—280).—The diffusion velocity of OH' in gelatin gel is increased by $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, and $Li^{\cdot}$, and decreased by $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Co^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$. The effects of two univalent ions or two multivalent ions are additive, whilst uni- and multivalent ions are antagonistic. E. S. H.

Dependence of osmotic pressure and micellar weight of gelatin solutions on the temperature and the previous history of the solution. J. Eggert and H. Binger (Biochem. Z., 1932, 247, 85).—Frankel's views (A., 1931, 1368) are criticised.
P. W. C.

Liesegang rings of silver chromate in gelatin. B. N. Desai and G. M. Nabar (J. Indian Chem. Soc., 1932, 9, 141—143).—Increase in the acidity of the gelatin causes the rings to become spiral-shaped and is accompanied by decrease in the time of appearance of the first ring, the distance between the same successive rings, and the no. of rings obtainable. The results do not support Hatschek's statement that addition of acid increases the width of the rings.
H. B.

Physico-chemistry of lecithin. I. Y. Suyeyoshi and K. Kawai (J. Biochem. Japan, 1932, 15, 277—283).—The isoelectric point of lecithin, as shown by the optimum of flocculation, is p_H 4·7, but after some days the val. shifts considerably to the acid side. At p_H vals. below the isoelectric point the micelles are positively charged and hence flocculated by anions; at p_H vals. above the isoelectric point they are negatively charged and flocculated by cations. The sensitivity towards flocculation by salts decreases with the age of the solution.
F. O. H.

Isoelectric points of glycine and alanine. M. Hiraki (J. Biochem. Japan, 1932, 15, 345—357).—Titration of dil. aq. HCl solutions of varying concn. against 0·02*N*-NaOH gave p_H 6·16 at 18° and 6·02 at 25° for glycine and 6·18 at 18° and 6·15 at 25° for alanine. F. O. H.

Relations between colloidal and constitutive changes in some proteins. W. Pauli (Austral. J. Exp. Biol., 1932, 9, 23—31).—The changes which occur when hydrotropic substances [salicylates, $HCO\cdot NH_2$, $CO(NH_2)_2$] act on coagulated protein (electrodialysed ovalbumin, serum-albumin, pseudoglobulin) depend on the nature of the protein, on that of the hydrotropic substance, and on the means by which coagulation was effected. The first stage in the interaction is the same in all cases, but subsequent changes, such as those in the optical activity of the solutions, vary with the protein. The differences suggest the formation of additive compounds (hydrotropic substance–protein). The nitroprusside reaction does not invariably serve as a test for denaturation. W. M.

p_H Stability region of proteins and osmotic swelling. D. J. Lloyd (Nature, 1932, 130, 24—25).—Protein structures giving evidence of a definite mol. orientation show, in contrast to gelatin, a p_H stability range with regard to osmotic swelling. For collagen fibres the range is p_H 4—8·5. L. S. T.

***X*-Ray study of the coagulation of ovalbumin.** W. S. Miller, K. G. Chesley, H. V. Anderson, and E. R. Theis (J. Amer. Leather Chem. Assoc., 1932, 27, 174—182).—The view that the coagulation of ovalbumin involves the elimination of H_2O between the free NH_2 and CO_2H groups is supported by *X*-ray studies. The structure developed when the coagulated albumin is resoaked indicates that the resulting linking is too firm to permit of the re-entry of H_2O. D. W.

Complex coacervation. X. Auto-complex coacervation of lecithin sols containing triolein, cholesterol, or oleic acid, and its biological significance. XI. Auto-complex coacervates of lecithin and their significance for the permeability problem. H. G. B. de Jong and R. F. Westerkamp (Biochem. Z., 1932, 248, 309—334, 335—374).—Hydrosols of soya-bean- or egg-lecithin containing triolein, cholesterol, or oleic acid are coacervated by cations of low valency, whilst the pure lecithin sols are not. In some cases the flocculation curves show several max. Multivalent cations produce a reversal of charge, which occurs at or near one of these max.; no such reversal was noted with NaCl. The point of reversal is approx. coincident with that previously noted for aq. non-electrolytes (this vol., 693). Neutral salts (*e.g.*, NaCl) at a concn. insufficient to cause coacervation inhibit the coacervation due to ions of higher valency (*e.g.*, $Ca^{\cdot\cdot}$); this inhibition is the more marked the greater is the valency of the anion of the added Na or K salt, or the smaller is the cation valency of an added chloride. These phenomena, which are in general similar to those observed in systems containing sol. non-electrolytes, are discussed in terms of changes in the degree of hydration of the complexes.

XI. The coacervates of lecithin vary with the conditions of formation; they may consist of liquid droplets, of granular masses, or of weakly solvated flakes. Their morphological characteristics are described and their behaviour in an electric field has been studied. The grouping of the particles in an electric field indicates a polar nature and the morphology of the clusters bears a relation to the electric charge. Under certain conditions polyphase liquid droplets are produced. The velocity of coacervation in these systems is increased strongly by adding capillary-active substances, thereby increasing the solvation of the auto-complex coacervate. Relations between solvation, electric charge, and permeability are discussed with special reference to processes occurring in biological media. The system lecithin–triolein (cholesterol, etc.)–H_2O is regarded as a model of the protoplasm surface, which is subject to an antagonistic action of $Ca^{\cdot\cdot}$ and $Na^{\cdot}$ as shown above. Factors which lower cell permeability reduce the degree of solvation of the coacervates described, whilst those which raise the permeability of the cell increase the solvation. E. S. H.

Biophysical chemistry of colloids and protoplasm. V. Cofman (Chem. News, 1932, 145, 1—3).

Union of biocolloids. VI. Coagulated egg-albumin and various carbohydrates. S. J. Przylecki and M. Z. Grynberg (Biochem. Z., 1932, 248, 16—38).—The combination of albumin with mono-, di-, and tri-saccharides, Mg hexosediphosphate, *iso*trihexosan, dextrins, amylose, amylopectin, starch, and glycogen has been examined. At a p_H below its isoelectric point the protein combines with phosphorylated carbohydrates. At a p_H above this point, association results from the union of the ionised group of the protein with the positively-charged polysaccharides. The union with amylose and dextrins is probably due to subsidiary valencies and with starch is conditioned by mol. size. P. W. C.

Osmosis and diffusion of some plant colloids. (Starch substances—ligninsulphonic acid—humates.) M. Samec [with L. Knop and Z. Pankovič] (Kolloid-Z., 1932, 59, 266—278).—Measurements of the osmotic pressure of amylopectin, ligninsulphonic acid, humates, and hymatomelanates suggest that the ion of opposite charge to the colloid particle is osmotically inactive. In dil. amylopectin solutions there is an approx. linear relation between concn. and osmotic pressure, but the relation is complicated in more conc. solutions. Amylopectin has an abnormally high diffusion velocity, in which the $H^{\cdot}$ plays a large part in spite of its osmotic inactivity in the same solution. The diffusion of the org. components (erythroamyloses) is normal in comparison. E. S. H.

Colloid-chemical reactions of rivanol. A. Steigmann (Kolloid-Z., 1932, 59, 343—344).—Aq. alkali halide solutions ppt. rivanol in the following order: $I'>Br'>Cl'>F'$. With I in KI rivanol forms a dark blue coloration resembling the starch reaction. E. S. H.

Swelling of graphite. H. Thiele (Z. anorg. Chem., 1932, 206, 407—415).—Graphite which has swollen in oxidising liquids (*e.g.*, $H_2S_2O_7$) exhibits a series of colours in reflected light. Incompletely swollen graphite gives blue, indigo, violet, red, orange, yellow, and grey. Swelling is a property of the graphite form of C and is exhibited by all the natural forms; the "amorphous" retort-graphite and sugar-charcoal do not swell. Liquids which do not cause swelling under ordinary conditions (*e.g.*, H_2SO_4, HNO_3, and 30% $HClO_4$) cause graphite to swell when it is anodically polarised. No swelling takes place under anodic polarisation in aq. HCl, HI, HBr, KCl, or KI. Probably the swelling in oxidising media is due to the formation of a labile oxide of graphite. E. S. H.

Flame temperatures of mixtures of ammonia and its products of dissociation. G. W. Jones, B. Lewis, and H. Seaman (J. Amer. Chem. Soc., 1932, 54, 2166—2170).—For mixtures of air, H_2, and N_2 the max. flame temp., T, is inversely proportional to the amount of N_2. For mixtures of NH_3 with its products of dissociation ($3H_2+N_2$), T is inversely proportional to the amount of NH_3. These data and calculation show that for NH_3–air mixtures T would be about 1700°, if a suitable burner could be developed (cf. B., 1928, 881; A., 1931, 572; this vol., 127). B. E. A. (*c*)

Gas-phase equilibrium between methyl nitrite, hydrogen chloride, methyl alcohol, and nitrosyl chloride. Absorption spectrum of nitrosyl chloride. J. A. Leermakers and H. C. Ramsperger (J. Amer. Chem. Soc., 1932, 54, 1837—1845).—The equilibrium $MeONO+HCl=MeOH+NOCl$, studied by means of the light absorption due to NOCl, is free from side reactions. The equilibrium const. is 0·521 at 298·1°, 0·753 at 323·1° abs. The calc. vals. for the free energy, the heat and the entropy of formation, and the entropy of MeONO at 25° are −100, −16,750 g.-cal., −55·9, and 64·2 entropy units. H. F. J. (*c*)

Vanishing line charts for the calculation of important technical gas equilibria. E. S. von Bergkampf (Z. anorg. Chem., 1932, 206, 317—327).—A method of representing schematically the dependence of four variables on one another is described, and also its application to various well-known equilibria. M. S. B.

Water-gas equilibrium. J. R. Partington and W. G. Shilling (J.S.C.I., 1932, 51, 82T, 222T).—The curves constructed by Bryant (A., 1931, 1233) do not support his choice of sp. heats. Attention is directed to an erroneous statement by Gordon and Barnes (this vol., 695).

Water-gas equilibrium. W. M. D. Bryant (J.S.C.I., 1932, 51, 222T).—A reply to Partington and Shilling (see preceding abstract).

Equilibrium $Fe^{\cdot\cdot\cdot}+I' \rightleftharpoons Fe^{\cdot\cdot}+\frac{1}{2}I_2$ in aqueous solution. H. M. Dawson and E. Spivey (J.C.S., 1932, 1838—1844).—The mass action coeff., K_1, for the above reaction at 25° in the presence of KCl falls from 19·4 to 6·85 as the concn. of KCl is increased from 0·5 to 3·5M, in qual. agreement with theory. Allowance must be made for the formation of ClI_2' and I_3', and for the salting-out effect of KCl on the solubility of I_2 (cf. A., 1926, 236, 244). For the equilibrium $ClI_2' \rightleftharpoons Cl'+I_2$, K_2 varies from 0·629 to 0·637, rising to 0·652 in the presence of 0·1M-HCl. For $I_3' \rightleftharpoons I'+I_2$, K_3 varies from 1·52 to $1·73\times10^{-3}$. The val. of K_1 given by Brönsted and Pedersen (A., 1923, ii, 61) is incorrect. D. R. D.

Perhalide equilibrium in non-aqueous solutions. E. A. Dancaster (J. Physical Chem., 1932, 36, 1712—1732).—The dissociation of Fe, Sn, and Sb perhalides in glacial AcOH has been determined by a distribution method, one solvent being air. Chloroperbromides exist mainly as trihalides in both aq.

and AcOH solution, whilst perbromides exist mainly as tribromides in aq. solution and pentabromides in AcOH. For a halide with a normal val. of the dissociation const., K, in H_2O, the val. is also normal in AcOH, and each val. is approx. const. from 15° to 40°. For Cd and Hg halides, Fe, Sn, and Sb chlorides, and Sn bromides K in either aq. or AcOH solution $>$ the normal val., and increases with the halide concn. In AcOH solutions of these compounds the percentage of simple mols. and ions increases with the halogen concn. and halide dilution. J. H. R. (c)

Salt-forming properties of iodine. M. I. Uschakov (J. Gen. Chem. Russ., 1931, 1, 1258—1265).—I dissociates in EtOH to yield uni- and ter-valent ions. I^I is pptd. by alcoholic $AgNO_3$, leaving $I(NO_3)_3$ in solution, and this, on addition of excess of I, yields INO_3. Salts of these nitrates with pyridine and quinoline are described. R. T.

Equilibrium between lactic and pyruvic acids. R. Wurmser and (Mlle.) N. Mayer (Compt. rend., 1932, 195, 81—83; cf. this vol., 813).—Previous results have been confirmed by the observation that under similar conditions at p_H 7·4 lactic acid reduces cresyl-violet and pyruvic acid oxidises phenosafranine. C. A. S.

Complex salts. V. Effect of di*iso*propyl substitution on the stability of the dimalonatocupriate ion. D. J. G. Ives and H. L. Riley (J.C.S., 1932, 1766—1770).—*Na* and *Cu*^{II} *diisopropylmalonates* have been prepared, the latter being deep blue and readily hydrolysed. Conductivity data are recorded for the Cu salt and the free acid. The val. $K=1·7\times10^{-5}$ for the complex Cu–di*iso*propylmalonate ion shows that this is much more stable than the corresponding Pr^a ion. D. R. D.

Classical dissociation constant of bromocresol-green, chlorophenol-red, and methyl-red in potassium chloride solutions. E. F. Chase and M. Kilpatrick, jun. (J. Amer. Chem. Soc., 1932, 54, 2284—2292).—The classical dissociation consts. in KCl solutions have been determined. The salt error in the colorimetric determination of $[H^{\cdot}]$ is expressed by the ratio of the classical dissociation const. of the indicator in the given solution to that in the standard solution of the same tint. R. H. C. (c)

Reversible two-step oxidation. L. Michaelis (J. Biol. Chem., 1932, 96, 703—715).—A mathematical development of the theory of two-step oxidation–reduction of org. dyes in which semiquinones are intermediate forms (cf. A., 1931, 1309). A. C.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XIV. Products of hydrolysis and aggregation processes in salt solutions of tervalent metals, especially in aqueous chromic salt solutions. G. Jander and W. Scheele (Z. anorg. Chem., 1932, 206, 241—251).—The curve representing the variation of diffusion coeff. with p_H for Cr in aq. $Cr(H_2O)_6(NO_3)_3$ is of similar form to the corresponding curves for Fe and Al solutions (A., 1931, 1369; this vol., 124), indicating the existence of a continuous and overlapping series of sol. Cr compounds, increasingly basic and more highly aggregated as the p_H of the solution increases. Below p_H 2, however, the unimol. ion $Cr(H_2O)_6(NO_3)_2'$ exists alone, but the mol. wt. increases very rapidly with increasing p_H. When the solution contains 2·35 mol. NaOH to 1 mol. $Cr(NO_3)_3$ the polymerised products of hydrolysis contain 600—700 Cr atoms and the mean mol. wt. is 84,000. When the proportion is 1 : 1 the prevailing hydrolysed product contains 2 atoms of Cr. The unimol. normal salts of Al, Cr, and Fe^{III} show increasing readiness to hydrolyse in this order, but the more basic compounds in the order Al, Fe^{III}, and Cr. The experimental data for Cr are in general agreement with those obtained by Bjerrum. M. S. B.

Activity coefficient of benzoic acid in solutions of neutral salts and of sodium benzoate. I. M. Kolthoff and W. Bosch (J. Physical Chem., 1932, 36, 1685—1694).—The solubility of BzOH in H_2O at 25° is $0·02775\pm0·00002$ mol. per litre. The activity of the undissociated acid is 0·0264. The solubility in aq. NaOBz and in aq. solutions of various alkali and alkaline-earth salts has been determined, and the influence of these salts on the activity is discussed. G. M. M. (c)

Ionisation constant of benzoic acid and activity coefficient of benzoate ion in presence of neutral salts. I. M. Kolthoff and W. Bosch (J. Physical Chem., 1932, 36, 1695—1701).—The ionisation const. of BzOH at 25° is $6·7\times10^{-5}$. The $H^{\cdot}$ activity of dil. solutions of BzOH and NaOBz has been determined by means of the quinhydrone and H electrodes, without correction for liquid junction potential. The activity coeff. of BzO′ in $0·01M$-NaOBz containing neutral salts and saturated with BzOH has been determined. G. M. M. (c)

Mean and individual ion activity coefficients of silver benzoate in salt solutions. I. M. Kolthoff and W. Bosch (J. Physical Chem., 1932, 36, 1702—1711).—The solubility of AgOBz at 25° is $0·01162\pm0·00002$ mol. per litre. The mean and individual ion activity coeffs. of AgOBz have deen determined in various salt solutions. Assuming that AgOBz is incompletely ionised in its saturated solution, the calc. vals. of the activity coeff. of BzO′ agree with those obtained from H electrode measurements with solutions containing BzOH, NaOBz, and a neutral salt, uncorrected for liquid junction potential. The normal potential of the Ag electrode against quinhydrone in $0·01M$-HCl and $0·09M$-KCl is $0·2269\pm0·0002$ volt. The activity coeff. of $Ag^{\cdot}$ in $0·01M$-$AgNO_3$ containing neutral salts has been determined. G. M. M. (c)

Thermodynamic properties of solid solutions of lead chloride and lead bromide. A. Wachter (J. Amer. Chem. Soc., 1932, 54, 2271—2278; cf. this vol., 700).—The electrode potentials of solid solutions in which N, the mol. fraction of $PbCl_2$, varies from 0·2 to 1·0 have been measured at 200—300°. If $N<0·9$ the activity of $PbCl_2<0·1$. The solid solution in which $N=0·75$ is the most stable. The Br ions are regularly arranged in the $PbCl_2$ lattice. A. F. (c)

Fusion curve of the system sodium nitrite–potassium nitrite. J. Ettinger (Rocz. Chem., 1932, 12, 362—365).—The existence of an unbroken series of solid solutions is indicated. R. T.

M.-p. curves in the system $NaNO_2$–KNO_2. J. Ettinger (Z. anorg. Chem., 1932, 206, 260—262).—$NaNO_2$ and KNO_2 form a continuous series of solid solutions with a min. m.p. of 230·5° for a mixture of 70% $NaNO_2$. M. S. B.

Fusion diagrams of the systems KF–AlF_3 and LiF–AlF_3. P. P. Fedotéev and K. Timofiev (Z. anorg. Chem., 1932, 206, 263—266).—Compounds of the cryolite type are formed in both cases: $3KF,AlF_3$, m.p. 1025°, and $3LiF,AlF_3$, m.p. 790°. There is probably an unstable compound KF,AlF_3, transition point 575°, but there is no evidence for the existence of a second compound of LiF with AlF_3. M. S. B.

Thermal analysis of isomeric dinitrobenzenes. O. Wyler (Helv. Chim. Acta, 1932, 15, 956).—A reply to van der Linden (cf. this vol., 574). R. S. C.

Crystallisation of binary mixtures of compounds of the malic–tartaric series. J. Timmermans (Rec. trav. chim., 1932, 51, 585—588).—*l*-Malic acid forms a eutectic with *l*-tartaric acid and an equimol. compound with *d*-tartaric acid. Similar behaviour is shown by the normal and acid NH_4 salts, diamides, and Et_2 esters. The term "racemoid" is proposed for compounds formed from optical antipodes of different substances. The different modes of behaviour of racemic mixtures when crystallised with an optically active third substance are classified. F. L. U.

System calcium chlorate–water. V. S. Egorov (J. Gen. Chem. Russ., 1931, 1, 1266—1270).—The solid phases consist of $Ca(ClO_3)_2$, eutectic 76°; dihydrate, eutectic −7·8°; tetrahydrate, eutectic −26·8°; and hexahydrate, eutectic −41°. R. T.

System silver nitrate–pyridine. R. Müller [with G. Wersitsch and H. Bauer] (Z. Elektrochem., 1932, 38, 449—450).—E.m.f. measurements of the element Ag|sat. solution of $AgNO_3$ in C_5H_5N between −20° and 85° show that four transitions occur in the solid phase; Ag begins to separate from the solution at about 50°. $AgNO_3,2C_5H_5N$ is stable between 44° and 35°, $2AgNO_3,5C_5H_5N$ between 35° and 11°, and $AgNO_3,3C_5H_5N$ between 11° and 0°; at lower temp. the solid phase is $AgNO_3$. H. F. G.

Equilibrium in binary systems under pressure. II. System K_2SO_4–H_2O at 25°. L. H. Adams (J. Amer. Chem. Soc., 1932, 54, 2229—2243; cf. A., 1931, 1370).—Compression measurements show a decrease in the compression of H_2O and an increase in fictive vol. of K_2SO_4, as observed for NaCl. The solubility, calc. thermodynamically, increases to a max. of 16·3% K_2SO_4 by wt. at 3800 bars. The solubility curve intersects the freezing pressure curve of ice$_{VI}$ at 10,750 bars and 13·3% K_2SO_4. The observed pressure at the pressure eutectic was 10,880 bars. A. F. (*c*)

Dissociation pressure of silver oxide below 200°. A. F. Benton and L. C. Drake (J. Amer. Chem. Soc., 1932, 54, 2186—2194).—Finely divided Ag slowly takes up O_2 at 160—170°, establishing at each addition a pressure which is independent of the amount already taken up. Decomp. pressures between 173° and 192° are about 17% lower than those obtained from other data at higher temp. These new data give −2450 g.-cal. for the free energy of formation of Ag_2O at 25°. E. J. R. (*c*)

Thermal dissociation of calcium carbonate in an atmosphere of carbon dioxide. II. Existence of primary and secondary dissociation points of Iceland spar. K. Bito, K. Aoyama, and M. Matsui (J. Soc. Chem. Ind. Japan, 1932, 35, 191—195B).—Iceland spar dissociates at 929° under a CO_2 pressure of 1 atm.; dissociation continues on cooling to 915°, but ceases at 914°. On cooling and reheating the specimen, dissociation commences at 915°. H. F. G.

Thermal change of bismuth nitrate in dry air. K. Bito, K. Aoyama, and M. Matsui (J. Soc. Chem. Ind. Japan, 1932, 35, 195—197B).—The behaviour of $Bi(NO_3)_3,5H_2O$, dried at 150°, on heating has been examined. Decomp. (loss of NO_2) commences at 440°; the product melts at 845°, and evaporation commences at 855°. H. F. G.

Pyrolysis of metallic arsenites. E. R. Rushton (J. Physical Chem., 1932, 36, 1772—1798).—The decomp. of arsenites on heating in inert atms. varies with the metal. Al, Mg, Zn, and Pb arsenites have a high dissociation pressure, *p*, and decompose into metal oxide and As_2O_3 only, whereas $Ca(AsO_2)_2$ and $Sr(AsO_2)_2$ also form a little As. Na, K, and Ba arsenites have low *p* and form largely As and arsenates. For Ag and Cu arsenites *p* is small, but owing to easy reducibility of their oxides the metals and As_2O_5 are the chief products. The Fe in $Fe(AsO_2)_3$ is slightly reduced. The extent of thermal dissociation increases with the As_2O_3 content, and the oxidation-reduction reaction is promoted by rapid heating to a high temp. When arsenites are heated in air, oxidation may be superposed on the other reactions. J. H. R. (*c*)

Equilibrium in the system bismuth–sulphur–oxygen. R. Schenck and F. Speckmann (Z. anorg. Chem., 1932, 206, 378—384).—The equilibrium $2Bi_2O_3+Bi_2S_3 \rightleftharpoons 6Bi+3SO_2$ has been investigated from both sides. Evolution of SO_2 begins at 150—200° and reaches a pressure of 1 atm. at 519°. Absorption of SO_2 in the reverse reaction is measurable at 400°. E. S. H.

System KCl–$PbCl_2$–H_2O at 25°. L. J. Burrage (Trans. Faraday Soc., 1932, 28, 529—531; cf. A., 1926, 908).—The system has been investigated with special reference to the conditions which obtain in the neighbourhood of the quadruple point characterised by the coexistence of the solids $PbCl_2$ and $KCl,2PbCl_2$. J. G. A. G.

System potassium nitrate–ammonium nitrate–water. E. Jänecke, H. Hamacher, and E. Rahlfs (Z. anorg. Chem., 1932, 206, 357—368).—The equilibrium diagram is recorded. A form of mixed crystal, not formerly described, is similar to the modification of KNO_3 produced under a pressure of 115 atm. E. S. H.

System $CuSO_4$–$CoSO_4$–H_2O. H. D. Crockford and D. J. Brawley (J. Physical Chem., 1932, 36, 1594—1596).—The 0° and 25° isotherms have been determined. At both temp. the solid phases are $CuSO_4,5H_2O$ and a series of solid solutions in which Cu partly replaces Co in $CoSO_4,7H_2O$. S. L. (*c*)

Compounds of lithium chloride with cobalt chloride. Water as a linking agent in polynuclear cations. H. Bassett and (Miss) I. Sanderson (J.C.S., 1932, 1855—1864).—The system $LiCl$–$CoCl_2$–H_2O has been investigated from 0° to 80° and previous results are found untrustworthy. The solid phases are $CoCl_2,6H_2O$; $CoCl_2,2H_2O$; $LiCl,2H_2O$; $LiCl,H_2O$ (I); and the double *salts* $7LiCl,2CoCl_2,18H_2O$; $3LiCl,2CoCl_2,6H_2O$; and $LiCl,CoCl_2,2H_2O$. In addition, (I) forms a series of solid solutions with $2LiCl,CoCl_2,2H_2O$. Hence, it is supposed that (I) is $(LiCl,H_2O)_3$. Structural formulæ are suggested in which several Li atoms are united in the same cation by means of H_2O mols. (*e.g.*, $[(H_2O)_2Li(H_2O)_2Li(H_2O)_2Li(H_2O)_2]^{\cdots}$). D. R. D.

Ternary system carbamide–water–hydrogen peroxide. E. Jänecke (Rec. trav. chim., 1932, 51, 579—584).—Solubilities of $CO(NH_2)_2$ in aq. H_2O_2 (3—98%) over the temp. range —10° to 40° have been determined, and the behaviour of the ternary system is shown in a triangular diagram. The only compounds formed are $H_2O_2,2H_2O$ and $CO(NH_2)_2,H_2O_2$, each of which forms a eutectic with the other and with $CO(NH_2)_2$. F. L. U.

Equilibrium $Sn+2CO_2 \rightleftharpoons SnO_2+2CO$. G. Meyer and F. E. C. Scheffer (Rec. trav. chim., 1932, 51, 569—573).—The composition of the mixture of CO and CO_2 in equilibrium with $Sn+SnO_2$ varies from 26·4% CO at 500° to 20·2% at 800°. The equilibrium const. is given by $\log K=420/T-0{\cdot}988$, and the calc. heat of the reaction $Sn+2CO_2=SnO_2+2CO$ is 3·8 kg.-cal. F. L. U.

Equilibrium and heat-toning of the reaction $NiO+H_2=Ni+H_2O$. A. Skapski and J. Dabrovski (Z. Elektrochem., 1932, 38, 365—370).—Equilibrium pressures of H_2 and H_2O over $NiO+Ni$ have been measured over the range 450—700°. The mean heat of reaction over this interval is calc. to be 4200 g.-cal. F. L. U.

Equilibria between mixtures of carbon monoxide and carbon dioxide at various pressures in contact with steels of different carbon concentrations at temperatures ranging from 750° to 1150°. A. Bramley and H. D. Lord (J.C.S., 1932, 1641—1669).—The main reactions are $2CO \rightleftharpoons C+CO_2$; $3Fe+2CO \rightleftharpoons Fe_3C+CO_2$; $Fe_3C \rightleftharpoons 3Fe+C$. The equilibria have been investigated by a static method over the range 0·25 to 2·0 atm., with steels containing 0·1—2·0% C, made by the gaseous cementation of pure Fe by CO. The results show that C vapour is monat., that the concn. of free C in the vapour and solid phases follows Henry's law, and that cementite is metastable to graphite at these temp. Carpenter and Keeling's data concerning the Fe–C diagram (B., 1904, 608) have been confirmed, and the graphite solubility line has been added. The following thermochemical data were obtained: $3Fe(\gamma)+2CO=Fe_3C$ (dissolved)$+CO_2+29{,}950$ g.-cal.; $3Fe(\gamma)+2CO=Fe_3C$ (pptd.)$+CO_2+36{,}950$ g.-cal.; $3Fe(\gamma)+C=Fe_3C-4750$ g.-cal.; $3Fe(\alpha)+C=Fe_3C-6950$ g.-cal. D. R. D.

Equilibria in reduction, oxidation, and carbonisation processes in iron. XI. R. Schenck, H. Franz, and A. Laymann (Z. anorg. Chem., 1932, 206, 129—151).—The effect of SiO_2, TiO_2, P_2O_5, and Cr_2O_3 on the reducibility of Fe_2O_3 (cf. A., 1930, 43) has been investigated at 800—1000°. In all cases the reducibility is diminished, due to the formation of less reducible compounds with the oxides. SiO_2 forms fayalite, $2FeO,SiO_2$; TiO_2 forms ilmenite, FeO,TiO_2, and also an orthotitanate, $2FeO,TiO_2$, and P_2O_5 forms $FePO_4$, a compound which appears to correspond with the formula $Fe^{II}{}_3P_4O_{13}$ or a mixture of pyro- and meta-phosphate, $Fe^{II}(PO_3)_2+Fe^{II}{}_2P_2O_7$, and a complex phase $Fe^{II}{}_3[Fe^{III}(PO_4)_2]_2$ which, on reduction, gives $Fe_3P_4O_{13}$ and Fe. Some Fe_3P is also present. The behaviour of Cr_2O_3 is similar to that of Al_2O_3 (*loc. cit.*). A spinel, FeO,Cr_2O_3, is formed, and a mixed crystal phase, Fe_3O_4–FeO,Cr_2O_3 is produced from mixed crystals of the oxides Fe_2O_3 and Cr_2O_3. M. S. B.

Reactions of carbon dioxide with silicates under high pressures. W. Weyl (Glastech. Ber., 1931, 9, 641—660; Chem. Zentr., 1932, i, 724).—The equilibria are displaced towards the carbonate by an increase in pressure and a fall in temp. This displacement is greater with K than with Na silicates, and in glasses of the composition $K_2O:SiO_2$ 1 : 3 separation of K_2CO_3 occurs. During its α–β-transition CaO,SiO_2 does not take up CO_2. Li silicate occupies an intermediate position between the alkali and alkaline-earth silicates, since Li_2SiO_3 can take up marked quantities of CO_2. The gas evolution with glasses containing carbonate indicates that a diffusion process and not a mol. reaction is involved. L. S. T.

Equilibria between metals and slags in melts. II. Dependence of equilibrium $FeO+Mn \rightleftharpoons MnO+Fe$ on temperature and the influence of addenda. W. Krings and H. Schackmann (Z. anorg. Chem., 1932, 206, 337—355; cf. this vol., 125).—The equilibrium const. is lowered by the addition of SiO_2, increased by CaO, and increased slightly by Ca_2SiO_4. The variations of equilibrium const. with the amounts of addenda are expressed graphically. $CaSiO_3$ has no influence. The const. increases with rise of temp. in accordance with the formula $\log K=-7280/T+1{\cdot}503$. The calc. heat of reaction is 33·2 g.-cal. E. S. H.

Dehydration of brucite. W. Büssem and F. Köberich (Z. physikal. Chem., 1932, B, 17, 310—326).—The heat of reaction calc. from the dissociation pressure agrees closely with the val. determined calorimetrically and thus affords no evidence for the formation of a pseudo-structure in the dehydration to MgO. This is confirmed by *X*-ray examination, which shows the product of dehydration to have the periclase structure. The periclase crystallites are oriented in two positions in relation to the original brucite lattice, and the brucite formed on rehydration is oriented. The periclase crystallites formed at low temp. are considerably deformed, but on ignition at 1150° the deformation disappears, and with it the optical double refraction and the last of the H_2O. Complete recrystallisation occurs at 2000°. R. C.

Representation of systems of several components. E. Denina (Rec. trav. chim., 1932, 51, 624—626).—A discussion of general principles. F. L. U.

History and analytical expression of first and second laws of thermodynamics, and rôle of differentials dW and $d\underset{=}{Q}$. G. Tunell (J. Physical Chem., 1932, 36, 1744—1771).—The close relation between thermodynamics and the theory of functions of a real variable is discussed. G. M. M. (c)

Axiomatic [basis] of Nernst's theorem and the limitations of thermodynamics. P. Kohnstamm (Rec. trav. chim., 1932, 51, 538—542).—A general theoretical discussion. F. L. U.

Maximum available work and entropy of formation of silver bromide from its elements. H. Woitinek (Z. Elektrochem., 1932, 38, 359—365).—The e.m.f. of the combination $Ag|AgBr|0{\cdot}5N\text{-}HBr|0{\cdot}5N\text{-}HBr+Br_2|Pt$ has been measured at 0° and 25°. The max. work of the condensed reaction is at 0° 22·96 and at 25° 22·88 kg.-cal. The reaction entropy calc. from the temp. coeff. of the e.m.f. is $-3{\cdot}08\pm0{\cdot}29$ g.-cal. per degree, a result in agreement with Nernst's heat theorem. F. L. U.

Heat of formation of cupric oxide. H. von Wartenberg and H. Werth (Z. Elektrochem., 1932, 38, 401—402).—Determination of the heat effect when H_2 is admitted to a vessel containing a pellet of CuO heated at about 400° in an atm. of CO_2 yields for the heat of formation of CuO from Cu and $\frac{1}{2}O_2$ $38{\cdot}5\pm0{\cdot}2$ kg.-cal. H. F. G.

Heat of formation of hydrogen fluoride. H. von Wartenberg and H. Schütza (Z. anorg. Chem., 1932, 206, 65—72; cf. A., 1931, 912).—Redetermination of the heat of formation of HF by direct combination gave $(H, F)=64{\cdot}45\pm0{\cdot}1$ kg.-cal. at 20°. The measurements were made at 100° to avoid error due to heat of polymerisation. F. L. U.

Heat of dissolution of sodium carbonate and the twin calorimeter. M. Matsui, S. Kambara, and K. Miyamura (J. Soc. Chem. Ind. Japan, 1932, 35, 227—232B).—Using a new form of apparatus the val. at 25° is found to be $5670{\cdot}8\pm8{\cdot}1$ g.-cal. per mol. J. W. S.

Heat of combustion of organic halogen compounds. I. A. Kablukov and F. M. Perelman (J. Gen. Chem. Russ., 1931, 1, 1249—1257).—The substance is placed within the calorimeter in a sealed, thin-walled glass bulb, which is burst by the pressure of the vapour at the beginning of the combustion. In this way loss due to vaporisation is avoided. A small amount of soot remains on the glass after combustion, but the error due to this does not exceed 10—20 g.-cal. The results, whilst of a higher order of accuracy than those of Berthelot or Thomsen, include a variable error due to free halogen and H halide in the products of combustion. R. T.

Thermochemistry of sulphides of antimony, arsenic, bismuth, cadmium, tin, and iron. E. V. Britzke and A. F. Kapustinski (Tzvet. Met., 1931, 1147—1156).—Equilibrium consts. for the reduction of the sulphides with H_2 have been determined. The values of log P_{S_1} (S v.p.) are given by (FeS) $-(14{,}329/T)+5{\cdot}80$; (SnS) $-(15{,}430/T)+8{\cdot}10$; (CdS) $-(15{,}130/T)+3{\cdot}02$; (Bi_2S_3) $-(16{,}270/T)+14{\cdot}25$; ($Sb_2S_3$) $-(12{,}660/T)+8{\cdot}95$. The heats of formation (g.-cal.) from diat. S and solid metals are calc. as: 2FeS, 65,460; 2SnS, 70,520; 2CdS, 69,140; Bi_2S_3, 111,540; Sb_2S_3, 86,490; As_2S_2, 51,430. Heats of formation from rhombic S and heats of roasting reactions are also calc. Ch. Abs.

Thermochemistry of calcium orthophosphates. C. Matignon and M. Séon (Compt. rend., 1932, 194, 2184—2187).—The heats of formation (in solution) of $CaH_4(PO_4)_2,H_2O$, $2(CaHPO_4,2H_2O)$, and $Ca_3(PO_4)_2$ from H_3PO_4 (sol.) and CaO (sol.) are respectively 53·92, 97·57, and 115·51 g.-cal.; the heats of hydration of the anhyd. salts are 4·95, 7·66, and 8·17. Addition of SiO_2 facilitates the reduction of $Ca_3(PO_4)_2$; the thermal data recorded are $Ca_3(PO_4)_2+5C=5CO+\frac{1}{2}P_4$ (vap.) $+3CaO-382{\cdot}9$ g.-cal.; and $Ca_3(PO_4)_2+5C+3SiO_2=5CO+\frac{1}{2}P_4$ (vap.) $+3CaSiO_3-297{\cdot}9$ g.-cal. C. A. S.

Heats of formation and combustion of cellulose nitrate. K. Tomioka (J. Cellulose Inst., Tokyo, 1932, 8, 88—94).—The heat of combustion and the heat of formation decrease linearly with increase in the N content of the material. The heat of formation changes by 75 g.-cal. for 1% N from 958·9 g.-cal. (7·66% N) to 568·7 g.-cal. (13·58% N), and the heat of combustion changes by 135 g.-cal. for 1% N, from 3071 g.-cal. (7·66% N) to 2286 g.-cal. (13·58% N). B. P. R.

Absolute magnitude of the diffusion current in stirred electrolytes. A. Eucken (Z. Elektrochem., 1932, 38, 341—345).—The limiting current in an electrolyte maintained in steady laminar flow parallel to the surface of a polarisable electrode is obtained by calculating the concn. gradient of the depolariser at right angles to the surface, the velocity gradient being assumed proportional to the distance from the electrode. This current $=0{\cdot}807Fch\sqrt{D^2y^2u/a}$, in which h and y are the respective dimensions of the electrode at right angles to and parallel with the direction of streaming, c is the bulk concn. of the depolariser, D its diffusion coeff., and u the velocity of a liquid lamina at a distance a from the electrode. An experimental arrangement has been devised for testing the applicability of the above expression, which is in agreement with observations. Measurement of the limiting current at known rates of stirring enables the diffusion coeff. of a depolariser to be calc. with an accuracy of 10%. F. L. U.

Transport number of magnesium chloride. C. Drucker (Rec. trav. chim., 1932, 51, 574—575).—The transport no. of the anion in aq. $MgCl_2$ exhibits a pronounced min. at about 0·005 mol. per litre, as with $CaCl_2$, $BaCl_2$, $BaBr_2$, and $CdBr_2$. The limiting val. is 0·605, whence it follows that the mobility of the Mg ion is < that usually assumed. F. L. U.

Hydration of ions. J. Baborovský (Arh. Hemiju, 1932, 6, 85—106).—By a modification of

Remy's method the following ionic hydration vals. have been found in *M* and 0·1*M* solutions, respectively: $K^{\cdot}$ 5, 29·3; $Na^{\cdot}$ 8—9, 44·5; $Li^{\cdot}$ 13—14, 62; $H^{\cdot}$ 1, 5; Cl' 4, 26·6; Br' 3, 29·6; I' 2, 31·4. A membrane of parchment-paper separated the anode from the cathode solution. Electro-osmotic action was neglected. The hydration nos. of the halogen ion appear to tend towards a common limit with increasing dilution, suggesting that in the more dil. solution hydration depends on physical rather than chemical forces. The results are compared with those of other investigators. M. S. B.

Hydration of solute ions of the heavier elements. L. H. Flint (J. Washington Acad. Sci., 1932, 22, 211—217).—Hydration vals. have been assigned to the ions of the heavier elements in accordance with the relation assumed for ions of the light elements (this vol., 467). These vals. have been tested by reference to experimental data for electrical conductivity etc., and are found to be, in general, of the right order. M. S. B.

Potential effect on conductivity of strong and weak acids. J. Schiele (Ann. Physik, 1932, [v], 7, 811—830).—The method of Wien and Malsch has been improved so that very small resistance changes can be measured. The effect with strong acids is small, as is to be expected from the theory. With weak acids the effect is much more marked. A. J. M.

Electrode potential of iron. E. Müller and J. Janitzki (Z. physikal. Chem., 1932, 160, 245—256).—The observed potential of an electrode of massive Fe in contact with an aq. solution of Fe^{II} salt is a limiting potential corresponding with equality in the rates of dissolution of $Fe^{\cdot\cdot}$ at active points and of diffusion of the H liberated at the remainder of the surface, which is inactive. By continual scraping of the electrode beneath the surface of a neutral solution its potential becomes less positive and approaches the reversible potential, which is not more positive than $-0{\cdot}512$ volt (ε_h) in *N*-$FeSO_4$. In contact with acid, gentle scraping renders the potential more positive. Experiments with Fe electrodes in aq. NaOH are described. R. C.

Electrode potential of iron. I. Measurements in a hydrogen atmosphere. K. Murata (J. Soc. Chem. Ind. Japan, 1932, 35, 209—214B).—E.m.f. measurements have been made with the cell Fe|$FeCl_2$ (0·1 or 0·01*M*)|sat.KCl|0·1*N*-KCl, Hg_2Cl_2|Hg, special precautions being taken to avoid formation of $Fe^{\cdot\cdot\cdot}$ salt. The Fe electrode consisted of reduced Fe sintered on to an electrolytic Fe wire. The e.m.f. becomes const. after a few days, but a green film is gradually formed on the surface of the Fe and high readings are then obtained. The shape of the electrode, when formed of solid wire, influences the e.m.f. to the extent of about 0·04 volt. The standard electrode potential of Fe at 25° is $-0{\cdot}4265$ volt, and the calc. free energy of formation of $Fe^{\cdot\cdot}$ at 25° is $-19{\cdot}670$ g.-cal. H. F. G.

Electrochemistry of iron. S. Bodforss (Z. physikal. Chem., 1932, 160, 141—157; cf. A., 1930, 423; 1931, 172).—The potential, *E*, in contact with an aq. solution at room temp. of an Fe electrode, the surface of which is continually renewed by grinding within the solution, depends on the p_H and the anions present. In a given buffer mixture *E* is a linear function of the p_H. Cations, even $Fe^{\cdot\cdot}$, do not affect *E*. In absence of grinding, *E* in a buffer solution is not appreciably affected by addition of $FeSO_4$. It is suggested that in these experiments the Fe is "inactive," and that none of the data so far published for the potential of Fe electrodes in solutions of Fe salts gives a real normal electrode potential. R. C.

Periodate[-iodate] potential. E. Abel and O. Smetana (Monatsh., 1932, 60, 181—188).—For the reduction of IO_4' to IO_3' the normal potentials are ${}_0\varepsilon_c = 1{\cdot}175(\pm 0{\cdot}005)$ and ${}_0\varepsilon_h = 1{\cdot}510(\pm 0{\cdot}005)$ volts; the free energy of formation of IO_3' from I and O_2 is $-18{,}500$ g.-cal. (all at 25°). In the determination the platinised Pt electrodes must be free from Cl. Vals. of ${}_0\varepsilon_h$ for a series of reactions of IO_4' with $H^{\cdot}$ and H_2O are tabulated. E. W. W.

Oxidation–reduction potential of system lactic acid–pyruvic acid. R. Wurmser and (Mlle.) Z. de Boe (Compt. rend., 1932, 194, 2139—2141).—A satisfactory catalyst for the reaction $OH{\cdot}CHMe{\cdot}CO_2H\ (I) \rightleftharpoons AcCO_2H\ (II)$ is an autolysate of *B. coli* prepared by Stephenson's method (cf. A., 1928, 549). In presence of PhMe this inhibits oxidation of (II), but accelerates that of (I). Colorimetric and electrometric observations indicate $-0{\cdot}200$ volt as the probable normal potential of the system. C. A. S.

Ammonium acetate as a neutral buffered standard. C. J. Schollenberger (J. Amer. Chem. Soc., 1932, 54, 2568; cf. this vol., 709).—The p_H of a solution of the commercial reagent may be far from 7·0. A mixture of equal vols. of 2*N*-AcOH and 2*N*-aq. NH_3 is invariably very nearly neutral. C. J. W. (*c*)

Potentiometric measurements with borax–sodium hydroxide and disodium hydrogen phosphate–sodium hydroxide buffer solutions. C. Naegeli and A. Tyabji (Helv. Chim. Acta, 1932, 15, 751—758).—The p_H vals. of buffer solutions of $Na_2B_4O_7$–NaOH (9·94—12·39) and of Na_2HPO_4–NaOH (10·87—11·42) are recorded. The inflexion in the p_H–NaOH concn. curve for the first-named is displaced somewhat to the alkaline side of the equivalence point. H. F. G.

Precipitation indicators. C. Naegeli and A. Tyabji (Helv. Chim. Acta, 1932, 15, 758—792).—A comprehensive survey is given of the theory and application of colloidal indicators which at a definite p_H undergo flocculation with or without a noticeable colour change; the sharpest end-point is obtained with sparingly sol. weak acids or bases of high mol. wt. the salts of which form so-called colloidal electrolytes. The flocculation point (p_H 9—11·8) and the range of p_H over which flocculation occurs (0·1—0·3), have been determined for certain azo-compounds containing N·OH and Ac groups. Details are given of the results obtained in titrating weak acids such as BzOH, PhOH, veronal, alanine, and As_2O_3 with these indicators. The results are usually reproducible within close limits, although a correction factor has frequently to be applied. H. F. G.

Physico-chemical studies of complex formation involving weak acids. VI. Solutions of complex cyanides of silver, zinc, cadmium, mercury, and nickel. H. T. S. Britton and E. N. Dodd. **VII. Glass-electrode titrations of vanadic acid.** H. T. S. Britton and R. A. Robinson (J.C.S., 1932, 1940—1954, 1955—1964).—The p_H of solutions obtained by adding aq. KCN to aq. metallic sulphates were determined, using a glass electrode. The conductivities of similar solutions, and of aq. KCN, were also measured, and the % hydrolysis of the Hg solutions was determined (cf. A., 1931, 1233). The concns. of simple metal cation in solutions of the cyanides in aq. KCN were determined potentiometrically, using electrodes of the respective metal or amalgam and (in most cases) a HgCl electrode. The results indicate formation of $Ag(CN)_2'$, $M(CN)_4''$ (M=Zn, Cd, Hg, Ni), and probably $Cd(CN)_3'$. The solubility product $Ag^{\cdot} \times Ag(CN)_2'$ is $5{\cdot}1 \times 10^{-12}$ at 25°; the other compounds do not give const. vals.

II. The data obtained when HCl is added to aq. Na_3VO_4, $Na_4V_2O_7$, and $NaVO_3$ indicate the formation, slow in the cold but immediate on boiling, of Na_2HVO_4 and NaH_2VO_4. A yellow compound, approx. $Na_2O,2{\cdot}5V_2O_5$, is also formed, which is not decolorised by boiling with HCl, but is converted into NaH_2VO_4, Na_2HVO_4, and Na_3VO_4 on boiling in alkaline solution. p_H curves for the back-titration of the acidified solution with NaOH, aq. NH_3, $Ca(OH)_2$, and $Ba(OH)_2$ indicate the formation of $Na_2O,2{\cdot}5V_2O_5$, but not of NaH_2VO_4, Na_2HVO_4, or Na_3VO_4, which are formed only on long keeping or boiling. The complex formed with excess of AcOH is approx. $Na_2O,2V_2O_5$. D. R. D.

Glass electrode. G. Haugaard (Z. physikal. Chem., 1932, **160**, 279—289).—The double layers set up on the opposite sides of a glass membrane separating two solutions are mutually independent. It is suggested that the boundary potentials are determined not by chemical interaction of membrane and solution so much as by physical effects, the membrane acting purely as a boundary wall. In a solution of a uni-univalent salt the smaller ion will be able to approach the membrane more closely than the other, and will therefore determine the sign of the charge of the double layer nearest the wall. The magnitude of the boundary potential will increase with the difference in radii of the two ions and with the salt concn. The effect of alkali chlorides agrees qualitatively with this theory. When the ions differ in valency, the difference in dielectric const. between the two phases at the interface may be a cause of the formation of a double layer. R. C.

New use of vacuum tube in electrometric titrations. I. Polarisation of platinum electrodes in oxidation and reduction reactions. J. L. Kassner, R. B. Hunze, and J. N. Chatfield (J. Amer. Chem. Soc., 1932, **54**, 2278—2284).—A positive grid bias is used, the resulting grid current polarising the Pt electrodes. The arrangement is insensitive to variations in circuit consts. up to 20%. The equiv. point is indicated by galvanometer "kick." R. H. C. (*c*)

Use of thermionic valves for measurement of the potential of cells. F. Müller [with G. Meyer] (Z. Elektrochem., 1932, **38**, 418—428).—Thermionic valve methods are especially suitable for determination of the e.m.f. of cells which have high resistance or are easily polarised. The theory and practical details of such methods are critically reviewed. H. F. G.

Limiting current in the anodic polarisation of metals in aqueous solutions. E. Müller and K. Schwabe (Z. Elektrochem., 1932, **38**, 407—418).—Current–voltage curves have been obtained for Th, Pb, Cd, Cu, and Zn anodes in saturated and unsaturated solutions of their salts. Increase of the anode potential from one const. val. to another causes always a transient rise of the current to a val. greater than its new const. val. Complete passivity is never produced. The results are discussed at length, particularly as regards the nature of the high-resistance film formed on the anode by polarisation; it is probable that friction between the ions in the solution and the walls of the pores in the film is the factor which determines the resistance. H. F. G.

Passivity of electrolytic iron in an alkaline medium. A. Travers and J. Aubert (Compt. rend., 1932, **194**, 2308—2309).—The negative potential of electrolytic Fe in *N*-NaOH increases by 0·72 volt when O_2 is completely removed. The passivity produced by anions such as CO_3 or PO_4 disappears in absence of O_2. The passivity produced in an alkaline medium is due to dissolved O_2, not to OH ions, and the protection of boilers due to addition of 0·5 g. of Na_2CO_3 per litre is diminished if the H_2O is degassed. C. A. S.

Electrochemical periodicities. E. S. Hedges (Nature, 1932, **129**, 870—871).—At low c.d., the potential of a Cu cathode in 10% HNO_3 oscillated continuously in periods lasting approx. 1 sec. with an amplitude of approx. 0·1 volt (cf. this vol., 575). L. S. T.

Peltier effect in the system Ag–$AgNO_3$–H_2O. E. Lange and T. Hesse (Z. Elektrochem., 1932, **38**, 428—442).—Thomson's equations are not directly applicable to electrolytic systems, in which transport of material takes place, and a modified equation for the rate of change of the effect with temp. is developed. Measurements with $Ag|AgNO_3$ aq., however, show that the first equation ($e=\pi/T$) is valid. The variation of π with the Ag concn. and activity is in agreement with that calc. on the basis of a simplified assumption regarding the isothermal heat of transfer. The Peltier effect at the interface between single crystals of the same metal cannot be explained unless the existence of a heat of transfer is assumed. H. F. G.

Affinity of chemical reactions. B. Macků (Publ. Fac. Sci. Univ. Masaryk, 1932, No. 151, 15 pp.).—The van 't Hoff expression is derived by two methods. H. J. E.

Difficulty of deducing the mechanism of a reaction from determination of its velocity. A.

Prins (Rec. trav. chim., 1932, **51**, 576—578; cf. A., 1930, 995).—A further example is given. F. L. U.

Mathematical representation of the course of chemical reactions. J. P. Treub (Rec. trav. chim., 1932, **51**, 543—548).—The usual velocity equations are transformed into others stated to be useful in supervising chemical processes, by taking as unit of time the time required for a given mol. species to reach a certain fraction of its initial concn. Examples are given. F. L. U.

Effect of foreign gases on unimolecular reactions. W. H. Rodebush and M. J. Copley (J. Amer. Chem. Soc., 1932, **54**, 2560). C. J. W. (*c*)

Explosion of oxy-hydrogen mixtures in soap bubbles. A. N. Mitra, H. N. Chatterjee, and H. K. Sen (J. Indian Chem. Soc., 1932, **9**, 163—170).—The ignition temp. of mixtures of O_2 and H_2 in soap bubbles is reproducible provided the same arrangement is used; the temp. depends on the length, shape, and surface of the Pt wire used for ignition (cf. A., 1929, 1016). The ignition temp. is lower for large than for small bubbles and becomes const. when the vol. is greater than 500 c.c. H_2O_2 and O_3 are produced in increasing quantities with 3 : 2, 2 : 1, and 1 : 1 mixtures of O_2 and H_2, but not with 8 : 2 or 7 : 3 mixtures. H. B.

Flame speeds during the inflammation of moist carbonic oxide–oxygen mixtures. W. Payman and R. V. Wheeler (J.C.S., 1932, 1835—1838).—The speed of "uniform movement," when flame travels from an open end towards a closed end of a horizontal tube, has been determined in mixtures of CO and O_2 saturated with H_2O vapour at room temp. The max. is obtained with mixtures near the composition $2CO+O_2$, thus conforming with the theoretical deduction of Payman (*ibid.*, 1920, **117**, 48). E. S. H.

Taylor's theory of active centres and kinetics of heterogeneous gaseous reactions. S. Horiba and T. Ri (Rec. trav. chim., 1932, **51**, 641—647; cf. A., 1928, 376).—The order of reaction in the decomp. of CO at 255° on reduced Ni is successively (1) retarded, (2) first, (3) zero, (4) fractional, (5) first. The initial retardation is caused by poisoning of the active centres by separated C. The peculiar course of the reaction can be best explained by assuming the presence of active centres of different kinds. F. L. U.

Thermal reaction between chlorine and ozone. A. Hamann and H. J. Schumacher (Z. physikal. Chem., 1932, **B**, **17**, 293—309).—At 35—60° there is a period of induction, after which $-d[O_3]/dt=k[Cl_2]^{1/n}[O_3]^{3/2}$, where n is about 3, and k for a given Cl_2 concn. diminishes towards the end of the reaction. The validity of the reaction scheme previously proposed (A., 1929, 1394) seems to have depended on the ClO formed by the reaction reacting rapidly with some impurity. In the present experiments the ClO is present in higher concns., the reaction $ClO+ClO=Cl_2+O_2$ being assumed to have a heat of activation, and by entering into side reactions complicates the course of the reaction. R. C.

Homogeneous combination of ethylene and hydrogen: second-order association reaction. R. N. Pease (J. Amer. Chem. Soc., 1932, **54**, 1876—1884).—In a pyrex vessel at 475—550° and under 1 atm. the reaction is homogeneous and bimol. A collision theory calculation indicates that 10% of the collisions between C_2H_4 and H_2 mols. possessing the activation energy of 43,150 g.-cal. per mol. result in formation of C_2H_6. The rates of formation and dissociation of C_2H_6 give a val. for the equilibrium const. of the reaction $C_2H_6 \rightleftharpoons C_2H_4+H_2$ which agrees with the observed val. S. L. (*c*)

Reaction between oxygen and propylene: activation, oxidation, and polymerisation. S. Lenher (J. Amer. Chem. Soc., 1932, **54**, 1830—1837).—The reaction at high C_3H_6 and low O_2 concns. has been studied at 500—600°. There occur both oxidation of C_3H_6 to MeCHO, CH_2O, HCO_2H, CO, CO_2, and H_2O, and its pyrolysis to higher mono-olefines, butylenes, amylenes, and hexylenes as primary, and olefines, paraffins, and H_2 as secondary products. The presence of a little O_2 lowers the temp. at which pyrolysis is appreciable greatly, and markedly accelerates the pyrolysis. A mechanism of the oxidation and pyrolysis of C_3H_6 and the mono-olefines generally based on activation of the double linking is outlined.
S. L. (*c*)

Kinetics of thermal dissociation of gaseous ethyl bromide. E. L. Vernon and F. Daniels (J. Amer. Chem. Soc., 1932, **54**, 2563—2564).—The reaction $EtBr=C_2H_4+HBr$ appears to be as satisfactory a unimol. reaction as any yet reported. Above 100 mm. at 390—420° the velocity coeff., k, is $3{\cdot}85\times10^{14}e^{-54800/RT}$. Below 120 mm. k falls, and at 20 mm. has about one third of its initial val. Under these low pressures the reaction appears to be purely bimol., and addition of N_2 or H_2 reduces k.
C. J. W. (*c*)

Chemical kinetics of high valency type electrolytes in dilute aqueous solutions. V. K. La Mer and R. W. Fessenden (J. Amer. Chem. Soc., 1932, **54**, 2351—2366).—The thiosulphate–bromoacetate reaction has been studied at 25°, at low concn., in presence of Na, K, Mg, Ca, Ba, and La ions. The kinetics agree with the Debye–Hückel limiting law in presence of univalent ions, and deviate by 40—80% with bivalent ions and by 440% with $La^{\cdot\cdot\cdot}$ at $\sqrt{\mu}=0{\cdot}09$. G. M. P. (*c*)

Speed of decomposition of hydrogen peroxide in presence of hydrochloric acid. E. A. Budge (J. Amer. Chem. Soc., 1932, **54**, 1769—1778).—The decomp. has been studied at 25°, 30°, and 35°. The reaction is strictly unimol., but when followed by observation of the rate of evolution of O_2 exhibits a short period of acceleration, ascribed to supersaturation. The velocity coeffs. obtained agree closely with those of Livingston and Bray (A., 1925, ii, 981). The temp. coeff. is about 3·1.
H. F. J. (*c*)

Reaction between sodium nitrite and hydroxylamine sulphate. R. Stratta (L'Ind. Chimica, 1932, 7, 435—438).—The evolution of N_2O in the reaction between $NaNO_2$ and $(NH_2OH)_2H_2SO_4$ is a unimol. reaction, in which the intermediate NH_2OH,HNO_2

is decomposed. The latter also decomposes to give small amounts of $H_2N_2O_2$. O. J. W.

Velocity of the reaction between sulphur trioxide and carbon tetrachloride. A. Sconzo (Gazzetta, 1932, 62, 295—299).—Errors in a previous paper (A., 1927, 432) are noted. Recalculation shows that the results do not serve to establish whether the reaction is uni- or bi-mol., and that the preliminary formation of an additive compound $2SO_3,CCl_4$ is doubtful. H. F. G.

Rate of hydrolysis of pyrophosphoric acid. A. Kailan (Z. physikal. Chem., 1932, **160**, 301).—Muus' vals. for the velocity coeff. (this vol., 576) agree with Pessel's data (A., 1923, ii, 396). R. C.

Rate of decomposition of xanthic acid. C. V. King and E. Dublon (J. Amer. Chem. Soc., 1932, 54, 2177—2186).—The decomp. of ethyl- and methylxanthic acids in presence of AcOH–NaOAc and NH_2Ph–NH_2Ph,HCl buffers has been followed. The primary and secondary salt effects are analysed. The temp. coeff. averages 6·75. E. J. R. (*c*)

Kinetics of a thermal *cis–trans* isomerisation. II. M. Nelles and G. B. Kistiakowsky (J. Amer. Chem. Soc., 1932, 54, 2208—2215).—For the isomerisation of gaseous Me_2 maleate at 300° up to 5 atm. $k=7{\cdot}7\times10^{-4}/(1+1400/P_{mm.})$ min.$^{-1}$ C_3H_8 accelerates the reaction slightly, CO_2 accelerates it markedly, with decomp. of the esters, and H_2 and N_2 have no effect. At equilibrium the amount of fumarate is >50%. H. A. B. (*c*)

Degradation of quaternary ammonium salts. VI. Effect of substitution on velocity of intramolecular rearrangement. J. L. Dunn and T. S. Stevens (J.C.S., 1932, 1926—1931).—The effect of substitution in the C_6 nucleus of the phenacyl radical on the velocity of the rearrangement $COPh\cdot CH_2\cdot N(CH_2Ph)Me_2X$ (I) $\longrightarrow$ $COPh\cdot CH(CH_2Ph)\cdot NMe_2$ (II) has been investigated for *o*-Br, *m*-Br, *o*-NO_2, *m*-NO_2, *p*-NO_2, *p*-Cl, *p*-Br, *p*-I, *p*-OMe, and *p*-Me. The reaction velocity is diminished by introducing negative substituents, the effect showing an approx. inverse proportion to the dissociation consts. of the similarly substituted benzoic acids. This effect is < and in the opposite sense to the influence of similar substitution in the CH_2Ph radical of (I). Probably the velocity of the process is determined by that of the conversion of the postulated intermediate $COPh\cdot\overset{-}{C}H\cdot\overset{+}{N}Me_2\cdot CH_2Ph$ into (II), which is due to the instability of the anionic C atom, and hence retarded by negative substitution near that point. E. S. H.

Velocity of evolution of hydrocarbons in the reaction between chloromagnesium phenylacetate and aliphatic magnesium compounds. D. Ivanov and A. Spassov (Bull. Soc. chim., 1932, [iv], 51, 619—622).—The reaction between $CH_2Ph\cdot CO_2MgCl$ and $R\cdot MgX$ follows two parallel courses. A hydrocarbon RH, together with the complex $CHPh(CO_2MgCl)(MgX)$ is formed in one reaction and the other leads to the formation of a *tert.* alcohol. The velocity of the first reaction may be taken as a measure of the force of attraction between R and MgX. The attraction increases in the order given for the following R groups: Me, Bu^{β}, *sec.*-Bu, Pr^{α}, Et, Pr^{β}. M. S. B.

Exponential analysis applied to the asymmetric hydrolysis of some β-glucosides with emulsin. S. Mitchell and I. MacArthur (J.C.S., 1932, 1669—1675).—Application of exponential analysis to the time–hydrolysis curve of *dl-sec.*-octyl glucoside gave 8·6 as the ratio of the reaction consts. of the two components, as compared with 8·4 obtained when the glucosides were hydrolysed separately. The β-glucoside of *dl-sec.*-hexyl alcohol gave the ratio 1·5; the β-glucoside of *dl-sec.*-butyl alcohol gave the ratio 5·5, but in this case the *l*-alkyl component was hydrolysed more rapidly than the *d*-alkyl component. E. S. H.

Kinetics of heterogeneous systems. B. Težak (Bull. Soc. Chim. Yougoslav., 1932, **3**, 25—31).—The Cl content (S) of $BaSO_4$ suspended in boiling N-HCl falls with time, according to the equation $-dS/dt=KS(S-S_{\infty})$, where S_{∞} is the val. of S at $t=\infty$ and K is const. This effect is ascribed to dissolution of primary particles, with growth of larger crystals of $BaSO_4$. R. T.

Corrosion with and without the co-operation of oxygen. U. R. Evans and C. W. Borgmann (Z. physikal. Chem., 1932, **160**, 194—204).—The intensity and distribution of the corrosion of a vertical Fe or steel surface under 0·1N-KCl are quite different according as the gas above the solution is air or O_2 or is N_2 or H_2. The corrosion of a horizontal surface under a drop of solution is not affected by variations in the relative humidity of the surrounding air. These findings cannot be reconciled with Liebreich's results (A., 1931, 1016). R. C.

Rusting under conditions of differential aëration. G. Schikorr (Z. physikal. Chem., 1932, **160**, 205—210).—Experiments supporting Evans' differential aëration theory of corrosion are described. It is suggested that Liebreich's results (A., 1931, 1016) are not wholly incompatible with this theory. R. C.

Theory of corrosion. E. Liebreich (Z. physikal. Chem., 1932, **160**, 211—224).—Experiments are described which cannot be explained by Evans' theory of rusting and indicate that the distribution and intensity of corrosion produced on an Fe surface by a liquid such as aq. KCl depend on the products of corrosion, and not on the electrode potential being rendered more positive by O_2. Criticisms (cf. preceding abstracts) are answered. R. C.

Mechanism of primary reaction between oxygen and graphite. Kinetics of combustion of carbon. L. Meyer (Z. physikal. Chem., 1932, B, **17**, 385—404).—The reaction between O_2 and graphite has been investigated under such conditions that mols. leaving the C could not return to it or undergo secondary reactions in the gas phase. Below about 1200° the rate of reaction is proportional to the O_2 pressure and CO_2 and CO appear as primary products in the mol. ratio 1 : 1, which is independent of the temp. and pressure and corresponds with $4C+3O_2=2CO_2+2CO$. This reaction is explained by supposing that the O_2 penetrates deeply into the graphite lattice by dissolution and at the same time passes into a reactive state and disintegrates the lattice. The basal planes are attacked preferentially. As the temp. rises above 1200°, the reaction rapidly slows down, and the ratio $CO_2 : CO$ falls, and at 1600° is about 0·5, the reaction then being of zero order. This change is attributed to diminution in the solubility of O_2 in C, as a consequence of which less and less of the combustion is effected by the above process until ultimately the slower surface reaction (cf. A., 1931, 321) becomes solely responsible. R. C.

Velocity of dissolution of aluminium in aqueous solutions of ferric salts. W. HELLER (Rocz. Chem., 1932, **12**, 341—361).—The velocity of dissolution V of Al in aq. $Fe_2(SO_4)_3$ is very small, in aq. $Fe(NO_3)_3$ greater, and is still greater in aq. $FeCl_3$. V is diminished by addition of SO_4'' to aq. $FeCl_3$, and increased by addition of Cl′ to aq. $Fe_2(SO_4)_3$. 90% of the H produced during the reaction is used for reduction of Fe‴ to Fe″, whilst the remaining 10% is liberated as H_2. The low temp. coeff. of the reaction (1·27 for the interval 25—35°) and the dependence of V on the rate of stirring indicate that its val. depends on the velocity of diffusion. For $FeCl_3$ the velocity coeff. is const. at concns. of 0·15—0·43M. V of Mg in aq. NH_4Cl, H_3PO_4, mandelic, fumaric, or gallic acid is a function of [H˙]. R. T.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, **41**, 234—247; cf. this vol., 577).—The influence of temp., streaming velocity, and other factors on the reduction of CuO by H_2 at 400—900° has been investigated. Under certain conditions CuH is formed intermediately. Photomicrographs of sections of CuO pastilles partly reduced by CO or H_2 show a sharply marked Cu/CuO boundary, indicating that the velocity of reduction is much greater than the velocity of diffusion into the interior. The grains of reduced metal are polyhedral when reduction has occurred at low temp., but this structure is lost at higher temp., whilst d is diminished simultaneously. The structure of the reduced Cu depends not only on the temp. but also on the structure of the original CuO. When CuO is reduced by H_2 at about 450° a section of the reduced pastille shows alternate bands of Cu in two different states, one of which has been produced probably by decomp. of CuH; in such cases the time curve shows periodic fluctuations in rate of reaction. E. S. H.

Reactions between gas and solid. III. Azotation of calcium carbide and effect of pressure of nitrogen on the reaction velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, **7**, 143—154).—The velocity of the reaction $CaC_2+N_2=CaCN_2+C$ has been studied over the range 786—1028°; $-dP/dt=KP/(1-\alpha P)$, where P=pressure, t=time, K and α are consts. depending on temp. and other conditions. The effect of coarseness and of addition of CaF_2 and $CaCl_2$ has been investigated. D. R. D.

Reaction between calcium carbonate and silica. W. MASKILL, G. H. WHITING, and W. E. S. TURNER (J. Soc. Glass Tech., 1932, **16**, 94—110T).—Mixtures of calcite and quartz (1 : 1, 1 : 2, and 1 : 3 mol.) were heated at 700°, 750°, and 800°. 1 mol. of quartz scarcely affected the rate of decomp. of $CaCO_3$, but marked acceleration was caused by 2 and 3 mols. At 700°, 99% dissociation was reached in 170 min. with $1SiO_2$, in 160 min. with $2SiO_2$, and in 80 min. with $3SiO_2$. Similar vals. at 800° were 30, 20, and 15 min. The results could be represented (see following abstract) by: $\log \alpha=K \log t+C$. Experiments using sillimanite grains in place of SiO_2 gave a rate of decomp. greater than that for calcite alone. Au grains also promoted the rate of decomp. The equation $K=\log_e [1/(1-x)]/t$ applied equally well for calcite with SiO_2 or Au. Microscopical and chemical examination for "sol. SiO_2" showed that reaction occurred between the SiO_2 and $CaCO_3$. Appreciable reaction was found at 610° in 5 weeks, at 700° in 3 hr., at 800° in 1 hr. The sol. SiO_2 with the equimol. mixture was after heating 1 hr. at 800°, 4—5%; at 1100°, 19%; at 1200°, 25%; at 1400°, 60%. The amount of reaction at 700—800° was small and its effect on the rate of liberation of CO_2 slight. At 1050° calcite was found to be more reactive than lime (cf. Hedvall, A., 1917, ii, 205, 208). The decomp. of $CaCO_3$ occurring on heating with SiO_2 was mainly the result of heat alone and not of chemical reaction. M. P.

Rate of decomposition of calcium carbonate. W. MASKILL and W. E. S. TURNER (J. Soc. Glass Tech., 1932, **16**, 80—93T; cf. A., 1931, 800).—The rate of decomp. was increased by enlarging the reaction chamber, and was affected by the depth of the layer of carbonate when >5 mm. Heating in a current of dry CO_2-free air (200 c.c. per min.) gave results slightly higher than those of the standard crucible method, but when the CO_2 evolved was absorbed in weighed U-tubes, good agreement was obtained. Attempts to study the effect of grain size by heating large single calcite crystals failed owing to disintegration of these even when the rate of heating was $<2°$ per min.; with limestone grains ($\frac{1}{8}$ in.), in one case evidence of a lower rate of decomp. was obtained.

Discrepancies between the results and those of Whiting and Turner are attributed to different dispositions of the thermocouple. The time t and degree of decomp. α were given by $\log \alpha=K \log t+C$, vals. of K and C being at 610°, 0·833 and −0·85; 700°, 0·633, 0·49; 750°, 0·75, 0·80; 800°, 0·80, 0·93, respectively. Decomp. and temp. T are related by $\log \alpha =K(10^4/T)+C$, where K has the common val. of −8/9. A numerically const. val. is obtained for the velocity coeff. K from the equation $K=\log_e [1/(1-x)]/t$, where x is the fraction decomposed in t min. Vals. for $K\times 10^4$ are at 610°, 6·3; 700°, 81; 750°, 485; 800°, 1000, respectively, giving a val. of approx. 2 for the temp. coeff. (10°). The crit. increment, 95,000 g.-cal., compares well with 80,000 (Brúzs) and 89,000 (Schaefer and Schubert). The authors consider that the process of decomp. is not so simple. M. P.

Velocity of crystallisation of supercooled liquids. W. REINDERS (Rec. trav. chim., 1932, **51**, 589—592).—The flatness of the max. sometimes observed in the curve connecting rate of crystallisation with the apparent degree of supercooling is due to the actual temp. being maintained near the m.p. by the latent heat of fusion, and is not found with substances which crystallise slowly. Regarding the velocity of crystallisation as a linear function of the difference between the free energy of the crystals and of the liquid, this velocity may be expressed by the formula $e^{B}(T_0-T)/e^{A/T}$, in which T_0 is the abs. m.p., and B and A are consts. which can be expressed in terms of the max. velocity of crystallisation, the corresponding temp., and the m.p. An example is given in which the agreement with observation is good. F. L. U.

Aldehyde hydrogen sulphite compounds. I. Rate of dissociation of benzaldehyde sodium hydrogen sulphite as measured by its first order reaction with iodine. T. D. Stewart and L. H. Donnally (J. Amer. Chem. Soc., 1932, 54, 2333—2340).—The rate of reaction with I depends on the velocity of the dissociation reaction yielding HSO_3' or SO_3'', and not on the I concn. It varies with the p_H, and is a min. at 1·8. The apparent heat of activation increases from 19,000 to 24,000 g.-cal., following a sigmoid curve, from p_H 6·5 to 0·03. H. A. B. (c)

Absorption of oxygen by benzaldehyde. H. J. Almquist and G. E. K. Branch (J. Amer. Chem. Soc., 1932, 54, 2293—2302).—If PhCHO purified by distillation until it shows no induction period, and containing 3% BzOH, is shaken with O_2 in the dark at 25° the reaction is of the first order with respect to O_2; in absence of BzOH it is autoinhibited. The rate of formation of peroxide and BzOH at const. O_2 pressure indicates that, with BzOH initially present, a peroxide–BzOH compound (I) is formed and reaches a const. concn. (I) readily oxidises PhCHO to BzOH and so acts as a weak inhibitor by removing active PhCHO. With no BzOH initially present, the primary peroxide changes to BzO_2H which oxidises PhCHO less rapidly than (I); the total concn. of BzO_2H thus passes through a max. In both cases, 3% of the O absorbed enters an unknown side reaction. H. A. B. (c)

Neutral salt effect in ionic reactions. V. Neutral salt effect in concentrated salt solutions. A. von Kiss [with I. Bossányi] (Z. physikal. Chem., 1932, 160, 290—294).—Criticisms are refuted (cf. this vol., 584). R. C.

Nature of the catalytic action of hydrochloric acid in the intramolecular change of *N*-chloroacetanilide. H. M. Dawson and H. Millet (J.C.S., 1932, 1920—1926).—The rate of transformation of *N*-chloroacetanilide as measured by the unimol. const. k is approx. proportional to $[H^\cdot][Cl']$. For the series of solutions represented by (1) cHCl+xNaNO$_3$, (2) cHCl+xNaCl, (3) cHCl+xHClO$_4$, and (4) xHCl (c const., x variable) the val. of $k/[H^\cdot][Cl']$ passes through a min., however, as x increases. The observed reaction velocities may be explained on the assumption that the active catalyst is the HCl mol., when due consideration is given to the change in degree of dissociation of the acid with the nature and concn. of the ions in the reaction medium. Since the ionisation const. K passes through a max. as the ionic strength μ of the solution increases, the concn. of the non-ionised acid will pass through a min. corresponding with the min. val. of $k/[H^\cdot][Cl']$. The variation of K for weaker acids is expressed by $\log K/K_0=a\sqrt{\mu}-b\mu$ when K_0 is the const. in absence of electrolyte. The results obtained for the above series of solutions can be explained by assuming that ionisation of the strong acids varies in the same way with the environment. The results are incompatible with the hypothesis that the reaction velocity is determined by the thermodynamic activities of the reactants. E. S. H.

Catalytic decomposition of hydrogen peroxide by iodine–iodide couple at 25°. H. A. Liebhafsky (J. Amer. Chem. Soc., 1932, 54, 1792—1806).—The mechanism previously proposed (A., 1931, 916) has been confirmed. For vals. of $a_{H^\cdot}<10^{-4}M$, the rate of decomp. is accounted for by the reactions (*a*) $I'+H_2O_2\longrightarrow IO'+H_2O$ and (*b*) $IO'+H_2O_2\longrightarrow I'+H_2O+O_2$. As $a_{H^\cdot}$ increases the reaction (*c*) $HIO+H_2O_2\longrightarrow H^\cdot+I'+H_2O+O_2$ becomes increasingly important, but at the steady state the abs. rate of (*a*) is always equal to the sum of the abs. rates of (*b*) and (*c*). H. F. J. (c)

Effect of salts on the reaction of esterification. A. V. Lozovoj (J. Gen. Chem. Russ., 1932, 2, 65—79).—NaOAc retards, AgCl, AgCNS, Li_2SO_4, $Ba(NO_3)_2$, Na_2WO_4, and $Tl_2(SO_4)_3$ slightly accelerate, and $Sr(NO_3)_2$, KI, Ag_2SO_4, Na_2SO_4, RbCl, $Pb(NO_3)_2$, HgCl, NaCl, $Th(SO_4)_2$, NH_4CNS, $UO_2(OAc)_2$, $Ti(SO_4)_2$, $CoCl_2$, $Ni(NO_3)_2$, $AgNO_3$, $HgNO_3$, $Ce(NO_3)_3$ and $Hg(NO_3)_2$ considerably accelerate reaction, in the order given, to an extent increasing with their mol. concn. At certain concns. of $AgNO_3$ the equilibrium point is shifted from 71·6 to 73% of EtOAc. The catalytic effect of salts is ascribed to elimination of H_2O as a result of hydration of their mols., and to orientation of acid and alcohol mols. within the sphere of hydration. R. T.

Shifting of equilibria by catalysts. N. A. Schlesinger [with E. I. Befort, N. A. Kuprianova, K. D. Panferova, E. A. Zabugina, A. D. Istiunina, E. I. Kamienskaja, and R. G. Malkina-Okun] (Thesis, Saratov, 1932, 1—170).—The esterification of AcOH and EtOH has been studied in the presence of H_2SO_4, HBr, or HCl alone, or together with the corresponding halide of K, Na, Li, Ca, Ba, Cd, or $Hg^{\cdot\cdot}$. Using low concns. of acids, no shifting of equilibrium in the direction of esterification was observed, whilst with high concns. the reaction is complicated by formation of Et_2O. In the presence of salts, the equilibrium const. K varies for low concns. of salt according to the equation $K=b-aC$, where a and b are const. for a given org. acid and salt, and C is the concn. of catalyst. The action of acids and salts is not due to hydration of their ions or mols., since it varies with the org. acid taken, it is greater at higher than at lower temp., and, finally, since glucose, which is hydrated in solution, has no catalytic action. The results are interpreted on the basis of the activity theory. R. T.

Impulse phenomena on heterogeneous catalysts, and possibility of detecting chain reactions. K. Bennewitz and W. Neumann (Z. physikal. Chem., 1932, B, 17, 457—459).—Attempts to repeat Cantor's radiometer experiment (Ann. Physik, 1897, 62, 482) have failed. The theory that the hydrogenation of C_2H_4 on Pt is a chain reaction occurring mainly in the gas phase (A., 1930, 715) must therefore be abandoned (cf. A., 1931, 1374). R. C.

Heterogeneous catalysis of binary gas reactions. II. C. Kröger (Z. anorg. Chem., 1932, 206, 289—303; cf. this vol., 579).—The following reactions are discussed with reference to the author's views of heterogeneous chemical catalysis of the first and second kinds: $2NH_3+3O_2=N_2O_3+3H_2O$; $2HCN+7O=H_2O+2NO+2CO_2$; $2CH_4+3O_2=2CO+4H_2O$; $CH_4+CO_2=2CO+2H_2$; $P_4+10H_2O \rightleftharpoons 2P_2O_5+10H_2$; $4HCl+O_2=2Cl_2+2H_2O$; $H_2+Cl_2=2HCl$; $N_2+3H_2=2NH_3$. M. S. B.

Activation of metals by the addition of foreign substances. II. R. Schenck, F. Kurzen, and H. Wesselkock (Z. anorg. Chem., 1932, 206, 273—288).—When Fe or W is mixed with MgO the formation of carbide by CH_4 (cf. this vol., 238) takes place to a much smaller degree than with the pure metal if the carbide is one in which the at. ratio of metal to $C>1$, as in Fe_3C or W_5C_2. If the ratio is 1, as in WC, the presence of MgO has no influence. The effect is apparently steric. The inhibited tendency to form carbide, however, is probably a cause of the catalytic activity of mixtures of metals of the Fe series with MgO in the formation of CH_4 from CO and H_2. M. S. B.

Effect of supports on the catalytic activity of nickel. C. R. Glass and L. Kahlenberg.—See B., 1932, 644.

Rôle of liquid stationary films in batch absorption of gases. III. Rates of hydrogen absorption and relative rates of catalytic hydrogenation in alcohol. H. S. Davis, G. Thomson, and G. S. Crandall (J. Amer. Chem. Soc., 1932, 54, 2340—2350).—The rates of hydrogenation of $CMe_2{:}CHMe$, Δ^{β}-pentene, and $CH_2{:}CHPr^{\beta}$ in EtOH with Pt–Pt oxide catalysts with particles $0{\cdot}1$—$0{\cdot}3\times10^{-4}$ cm. in diameter have been measured. In the hydrogenation of mixtures of olefines the order of reduction is mono-, di-, and tri-substituted. P. T. N. (*c*)

Decomposition of nitrous oxide on glowing platinum. II. H. Cassel and E. Glückauf (Z. physikal. Chem., 1932, B, 17, 380—384; cf. A., 1930, 1380).—Measurements of the rate of decomp. at 900—1100° abs. with the partial pressure of N_2O kept const. at about 10^{-4} mm. have shown that under this pressure the retardation by O is due to the adsorption, not of O_2, but of at. O. R. C.

Thermal combination of ethylene and bromine at glass surfaces. I. General kinetics at 16°. II. The influence of water. G. Williams (J.C.S., 1932, 1747—1758, 1758—1765).—I. The combination of C_2H_4 and Br_2 is a surface reaction in a glass vessel at room temp. The reaction is a simple addition of Br to the double linking unless Br is in excess, when some supplementary reaction is induced. The kinetics of the reaction are complex: (*a*) the rate of reaction decreases with rising temp.; (*b*) the order of reaction varies in different reaction vessels. For a given surface, lowering the temp. or raising the pressures of the reactants tends to lower the order of reaction. (*c*) For a given surface and reaction order, the velocity coeff. is independent of the initial pressure of C_2H_4, but rises with increasing initial pressure of Br. It does not seem probable that the variation of the adsorption of the reactants with temp. and pressure can account for the magnitude of the observed effects, which imply that the reaction involves more than one stage.

II. H_2O vapour accelerates the C_2H_4–Br_2 reaction, partly by participating in some action at the glass surface. Transition from a second- to a first-order reaction is favoured by (*a*) a wet surface, (*b*) high initial proportion of Br to C_2H_4, (*c*) low temp. Probably Br is hydrated at the glass surface and C_2H_4 reacts with the complex. The rate of reaction becomes independent of the bulk Br pressure when the surface concn. of hydrated Br is relatively high. Chains may start at the glass surface and spread into the gaseous phase. Introduction of $C_2H_4Br_2$ vapour before the reaction increases the rate of reaction. E. S. H.

Catalytic activity of reduced copper chromate and of vanadium oxide in reduction of nitro-compounds. H. A. Doyal and O. W. Brown (J. Physical Chem., 1932, 36, 1549—1561).—The Cu chromate catalysts are superior to the V oxide catalysts for the production of high-grade NH_2Ph by reduction of $PhNO_2$ with H_2, the yield being 99% of theoretical, as against 91·8%, and less $NHPh_2$ is formed. S. L. (*c*)

Reactions of ethyl alcohol on nickel–chromium catalysts. E. H. Boomer and H. E. Morris (Canad. J. Res., 1932, 6, 471—484).—The composition of the gaseous products of the decomp. of EtOH–H_2O mixtures at a series of catalysts containing Ni and Cr has been determined. Mixtures of hydroxides or $NiCrO_4$ are the most active catalysts, but the effect varies with the method of prep. and the temp. The dehydrating power of Cr is largely suppressed by the presence of Ni; with use, the Ni loses its activity more rapidly than the Cr and the dehydrating efficiency of the mixed catalyst may rise. Secondary reactions, producing C and complex org. liquids, usually occur, resulting in the formation of CO_2. E. S. H.

Addition of hydrogen chloride to acetylene and to vinyl chloride in the gaseous phase under the influence of catalysts. J. P. Wibaut and J. van Dalfsen (Rec. trav. chim., 1932, 51, 636—640; cf. A., 1931, 598, 1393).—HCl reacts smoothly with C_2H_2 at 25—195° in presence of $HgCl_2$ on SiO_2 gel (0·1 mol. per 100 g.) to form $CH_2{:}CHCl$. With $BiCl_3$, $FeCl_3$, or $ZnCl_2$ the yield is poor. $ZnCl_2$ catalyses the addition of HCl to $CH_2{:}CHCl$, the product being exclusively $CHMeCl_2$. F. L. U.

Mechanism of hydrogenation catalysis with sodium hydride. II. G. Hugel and Gidaly (Bull. Soc. chim., 1932, [iv], 51, 639—644).—The catalytic activity of NaH is limited to those parts of the mol. which can take up Na. Under suitable conditions Na is then replaced by H. This conclusion has been confirmed by the hydrogenation of styrene to dibenzyl, anisylidenefluorene to 9-methylfluorene, benzylidenefluorene to fluorene and methylfluorene, owing to the removal of PhMe or C_6H_6 from the hydrogenated mol., and diphenylbutadiene to αδ-diphenylbutane. M. S. B.

Transformations of cyanogen. Polymerisation and action of potassium carbonate and sodamide. A. Perret and A. Krawczynski (Bull. Soc. chim., 1932, [iv], **51**, 622—636).—Polymerisation of $(CN)_2$ takes place very slowly at 450—500° under a pressure of approx. 1 atm., but it is catalysed by certain solid surfaces, especially salts. Powdered quartz has a slightly catalytic effect and powdered Thuringian glass a somewhat greater one. KCN has a strong catalytic activity at 440° and remains unaltered. K_2CO_3 shows a still greater activity beginning at 120°, but the salt itself is transformed into KCN to the extent of 21·6%, when heated to 370°. $NaNH_2$ catalyses without chemical change at 90—105°, but above that temp. Na_2NCN and NaCN are obtained, NaHNCN being probably formed as an unstable intermediate product. Above 300° Na_2NCN is gradually changed into NaCN by the action of $(CN)_2$. HCN on $NaNH_2$ gives Na_2NCN and NaCN directly, but more slowly than $(CN)_2$. The N_2 formed in these reactions is probably due to the oxidation of $NaNH_2$ at approx. 160° by its products of decomp. in presence of air. M. S. B.

Zinc electrolytes. I. Purification from nickel. L. Cambi and V. Toja [with F. Cremascoli].—See B., 1932, 607.

Electro-deposition of alloys from metallic cyanides in cyanide solution. K. Masaki (Bull. Chem. Soc. Japan, 1932, **7**, 158—168).—The p.d. between electrodes of Cu, Cd, Ag, Ni, Co, Hg, and Zn, and solutions of their cyanides in aq. NaCN, have been determined. From the curves obtained, the best compositions for depositing Cu–Cd, Ag–Ni, Ag–Co, Cu–Ni, and Ni–Co alloys are deduced, experimental details being given for the first three. D. R. D.

Electro-deposition of platinum, palladium, and rhodium. W. Keitel and H. E. Zschiegner.—See B., 1932, 645.

Reaction of ammonia with active nitrogen, and existence of free NH and OH radicals. J. K. Dixon and W. Steiner (Z. physikal. Chem., 1932, **B**, **17**, 327—352).—The amount of NH_3 formed by interaction of active N and H atoms is proportional to the concn. of H atoms as long as N atoms are present in excess. NH_3 reacts very slowly with active N. Calculation from the observed rate of reaction shows that various of the exothermic exchange reactions of NH_3 with constituents of active N involve a heat of activation, and even N atoms in the metastable ^2P state exhibit reaction inertia. Attempts to draw off NH from the region of discharge when a high-voltage alternating discharge is passed through NH_3 have failed. It is probable that NH is either resolved into N and H by the discharge, or is decomposed by chemical reaction in the region of discharge. It has proved impossible to draw off OH from H_2O vapour through which a discharge is passing (cf. A., 1931, 1215). R. C.

Chemical action of the electric discharge. VI. Influence of the nature of the electrodes on the fixation of nitrogen as nitric oxide, ammonia, and hydrogen cyanide. Measurement of the power factor of the arc. E. Briner and C. H. Wakker. **VII. Study of a 3-kw. furnace using copper electrodes containing small quantities of lithium and calcium.** E. Briner, C. H. Wakker, and H. Paillard (Helv. Chim. Acta, 1932, **15**, 959—969, 970—977).—VI. The increase of yield (per unit power consumption) obtained by using Cu electrodes containing alkali or alkaline-earth metals for the direct synthesis of NO has been determined; with 3% of Li the increase is 152%, and with 1% Li and 1% Ca 116%. With electrodes containing 9·6% of Ag and 3·8% of Li the increase is 120%, and the potential across the arc (10 mm. long, 140 milliamp.) is only 380 volts. The increase of yield is due not only to the lower voltage required but also to the larger quantity of NO formed. In similar experiments on the synthesis of NH_3 the formation of Li and Ca nitrides interfered. An increase of the yield of HCN, at 730 mm. pressure, of 65% has been obtained by using electrodes containing 1·7% Li. The power factor of the arc is 0·92—0·96, and is practically independent of the composition of the electrodes. The results are discussed from the viewpoint of electron emission by the electrodes.

VII. The results obtained previously with small arcs have been confirmed by using 2—4-kw. arcs 40—60 cm. long between electrodes containing Li or Li and Ca. Spectroscopical examination of the radiation emitted by the arc shows that Li (and Ca) atoms are present in certain regions, in confirmation of the view that the increase of yield is due to increased ease of ionisation. H. F. G.

Photokinetics of ozone. I. Decomposition in red light. H. J. Schumacher. **II. Decomposition in ultra-violet light.** U. Beretta and H. J. Schumacher (Z. physikal. Chem., 1932, **B**, **17**, 405—416, 417—428).—I. The kinetics of the decomp. in red light may be quantitatively deduced from the scheme (1) $O_3+E=O_2+O$, (2) $O+O_3=2O_2^*$, (3) $O+O_2+M=O_3+M$ ($M=O_2$ or O_3), (4) $O_2^*+O_3=O_2+O_2+O$, (5) $O_2^*+O_3=O_2+O_3$, (6) $O_2^*+O_2=2O_2$. The absorption spectrum in the yellow and red shows the primary process to be decomp. into normal O_2 ($^3\Sigma$) and normal O (^3P).

II. The decomp. in light of wave-length 313 mμ follows the above scheme, the velocity coeffs. having the same vals. In the primary process excited O_2 mols. ($^1\Sigma$) or O atoms (^1D) may be produced, but must react in the same way as when unexcited. The temp. coeff. of 1·25 is partly due to (2), which has a heat of activation of 4—6 kg.-cal. Reaction (3) occurs once in 10^3—10^5 collisions. In presence of a foreign gas (X) the reactions (7) $O+O_2+X=O_3+X$ and (8) $O_2^*+X=O_2+X$ also play a part. In respect of (7) He and A have about one tenth and N_2 has about half the effect of CO_2 and O_2 in retarding the reaction, and the effects in (8) are qualitatively similar. R. C.

Photochemical dissociation of carbonyl sulphide. W. Lochte-Holtgreven, C. E. H. Bawn, and E. Eastwood (Nature, 1932, **129**, 869—880).—With a H discharge tube as light source, COS shows a continuous absorption spectrum from a sharp limit at 2550±20 Å. extending far towards the ultra-violet. The spectrum appears to correspond with the dissociation of the COS mol., and the observed photochemical dissociation energy of 111±1 kg.-cal. indicates a reaction $COS \longrightarrow CO+S-76$ kg.-cal. The difference, 35 kg.-cal., between the calc. and observed vals. corresponds with the excitation energy of the S atom. L. S. T.

Study of photochemical reactions using photogalvanic elements. S. Schlivic (Bull. Soc. Chim. Yougoslav., 1931, 2, 129—137).—A photovoltaic accumulator is prepared by immersing Pt electrodes in a solution of Na fluorescein in aq. glycerol. The fluorescein is reduced in the presence of light, and is re-oxidised in the dark. This element has a const. e.m.f. Elements containing methylene-blue in place of fluorescein give a higher e.m.f. under diminished than under atm. pressure. R. T.

Photo-reduction of metallic oxides. C. Renz (Helv. Chim. Acta, 1932, 15, 839—842).—When in contact with a liquid possessing reducing properties, such as PhCHO, the yellow form of In_2O_3 is light-sensitive, becoming first grey and then black; the product resembles that obtained by heating In_2O_3 in H_2, and is reconverted into the yellow oxide by air. Neither aldehydes nor light, separately, have any action on In_2O_3. The phenomenon does not occur with Sm_2O_3. H. F. G.

Silver nucleus theory of the latent image. I. Critical nuclear size. W. Reinders and L. Hamburger (Z. wiss. Phot., 1932, 31, 32—53).—In experiments with attenuated Ag layers formed by sublimation in high vac., the limit of physical developability is reached when the average thickness of the layer is equiv. to 0·001—0·005 atom (cf. Esterman and Stern, Z. physikal. Chem., 1926, 106, 399). Only Ag aggregates of 3—4 or more atoms are developable. Reversal may occur in layers of more than 0·01 atom equiv. thickness. The developed solarised layers have a fine-grain structure and a smoother surface than usual. Solarisation in photographic plates is ascribed to the formation of more or less complete Ag layers on the surface of the grains in the first stages of development. J. L.

Nature of the latent image for physical development. II. H. Arens (Z. wiss. Phot., 1932, 31, 68—76; cf. A., 1929, 1382).—For artificially prepared suspensions of Ag (Ag_2S or Au) nuclei in gelatin, the amount of Ag physically developed is dependent only on the no. of grains per sq. cm. and is independent of their size or nature; for a given wt. of Ag per sq. cm., it increases with the degree of dispersion. These relations are shown to hold also for the Ag nuclei in a latent image. J. L.

Photo-electric theory of the latent image. G. Schwarz and F. Urbach (Z. wiss. Phot., 1932, 31, 77—79).—Experiments are briefly summarised in support of the theory that unexposed Ag halide grains possess a protective negative charge on the surface (repelling negative reducing ions) which is removed by exposure to light. Part, at least, of the electrons so displaced are taken up by Ag ions in the cryst. lattice to form Ag nuclei, which are hence only a by-product indicative of latent image formation. The protective action of gelatin is also considered. J. L.

Ultramicroscopic observations on light-sensitive crystals. I. K. Schaum and F. Kolb (Z. wiss. Phot., 1932, 31, 2—31).—The photolysis occurring in crystals when dry, or in Canada balsam or in H_2O has been examined microscopically by direct illumination, with dark-ground illumination, and with vertical and grazing incidence illumination. The substances examined were Ag, Cu^{I}, Cu^{II}, Hg^{I}, Hg^{II}, and Tl halides, Ag oxalate, tartrate, and benzoate, and mixed crystals of Ag and Tl halides. Photographs are given. The rate of darkening, occurrence of diffraction spots, etc. have been observed. Photolysis occurs in weak points of the cryst. lattice, especially at the surface and edges. Greatest sensitivity is found in skeleton and similar shaped crystals. Foreign substances in the crystals, as is to be expected, form centres of disturbance. J. L.

Einstein relation and temperature coefficient in photobromination of cinnamic acid. W. H. Bauer and F. Daniels (J. Amer. Chem. Soc., 1932, 54, 2564—2565).—When accompanying thermal reactions are suppressed a quantum efficiency temp. coeff. of unity may be obtained. The temp. coeff. is 1 at infinite dilution and increases to a limiting val. of 2 at higher concns. The temp. coeff. of the total reaction may vary with the concn. C. J. W. (c)

Light and dark reactions of alcoholic crystal-violet leucocyanide solution with and without addition of potassium cyanide. E. Weyde, W. Frankenburger, and W. Zimmermann (Z. physikal. Chem., 1932, B, 17, 276—284).—In the photochemical conversion of the leucocyanide into the cyanide of the dye one mol. of the latter is formed for each quantum absorbed, and the velocity between −6° and 40° is independent of the temp. The velocity of the reverse dark reaction, brought about by KCN, is proportional to the dye concn., has a temp. coeff. of 5, and is greatly diminished by the presence of a little H_2O. On prolonged irradiation of leucocyanide solutions containing KCN the leucocyanide is completely destroyed, probably by oxidation. The absorption spectra of the various reactants have been determined. R. C.

Examination with ultra-violet light. M. Guyot (Ann. Falsif., 1932, 25, 263—267; cf. B., 1931, 765).—Fluorescence is measured photographically by comparison with light passed through ordinary coloured screens and the use of panchromatic plates. Alternatively it may be determined by means of a photo-electric cell and a mirror galvanometer. T. McL.

Photographic action of slow electrons. R. Whiddington and J. E. Taylor (Proc. Roy. Soc., 1932, A, 136, 651—662).—The photographic action of slow electrons (60—300 volts) has been experimentally determined. L. L. B.

Reducing power of β-radiation. H. A. Colwell (Lancet, 1932, 222, 932—933).—β-Radiation from radon decolorises solutions of methylene-blue, brilliant-green, acid fuchsin, and safranine; it also reduces

Fehling's solution, ammoniacal $AgNO_3$, alkaline picrate, $KMnO_4$, and KNO_3 (to nitrite) solutions.
L. S. T.

Combination of carbon monoxide and oxygen under the influence of radon. S. C. LIND and C. ROSENBLUM (Proc. Nat. Acad. Sci., 1932, **18**, 374—386).—An investigation of the influence of CO_2 on the rate of the α-ray reaction between CO and O_2. The recoil atom effect on the oxidation was also investigated.
A .B. D. C.

Pyrogenic decomposition of sodium sulphate. K. I. LOSEV, N. I. NIKOLSKAYA, and T. G. GUSEVA.—See B., 1932, 597.

Sodium thiocyanate. C. K. BUMP (J. Physical Chem., 1932, **36**, 1851—1852).—On cooling aq. NaSCN, saturated at 60°, monoclinic needles of $NaSCN,H_2O$ separate, the v.p. of a saturated solution of which is 5·2 mm. at 17°, and 7·5 mm. at 25°.
J. H. R. (*c*)

Solid polybromide of potassium. I. W. H. HARRIS (J.C.S., 1932, 1694—1697).—The solubility curves in the system $KBr–Br–H_2O$ have been determined at 0° for the more conc. solutions. Solid $2KBr_6,3H_2O$, but no anhyd. polybromide, exists. The assumed presence of Br_3' and Br_5' in considerable proportion is doubtful. Na gives no polybromide at 0°.
E. S. H.

Topochemical transformations. V. Mechanism of formation of filiform silver on silver sulphide. H. W. KOHLSCHÜTTER (Z. Elektrochem., 1932, **38**, 345—353; cf. this vol., 131).—The growth of filaments of Ag during reduction of Ag_2S by H_2 has been studied in relation to the velocity of reaction and the condition of the Ag_2S. The presence of excess of S in the Ag_2S, and a moderate temp. (440°) of reduction favour the formation of long filaments. Admixture of Ag powder suppresses it completely. One or two Ag nuclei are developed on each grain of Ag_2S and subsequent growth takes place exclusively on these, the Ag required for it being conveyed from other parts of the grain, probably by reason of the higher solution pressure of sub-microscopic particles of Ag formed by reduction. Possible causes of the peculiar growth form are discussed.
F. L. U.

Composition of magnesium oxychloride. H. S. LUKENS (J. Amer. Chem. Soc., 1932, **54**, 2372—2380).—MgO dissolves in aq. $MgCl_2$ of $d > 1{\cdot}16$ and a compound $5MgO,MgCl_2,xH_2O$ subsequently separates. The velocity of the reaction depends on the previous thermal history of the MgO and the temp. On continued treatment with the $MgCl_2$ solution the compound passes into $3MgO,MgCl_2,yH_2O$. The H_2O is loosely combined.
F. D. S. (*c*)

Calcium aluminates. I. Synthesis. II. Micro-structure. S. KONDO and T. YAMAUCHI (J. Japan. Ceram. Assoc., 1932, **40**, 81—87, 87—91).—I. Mixtures of $CaCO_3$ and Al_2O_3 (3 : 1, 5 : 3, 1 : 1, 3 : 5) were heated at 1200—1700° for 1—7 hr.; the free CaO and Al_2O_3 in the products were then determined. In Rathke's method the CaO was dissolved by heating the substance with glycerol at 75° for 25 min. with const. shaking, and then keeping at 75° for 1 hr. Practically pure 3 : 1, 5 : 3, and 1 : 1 aluminates were obtained in 2 hr. at 1540°, 1450°, and 1600°, respectively. The 3 : 5 mixture after 2 hr. at 1700° contained 1% Al_2O_3.

II. For $3CaO,5Al_2O_3$ $n_{D\omega}=1{\cdot}621$; $n_{D\alpha}$ 1·665, $n_{D\beta}$ 1·660, $n_{D\gamma}$ 1·645. The crystals were biaxial and optically negative.
CH. ABS.

Hydrothermal syntheses of calcium aluminates and silicates from lime and alumina or kaolin. II. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, **35**, 256—260B; cf. A., 1931, 1020, 1380; this vol., 707).—On heating a CaO–kaolin mixture, reaction occurs at $\nless$700°, the extent of reaction increasing with rise of temp. up to 1100°. Compounds $xCaO,yAl_2O_3,zH_2O$ can be obtained by heating $CaO–Al_2O_3$ or $CaO–Al_2(OH)_6$ mixtures under H_2O v.p. in an autoclave. Under similar conditions CaO reacts with kaolin at 150°.
J. W. S.

Double salts of zinc iodide. E. VOYATZAKIS (Bull. Soc. chim., 1932, [iv], **51**, 670—672).—The following *compounds* of ZnI_2 or $ZnI_2,KI,2H_2O$ with bases have been obtained: $ZnI_2,2B$ ($B=m\text{-}C_6H_4Me{\cdot}NH_2$), white needles becoming red on exposure to air with the probable loss of 1 mol. of PhMe; $ZnI_2,KI,2B$, white cubes which become green in the air probably losing 1 mol. of B; $ZnI_2,KI,2C_6H_4Me{\cdot}NH_2(o)$, white prisms sol. in H_2O; $ZnI_2,2({\cdot}C_6H_4{\cdot}NH_2)_2$, white crystals; $ZnI_2,KI,2({\cdot}C_6H_4{\cdot}NH_2)_2$, yellow crystals sol. in H_2O; $ZnI_2,KI,2C_9H_7N$, white crystals sol. in dil. HCl.
M. S. B.

Action of mercuric oxide on zinc chloride and of zinc oxide on mercuric chloride. H. PÉLABON and (MLLE.) DELWAULLE (Bull. Soc. chim., 1932, [iv], **51**, 650—653).—If aq. $ZnCl_2$ is shaken up with increasing proportions of HgO, Hg completely displaces Zn at first and the ZnO formed combines with excess of $ZnCl_2$ to form $ZnCl_2,3ZnO,3H_2O$. If the mol. proportion of HgO is greater than that of $ZnCl_2$ the reverse reaction of ZnO on $HgCl_2$ becomes possible. $HgCl_2$ also crystallises as a new solid phase and excess of HgO combines with $HgCl_2$ to form a series of oxychlorides. The colour changes from white, through grey, to maroon as the proportion of Hg increases. 0·02 mol. ZnO with 0·02 mol. $HgCl_2$ in 20 c.c. H_2O gives the same equilibrium as the same proportions of $ZnCl_2$ and HgO. By reducing the quantity of ZnO in the first case the same equilibrinm is still obtained. Hence ZnO forms a pure phase. The HgO formed combines with excess of $HgCl_2$ to give $2HgCl_2,HgO$.
M. S. B.

Mercuric chlorobromide. R. STRATTA (L'Ind. Chimica, 1932, **10**, 726—727).—The Debye–Scherrer diagram of the product obtained by melting equimol. mixtures of $HgCl_2$ and $HgBr_2$ confirms the formation of the compound HgClBr which Losana (cf. A., 1926, 908) had foreseen from thermal analysis.
O. F. L.

Analysis of solutions of basic aluminium chloride. W. D. TREADWELL and M. ZÜRCHER [with W. WEBER and J. W. HOEKSTRA-KLEIN] (Helv. Chim. Acta, 1932, **15**, 980—995).—When a solution of basic $AlCl_3$ is titrated potentiometrically, breaks in the curve occur at p_H 3, due to neutralisation of acid, at p_H 5—6 (AlOCl), p_H 8·5 [$Al(OH)_3$], and p_H 11 (aluminate). F.-p. measurements with solutions having an Al : Cl ratio of 1 indicate the presence of AlOCl. Potentiometric titration shows that several hr. are required for complete conversion of the basic salt into normal $AlCl_3$. Basic $AlCl_3$ solutions yield with $Na_2C_2O_4$ solution a cryst. ppt. of probable structure $(HO\cdot Al\dot{:}O_2\dot{:}Al)_2C_2O_4$; the reaction will detect 5% of basic chloride in solution. When NaOH is added to a solution containing AlOCl, the $AlO^{\cdot}$ is converted first into $Al_2O_2\cdot OH$, and then into a form of $Al(OH)_3$ which is much less sol. in NaOH than is the normal form. Analysis of a basic $AlCl_3$ solution may be effected by adding an excess of $Na_2C_2O_4$, to remove $AlO^{\cdot}$, and then KI and KIO_3, and titrating the I liberated with $Na_2S_2O_3$ solution, but electrometric titration with NaOH is more satisfactory; for accurate determination of the basic salt content the solution should be heated for 1 hr. on the water-bath with an excess of dil. HCl, the excess of acid being titrated with NaOH. Basic Al perchlorates are formed in solution, but have little stability, probably because of the great affinity of ClO_4' for H_2O; conditions are similar in nitrate solutions, whilst solutions of sulphate occupy a position intermediate between those of perchlorate and chloride. H. F. G.

Preparation and properties of titanium tetrabromide and titanium tribromide hexahydrate. J. C. Olsen and E. P. Ryan (J. Amer. Chem. Soc., 1932, **54**, 2215—2218).—The solubility of $TiBr_4$, d_4^{20} 3·25, in g. per 100 c.c. at 20° is: EtOH, 287; Et_2O, 3·6. It is sol. in CCl_4, $CHCl_3$, HBr, and HCl, and decomposed by HNO_3, H_2SO_4, aq. NH_3, and aq. NaOH. $TiBr_3,6H_2O$ has m.p. 115°. F. D. S. (*c*)

Heteropoly-acids of germanium. III. A. Brukl and B. Hahn (Monatsh., 1932, **60**, 145—149; cf. this vol., 351).—Electrometric titration of 12-molybdogermanic acid (A., 1930, 1537; 1931, 322) shows no unsaturated complex acids; in neutral 4-basic Na, Ba, or $Hg^{\cdot}$ *salts* the complex is unstable, only acid salts being stable. E. W. W.

Lead suboxide, Pb_2O. M. Le Blanc and E. Eberius (Z. physikal. Chem., 1932, **160**, 129—140).—The thermal decomp. of PbC_2O_4 may be represented by $2PbC_2O_4=PbO+Pb+3CO_2+CO$. The proportion of CO in the gas given off diminishes as reaction proceeds, due to its reducing PbO. *X*-Ray and microscopic examination shows the residue to consist of Pb and PbO only. R. C.

Hydrazine tetrathionate. J. Voríšek (Chem. Listy, 1932, **26**, 286—287).—In the presence of air oleic acid is reduced to stearic acid by $(N_2H_5)_2S_x$, part of which is simultaneously oxidised to N_2H_4 tetrathionate. R. T.

Reversibility of the reaction $NaNO_2+NO_2=NaNO_3+NO$. J. Szper and K. Fiszman (Z. anorg. Chem., 1932, **206**, 257—259).—In the electrolysis of fused $NaNO_2$ pure NO separates at the anode in the early stages. This is due to a secondary reaction: $NaNO_2+NO_2=NaNO_3+NO$. When heated in a stream of NO_2 for 3—4 hr. at 315—450° $NaNO_2$ is completely oxidised to $NaNO_3$. The process may be reversed, but by heating $NaNO_3$ in NO for 6—7 hr. at 315° only about 5% is reduced to $NaNO_2$. M. S. B.

Decomposition of metallic nitrates and nitrites. III. Manganous nitrite. C. Montemartini and E. Vernazza (L'Ind. Chimica, 1932, **10**, 577—582).—By mixing anhyd. $MnSO_4$ and $Ba(NO_2)_2$ in presence of abs. EtOH and rapidly evaporating the EtOH solution, minute crystals of $Mn(NO_2)_2$ were obtained. The decomp. of $Mn(NO_2)_2$ on ebullition is complex and produces NO, NO_2, N_2, MnO, Mn_2O_3, and $Mn(NO_3)_2$. O. F. L.

Reaction of gases with incandescent tantalum. M. R. Andrews (J. Amer. Chem. Soc., 1932, **54**, 1845—1854).—Ta filaments have been heated at 3400° abs. in gases under low pressure. With N_2 absorption increases with the pressure until 100 vols. are absorbed, beyond which the equilibrium pressure falls as absorption increases. Absorption continues until TaN is formed. The amount of H_2 absorbed depends on the concn. of H atoms in the gas. With O_2 absorption is followed by oxide formation. In hydrocarbons the carbides Ta_6C_5 and TaC, both of high m.p., and with the sp. resistances of 180×10^{-6} and 18×10^{-6}, respectively, are formed. S. L. (*c*)

Behaviour of tungstic acids towards sodium hydroxide. A. M. Morley (J. Physical Chem., 1932, **36**, 1655—1671).—WO_3 and four standard tungstic acids (A., 1930, 1262) were digested in various concns. of NaOH at 25° for about 200 days. At intervals the amounts of W in solution were determined before and after ultrafiltration. p_H measurements showed that neutralisation occurs at once. The WO_4'' formed reacts with the excess of acid to form negative colloids, which are dispersed by low concns. of NaOH, but coagulated by higher concns. The max. amount of acid thus peptised varies with the type of acid. Variation in results may be due to change in the dispersing medium owing to formation of intermediate tungstates, or in the solid or disperse phase, or to the hydrolytic formation of colloidal tungstic acid. J. H. R. (*c*)

Polyhalides containing fluorine. H. S. Booth, C. F. Swinehart, and W. C. Morris (J. Amer. Chem. Soc., 1932, **54**, 2561—2562)—These compounds may be prepared by chlorinating a mixture of a saturated alkali fluoride solution with 1 equiv. of I, preferably acidified with HCl, until the colour of I disappears, by chlorinating a mixture of 1 mol. of alkali fluoride with 1 g.-atom of I to const. wt., or by treating the acidified saturated fluoride solution with a slight excess of aq. ICl_3 The *compounds* $CsFICl_3$, m.p. 194°, *d* 3·565, decomp. above 300° to give CsF, and $RbFICl_3$, m.p. 172°, *d* 3·159, decomp. at about 300°, have been prepared. C. J. W. (*c*)

Reduction of permanganate by manganous sulphate. P. Dubois (Compt. rend., 1932, **194**, 2213—2215; cf. A., 1891, 270; 1929, 1156).—The interaction of $KMnO_4$ and $MnSO_4$ has been examined by varying relative amounts, concn., temp., and p_H of the reactants and solutions; in no case is it represented by $2KMnO_4+3MnSO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4$, but the oxide varies from $MnO_{1\cdot65}$ to nearly MnO_2. C. A. S.

Preparation and properties of iodine monochloride. J. Cornog and R. A. Karges (J. Amer.

Chem. Soc., 1932, **54**, 1882—1887).—ICl, m.p. 27·19°, is prepared by adding solid I to an excess of liquid Cl_2, driving off part of the Cl_2 by warming, again adding I to make the composition correspond with ICl, and keeping above the m.p. for 24 hr. V.-p. measurements indicate that ICl is a polar liquid. At a vapour concn. of 0·00507 mol. per litre the entropy of vaporisation is 33·4 g.-cal. The liquid acts as a dissociating solvent for KCl and NH_4Cl.
H. F. J. (*c*)

Rhenium and its compounds. N. Pushin (Bull. Soc. Chim. Yougoslav., 1931, **2**, 111—128).—A review of the chemistry of Re. R. T.

Dark blue nickel oxide. M. Centnerszwer and H. Zyskowicz (Z. anorg. Chem., 1932, **206**, 252—256).—NO has no action on Ni foil between 50° and 150°, but it reacts with Ni powder with the formation of a dark blue Ni oxide. The same oxide is obtained with increasing ease as the temp. rises to 290° in NO, air, or O_2, the readiness of formation increasing for the gases in the order given. Above 290° it passes into yellowish-green NiO. M. S. B.

Supposed isomerism among the pallado-diammines. H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw (J.C.S., 1932, 1895—1909).—The pink and yellow series of compounds of formula PdA_2X_2 (where A is an amine and X an acid radical) are not isomeric. The pink compounds, $[PdA_4]PdX_4$, are analogues of Magnus' salts. This is shown by the formation of pink compounds from the pallado-tetrammines, $[PdA_4]Cl_2$, and K_2PdCl_4, by the formation of $[PdA_4]PtCl_4$ and $[PtA_4]PdCl_4$, by decomp. of the pink compounds with $AgNO_3$ (giving $[PdA_4](NO_3)_2$), and by chlorination under various conditions to give the anticipated products. Similar reactions show the yellow series to consist of monomeric substances corresponding with the α-platinous diammines. Mixed α-tetrammines, $[PdA_2A'_2]Cl_2$, have been prepared and their decomp. with HCl has been studied. β-Diammines and β-tetrammines are absent from the Pd series. The stereochemistry of the Pd atom is compared with that of the Pt atom (cf. this vol., 562). There are no longer any chemical grounds for assuming *cis-* and *trans-*planar isomerism among Pd compounds. E. S. H.

Spark-in-flame method of spectrographic analysis, and mutual effects of elements on one another's emission. R. Hultgren (J. Amer. Chem. Soc., 1932, **54**, 2320—2328).—A new method of spectrographic analysis, utilising the spectrum of a spark discharge through a flame, overcomes the disadvantages of the low excitation of the flame, and has the advantage that the sample is introduced uniformly into the exciting spark. Elements of low resonance potential, notably Na, introduce error into the determination of other elements. A new type of step sector photometer is described. H. A. S. (*c*)

Disgregation of insoluble mixtures. A. Sconzo (L'Ind. Chimica, 1932, **7**, 145—147).—In the analysis of mixtures of salts containing a constituent insol. in acid, only such constituent and not the whole mixture should be fused with Na_2CO_3 and K_2CO_3. Volatile compounds are liable to be lost entirely during the fusion. T. H. P.

Short method for calculating moisture percentages. N. McKaig, jun. (Science, 1932, **75**, 612—614). L. S. T.

Photometric micro-analysis of drinking and service water. II, III. C. Urbach.—See B., 1932, 658.

Determination of active chlorine. J. C. Harral and F. W. M. Jaffé.—See B., 1932, 641.

Determination of traces of hydrochloric acid in the presence of hydrobromic acid. G. G. Longinescu and T. Pirtea (Bul. Chim. Soc. Române Stiinte, 1930, **33**, 65—67).—The mixture of chloride and bromide is pptd. completely by $AgNO_3$ after acidifying with HNO_3. The washed ppt. is extracted with dil. aq. NH_3. 1 c.c. of 0·1% KBr is added, the solution acidified with HNO_3, and filtered. Any chloride in the original ppt. now appears as KCl in the filtrate (AgCl+KBr=KCl+AgBr). If on the addition of $AgNO_3$ the ppt. formed is pure white, and therefore contains no AgBr, the original ppt. must have contained at least 1 mg. of AgCl. The operation may be repeated with successive amounts of 1 c.c. of the KBr solution until a yellow ppt. is obtained; from the amount of KBr used the Cl content of the original mixture can be calc.
A. B. M.

Colour reagents for detecting Cl′, Br′, and I′. C. Palmeri and G. Rizzi (L'Ind. Chimica, 1932, **7**, 147—149).—The reagents recommended are: (1) microcryst. Hg_2CrO_4 mixed with pptd. $CaCO_3$; (2) powdered Ag_2CrO_4 mixed with pptd. $CaCO_3$; (3) powdered mixture of AgCNS and $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$; (4) solution of Cl_2 in CCl_4. (1) and (2) keep indefinitely and react with halide salts, either dry or in neutral or slightly acid solution, to give sol. chromates, which form yellow solutions; 0·0005% of Cl′ is detectable in solution. Reagent (3), which must be stored in a closed vessel in the dark, gives red $Fe(CNS)_3$ with halide salts, even in highly acid solution. Reagent (4) remains unchanged almost indefinitely. The prep. of the reagents is described. T. H. P.

Colour reaction for the identification of Cl′, Br′, and I′. A. Sconzo (L'Ind. Chimica, 1932, **10**, 573—575).—The test proposed by Palmeri and Rizzi (preceding abstract) is not characteristic of these ions. $BaCl_2$, forming insol. $BaCrO_4$, gives no reaction, whilst $HgCl_2$ producing a slightly sol. chromate shows only a weak coloration. Dil. solutions of KCNS, Na_2S, KIO_3, $Na_2S_2O_3$, and cyanides as well as $CaCO_3$ in presence of NH_4 salts give a positive reaction. O. F. L.

Determination of bromides in presence of iodides and chlorides. A. G. Baitschikov (J. Chem. Ind., Russia, 1931, **8**, No. 15—16, 54—58).—Conditions for oxidation with $KMnO_4$ of I′ to IO_3', Br′ to Br, and Cl′ to Cl_2 are specified. Br and Cl_2 are removed with $CHCl_3$ and treated with $NaHSO_3$ giving Br′ and Cl′. Treatment with MnO_4' under other conditions gives Br but not Cl_2; the Br is then determined iodometrically. Ch. Abs.

Analytical application of the reduction of sulphurous acid to hydrogen sulphide. E. Donath

(Chem.-Ztg., 1932, 56, 483).—SO_2 is reduced to H_2S by $SnCl_2$ in hot HCl. As and Sb if present are successively pptd. as sulphides. The reaction is sensitive. H. J. E.

Analysis of nitrous oxide by solubility in water. A. L. Chaney and C. F. Lombard.—See B., 1932, 598.

Rationalisation of gravimetric analysis. II. Colorimetric determination of phosphoric acid. III. Colorimetric determination of phosphoric acid in fertilisers. N. E. Pestov (J. Chem. Ind., Russia, 1931, 8, No. 15—16, 22—36; No. 20, 15—22). —II. Optimal conditions are specified, and a considerable increase in accuracy is recorded.

III. Details of procedure are given. Ch. Abs.

Reduction of phosphomolybdic acid to "molybdenum blue," and the determination of phosphate in biological materials in presence of silicate and arsenate. Ernst Tschopp and Emilio Tschopp (Helv. Chim. Acta, 1932, 15, 793—809).—The literature relating to the formation of molybdenum blue, especially by reduction of phosphomolybdic acid by means of phenolic and NH_2-compounds, is reviewed. The relative reducing activities of many amines and phenols in a solution containing $NaHSO_3$ and Na_2SO_3 have been determined; reduction occurs in all cases, but is relatively slow for *m*- and *o*-derivatives as compared with *p*-derivatives, and is most rapid and complete with compounds containing an NH_2 group para to an OH group. *p*-Methylaminophenol sulphate in 0·2% solution is suitable for the quant. reduction of phosphomolybdate, since its action is, within wide limits, independent of the acidity of the solution, relatively high salt concns. do not interfere, the depth of colour produced is proportional to the P present, and no reduction of excess MoO_3 takes place; $Fe^{\cdot\cdot}$ and (after addition of HSO_3') $Fe^{\cdot\cdot\cdot}$ do not interfere, but oxalate, citrate, and tartrate must be absent. For determination of PO_4''' in presence of SiO_3'' or arsenate an excess of HSO_3' should be added to inhibit formation of complex molybdic acids. Methods based on these considerations for the determination of PO_4''' in, especially, org. materials such as urine, egg, milk, bile, etc., are given in detail. H. F. G.

Colorimetric determination of arsenic. G. E. Youngburg and J. E. Farber (J. Lab. Clin. Med., 1932, 17, 363—366).—The biological material is oxidised with H_2SO_4, HNO_3, and perhydrol; As is pptd. as sulphide, which is oxidised and the As determined colorimetrically after addition of Na_2MoO_4 and $SnCl_2$ Ch. Abs.

"Chloramine" as reagent. O. Tomíček and B. Sucharda (Časopis Českoslov. Lék., 1931, 11, 285—289, 309, 320; Chem. Zentr., 1932, i, 1123).—0·1*N*-Chloramine-*T*, which is stable when kept in brown bottles, is applicable to the determination of As^{III}, Sb^{III} (with Me-red), As^{III}, Sb^{III}, Sn^{II}, Fe^{II}, $Fe(CN)_6''''$, and I' (potentiometrically). A. A. E.

Determination of soluble silica in volcanic tuffs. A. Steopoe (Bul. Chim. pura apl. Bukarest, 1929, 32, 37—44; Chem. Zentr., 1932, i, 710; cf. this vol., 588).—Extraction with 10% Na_2CO_3+1%NaOH or 1% NaOH gives vals. which vary according to the fineness of the material and the duration of treatment. Al_2O_3 and Fe_2O_3 are also dissolved. L. S. T.

Detection of traces of alkali metals. R. Bossuet (Bull. Soc. chim., 1932, [iv], 51, 681—686).—A solution of the alkali salts is absorbed on a small plate of $Mg_2P_2O_7$ obtained by calcining $Mg(NH_4)PO_4$. The $Mg_2P_2O_7$ is heated on graphite supports in the O_2–C_2H_2 flame, when it melts to a small ball and practically disappears, the alkali salt having thus been practically all employed in colouring the flame, which is examined spectrographically. The principal spectral rays of the alkali metals are obtained without interference from other rays and the method is extremely sensitive. The following limiting wts. (mg.) were detected: Li 0·5, Na 0·03, K 0·015, Rb 0·015, and Cs 0·03. M. S. B.

Double ferrocyanides and some of their applications. T. Gaspar (Anal. Fís. Quím., 1932, 30, 398—405).—A review of the author's work on the use of double ferrocyanides for the detection and determination of the alkali metals and Tl, determination of Mg, separation of Ca and Mg from Ba and Sr and of Sn from Sb, and for determination of Co. H. F. G

Determination of sodium. G. B. van Kampen and L. Westenberg (Chem. Weekblad, 1932, 29, 385—386).—For (*e.g.*) vegetable matter, the sample (5 g.) is ignited and the ash is boiled for a few min. with HCl; powdered CaO is added until, after boiling for 10 min., the solution is alkaline. The mixture is filtered and the filtrate evaporated to dryness with $HClO_4$; after separation of the pptd. $KClO_4$, which should be washed first with 1% $HClO_4$ solution and then with 96% EtOH, the solution is evaporated to dryness, a small quantity of MgO being added to reduce the danger of explosion. The residue is dissolved in H_2O, the filtered solution is evaporated to about 2 c.c., and a solution of Mg U acetate, prepared by Kahane's method, is added to ppt. Na. The ppt., after drying at 105°, contains 1·5% Na. H. F. G.

Reagent for the lithium ion. Separation of lithium from magnesium. Determination of lithium. Separation of arsenite from arsenate. T. Gaspar (Anal. Fís. Quím., 1932, 30, 406).—The reagent is prepared by adding to a 5% solution of Na_3AsO_4 an excess of aq. NH_3 and then sufficient EtOH to produce turbidity; the solution is filtered, or sufficient H_2O is added to yield a clear solution. With $Li^{\cdot}$ the reagent gives a quant. copious faintly pink ppt., which may be dried or ignited, and weighed. If Mg is present it may first be pptd. with $NaAsO_2$ solution. AsO_4''' may be separated from AsO_2' by addition of an ammoniacal solution of LiCl containing EtOH. H. F. G.

Indicator for titration of silver. I. F. Sierra and F. Burriel (Anal. Fís. Quím., 1932, 30, 366—371).—KI solution is added slowly to a mixture of 20 c.c. of the solution containing Ag, 1 c.c. of 5% $Cu(NO_3)_2$ solution, and a few drops of benzidine sulphate suspension or, for dil. solutions, of benzidine acetate solution; if the solution is stirred vigorously a characteristic greenish-yellow to blue coloration is produced at the end-point, owing to adsorption of Cu benzidine iodide and oxidation products of benzidine by the pptd. AgI. The method is satisfactory for

N—0·001*N*-Ag solutions and the result is independent of the quantity of indicator present and of the acidity, within fairly wide limits. The error is < 0·5%.
H. F. G.

Colorimetric determination of small amounts of silver. E. E. Jelley (J.S.C.I., 1932, 51, 191—193T).—A rapid and accurate colorimetric method of determining Ag in solutions and suspensions containing 1—20 mg. Ag per litre is based on reduction of ammoniacal Ag solutions by $Na_2S_2O_4$ in presence of gelatin to form clear yellow Ag sols of reproducible shade. The Ag content of Ag and Ag_2S deposits may be determined by adding Br–H_2O to convert the Ag into AgBr and then adding NH_3 to bring the Ag into a solution suitable for reduction by $Na_2S_2O_4$. Cu, Co, Ni, and Cd interfere, and must be separated if present. In particular, a trace of Cu in any of the reagents used gives the sols an orange instead of a yellow colour, and so vitiates the accuracy of the result. As gelatin is added to the ammoniacal Ag solution prior to reduction, any gelatin present in the material for analysis need not be removed.

Volumetric determination of magnesium in presence of free acid and alkali metals. J. Clarens and J. Lacroix (Bull. Soc. chim., 1932, [iv], 51, 667—668).—Mg can be completely pptd. as $MgCO_3$ by just neutralising the acid solution to the yellow of Me-red with KOH, boiling for about 10 min. with Na_2CO_3 in presence of a little pptd. and dried Al_2O_3, and titrating the excess Na_2CO_3 in the boiling solution using Me-red as indicator. If Ca is also present the total Mg and Ca must be determined as carbonate and Ca then determined in another sample as oxalate.
M. S. B.

Antimony electrode in electrometric determination of magnesium. B. B. Malvea and J. R. Withrow (J. Amer. Chem. Soc., 1932, 54, 2243—2247).—An electrode of commercial stick Sb, sand-papered smooth, may satisfactorily replace the H electrode in the electrometric determination of Mg in its salts and in presence of Ca salts, if there is not less than 0·10 g. of MgO in 150 c.c. of solution. In fairly conc. solutions a large excess of Ca does not influence the result, but in dil. solutions much smaller amounts cause error. The graph of potential against vol. of alkali added exhibits a sharp inflexion corresponding with the commencement of the pptn. of Mg. A second inflexion marks the completion of pptn., but is so indefinite that the exact end-point of the titration is not readily located. The graph of $\Delta E/\Delta V$ against the vol. of alkali, however, has two well-defined maxima.
E. B. S. (*c*)

Quantitative spectrum analysis. III. Cadmium contained in zinc oxide. IV. Copper in lead. A. Iwamura (Mem. Coll. Sci. Kyoto, 1931, A, 14, 327—331, 332—335; cf. A., 1931, 1143).—III. The ZnO is made into a pellet with a little HCl and the intensity of the Cd line at 2288 Å. measured. The method will detect 0·00015% Cd in ZnO.

IV. For the determination of traces of Cu, an org. compound is melted with 20 g. of Pb and the intensity of the Cu line 3274 Å. in the emission spectrum is measured. The sensitivity is 0·00035% Cu in the Pb.
A. R. P.

Traces of copper and lead in conductivity water. N. Schoorl (Chem. Weekblad, 1932, 29, 338—343).—Methods for the determination of traces of Pb and Cu are reviewed. Removal of Pb from H_2O by shaking with pptd. $CaCO_3$, and determining the Pb colorimetrically, gives accurate results if the $CaCO_3$ is sufficiently fine; with Cu the removal is less complete. Freshly-pptd. $Mg(OH)_2$ removes the last traces of Cu, but it also readily adsorbs humus etc., which interferes with the subsequent colour reaction; Br–H_2O should therefore be added if necessary before the $Mg(OH)_2$ treatment. By this method, also, all As present is transferred to the ppt. Traces of Pb may be removed by $CaCO_3$ in presence of large quantities of Cu if KCN is first added to the slightly alkaline H_2O, and the Cu may be subsequently removed by acidifying the solution and shaking with $Mg(OH)_2$. Full practical details are given.
H. F. G.

Adsorption indicators. I. Iodometry of copper. F. Sierra (Anal. Fís. Quím., 1932, 30, 359—365).—When a solution of a Cu salt [$CuSO_4$, or preferably $Cu(NO_3)_2$] is added drop by drop to a solution containing $Na_2S_2O_3$, an excess of KI, and 2—3 c.c. of 4% benzidine acetate solution, $Na_2Cu_2(S_2O_3)_2$ is formed under certain conditions of concn. On addition of an excess of $Cu^{\cdot\cdot}$ beyond the quantity equiv. to the $Na_2S_2O_3$ originally present the momentary liberation of I causes the appearance of a deep blue coloration, but subsequently a Cu benzidine iodide is produced; this compound forms with the oxidation products of the benzidine present and the $Na_2Cu_2(S_2O_3)_2$ an adsorption complex, and the end-point of the reaction is rendered evident by a characteristic and sharp colour change. The result is influenced considerably by variations of the concns. of the solutions used; a suitable solution contains 20 c.c. of 0·02*N*-$Na_2S_2O_3$, 10—15 c.c. of 0·2*N*-KI, and 3 c.c. of 5% benzidine acetate solution, whilst the Cu solution should contain 0·79—7·9 g. of Cu per litre. For more dil. solutions a greater excess of KI should be used with 1 c.c. of indicator solution. Benzidine gives a sharper end-point than does starch in iodometric titrations, but a correction, dependent on the concn. of the solutions used, is usually necessary.
H. F. G.

Volumetric determination of aluminium. J. Clarens and J. Lacroix (Bull. Soc. chim., 1932, [iv], 51, 668—670).—The free acid is first neutralised by KOH until the red colour of Me-orange added to the solution suddenly decreases in intensity. Me-red is then added and the solution boiled and titrated with KOH to a permanent yellow, the difference between the two readings giving the val. required. When the initial solution is only slightly acid it is advisable to add excess of HCl. The same method is employed if Ca or Mg is present, but in the latter case a little $Mg(OH)_2$ may also be pptd. This can be determined by back-titration with acid and a correction applied. Mg in the solution may then be determined as previously described (see above).
M. S. B.

Physical method of determining ferrous and ferric iron formed by the actions of potassium dichromate and potassium permanganate on ferrous salt. M. Prasad and P. Y. Deshpande

(J. Indian Chem. Soc., 1932, 9, 133—136).—The amounts of $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ in solutions obtained by incomplete oxidation of $Fe^{\cdot\cdot}$ with $K_2Cr_2O_7$ or $KMnO_4$ are determined by measuring the absorption borders and comparing them with those of known solutions.
H. B.

Characterisation of tervalent iron with thiocyanates. C. H. LIBERALLI (Rev. Soc. Brasil. Chim., 1931, 2, 485—492).—The well-known interference of certain salts etc. with the CNS test for $Fe^{\cdot\cdot\cdot}$ is attributed to interaction of the coloured complex ion $[Fe(CNS)_6]'''$ (cf. Schlesinger and van Valkenburgh, A., 1931, 670) with Cl', F', Br', NO_2' ($[Fe(NO_2)_6]'''$ is probably formed), etc. in neutral media, and can be obviated in many cases by performing the test in a slightly acid solution. Contrary to the observations of Treadwell, small amounts of NO_3' do not interfere with the test; excess of HNO_3, as of any other mineral acid, destroys the red colour as $H^{\cdot}$ interacts with the $[Fe(CNS)_6]'''$ complex, forming $Fe^{\cdot\cdot\cdot}$ and HCNS. PO_4''' and HPO_4'' interfere in neutral or only slightly acid solutions, $FePO_4$ being pptd. (with H_3PO_4, complex ferriphosphate ions may be formed), but in the presence of HCl, PO_4''', like AsO_4''', does not interfere. $Cu^{\cdot\cdot}$ (cf. Ag) gives an insol. thiocyanate, and $Au^{\cdot\cdot\cdot}$ an insol. complex thiocyanate of unusual type, but with excess of the reagent the colour due to $Fe^{\cdot\cdot\cdot}$ appears in the filtrate.
E. L.

Separation of common elements into groups. I. Precipitation by ammonium hydroxide. E. H. SWIFT and R. C. BARTON (J. Amer. Chem. Soc., 1932, 54, 2219—2229).—The separation of Fe, Cr, and Al from Mn, Ni, Co, and Zn by adding aq. NH_3 to the dil. solution in presence of NH_4Cl is most effective when the amount of aq. NH_3 is sufficient to make the solution alkaline to methyl-red, and excess is avoided. If the solution has a vol. of only 3—5 c.c. and is saturated with NH_4Cl, addition of a large excess of aq. NH_3 causes a better separation of Fe from Mn, Ni, Co, and Zn, but 5 mg. of Al and considerably more Cr remain in solution. An excess of aq. NH_3 is essential for separating Bi from Cu, but not for separating Bi from Cd.
W. T. H. (c).

Separation of the ammonium sulphide precipitate. J. KUNZ (Helv. Chim. Acta, 1932, 15, 854—855).—CoS and NiS are separated from the group ppt. by means of dil. HCl. To the acid solution is added NaOAc, and Zn is pptd. by H_2S. The solution is then boiled and rendered strongly alkaline with NaOH, and NaOCl solution is added to ppt. Fe and Mn, Cr and Al remaining in solution as CrO_3'' and aluminate, respectively. The ppt. is dissolved in HCl, and basic $Fe^{\cdot\cdot\cdot}$ acetate is pptd. from the neutral solution; the Mn may then be pptd. as MnS.
H. F. G.

Transformations of salts of tervalent metals in solution. II. Separation and determination of the violet and green forms of chromic sulphate and of chrome alum. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 1932, 7, 432—435).—The violet and green forms of $Cr_2(SO_4)_3$ can be separated quantitatively by pptg. the former with EtOH. If not already present in the solution an amount of K_2SO_4 equiv. to that necessary for the formation of Cr alum should be added, and the concn. of the latter adjusted to about 4—5% before the addition of EtOH, sufficient of which should be added to make its concn. 70%.
O. J. W.

Determination of uranium in carnotite ore. W. W. SCOTT.—See B., 1932, 598.

Determination of tin in ferrotungsten and tungsten ores. K. KIEFER.—See B., 1932, 644.

Automatic micro-compensation calorimeter. L. ALGERA (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 906—917).—An automatic micro-compensation calorimeter for botanical use is described and the accuracy of measurement discussed. W. R. A.

Apparatus for optical studies at high pressure. T. C. POULTER (Physical Rev., 1932, [ii], 40, 860—871).—Selection of materials and constructional methods for high-pressure equipment up to 30,000 atm. are discussed.
N. M. B.

Lens effect of pressure windows. T. C. POULTER and C. BENZ (Physical Rev., 1932, [ii], 40, 872—876; cf. preceding abstract).—Measurements and methods of correction of the lens effect for glass or quartz windows in high-pressure optical systems are discussed.
N. M. B.

Colorimetric determinations. E. CANALS and E. CABANES (Bull. Soc. Chim. biol., 1932, 14, 238—262).—Experiments carried out with I, $CuSO_4$, $KMnO_4$, methylene-blue, glucose (Lewis–Benedict method), and cholesterol (Grigaut method) to compare the accuracy of colorimetric determinations using the Duboscq colorimeter, the Arsonval differential spectrometer, the Pellin spectrocolorimeter, the method of comparison with standards, and the dilution method, indicate that the first of these gives the best results. The determinations should be made in a dark room using artificial light from a source of variable intensity placed behind a ground-glass screen. The liquid column should be 5—30 mm. high. A technique for the colorimetric determination of cholesterol based on Grigaut's method (J. Pharm. Chim., 1910, 1, 138) is described.
A. L.

C.I.E. colorimetric standards and their use. T. SMITH and J. GUILD (Trans. Opt. Soc., 1932, 33, 73—134).—A discussion based on resolutions of the Commission Internationale de l'Eclairage, 1931.
C. W. G.

New type of interference refractometer. W. E. WILLIAMS (Proc. Physical Soc., 1932, 44, 451—464).—The beam from the central part of the collimator is divided into halves, which are then laterally displaced, and reunited after passing through the gas tubes. Interference patterns are formed at the focal plane of the telescope. A new method of combining it with a spectrograph for dispersion measurements is developed.
C. W. G.

Photochemical technique. I. Simple capillary mercury-vapour lamp. F. DANIELS and L. J. HEIDT. **II. Construction and tests of a quartz monochromator.** L. J. HEIDT and F. DANIELS (J. Amer. Chem. Soc., 1932, 54, 2381—2384, 2384—2391).—I. A cheap quartz lamp useful as an intense source of ultra-violet for photochemical investigations and for illuminating the slit of a monochromator is described.

II. Attempts have been made to increase the radiation intensity by using a large monochromator and working under favourable optical conditions.
M. M. (c).

Preparation of dust specimens for microscopical examination. W. Scheffer (Angew. Chem., 1932, **45**, 148).—The dust is sprinkled sparingly on a slide coated with a thin film of warm gelatin solution; alternatively, the slide may be pressed lightly on the surface from which the specimen is to be taken. Cellulose ester solution or linseed oil films should be used for dusts which may not be wetted. For fine particles which exhibit Brownian movement a 7% gelatin solution is heated for 30 min. on the water-bath with albumin and a little PhOH; the solution, after decantation, is optically clear.
H. F. G.

Preparation of purified gold electrodes for the spectrograph. T. A. Wright (Met. and Alloys, 1932, **3**, 146—150).—Ag is removed as AgCl from the solution in aqua regia; Au is pptd. by SO_2 and aq. NH_3, redissolved in aqua regia, diluted, and repptd. by $H_2C_2O_4$ and aq. NH_3. The metal is spectroscopically free from Cu, Ag, Ni, Zn, and the Pt group metals. In view of its extreme softness, special precautions are required for cold-rolling or drawing.
E. S. H.

Electroanalysis with rectified alternating currents. I. A. Atanasiu and T. Ionescu (Bul. Chim. pura apl. Bukarest, 1931, **33**, 69—74; Chem. Zentr., 1932, i, 707—708).—Pulsating direct current from rectified alternating current is suitable for analysis. The rectifier consists of a Ta plate, 6×1—1·5 cm., as anode, a Pb wire 0·9 cm. diameter as cathode, and 750 c.c. of H_2SO_4, d 1·2, with 1% $FeSO_4$, as electrolyte.
L. S. T.

Apparatus for the continuous recording of p_H. A. E. J. Vickers, J. A. Sugden, and R. A. Bell (Chem. and Ind., 1932, 545—554, 570—574).—The construction and technique of an apparatus consisting of a glass electrode, a thermionic potentiometer, and a milliammeter or Cambridge thread recorder are described. A pair of matched valves is used as resistances in the potentiometer; the principles of design of thermionic potentiometers are discussed fully. It is claimed that the apparatus eliminates the drift of zero usually experienced with the use of the thermionic valve. Whilst designed particularly for measuring $[H^{\cdot}]$ of soils, clays, coloured liquids, cloudy suspensions, and materials which are strongly reactive with dye indicators, or which may have a poisoning effect on the H or quinhydrone electrode, the apparatus is of general applicability, especially when a continuous record is required.
E. S. H.

Mercury electrodes. P. S. Tutundžić (Bull. Soc. Chim. Yougoslav., 1931, **2**, 163—174).—A rotating Hg electrode giving accurate results in the electrotitration of Hg and Cu is described. The results obtained for Zn are high owing to oxidation of the amalgam.
R. T.

New gravimetric microanalytical method. J. Donau (Monatsh., 1932, **60**, 129—140).—The author's filtering cup (A., 1912, ii, 199; 1913, ii, 424) has been improved.
E. W. W.

Surface-tension measurement. A. Ferguson and S. J. Kennedy (Proc. Physical Soc., 1932, **44**, 511—520).—A capillary tube method for determining surface tension, not involving a knowledge of the d of the liquid, is developed. The surface tensions of aq. solutions containing up to 0·6% of p-$C_6H_4Me\cdot NH_2$ have been determined.
C. W. G.

Apparatus for accurate and rapid gas analysis. E. Martini (Biochem. Z., 1932, **247**, 86—88).—An absorption pipette is described.
P. W. C.

Distillation apparatus for the preparation of very pure water. L. Ramberg (Svensk Kem. Tidskr., 1932, **44**, 130—135).—Two forms of laboratory stills, fitted with special spray arresters and quartz condenser tubes, are described; these are utilised for redistilling ordinary distilled H_2O when a very pure product is required, as in conductivity experiments.
H. F. H.

Apparatus for continuous extraction by chloroform. H. Paget (J.S.C.I., 1932, **51**, 190T).—The apparatus depends on the principle that the vessel containing the aq. solution to be extracted is closed, so that the solvent is forced back into the reservoir.

Direct-reading γ-ray electroscope. L. G. Grimmett (Proc. Physical Soc., 1932, **44**, 445—450).—A Lindemann electrometer, a high resistance, and a special ionisation chamber are used. The γ-ray activity of 1 mg. Ra can be determined to 0·5% in 3 sec.
C. W. G.

Evaporation of Ag, Be, Cr, and Si. C. H. Cartwright (Rev. Sci. Instr., 1932, [ii], **3**, 298—304).—Full experimental details for the prep. of thin films of these elements by evaporation are given.
C. W. G.

Nomogram for determining the solubility of brushite in dilute sodium chloride solutions. J. W. H. Lugg (Austral. J. Exp. Biol., 1932, **9**, 231—233; cf. A., 1931, 911).—If the p_H is known it is possible, with the aid of the nomogram, to calculate, from the inorg. analytical figures of solutions containing small amounts of Ca and P and a preponderance of NaCl over all other salts present, whether there is saturation, under-saturation, or supersaturation with regard to $CaHPO_4,2H_2O$.
W. M.

Calibration of volumetric glassware and analytical weights. Anon. (Paper Trade J., 1932, **94**, T.A.P.P.I. Sect., 270—271).—The T.A.P.P.I. tentative standard methods are described.
H. A. H.

Preparation and standardisation of volumetric solutions. Anon. (Paper Trade J., 1932, **94**, T.A.P.P.I. Sect., 272—274).
H. A. H.

Determination of coefficients in chemical equations. C. H. Liberalli (Rev. Soc. Brasil. Chim., 1930, **2**, 256—265).—The method of working out the coeffs. for equations of oxidation–reduction reactions by equating the electric charges (valencies) of the participating elements is illustrated.
E. L.

Geochemistry.

Lysimeter investigations. II. Composition of rain water at Geneva, N.Y., for a 10-year period. R. C. Collison and J. E. Mensching (New York State Agric. Exp. Sta. Tech. Bull., 1932, No. 193, 19 pp.).—The annual average pptn. contained 9 lb. of N (>86% of this as NH_3 and remainder as NO_3'), 41 lb. of S, and 16 lb. of Cl per acre. Variations in the proportion of S per annum were less than those of N. HCO_3' occurred at the rate of 12—92 lb. per acre. The mineral contents of rainfall are sufficient to necessitate their consideration in lysimeter trials. A. G. P.

Conductivity of Belgrade drinking water. P. S. Tutundžić (Bull. Soc. Chim. Yougoslav., 1931, 2, 77—95).—The content of dissolved substances may be deduced from the conductivity of drinking water. R. T.

Mineral water of Rogaške Slatine. A. Režek (Bull. Soc. Chim. Yougoslav., 1931, 2, 213—223).—The temp. and composition of the waters of two springs have not changed since 1907. R. T.

Conductivity of Makisch and Sava River water. P. S. Tutundžić (Bull. Soc. Chim. Yougoslav., 1932, 3, 33—42).—The conductivity method for determination of salt content gives good results for river and other natural waters. R. T.

Salts in subterranean waters around Palmyra. V. Frolow (Compt. rend., 1932, 194, 2153—2155).—The total salts in the waters of a spring at Palmyra, and of two wells, determined throughout a year, vary between 1·27 and 2·29; 1·27 and 3·07; and 1·61 and 6·97 g. per litre, respectively. C. A. S.

Microbiological lime precipitation in tropical seas. W. Bavendamm (Arch. Mikrobiol., 1932, 3, 205—276).—The calcareous sludge from waters surrounding the Bahamas contains S bacteria, cellulose- and carbamide-decomposing organisms, SO_4-reducing and N-fixing bacteria. Chalk pptn. is essentially a biological process, the mechanism of which is discussed. A. G. P.

Liquid carbon dioxide in the depths of the ocean. H. Wattenberg (Nature, 1932, 130, 26).—A crit. discussion relating to the occurrence of plankton. L. S. T.

"Rain of ashes" at Bucharest in February, 1929. A. Steopoe (Bul. Chim. Soc. Române Stiinte, 32, 1932, 51—54).—A yellow dust which fell together with snow in a gale of wind in various parts of Roumania consisted mainly of SiO_2, and was in many respects similar to a volcanic tuff. The presence of humic acid, however, indicated that the dust originated from wind-swept fields bare of snow. C. I.

Volatile constituents in magma and formation of magmatic residual solutions. P. Niggli (Rec. trav. chim., 1932, 51, 633—635).—A general theoretical discussion. F. L. U.

Minerals containing calcium and antimony. G. Natta and M. Baccaredda (Atti R. Accad. Lincei, 1932, [vi], 15, 389—395).—Various Sb ochres containing Ca have been examined. Those containing less than about 4% of CaO consist essentially of partly hydrated Sb_2O_4, but in those containing >12% of CaO the Sb is present as Sb_2O_5; the composition of ochres of this second group ranges from $CaO,Sb_2O_5,3H_2O$ to $3CaO,2Sb_2O_5,8H_2O$. The *X*-ray spectra of several such ochres have been determined; the crystals are cubic, with *a* 10·25—10·26 Å. Vals. of $d_{\text{calc.}}$, $d_{\text{obs.}}$ after heating at 750°, and no. of mols. in the unit cell are: romeite, 4·98, 4·71—5·07, 4; atopite, 5·32, 5·03, 8; Galicia ochre, 5·00, 4·30, 4; Cordova ochre, 4·66, 4·21, 8; and China ochre, 4·28, 4·44, 2. H. F. G.

Ferro-titaniferous mineral from Alto Egitto, in the Arabian Desert. A. Stella (Atti R. Accad. Lincei, 1932, [vi], 15, 336—339).—A detailed description of a mineral containing about 40% of TiO_2 is given. H. F. G.

Original materials of oölites of Lorraine and Luxemburg. J. P. Arend (Compt. rend., 1932, 195, 54—56; cf. this vol., 595).—The suggested origin of these deposits is substantiated by analyses of the dried mud deposited from the ferruginous spring at Mondorf, the accompanying marls, the dried parts of molluscs and fish, and of the "green layer." C. A. S.

Formation of kaolin and alunite in the eastern part of the Polish Mittelgebirge. J. Kuhl (Bull. Acad. Polonaise, 1931, A, 665—675).—The kaolin in the clefts in the shale and quartzite in the Mittelgebirge was probably formed by the action on the aluminosilicates of traces of H_2SO_4, a decomp. product of the co-existing pyrites. The kaolin contains particles of Na_2SO_4 and $Al_2(SO_4)_3$, probably formed by the further action of H_2SO_4. J. W. S.

Origin of auriferous deposits of jacutinga. E. de Oliveira (Ann. Acad. Brasil. Sci., 1931, 3, 151—157).—The Au contained in Brazilian jacutinga deposits is of secondary origin. H_2SO_4 formed by oxidation of pyrites reacts with the NaCl and MnO_2 which are also present, and the resulting solution containing free Cl dissolves the Au from the surface deposits and carries it, as $AuCl_3$, to the lower strata, where it is reduced to Au by $FeSO_4$. Au is found in jacutinga only when the latter occurs below deposits of auriferous quartz pyrites. H. F. G.

Two nepheline-sodalite-syenites from new localities in Northern Rhodesia. F. D. Adams and F. F. Osborne (Canad. J. Res., 1932, 6, 571—576).—These rocks, which are similar in chemical composition to lavas found at the north end of Lake Nyassa, are characterised by a low content of binary oxides and the presence of an aluminous ægirine. E. S. H.

Twin structure and surface indications of rock quartz with reference to the temperature of its formation. O. Mügge (Z. Krist., 1932, 82, 451—467).—The effect of heating at 600° on quartz of various origins is examined, and from the changes effected in the crystal form etc. a method of determining the probable conditions as to temp. etc. of the rocks in which it occurs is deduced. C. A. S.

Spinel structures, with and without variate atom equipoints. T. F. W. Barth and E. Posnjak (Z. Krist., 1932, 82, 325—341; cf. A., 1931, 1001).—The variate atom equipoint structure is possessed by $MgFe_2O_4$ (a 8·36 Å.), $MgGa_2O_4$ (a 8·26), $MgIn_2O_4$ (a 8·81), $TiMg_2O_4$ (a 8·41), $TiFe_2O_4$ (a 8·50), and $SnZn_2O_4$ (a 8·61); the normal spinel structure by XAl_2O_4 (X=Co, Fe, Mn, Ni, and Zn). $MgIn_2O_4$, $TiMg_2O_4$, and $SnZn_2O_4$ are prepared by prolonged heating of the constituent oxides in the required proportions at temp. ≯1300° for $MgIn_2O_4$; $TiFe_2O_4$ by heating in vac. TiO_2, Fe_2O_3, and Fe at 1150°. C. A. S.

Magnesium–gallium spinel. F. Machatski (Z. Krist., 1932, 82, 348—354; cf. this vol., 12, and preceding abstract).—The distribution of cations in $MgGa_2O_4$ is different from that required by strict structure theory, Ga and Mg being largely interchangeable. This may be due to rapid cooling of the artificial crystals, or to the two cations having nearly identical space requirements, but is certainly not uncommon in similar compounds (cf. A., 1930, 1137). C. A. S.

Spanish vanadinite. F. M. Martin (Anal. Fís. Quím., 1932, 30, 377—383).—A specimen of vanadinite from Albuñuelas had d^{15} 6·94 and contained Pb 71·98%, VO_4 22·33%, AsO_4 2·33%, and Cl 2·49%. The AsO_4 content is thus intermediate between the amounts found in vanadinite from Arizona (5·2%) and in that from Sierra Grande (1·6%). V should not be determined as V_2O_5 if As is present. H. F. G.

Presence of germanium in Brazilian metallic meteorites. H. E. de Araujo (Rev. Soc. Brasil. Chim., 1931, 2, 365—369).—0·1% of Ge sulphide was isolated from a meteorite from Sta. Lucie de Goyaz, where it occurs in the "graphitic fraction." Ge was also found and identified spectroscopically in two other meteorites and may be of more general occurrence. E. L.

Collinsics of minerals. XXII. H. Collins (Chem. News, 1932, 144, 427—430).

Organic Chemistry.

Co-ordinative theory of the constitution of organic compounds. G. Urbain (Compt. rend., 1932, 194, 1993—1997).—The electrovalency of C in org. compounds varies from +4 (as in CCl_4, where C has lost all its peripheral electrons) to −4 (as in CH_4, where C has 8 electrons in its second group). Various examples are discussed. H. B.

Simple organic compounds of radial structure. H. J. Backer (Natuurwetensch. Tijds., 1932, 14, 175—177).—Radial compounds CX_4 are characterised by small mol. cohesion, stability of the cryst. phase, small temp. range of the liquid phase, simple cryst. form, inertness, and tendency to ring formation. H. F. G.

Active product of the reaction of sodium vapour with alkyl halides. M. Polanyi and D. W. G. Style (Naturwiss., 1932, 20, 401—402).—When the reaction products of Na vapour on MeBr or EtBr (cf. A., 1931, 174) are immediately swept into an atm. of Cl_2 or I the corresponding alkyl chloride or iodide is formed, thus affording additional evidence of the momentary existence of the free alkyl radical. A. R. P.

Thermal decomposition of *iso*pentane in presence of silica gel. Mailhe and Creusot (Compt. rend., 1932, 194, 2220—2222).—Thermal decomp. of 1000 g. of *iso*pentane in presence of silica gel at 680°/atm. pressure affords 750 litres of gas containing CH_4, C_2H_4, C_3H_6, and butadiene and 245 g. of liquid, b.p. <20° to >280° (condensed by solid CO_2), rich in ethylenic and aromatic hydrocarbons. J. L. D'S.

Polymerisation of diolefines with olefines. I. Isoprene and Δ^{β}-pentene. C. A. Thomas and W. H. Carmody (J. Amer. Chem. Soc., 1932, 54, 2480—2484).—Isoprene and Δ^{β}-pentene (I) react in presence of $AlCl_3$ to form hydrocarbon-sol. and -insol. polymerides. The quantity of the sol. polymeride formed is a function of the amount of (I) present, whilst its hardness is an inverse function of the quantity of (I) used. The quantity of the insol. polymeride is also an inverse function of the (I) present. The sol. resin polymeride, exposed in a thin film to air, slowly oxidises, thereby becoming harder; the I val. gradually decreases whilst the acid val. increases; O_3 is rapidly absorbed by this polymeride in CCl_4, but the product, after absorption ceases, has an I val. as high as 140 (in some cases). The insol. polymeride, $(C_5H_8)_x$, begins to depolymerise about 116°; it is decomposed by strong acids and gives reddish-violet colorations (with decomp.) with phenols. No insol. polymeride is formed when (I) is treated with $AlCl_3$. C. J. W. (b)

Preparation of pure octene. H. I. Waterman and T. W. Te Nuyl (Rec. trav. chim., 1932, 51, 533—537).—The preps. of octan-β-ol from castor oil and thence of octene, b.p. 121·6—123·6°/760·2 mm., are described. Octan-α-ol gives an octene similar in physical properties. R. S. C.

Fluorine derivatives of chloroform. H. S. Booth and E. M. Bixby (Ind. Eng. Chem., 1932, 24, 637—641).—$CHCl_2F$, b.p. 13·5—15·5°, m.p. −127°, is prepared from $CHCl_3$ (containing a little CS_2), SbF_3, and a little $SbCl_5$ at room temp., whilst *chlorodifluoromethane*, b.p. −39·8°, m.p. −147° to −146°, is formed from $CHCl_3$, SbF_3, and $SbCl_5$ at 100° under pressure. CHF_3 could not be obtained from $CHCl_3$, SbF_3, and $SbCl_5$ at 200° (bath) under pressure. The toxicity (towards guinea-pigs) of the above compounds decreases with increase in the no. of F atoms substituted for Cl. H. B.

Action of ultra-violet light on halogenated hydrocarbons. I. Action on tetrachloroethane.

E. Müller and A. Luber (Ber., 1932, 65, [*B*], 985—987).—Irradiation of $CHCl_2·CHCl_2$ through which moist air is passing results in the production of HCl, $CHCl_2·CO_2H$, and *octachlorobutane*, m.p. 81°. The hypothesis that the primary change is loss of HCl with formation of $CHCl_2·CCl$, which combines with activated O to produce $CHCl_2·COCl$, is supported by the production of $CHCl_2·CO·NH_2$ by the action of NH_3 on the solution remaining when dry air is used. $H_2C_2O_4$ is produced in small amount. $C_2H_2Cl_4$ appears stable towards O_3 at room temp. Similar irradiation of $CHCl_3$ produces $COCl_2$ and C_2Cl_6.
H. W.

Synthesis of aliphatic alcohols by catalytic reduction of carbon monoxide. G. Natta and R. Rigamonti (Giorn. Chim. Ind. Appl., 1932, 14, 217—225; cf. B., 1931, 874).—The catalytic reduction of CO by H_2 under pressure and in presence of ZnO and KOAc yields MeOH, higher aliphatic alcohols, about 0·9—1·1% of aldehydes and ketones, 0·02—0·5% of hydrocarbons, 1·4—2·4% of free acids, and 2·5—2·6% of esters. The proportion of alcohols higher than MeOH may be increased somewhat by increasing the amount of alkali metal in the catalyst, but the effect is small over the range 14—9% K_2O. The methods used for separating and identifying the different alcohols are described in detail. Besides MeOH, the following are formed: $Bu^{\beta}OH$, 51·3—46·6; PrOH, 13·1—11·6; $CHMeEt·CH_2·OH$, 4·9—4·8; EtOH, 3·3—4·2; $Pr^{\beta}OH$, 2·6—3·7; $CHMePr·CH_2·OH$, 2·5; BuOH, 1·8—2·0; *n*-$C_5H_{11}·OH$, 0·4, and β-methylhexanol, 1·6%; γ-methylpentanol, *iso*-$C_5H_{11}·OH$, $CHMePr^{\beta}·CH_2·OH$, $CHEtPr^{\beta}·OH$, $CHPr_2^{\beta}·OH$, $CHPrPr^{\beta}·OH$, *tert.*-BuOH, and *tert.*-$C_5H_{11}·OH$, all in small proportions. The alcohols formed contain 94·7—98·4% or, excluding MeOH, 87·5—90·1% of primary alcohols. Among the normal-chain alcohols, those with odd nos. of C atoms predominate, and among the ones with branched chains, those with the Me in the β-position to the OH. T. H. P.

Preparation of mixed ethers. R. Truchet and M. Graves (Bull. Soc. chim., 1932, [iv], 51, 686—689).—The action of alkyl arylsulphonates on Na alkoxides gives 55% yield of ethers. A. A. L.

Ethyl ethers of α-glycols, and the ketones obtained by their dehydration. IV. D. Bardan (Bul. Chim. Soc. Române Stiinte, 1930, 33, 25—32; cf. this vol., 368).—*iso*Valeryl chloride (from the acid with $SOCl_2$) gives the α-Br-derivative, converted into the Et ester, which gives *Et α-ethoxy*iso*valerate*, b.p. 73—76°/31 mm. From this the following are obtained with the appropriate Grignard reagent: *γ-ethoxy-β-methyl-δ-ethylhexan-δ-ol*, b.p. 74—77°/19 mm. (60%); *γ-ethoxy-β-methyl-δ-propylheptan-δ-ol*, b.p. 105—109°/20 mm. (70%); *γ-ethoxy-β-methyl-δ-butyloctan-δ-ol*, b.p. 143—145°/26 mm.; and *γ-ethoxy-β-methyl-δδ-diphenylbutan-δ-ol*, b.p. 204—209°/17 mm. Conversion of these substances into the following ketones is best effected by treatment with P_2O_5 in anhyd. pyridine, followed by hydrolysis with 20% H_2SO_4: *β-methyl-δ-ethylhexan-γ-one*, b.p. 52—54°/21·5 mm. (yield 80%); *β-methyl-δ-propylheptan-γ-one*, b.p. 74—78°/23 mm.; *β-methyl-δ-butyloctan-γ-one*, b.p. 116—121°/14 mm.; and *δδ-diphenyl-β-methylbutan-γ-one*, b.p. 159—165°/21 mm. A. A. L.

Alkyl peroxides and ozonides. A. Rieche (Angew. Chem., 1932, 45, 441—444).—A review.

Glycerophosphoric acids. G. Carrara (Giorn. Chim. Ind. Appl., 1932, 14, 236—237).—The two free OH of the glycerol residue in α-glycerophosphates are vicinal and, like analogous glycols (Criegee, A., 1931, 461) and unlike β-glycerophosphates, these compounds are readily oxidised by $Pb(OAc)_4$, which is converted into $Pb(OAc)_2$. As the tetra-acetate liberates I from KI, α-glycerophosphates may be determined accurately by means of this reaction. When tested in this way, Ca glycerophosphate polv. F.U.VI (Erba) proves to be the almost pure α-compound; it is readily convertible into the Na salt (Charpentier and Bocquet, this vol., 251). The quinine α- and β-compounds show the m.p. given by King and Pyman (J.C.S., 1914, 105, 1238). During the alkaline hydrolysis of the di-esters of glycerophosphoric acid, 20—40% of a polyglycerol polyphosphate (?) is formed. T. H. P.

Metallic compounds of the enolic forms of monocarbonyl compounds. XIV. Action of sodium alkoxide on esters, ester-condensation, and substitution reactions of metallic compounds of esters. H. Scheibler (Ber., 1932, 65, [*B*], 994—999).—Mainly a reply to Adickes (this vol., 599) and Hückel ("Theoret. Grundlagen d. organ. Chemie," 1931, Vol. I, p. 188). The course of the reaction between BzOEt and NaOEt is represented, $BzOEt+NaOEt=NaOBz+C_2H_4+EtOH$. The production of the salt is not quantitatively explicable by assuming the action of "traces of H_2O." H. W.

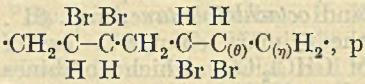
Addition of alkali alkoxides to esters. VII. Kinetics and statics of the decomposition of ethyl formate by sodium ethoxide. F. Adickes and G. Schäfer [with, in part, W. Brunnert] (Ber., 1932, 65, [*B*], 950—955; cf. this vol., 614).—The course of the change is observed by measurement of the CO evolved during the action of alkali alkoxide on HCO_2Et in EtOH. The rate is independent of the initial concn. of ester and directly proportional to the NaOEt concn. $Na^{\cdot}$ (HCO_2Na, NaOAc) is without catalytic action. KOEt is more powerful than NaOEt, whilst $Ca(OEt)_2$ is still less active and $Al(OEt)_3$ without action. The results do not throw light on the mechanism of the change. Solubility data of HCO_2Na in anhyd. EtOH and in NaOEt–EtOH are recorded. H. W.

Oxidation and degradation of various sugars and their decomposition products. XIII. Conversion of acetic into succinic acid. K. Bernhauer and W. Stein (Biochem. Z., 1932, 249, 219—222).—AcOH (50 g.) on oxidation with $K_2S_2O_8$ gave 0·2 g. succinic acid. The smallness of the yield is due to further oxidation of succinic acid to HCO_2H, AcOH, and CO_2. P. W. C.

Preparation of branched-chain fatty acids of high mol. wt. H. Rupe and E. Will (Helv. Chim. Acta, 1932, 15, 842—853).—Heptaldehyde, $COMe_2$, and 3% NaOH first at 0° and then at room temp. give *Me β-hydroxyoctyl ketone* (I), b.p. 128—129°/10 mm., *di-β-hydroxyoctyl ketone* (3—5% yield), m.p. 85—86°, and Δ^{γ}-decen-β-one (II), b.p. 105°/10 mm. (*β-semicarbazidosemicarbazone*, m.p. 172°) [also formed when (I) is heated in vac. with a little I]. (II), when hydrogenated (Ni) in 75% EtOH and subsequently oxidised by Beckmann's mixture, gives n-*decan-β-one*, b.p. 92°/10 mm., m.p. 2·5° (*semicarbazone*, m.p. 126°), which with $CH_2Br\cdot CO_2Et$ and Zn in hot, dry C_6H_6 yields *Et* β-*hydroxy*-β-*methylundecoate*, b.p. 157°/10 mm., dehydrated, best by distillation at 60—70 mm. with anhyd. $ZnCl_2$, to *Et* β-*methyl*-Δ^{α}-*undecenoate*, b.p. 142—143°/10 mm. This was hydrogenated (Ni), best in 90% EtOH at 60—70 atm., to *Et* β-*methylundecoate*, b.p. 134°/10 mm., hydrolysed to the corresponding *acid*, b.p. 165·5°/10 mm. (*K*, *Na*, and *Cu* salts) (together with a small amount of an *acid*, b.p. 185°/10 mm.), the *acid chloride* of which, an oil (prepared by $SOCl_2$), with $ZnMe_2$ gives *Me* β-*methyldecyl ketone*, b.p. 129°/10 mm. (*semicarbazone*, m.p. 81·5°). From this by similar methods were prepared: *Et* β-*hydroxy*-βδ-*dimethyltridecoate*, b.p. 170—175°/11 mm., *Et* βδ-*dimethyl*-Δ^{α}-*tridecenoate*, b.p. 160°/10 mm., βδ-*dimethyltridecoic acid*, b.p. 183—184°/10 mm. (*Et* ester, b.p. 153°/10 mm.; *Na* salt; *acid chloride*, b.p. 162—163°/10 mm.), *Me* βδ-*dimethyldodecyl ketone* (III), b.p. 162°/10 mm. (*semicarbazone*, m.p. 77°), *Et* β-*hydroxy*-βδζ-*trimethylpentadecoate* (impure), b.p. 203—205°/11 mm., *Et* βδζ-*trimethyl*-Δ^{α}-*pentadecenoate* (IV), b.p. 191—192°/10 mm., βδζ-*trimethylpentadecoic acid*, b.p. 209—210°/10 mm. (*Na* salt; *Et* ester, b.p. 189°/10 mm.). (IV) was reduced only at 50°. (III) with $MgBu^{a}Br$ gives impure εηι-*trimethylheptadecan*-ε-*ol*, b.p. 173—175°/9 mm., yielding (probably) impure εηι-*trimethyl*-Δ^{δ}-*heptadecene*, b.p. 168°/10 mm. η is recorded for the new compounds, whence the average val. $+0\cdot272\times10^{-5}$ for log η is obtained for the grouping $\cdot CHMe\cdot CH_2\cdot$ in agreement with the lit. R. S. C.

Fatty acids associated with cassava starch. L. Lehrman (J. Amer. Chem. Soc., 1932, 54, 2527—2530).—The fatty acids liberated during the hydrolysis of cassava starch (free from extraneous fatty materials) are palmitic, oleic, linoleic, and linolenic. The detection of small amounts of linolenic acid in presence of oleic and linoleic acids by bromination is better than oxidation. The test for phytosterol was negative. C. J. W. (*b*)

Unsaturated fatty acids and their derivatives. II. Configuration of tetrabromostearic acid from linoleic acid. T. Maruyama and B. Suzuki (Proc. Imp. Acad. Tokyo, 1932, 8, 186—189).—The tetrabromostearic acid, m.p. 114°, from linoleic acid is treated with EtOH–KOH at 0° for 120 hr. or at 20° or 35° for 20 hr. and the Me ester of the resulting Br_2-acid (I) oxidised by Armstrong and Hilditch's method (A., 1925, i, 355); Me H sebacate and tartronic [from $CHBr(CO_2H)_2$] and *n*-valeric acids are thereby obtained. (I) is, therefore, θλ-dibromo-$\Delta^{\iota\mu}$-octadecadienoic acid. Dehalogenation at 50° gives θ-bromo-$\Delta^{\iota\kappa\mu}$-octadecatrienoic acid (oxidation products, $H_2C_2O_4$, *n*-valeric and α-hydroxysebacic acids); at 80°, $\Delta^{\eta\iota\kappa\mu}$-octadecatetraenoic acid (oxidised to $H_2C_2O_4$, suberic and *n*-valeric acids) results. Elimination of HBr occurs simultaneously with almost equal readiness between the ι- and κ- and the μ- and ν-C atoms to give (I). Linoleic acid is considered to have the *cis-cis*-structure; the grouping,



$\cdot CH_2\cdot\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}\cdot CH_2\cdot\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}_{(\theta)}\cdot C_{(\eta)}H_2\cdot$, probably occurs in the Br_4-acid. H. B.

Action of hydrazine polysulphide on oleic acid. J. Vorišek (Chem. Listy, 1932, 26, 285—286).—N_2H_4 polysulphide and oleic acid yield a mixture of the hydrazones of oleic and stearic acid. R. T.

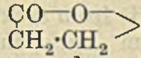
Hydrogenation of linoleic acid. I. Ethyl linoleate. H. van der Veen (Chem. Umschau, 1932, 39, 104—109).—Et linoleate (prepared from linoleic acid tetrabromide by Rollett's method) was hydrogenated at 200° with a Ni–kieselguhr catalyst (reduced at 500°), and the reaction was followed by thiocyanometric analysis. The first stage of the reaction converting linoleic into Δ^{θ}-octadecenoic acid was highly selective, <9% of stearic acid (checked by the Bertram method) being formed. Under the given conditions no wandering of the double linking occurred, the octadecenoic acids produced consisting of about equal proportions of Δ^{θ}-oleic and elaidic acids (cf. Suzuki and Inoue, B., 1930, 956). E. L.

Odour and constitution of some alkoxy-acids and their esters. I. B. Rothstein (Bull. Soc. chim., 1932, [iv], 51, 691—696).—The action of $CH_2Cl\cdot CO_2H$ on the appropriate Na alkoxide gives the following alkoxyacetic acids: n-*heptyl*-, b.p. 157°/18 mm. (*Me* ester, b.p. 115°/18 mm.; *Et* ester, b.p. 123·5°/16 mm.) (60%); octyl-, b.p. 162°/15 mm. (*Me* ester, b.p. 119°/15 mm.; *Et* ester, b.p. 125°/13 mm.) (A., 1929, 1174); *benzyl*-, b.p. 180—182°/15 mm. (*Me* ester, b.p. 136·5°/15 mm.; *Et* ester, b.p. 143°/15 mm.); phenylethyl-, m.p. 46°, b.p. 183°/14 mm. (*loc. cit.*) [Me ester, b.p. 145°/13 mm.; *Et* ester, b.p. 153°/16 mm.] (50%); *phenylpropyl*-, m. p. 55°, b.p. 198°/15 mm. (*Me* ester, b.p. 157°/14 mm.; *Et* ester, b.p. 162—163°/15 mm.); *rhodinyl*-, b.p. 180—181°/ 16mm.: and *geranyl*-, b.p. 180°/16 mm., 143°/0·86 mm. (*Et* ester, b.p. 155—157°/16 mm.). A. A. L.

Electrolytic oxidation of aliphatic dicarboxylic acids. E. A. Tommila (Ann. Acad. Sci. Fennicæ, 1932, 36, 114 pp.).—The anodic oxidation products of a no. of aliphatic dicarboxylic acids have been determined, mostly in strongly alkaline solutions (5*N*-NaOH), but in some cases in presence of 2*N*-H_2SO_4 or without any addition. Electrodes of polished and platinised Pt, Fe, and Ni were used in the alkaline solutions, and Pt and PbO_2 in the acid solutions. The course of the oxidation varies with the composition of the electrolyte, and with the nature and material of the anode. In general, the anodic oxidation of malic acid in alkaline solution gives relatively large yields of malonic acid (by oxidation of the univalent malate ion), MeCHO (from the bivalent malate ion), and $H_2C_2O_4$ (especially at low potentials and at anodes of Ni or Fe). Secondary changes and the mechanisms of the reactions involved are discussed. In H_2SO_4 solution the current efficiency is low, except with PbO_2 anodes, and the products of oxidation are malonic acid, HCO_2H, AcOH, MeCHO, CO, and CO_2, no $H_2C_2O_4$ being obtained; in this case the undissociated malic acid is the depolariser, rather than the malate ions. The anodic oxidation products of oxaloacetic acid are mainly CO_2 and MeCHO in acid solution, but in alkaline solution a yellowish-red condensation product of unknown composition is produced. Malonic acid in alkaline solution is oxidised electrolytically mainly to CO_2, with some $H_2C_2O_4$ and HCO_2H (probably indicating tartronic acid as intermediate). No CO or hydrocarbon is formed. Alkaline mesoxalic acid gives equiv. amounts of CO_2 and $H_2C_2O_4$ in quant. yield, whilst the acid solution is oxidised to CO_2 alone. Succinic acid is oxidised with difficulty to CO_2, accompanied by traces of org. acids. Alkaline solutions of maleic or fumaric acid are oxidised anodically with difficulty; the products are CO_2, a little $H_2C_2O_4$ (not found with fumaric acid), and traces of MeCHO and HCO_2H. Tartaric and meso-tartaric acids give approx. equal yields of HCO_2H and CO_2. A comparison of the c.d.–p.d. curves shows oxaloacetic and mesoxalic acids to be the best depolarisers. The following general conclusions are reached: (1) ease of electrolytic oxidation increases with the no. of O atoms in the mol.; (2) a double linking has no special influence on anodic oxidisability; (3) a CH_2 group is more easily oxidised when situated between two CO_2H groups than in any other position; (4) oxidation proceeds more readily the lower is the $[H^{\cdot}]$ of the solution; (5) the products contain a smaller no. of C atoms than the original substance; (6) univalent ions having OH attached to a middle C atom produce aldehydic acids, which subsequently undergo further oxidation, but, if two OH radicals are attached, acids are produced directly; (7) bivalent ions having O attached to a middle C atom are oxidised with elimination of both CO_2H groups; (8) hydroxylation is the first process to occur when the acid does not already contain a OH radical attached to a central C atom. E. S. H.

Chromic acid oxidation of dicarboxylic acids. L. Semichon and M. Flanzy (Compt. rend., 1932, 194, 2063—2065).—Oxidation of dibasic acids (oxalic—adipic) (0·05 g. in 10 g. of H_2O) with CrO_3 (0·525 g.) in 5 c.c. of H_2SO_4 (*d* 1·71) proceeds more slowly than with the monobasic acids (this vol., 719). Oxidation of the acids above succinic is favoured by the presence of β-CH_2 groups (adipic is oxidised more rapidly than glutaric at 100°), and succinic acid (which is oxidised slowly at 100° after 3 hr.) is the intermediate. OH-acids are oxidised to CO_2 and H_2O; CH_2O is an intermediate. H. B.

Action of peracetic acid on mono- and di-allyl-malonic and -acetic acid. J. Böeseken (Rec. trav. chim., 1932, 51, 551—556).—Mono- and di-allyl-malonic and -acetic acids are slowly oxidised by AcO_2H in AcOH. Oxidation is fastest if the unsaturated group contains a CH_2 group and is affected by the nature of the other substituents. The following are described: *Et_2 β-hydroxy-γ-acetoxy-*n-*propylmalonate*, b.p. 127—145°/cathode vac.; β-*lactone* of βγ-*dihydroxy-*n-*propylmalonic acid*, an oil, and its γ-*Ac* derivative, an oil; *compound*



$\begin{matrix}CO{-}O{-}\\ CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}CH_2{\cdot}CO_2Me$, an oil; ι-*hydroxy*-κ-*acetoxy*-n-*undecenoic acid*, an oil. R. S. C.

Ether-like compounds. VI. Synthesis of ether-lactones from di-ethereal acids. M. H. Palomaa and Y. T. Järvenkylä (Ber., 1932, 65, [*B*], 923—925; cf. A., 1931, 1033).—Hydroxyethoxy-acetolactone, b.p. 213°, m.p. 26·7°, is obtained in 70% yield by gradually heating β-methoxyethoxy-acetic acid with 67% HBr to 150°, distilling the residue under atm. pressure, repeated addition and expulsion of small amounts of H_2O, and final distillation; m.p., *d*, and *n* increase with age of the product. α-β′-*Methoxyethoxypropionic acid*, b.p. 105—108°/1·5 mm., does not yield the corresponding ether-lactone when similarly treated, probably because of the secondary linking of the intermediate O atom. H. W.

Preparation of ammonium *l*-tartrate. E. G. Kellett (J.S.C.I., 1932, 51, 204T).—*d*-Tartaric acid is racemised by boiling with excess of NaOH, and the concn. and acidity of the resulting solution are so adjusted that Na H racemate is salted out practically pure. Cinchonine H tartrate is prepared by direct interaction of Na H racemate and cinchonine hydrochloride. A rapid method of controlling the process of resolution by observations of crystal form is described.

Sugar acids. I. Products obtained by the action of phosphorus pentachloride on mucic acid. K. Bernhauer and A. Iglauer. **II. Preparation of *d*-mannonic acid. III. Preparation of gluconic acid.** K. Bernhauer and K. Irrgang (Biochem. Z., 1932, 249, 211—215, 216—218, 227—233).—I. By the action of PCl_5 on mucic acid two *chloro-hydroxymuconic acids* are obtained (as Me esters), one, m.p. 196°, probably the precursor of Me_2 *d*-dichloromuconate, m.p. 156°, and the other, m.p. 110°, the precursor of Me_2 β-dichloromuconate. Hydrolysis of the first ester gives an acid which sublimes without melting above 260°.

II. The hydrolysis of ivory-nut meal and the electrolytic oxidation of the mannose syrups are described. The yield of crude Ca mannonate was 110% on the mannose oxidised.

III. The oxidation of glucose to gluconic acid by Br under various conditions is studied. P. W. C.

Selenium dioxide, a new oxidising agent. I. Its reaction with aldehydes and ketones. H. L. Riley, J. F. Morley, and N. A. C. Friend (J.C.S., 1932, 1875—1883).—SeO_2 has a sp. oxidising action on aldehydes ($CH_2R{\cdot}CHO$) and ketones ($CH_2R{\cdot}COR'$); α-ketoaldehydes and αβ-diketones are thereby produced. When the CH_2 is activated by proximity to a negative group, oxidation proceeds at moderately low temp. The reactions are sometimes carried out in presence of EtOH. The SeO_2 is recovered by ignition or oxidation of the pptd. Se with HNO_3 and sublimation. The following are prepared: $(CHO)_2$ from MeCHO; AcCHO from $COMe_2$ and EtCHO; EtCO·CHO from COMeEt and PrCHO; BzCHO from COPhMe and $CH_2Ph{\cdot}CHO$; Ac_2 from COMeEt; AcCOEt from $COEt_2$; AcCOPh from COPhEt;

*cyclo*hexane-1 : 2-dione (I) from *cyclo*hexanone; *cyclo*pentane-1 : 2-dione from *cyclo*pentanone; buchu-camphor (diosphenol) from menthone. The enol content of freshly-distilled (I) is small; the amount increases gradually during 2 months to an equilibrium val. of about 40%. Fructose gives a red ppt. of Se when boiled with SeO_2 in acid solution; glucose, lactose, and maltose do not, whilst prolonged boiling is necessary with sucrose. H. B.

Stereoisomerism of unsaturated compounds. I. Composition of crotonaldehyde. W. G. Young (J. Amer. Chem. Soc., 1932, 54, 2498—2503).—Oxidation of commercial ("niacet") and *trans*-crotonaldehydes (prepared from the commercial material by treatment with HCl and sunlight) with O_2 below 30° and Ag_2O–H_2O at 15—20° gives *trans*-crotonic acid in each case; some *cis*-acid is produced when the temp. is not controlled. The *cis*-acid obtained by Kaufler (A., 1929, 1423) is probably formed by stereomutation of the *trans*-form during the oxidation. C. J. W. (*b*)

Polyene compounds. I. Condensation products of crotonaldehyde and β-methylcrotonaldehyde. K. Bernhauer and E. Woldan (Biochem. Z., 1932, 249, 199—210).—The prep. of β-*methylcrotonaldehyde*, b.p. 24—37°/12 mm. (*acetal*, b.p. 55—62°/12 mm.), is described. Fractionation of its condensation products gives a fraction, b.p. 72—74°/0·5 mm., probably *dimethyloctatrienal* (p-*nitrophenylhydrazone*, m.p. 139°; *semicarbazone*, m.p. 195°; *azide*, m.p. 140°), and a fraction, b.p. 132—135°/0·4 mm. probably β-*methylcrotonaldehyde aldol* (p-*nitrophenylhydrazone*, m.p. 234°; *semicarbazone*, m.p. 222°). P. W. C.

Glyceraldehyde-γ-phosphoric acid. II. Calcium salt. H. O. L. Fischer and E. Baer (Ber., 1932, 65, [*B*], 1040—1041; cf. this vol., 364).—*Ca glyceraldehyde-γ-phosphate dihydrate* is obtained from the acid and $Ca(OAc)_2$ in H_2O. H. W.

Mechanism of the diacetyl reaction of guanidines, their reactions and application to the colorimetric determination of creatine and arginine. K. Lang (Z. physiol. Chem., 1932, 208, 273—280).—Diketones of the type of Ac_2, combine with guanidines in alkaline solution, giving violet-coloured products. 2 mols. of AcBz unite with 3 mols. of creatine. This is the basis of a colorimetric micromethod for the determination of creatine in muscle extracts and of arginine in proteins. The error does not exceed 5%. J. H. B.

Thermal decomposition of acyloins. M. Urion (Compt. rend., 1932, 194, 2145—2146; cf. A., 1930, 1160).—δ-Ketohexan-γ-ol at 320° in presence of Al_2O_3 and pumice gives EtCHO and dipropionyl. Similarly, acetol gives MeCHO and Ac_2, and glycide gives acraldehyde, acetol, and the products from the latter. Pyruvic acid at 300° in presence of Cu gives mainly methylsuccinic acid, MeCHO, Ac_2, methylglyoxal, and CO_2. A. A. L.

Preparation of tetrathiopentone. S. A. Karasiewicz (J. Amer. Chem. Soc., 1932, 54, 2556—2557).—I (20 g.) in $COMe_2$ (60 c.c.), treated with H_2S for 7 hr., gives 20 g. of tetrathiopentone, m.p. 170—171°; reduction with Na in liquid NH_3 gives $Pr^{\beta}SH$. C. J. W. (*b*)

Course of the oxidation of aldose sugars by bromine water. H. S. Isbell and C. S. Hudson (Bur. Stand. J. Res., 1932, 8, 327—338).—When a slightly acid buffered glucose solution is oxidised by Br–H_2O the rotation first rises rapidly to a point corresponding approx. with that of the δ-gluconolactone, then decreases to a min. val. at a rate corresponding with the hydrolysis of this lactone, and finally increases slowly to a point corresponding with the equilibrium rotation of gluconic acid. Mutarotation occurs in the solution if the oxidation is interrupted by removal of Br with either olive oil or $Na_2S_2O_3$. This suggests that the initial oxidation product of the glucopyranose is the δ-lactone which then becomes hydrolysed to the gluconic acid. The latter finally reaches equilibrium with the δ- and γ-lactones. This view is confirmed by similar observations with *d*-galactose, *l*-arabinose, *d*-xylose, and lactose, and in the last case, no final rise in rotation occurs owing to the impossibility of γ-lactone formation. J. W. B.

Reaction between potassium cyanide and sugars. Its relation to the forms of sugars in aqueous solution. F. Lippich (Biochem. Z., 1932, 248, 280—308).—Hexoses (also hexosephosphates) and reducing and mutarotatory bioses combine under suitable conditions with definite amounts of HCN. Study of these amounts and of the variations which they undergo in certain circumstances (presence of alkali, acid, phosphate, proteins, NH_2-acids, synthalin, insulin, or thyroxine) leads to conclusions concerning the various forms in which the sugars exist and the alterations which take place in equilibrium mixtures of these forms. W. M.

X-Ray evidence of structure of the furanose and pyranose forms of α-methylmannoside. E. G. Cox and T. H. Goodwin.—See this vol., 798.

Passage from the hexose to the cyclitol series. F. Micheel (Annalen, 1932, 496, 77—98).—Successive treatment of mannitol with CPh_3Cl and BzCl in pyridine gives 1 : 6-*di*(*triphenylmethyl*)*mannitol* 2 : 3 : 4 : 5-*tetrabenzoate* (I), m.p. 185°, $[\alpha]_D^{18}$ +46·9°, hydrolysed by HBr in AcOH–$CHCl_3$ at 0° to *mannitol* 2 : 3 : 4 : 5-*tetrabenzoate*, m. p. 155°, $[\alpha]_D$ ±0° in $CHCl_3$, which is convertible into (I) and with PCl_5 in $CHCl_3$ at 130—150° (bath) affords 1 : 6-*dichloromannitol* 2 : 3 : 4 : 5-*tetrabenzoate*, m.p. 108—109°, $[\alpha]_D^{20}$ +20·6° in $CHCl_3$, also formed by benzoylation of the (1 : 6-)dichloromannitol (II) of Siwoloboff (A., 1886, 681). (II), $COMe_2$, anhyd. $CuSO_4$, and a little conc. H_2SO_4 give 1 : 6-*dichloro*-3 : 4(or 2 : 3)-iso*propylidenemannitol*, m.p. 75°, $[\alpha]_D^{21}$ +25·7° in $CHCl_3$ (*diacetate*, m.p. 46°, $[\alpha]_D^{20}$ +21·8° in $CHCl_3$), whilst saturation of a mixture of (II) (1 pt.) and 40% CH_2O (1·5 pts.) with HCl affords 1 : 6-*dichloro*-2 : 3 : 4 : 5-*dimethylenemannitol* (III), m.p. 156°, $[\alpha]_D^{20}$ +74·7° in $CHCl_3$, converted by NaI in $COMe_2$ at 110—115° into the 1 : 6-*di-iodo*-derivative (IV), m.p. 194—195°, $[\alpha]_D^{16}$ +50° in $CHCl_3$. (IV) and K in xylene and N_2 give βγδε-*di*(*methylenedioxy*)-$\Delta^{\alpha\epsilon}$-*hexadiene*, m.p. 81°, $[\alpha]_D^{18}$ +280·3° in $CHCl_3$, which consumes approx. 2O per mol. when titrated with BzO_2H and is hydrolysed by 5% HCl to *γδ-dihydroxy-βε-diketohexane*, m.p. 74°. (IV) and "mol." Ag in PhMe or xylene at 165—170° afford 1 : 6-*deoxy*-2 : 3 : 4 : 5-*dimethylenemannitol* [*βγδε-di(methylenedioxy)hexane*], b.p. 70—71°/0·04 mm., m.p. 60°, $[\alpha]_D^{18}$ +54·8° in $CHCl_3$ [also formed from (IV), H_2, and Pd–$CaCO_3$], and the *dimethylene ether*, b.p. 103°/0·04 mm., m.p. 215°, $[\alpha]_D^{18}$ +17·03° in $CHCl_3$, of *tetrahydroxymannocyclitol* [1 : 2 : 3 : 4-*tetrahydroxy*cyclo*hexane*] (V), m.p. 229°, $[\alpha]_D^{19}$ +31·6° in H_2O. *αζ-Deoxymannitol* [*βγδε-tetrahydroxyhexane*] has m.p. 148°, $[\alpha]_D^{18}$ −17·6° in $CHCl_3$. (V) and Zn dust at 250—280° give C_6H_6, whilst oxidation with HNO_3 (*d* 1·4) affords succinic acid. 6-*Chloro*-1-*deoxydimethylenemannitol* [*α-chloro-βγδε-di(methylenedioxy)hexane*], b.p. 98°/0·04 mm., m.p. 81°, $[\alpha]_D^{19}$ +55·9° in $CHCl_3$, is the sole cryst. product isolated from (III) and "mol." Ag in xylene at 180°. H. B.

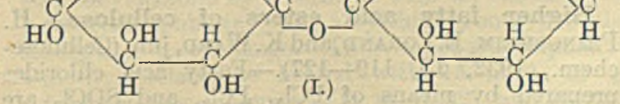
α- and β-*d*-Glucose 2 : 3 : 4 : 6-tetra-acetate, and a source of error in the determination of m. p. in a capillary tube. A. Georg (Helv. Chim. Acta, 1932, **15**, 924—935).—The prep. of β-*d*-glucose tetra-acetate (I), m.p. 137·5—138°, $[\alpha]_D^{22}$ −3·0° to +80·25° in 95% EtOH (*c*=4), and $[\alpha]_D^{18}$ +14·8° (const.) in $CHCl_3$ (*c*=4·116), is modified to give a 92% yield. Acetobromoglucose with "active" $AgNO_3$ (prepared by pouring a 10% solution in warm MeOH into 2 vols. of Et_2O) in dry Et_2O gives tetra-acetyl-β-glucosidyl nitrate; in presence of a little H_2O, excess of $AgNO_3$, and some HNO_3 (formed by hydrolysis), the β-nitrate is (*a*) partly inverted to the α-nitrate, which hydrolyses to yield (I), and (*b*) partly hydrolysed to yield by inversion α-glucose tetra-acetate, dimorphic, plates, m.p. 99—100° (from Et_2O–ligroin), and needles, m.p. 112·5—113° (from Et_2O alone), $[\alpha]_D^{21}$ +142° to +80·2° in 3 days in 95% EtOH (*c*=4), $[\alpha]_D^{18}$ + 135·1° in $CHCl_3$ (*c*=4·36). Hudson's rule is not accurately obeyed by these substances. The m.p. of sugars containing a free *ψ*-aldehydic or -ketonic group may be depressed if the surface of the capillary tube contains free alkali. This may be obviated by heating the tube with 1 : 1 HCl. Traces of acid remaining after this treatment depress the m.p. of sucrose, but not of substances less sensitive to acids. R. S. C.

Physical properties of fructose and its determination by copper reduction methods. R. F. Jackson and J. A. Matthews (Bur. Stand. J. Res., 1932, 8, 403—444).—Accurate data for the densities of 0—70% aq. solutions of cryst. fructose (*d* 1·598) at 20° and 25° are tabulated: $d_4^{20}=0·99823+0·0_238893p+0·0_4140p^2$ and $d_4^{25}=0·99708+0·0_23855p+0·0_4139p^2$ (0—20%) and $d_4^{20}=0·99936+0·0_237842p+0·0_41636p^2$ (24—70%), whence the mean expansion of such solutions between 20° and 25° is given by $\Delta D/\Delta t=-(0·0_3231+0·0_5672p-0·0_7224p^2$ (0—20°) and $-(0·0_32145+0·0_5795p-0·0_7·136p^2)$ (20—70%), respectively. The vals. of n_D^t for such solutions are given by similar interpolation formulæ, the vals. of the consts. being 1·33300, $0·0_214159$, $0·0_5491$ (0—20%); 1·33344, $0·0_213625$, $0·0_56645$ (20—63%); and 1·33377, $0·0_213570$, $0·0_56680$ (63—90%), all for *t*=20°; the vals. for *t*=25° are 1·33252, $0·0_214059$, $0·0_5487$; 1·33312, $0·0_213415$, $0·0_56722$; and 1·33345, $0·0_213360$, $0·0_56800$, respectively. The saccharimetric rotations of fructose solution at 20° and 25° are submitted to similar analysis, the saccharimetric normal wt. of cryst. fructose being 18·407 at 20° and 19·003 at 25°. Between room temp. and 75° the change in rotation of 1 g. of fructose in 10 c.c. is −0·0344° *S* per 1°. The reducing powers of glucose and fructose by Munsen and Walker's method (A., 1906, ii, 634) are not const., but are a function of the sugar concn. Nyn's method (B., 1925, 21) for the selective determination of fructose is improved by effecting the reduction for 75 min. at 55° and determination of the pptd. Cu_2O by oxidation with an excess of standard $K_2Cr_2O_7$ and electrometric titration of the excess with Fe_2SO_4. Under these conditions the fructose/Cu ratio, which varies with the concn. of the sugar, has been determined over a wide range of concn. Except in very high concn. the reducing power of glucose in mixtures containing fructose is essentially independent of the concn. of either sugar, 12·4 mg. of glucose being equiv. in reducing power to 1 mg. of fructose. In sucrose–fructose mixtures, containing *S* g. of sucrose, the reducing effect of the former is represented by mg. $Cu=3·32S-0·31S^2+0·27$, for quantities between 1 and 5 g. of sucrose. The above data and other analytical processes are applied to deduce methods of calculating the fructose concn. in various sugar mixtures. J. W. B.

Sir James Irvine's view on the constitution of di- and poly-saccharides. E. L. Hirst (J. Amer. Chem. Soc., 1932, **54**, 2559—2560).—Polemical with Irvine and McGlynn (this vol., 255). C. J. W. (*b*)

Possible source of error in determining the constitution of di- and poly-saccharides. J. C. Irvine (J. Amer. Chem. Soc., 1932, **54**, 2567—2568).—A reply to Hirst (preceding abstract). C. J. W. (*b*)

Polysaccharides. XLVI. A new maltose anhydride, α-4-glucosido-*l*-glucosan. P. Karrer and L. Kamienski (Helv. Chim. Acta, 1932, **15**, 739—745; cf. this vol., 46).—β-Octa-acetylmaltosidyl bromide (modified prep.) with 33% alcoholic NMe_3 at 70° or, better, with $NHMe_2$ in $CHCl_3$ at room temp. gives 1-*dimethylaminomaltose hepta-acetate*, m.p. 164°, the *methiodide* of which (prepared in boiling MeOH) with boiling aq. $Ba(OH)_2$ yields *glucosido*-l-*glucosan* (I), + (?) H_2O (lost at 125° in a high vac.), m.p. (dried at 100°, + approx. $0·5H_2O$) 157—158° (*Ac*$_6$ derivative, m.p. 184°). (I) is stable to Fehling's solution, Br and I solutions, malt diastase, and emulsin, but a hepatopancreatic extract gives glucose (not isolated) and *l*-glucosan, identical with that obtained from starch. (I) is methylated with



(I.)

difficulty by Me_2SO_4 and NaOH in $COMe_2$–H_2O, and a product containing 37·8% OMe gives, when hydrolysed, tetramethylglucose. The constitution of (I) is thus proved. R. S. C.

Synthesis of anthocyanins. Isomeric glucosides of pelargonidin chloride. A. Léon and others. See this vol., 859.

Chemical constituents of tobacco. II. Glucosides of tobacco leaf. I. K. Yamafuji.—See this vol., 888.

Crotonoside. E. Cherbuliez and K. Bernhard (Helv. Chim. Acta, 1932, **15**, 978—980).—The sugar from crotonoside (I) is *d*-ribose, the structure of (I) as 6-amino-2-hydroxypurine-*d*-riboside being thus confirmed. "Hydroxyadenine" (A., 1927, 584) is not identical with *iso*guanine and may, therefore, be an unknown isomeride. R. S. C.

Vanillin as a colour reagent. L. Pavolini (L'Ind. Chimica, 1932, **7**, 149—152).—Purified starches (1—2 g.) give little colour with a few drops of 2% solution of vanillin in EtOH (95%) and 4—5 c.c. of conc. HCl, but flours yield a pink colour changing to violet with an intensity depending on the proportion of protein present; bran gives this colour, but sawdust an indistinct green. Casein, albumin, and peptone give reddish-violet colorations. Bleached cotton, artificial silk, flax, and hemp yield no colour, the first two dissolving in the reagent. Raw vegetable fibres give greenish colorations (lignin), but animal fibres show the same colour as flour, silk dissolving and wool remaining undissolved. Glucose and lactose remain colourless, but fructose and sucrose gradually yield a pink or red colour. Resin (in EtOH) turns pink or reddish-violet. T. H. P.

Glycogen. W. S. Reich (Compt. rend., 1932, **194**, 2141—2143).—Repeated treatment of glycogen with 33% KOH combined with electrodialysis gives a product containing $<0{\cdot}002\%$ P_2O_5, and giving a true solution in resorcinol, in which the mol. wt. corresponds with $4C_6H_{10}O_5$. A. A. L.

Measurements by methods based on dialysis. Mol. wt. and thermal degradation of inulin and inulan in aqueous solution. H. Brintzinger, K. Maurer, and J. Wallach (Ber., 1932, **65**, [*B*], 988—994).—Application of Brintzinger's method (A., 1931, 416) shows the mol. wt. of inulin purified by the method of Irvine and Steele and of a technically pure inulin to be about 80,000 and above 100,000, respectively. Hydrolysis of inulin to fructose by hot H_2O without catalyst is complete in 30—40 hr.; uniform intermediate products of measurable life period are not produced. Investigation of inulan, prepared by heating inulin in glycerol at 90—95°/vac., discloses the presence of compounds of low mol. wt. (glycerol, EtOH; cf. Berner, A., 1931, 716, 941) and shows that depolymerisation has not taken place. Thermal degradation of inulan proceeds similarly to but rather more slowly than that of inulin. H. W.

Higher fatty acid esters of cellulose. H. Pringsheim, E. Lorand, and K. Ward, jun. (Cellulosechem., 1932, **13**, 119—127).—Fatty acid chlorides prepared by means of PCl_5, PCl_3, and $SOCl_2$ are allowed to act on cellulose in presence of pyridine and an inert solvent, *e.g.*, C_6H_6. In preparing insol. esters the method of drying the cellulose is important, and the esters are weak if the treatment with acyl chloride is prolonged. These esters become sol. when heated at a high temp., *e.g.*, 180°, with tetrahydronaphthalene, EtOAc, camphor, or $CH_2Ph{\cdot}OAc$, the last being the best. This is essentially a heat effect catalysed by $PhSO_3H$, etc. Such esters are somewhat coloured in solution and their films are weak. If cellulose is esterified at a high temp., *e.g.*, in boiling xylene, sol. esters are formed directly and contain 2—2·8 acyl groups per C_6, but their quality is inferior. A. G.

Alkali-cellulose. I. O. Schwarzkopf (Z. Elektrochem., 1932, **38**, 353—358).—The distribution of NaOH between cellulose (ramie and Cu-silk) and an aq. solution has been studied by analysing the liquid and residue furnished by a hydraulic press at different pressures. The amount of H_2O taken up was determined by the use of an unabsorbed solute (NaCl) as reference substance. The results agree with *X*-ray evidence in showing that H_2O as well as NaOH is fixed by the cellulose. In the case of cellulose hydrate the process is reversible. F. L. U.

Additive compound of diethylamine and phenylboric acid. G. E. K. Branch and D. L. Yabroff (J. Amer. Chem. Soc., 1932, **54**, 2569).—$BPh(OH)_2$ and $NHEt_2$ in Et_2O give the *compound* $3BPh(OH)_2,NHEt_2$, m.p. 85°. $BPh(OH)_2$, like H_3BO_3, can be titrated in presence of glycerol. C. J. W. (*b*)

Glycine anhydride. I. H. Sanborn (J. Physical Chem., 1932, **36**, 1799—1830).—Glycine anhydride (I) forms an adsorption complex with HCl (the amount of which is determined volumetrically) and a series of compounds with HF [the mol. ratio depends on time of contact and concn., and is a max. at 4 mols. of HF per mol. of (I)]. A compound of 2 mols. of $HClO_4$ and 1 mol. of (I) and a disulphate of (I) are described. The formation of these compounds favours the enolic structure of (I). Previous work on the structure of (I) is reviewed. R. B. (*b*)

Knoop's degradation of amino-acids, F. Ehrlich's alcoholic fermentation of amino-acids, and C. Neuberg's fourth fermentation form. E. Baur (Helv. Chim. Acta, 1932, **15**, 734—738).—Aminolysis of alanine in presence of C is considered to occur by the following stages: alanine $\longrightarrow NH_3+AcCHO$ (I); (I) $\longrightarrow$ lactic acid $+AcCO_2H$ (II) + glycerol (III); (II) $\longrightarrow MeCHO+CO_2$; (III) $\longrightarrow EtOH+HCO_2H$. However, failure to detect (I) amongst the reaction products renders this hypothesis uncertain. R. S. C.

Aminolysis of alanine. K. Wunderly (Helv. Chim. Acta, 1932, **15**, 721—734; cf. A., 1931, 1015).—When degassed animal charcoal is used, NH_4 lactate (I) is almost the sole product of aminolysis of alanine. This is not an oxidation process, since it is unaffected by replacement of air by H_2, N_2, CO_2, or H_2O vapour when the C is not degassed. The products of the reaction with ordinary C include (I), EtOH, NH_4HCO_3, HCO_2NH_4, $AcCO_2NH_4$ (II), and MeCHO, but AcCHO and glycerol are absent. The proportions in which the products are formed, however, vary in different experiments. Aminolysis is brought to a premature end by lactate and pyruvate ions. NH_4 pyruvate and lactate are unaffected by C at 90°. The determination of (I) and (II) is modified. R. S. C.

Configuration of natural valine. P. Karrer and F. C. van der S. Veer (Helv. Chim. Acta, 1932, **15**, 746—750).—Natural valine is *l*(+)-, since the vals. of $[\alpha]_D$ for a no. of *N*-acylvaline esters are parallel to those for the corresponding *l*-leucine derivatives. Parallelism is not complete between derivatives of the corresponding acids owing to the free CO_2H group. The following *N*-acyl derivatives of *l*-valine are described, the rotations quoted being all $[\alpha]_D^{20}$ in EtOH : *Bz*-, m.p. 127°, +17·18° (*Et* ester, m.p. 82°, −3·44°); *$PhSO_2$*-, m.p. 153°, +18·35° (*Et* ester, m.p. 56°, −1·04°); p-*toluenesulphonyl*-, m.p. 147°, +25·0° (*Et* ester, m.p. 59°, +3·99°); β-*naphthalenesulphonyl*-, m.p. 173°, +6·19° (*Et* ester, m.p. 99°, −24·7°). The *Et* esters of N-p-*nitrobenzoyl*-l(+)- and -d(−)-*valine* have m.p. 88° and $[\alpha]_D^{20}$ +4·12° and −3·5° in EtOH, respectively. *N*-*p*-Toluenesulphonyl-*l*-leucine has $[\alpha]_D^{20}$ −4·05° (lit. +4·50°). R. S. C.

Synthesis of peptide-like substances from amino-sugars and amino-acids. II. *N*-Dialanylglucosamine. A. Bertho and J. Maier (Annalen, 1932, **495**, 113—121).—Glucosamine hydrochloride and *dl*-α-azidopropionyl chloride (I) in *N*-NaOH give N-α-*azidopropionylglucosamine*, decomp. 188°, $[\alpha]_D^{20}$ (in H_2O) $+60° \longrightarrow 23·3°$ (24 hr.), reduced catalytically (Adams) or by Al–Hg in H_2O to impure *N*-alanylglucosamine, which when heated with a little NaOH in EtOH passes into *N*-alanyldehydroglucosamine anhydride (A., 1931, 470). Tetra-acetylglucosamine and (I) in $CHCl_3$–pyridine give *tetra-acetyl*-N-α-*azidopropionylglucosamine*, m.p. 146° (slight decomp.), $[\alpha]_D^{20}$ +13·6° in $CHCl_3$, reduced catalytically (Adams) in EtOAc to *tetra-acetyl*-N-*alanylglucosamine*, m.p. 180° (decomp.), $[\alpha]_D^{20}$ +3·0° in $CHCl_3$, converted by α-bromopropionyl chloride in $CHCl_3$–pyridine into *tetra-acetyl*-N-(*α-α′-bromopropionamidopropionyl*)*glucosamine*, m.p. 156—162°, $[\alpha]_D^{20}$ +18·7° and +26·4° in $CHCl_3$ (according to solvent used for crystallisation). This with $MeOH–NH_3$ at room temp. for 4 days gives N-(*α-α′-aminopropionamidopropionyl*)*glucosamine* (N-*dialanylglucosamine*), decomp. about 125°. H. B.

Identification of nitriles. H. P. Howells and J. G. Little.—See this vol., 854.

Reducing action of the Grignard reagent. II. Comparison with the ease of removal of hydrogen bromide from alkyl bromides and with the amount of magnesium dialkyl in the Grignard reagent. C. R. Noller and F. B. Hilmer (J. Amer. Chem. Soc., 1932, **54**, 2503—2506; cf. this vol., 474).—There is no relationship between the amount of reduction of $COPh_2$ by Grignard reagents from 7 alkyl bromides and the relative ease of formation of alkenes from these bromides. The amount of reduction increases (not proportionally) with rise in the Mg dialkyl content of the solutions. The amount of Mg dialkyl present in Grignard solutions appears to be influenced more by the structure than by the mol. wt. of the hydrocarbon radical. The following figures give the equiv. % of Mg dialkyl and % of benzhydrol formed, respectively: *tert.*-Bu 32, 0; Et 51, 2; Pr$^\beta$ 59, 13; *sec.*-Bu 62, 40; Pr 71, 58; Bu 74, 59; Bu$^\beta$ 78, 86. C. J. W. (*b*)

Stereoisomeric-1 : 2-dimethyl*cyclo*hexanes. O. Miller (Bull. Soc. chim. Belg., 1932, **41**, 217—227). —*o*-Xylene, b.p. 143·95—144·15°, m.p. −25·0°, when hydrogenated in presence of Pt, gives *cis*-1 : 2-dimethyl*cyclo*hexane, b.p. 130·0°, m.p. −50·2°, mixed with 9% of the *trans*-isomeride, b.p. 123·7°, m.p. −89·6°. Reduction could not be effected using activated Ni catalysts. Physical consts. for the isomerides are recorded. R. S. C.

Slow oxidation of 1 : 2-dimethyl*cyclo*hexane. M. G. Chavanne, (Mlle.) Katzenstein, and (Mme.) Pahlavouni (Bull. Soc. chim. Belg., 1932, **41**, 209—216).—1 : 2-Dimethyl*cyclo*hexane (I) is more rapidly oxidised by O_2 than are the 1 : 3- and 1 : 4-isomerides. (I), when prepared from *o*-xylene by hydrogenation in presence of Pt, has b.p. 128·9—129·7°, d_4^{15} 0·7978, and is more rapidly oxidised than the product, b.p. 125·5—127·1°, d_4^{15} 0·7884, obtained by use of Ni. 2-Methyl*cyclo*hexanone gives by the Grignard reagent a product, b.p. 129—130°, d_4^{15} 0·7977. Oxidation at room temp., more rapidly in direct light, gives peroxides. At 100—110° there are formed much AcOH with some HCO_2H, *n*-hexoic acid, and δ-keto-*n*-hexoic acid, 1 : 2-dimethyl*cyclo*hexan-1-ol, Me *n*-hexyl ketone, βε-diketohexane, and an oil, transformed by boiling HCO_2H into an unsaturated *ketone*, $C_8H_{14}O$ (*semicarbazone*, m.p. 107°). Oxidation thus starts at a >CH· group. R. S. C.

Mobility of groups containing a sulphur atom. D. T. Gibson (J.C.S., 1932, 1819—1826).—*Me benzenethiolsulphonate* (I), b.p. 123°/1 mm. (from Na benzenethiolsulphonate and Me_2SO_4) (1 mol.), and benzenesulphonylacetone (II) (1 mol.) with Na_2CO_3 (1 mol.) in EtOH give *α-benzenesulphonyl-α-methylthiolacetone* (III), m.p. 60°, hydrolysed to *benzenesulphonylmethylthiolmethane*, which is oxidised by $KMnO_4$ to benzenesulphonylmethanesulphonylmethane (A., 1931, 1394). Me *p*-toluenethiolsulphonate (IV) (1 mol.) and (II) (5 mols.) with Na_2CO_3 also give (III), which is converted by the further action of (IV) into α-*p*-toluenesulphonyl-α-methylthiolacetone (V), m.p. 81° (cf. *loc. cit.*) [also formed from equimol. amounts of *p*-toluenesulphonylacetone and (IV)], which is reconverted into (III) by an excess of (I), and on hydrolysis and subsequent oxidation affords p-*toluenesulphonylmethanesulphonylmethane*, m.p. 158°. (III) is also obtained from *p*-toluenesulphonylacetone (1 mol.) and (I) (3 mols.). It is suggested that the interconversion of these derivatives involves the separation of $PhSO_2^{\ominus}$ and its replacement by *p*-$C_6H_4Me{\cdot}SO_2^{\ominus}$; the excess or deficiency of the attacking ions determines the main course of the reaction. The SMe group is essential for the change, since benzenesulphonylacetone is not converted into *p*-toluenesulphonylacetone by treatment with an excess of Na *p*-toluenesulphinate. The alkylthiol groups are also susceptible to exchange. Thus, α-benzenesulphonyl-α-methylthiolacetone heated with 15 mols. of Et *p*-toluenethiolsulphonate (VI), m. p. 32°, and Na_2CO_3 (1 mol.) in EtOH is converted into α-p-*toluenesulphonyl-α-ethylthiolacetone*, m. p. 93—94°, also prepared from *p*-toluenesulphonylacetone and (VI). The replacement of SR is not necessarily accompanied by replacement of $Ar\cdot SO_2$; thus, 2 : 5-dichlorophenyl 2′ : 5′-dichlorobenzenethiolsulphonate, (V), and NaOEt give a mixture of 2 : 5 : 2′ : 5′-tetrachlorodiphenyl disulphide, 2 : 5-dichlorobenzenesulphinic acid, and α-p-*toluenesulphonyl*-α-2 : 5-*dichlorophenylthiolacetone*, m.p. 111°. Exchange of groups is also observed with Et benzenesulphonylacetate (VII) and (IV) (3 mols.) (whereby impure Et α-*p*-toluenesulphonyl-α-methylthiolacetate results) and with ω-benzenesulphonylacetophenone and (IV) (5 mols.); saturation of the solution obtained in the last case with CO_2 gives the *salt*, p-$C_6H_4Me\cdot SO_2\cdot CH(SMe)\cdot COPh,Na_2CO_3$, hydrolysed to *p*-toluenesulphonylmethylthiolmethane. *Et* α-*benzenesulphonyl*-α-*methylthiolacetate*, m. p. 84°, is obtained from equimol. amounts of (I), (VII), and Na_2CO_3. Equimol. amounts of (II) and diphenyl disulphoxide with NaOEt give α-*benzenesulphonyl*-α-*phenylthiolacetone*, m.p. 69—70°, whilst di-*p*-tolyl disulphoxide and *p*-toluenesulphonylacetone afford α-p-*toluenesulphonyl*-α-p-*tolylthiolacetone*, m.p. 98°. Exchange of $Ar\cdot SO_2$ occurs very slowly (if at all) with purely aromatic disulphoxides; thus, *p*-toluenesulphonylacetone and diphenyl disulphoxide (5 mols.) give α-p-*toluenesulphonyl*-α-*phenylthiolacetone*, m.p. 83°, whilst (II) and di-*p*-tolyl disulphoxide (4 mols.) afford α-benzenesulphonyl-α-*p*-tolylthiolacetone. p-*Chlorobenzenesulphonylacetone*, m.p. 79° (from Na *p*-chlorobenzenesulphinate and $Ac\cdot CH_2Cl$), reacts with (IV) (5 mols.) in $EtOH$–Na_2CO_3 forming (V) and p-$C_6H_4Cl\cdot SO_2H$; with a deficiency of (IV), there results (after hydrolysis) p-*chlorobenzenesulphonylmethylthiolmethane*, m.p. 93°, also formed from (V), p-$C_6H_4Cl\cdot SO_2Na$, and a little Na_2CO_3 in EtOH.

No indication of exchange of $R\cdot SO_2$ is observed with $CH_2(SO_2R)_2$ and an excess of alkyl thiolsulphonate. Thus, *benzenesulphonyldi*(*methanesulphonyl*)*methane*, m.p. 225°, is formed from benzenesulphonylmethanesulphonylmethane (VIII) and (IV) (with subsequent oxidation) and from $CH_2(SO_2Me)_2$ and diphenyl disulphoxide. p-*Toluenesulphonyldi*(*methanesulphonyl*)-*methane*, m.p. 185°, is prepared similarly. Di-*p*-tolyl disulphone, (VIII), and NaOEt give a little benzenesulphonylmethanesulphonyl-*p*-tolylthiolmethane and not the expected trisulphone, whilst (VIII), p-$C_6H_4Me\cdot SO_3Me$, and NaOEt afford α-benzenesulphonyl-α-methanesulphonylethane.

The sulphones obtained by Posner (A., 1905, i, 279; 1908, i, 21) from PhSH and acrylic and cinnamic acids are probably mixtures resulting by (partial) migration of the sulphonyl group. H. B.

Quantitative nitration of *p*-chloro- and *p*-bromo-toluene. (Miss) F. R. Shaw and E. E. Turner (J.C.S., 1932, 1884—1888).—p-C_6H_4MeCl and HNO_3 (*d* 1·5) at 0° and −15° give 38 and 35·6±0·2%, respectively, of 3-NO_2-derivative; the amounts are determined by the piperidine method (this vol., 259). p-C_6H_4MeBr gives 38·1 and 36·3±0·7% at 0° and −15°, respectively. The ratio of 3 : 2-nitration increases more rapidly with rise of temp. for p-C_6H_4MeCl than for p-C_6H_4MeBr. H. B.

Substitution in compounds containing two or more phenyl groups. I. Nitration of 4-methyldiphenyl. W. S. M. Grieve and D. H. Hey (J.C.S., 1932, 1888—1894).—Nitration of 4-methyldiphenyl [with HNO_3 (*d* 1·42) in AcOH] gives rise to both homo- and hetero-nuclear substitution; substitution is primarily controlled by the strongly *op*-directing Ph and *p*-tolyl groups. 4-Nitro-4′-methyl- (I), m.p. 140° (40—45%), 2-nitro-4′-methyl-, and 2-nitro-4-methyl-diphenyls are formed. The oil remaining after separation of (I) from the nitration product is oxidised by $KMnO_4$ to 2-*nitrodiphenyl*-4′-*carboxylic acid* (II), m.p. 250° (nitrated further to 2 : 2′-dinitrodiphenyl-4-carboxylic acid); oxidation with CrO_3–AcOH gives also some 2-nitrodiphenyl-4-carboxylic acid. Reduction of the oil with $SnCl_2$ and EtOH–conc. HCl and subsequent acetylation affords 2-*acetamido*-4-*methyldiphenyl*, m.p. 145°, oxidised by neutral $KMnO_4$ to 2-*acetamidodiphenyl*-4-*carboxylic acid*, m.p. 222°, also prepared by acetylation of the reduction product of 2-*nitrodiphenyl*-4-*carboxylic acid*, m.p. 191° (formed together with 2 : 2′-dinitrodiphenyl-4 : 4′-dicarboxylic acid by hydrolysis of the reaction product from PhI, Et 4-bromo-3-nitrobenzoate, and Cu-bronze). 2-*Benzamido*-4-*methyldiphenyl* has m.p. 221°. p-$C_6H_4Me\cdot N_2Cl$, $PhNO_2$, and 40% NaOH below 5° give 2- and 4-nitro-4′-methyldiphenyl; the former is reduced to 2-amino-4′-methyldiphenyl (*Ac* derivative, m.p. 103°) and oxidised (CrO_3) to (II). 3-*Acetamido*-4-*methyldiphenyl*, m.p. 150°, is prepared similarly by way of 2-nitro-*p*-toluenediazonium chloride and C_6H_6. (I) is nitrated further to 2(or 3) : 4′-*dinitro*-4-*methyldiphenyl*, m.p. 178°, and oxidised by CrO_3–AcOH to 4-*nitrodiphenyl*-4′-*carboxylic acid*, m.p. 340° [the acid thus described by Kühling (A., 1895, i, 290; 1896, i, 236) is the 2′-carboxylic acid], which is nitrated to 2 : 4′-dinitrodiphenyl-4-carboxylic acid. H. B.

Benzhydryl rule and the constitution of alkali triphenylethides which are stable in liquid ammonia. C. B. Wooster and J. F. Ryan (J. Amer. Chem. Soc., 1932, 54, 2419—2424).—Reaction between $NaNH_2$ or KNH_2 and phenylated paraffins in liquid NH_3 at its b.p. occurs only when the $\cdot CHPh_2$ group is present in the hydrocarbon; this generalisation is termed the "benzhydryl rule." $CPh_2{:}CHPh$ and Na in liquid NH_3 give $CNaPh_2\cdot CHNaPh$, which is then ammonolysed to $CNaPh_2\cdot CH_2Ph$, which with EtBr gives αββ-*triphenylbutane*, m.p. 79—79·5°, also synthesised from $CPh_2{:}CHMe$ and K in liquid NH_3 followed by CH_2PhCl. In one experiment in which NH_3 was condensed on $CPh_2{:}CHMe$ and then K slowly added until present in slight excess, reaction with CH_2PhCl gave ααδ-*triphenyl*-Δ^{α}-*butene* (?), m.p. 122—124°. $CHPh_2\cdot CH_2Ph$ and KNH_2 in liquid NH_3 with CH_2PhCl give αββγ-*tetraphenylpropane* (?), m.p. 125—127°, also obtained from $CPh_2{:}CHPh$ and Na in liquid NH_3 with CH_2PhCl, but not from CPh_2Cl_2 and $CH_2Ph\cdot MgCl$. $CPh_3\cdot CH_2Cl$ and Na give the compound, $C_{20}H_{17}Na$, which with NH_4Cl gives $CHPh_2\cdot CH_2Ph$ (showing that mol. rearrangement occurs) and with EtBr affords $CH_2Ph\cdot CPh_2Et$; the initial reaction gives $CPh_3\cdot CH_2Na$, which rearranges to $CNaPh_2\cdot CH_2Ph$. C. J. W. (*b*)

Photosynthesis of *cis*- and *trans*-isomerides of organic halogen compounds. S. Kato (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 765—768).—

Bromination of $CPh\vdots CPh$ in CCl_4 affords the *cis*-Br_2-derivative (30% yield), whilst bromination of $CHPh{:}CHPh$ in MeOH gives a 90% yield of the *trans*-Br_2-derivative, these solvents having approx. the same fundamental mol. frequencies as those calc., respectively, for the two reactions. J. W. B.

1-Vinylnaphthalene and polyvinylnaphthalene resins. L. Palfray, S. Sabetay, and (Mlle.) D. Sontag (Compt. rend., 1932, **194**, 2065—2068).—β-1-Naphthylethyl alcohol heated with KOH under 30—40 mm. gives 1-vinylnaphthalene, b.p. 126—128°/15 mm. (with appreciable resinification) [*picrate*, m.p. (Maquenne block) 101—102°; *styphnate*], which is readily polymerised (by heat) to a resin, sol. in $CHCl_3$, C_6H_6, and PhMe, which does not decolorise Br. Benzylmethylcarbinol and αβ-diphenylethyl alcohol are partly dehydrated by KOH to propenylbenzene and stilbene, respectively; benzyldimethylcarbinol is largely decomposed to PhMe and $COMe_2$. The ease of dehydration of the alcohols, $CH_2Ph{\cdot}CR_2{\cdot}OH$, decreases in the order $\cdot CR_2{\cdot}OH$=primary, *sec.*, and *tert.* H. B.

Syntheses of 2 : 6- and 2 : 7-dibenzylnaphthalene and of ketone derivatives of the ββ-naphthalene series. K. Dziewoński and S. Wodelski (Rocz. Chem., 1932, **12**, 366—377).—CH_2PhCl reacts with $C_{10}H_8$ at 170° in the presence of $AlCl_3$ to yield 2-benzylnaphthalene, 2 : 7-, m.p. 91°, and 2 : 6-*dibenzylnaphthalene*, m.p. 123° (*NO_2*-derivative, m.p. 133°), which on oxidation gives 2 : 6-dibenzoylnaphthalene (*diphenylhydrazone*, m.p. 235°; *dioxime*, m.p. 281°). 2 : 6-*Dibenzamidonaphthalene*, m.p. 306°, is prepared by applying the Beckmann change to the dioxime, and also by benzoylation of 2 : 6-diaminonaphthalene. 2 : 7-Dibenzylnaphthalene yields on oxidation 2 : 7-dibenzoylnaphthalene (*dioxime*, m.p. 176°). 2-Benzylnaphthalene yields 6-*benzoyl-2-benzylnaphthalene*, m.p. 126—127°, with BzCl in the presence of $ZnCl_2$, and 6-*acetyl-2-benzylnaphthalene* (I), m.p. 96° (*oxime*, m.p. 127°), with AcCl in presence of $AlCl_3$. The oxime is converted into 6-*acetamido-2-benzylnaphthalene*, m.p. 189°, which on hydrolysis yields 6-*amino-2-benzylnaphthalene*, m.p. 95°. 2-*Benzoyl-6-naphthoic acid*, m.p. 98°, is obtained by the oxidation of (I). R. T.

Acenaphthenesulphonic acids. II. Derivatives of acenaphthene-α-sulphonic acid. K. Dziewoński, (Mlle.) J. Krasowska, and (Mlle.) J. Schoenowna (Bull. Acad. Polonaise, 1931, A, 400—405).—Na acenaphthene-5-sulphonate with PCl_5 gives the *chloride* (I), m.p. 109—111° (*anilide*, m.p. 177—178°), reduced by Zn and dil. H_2SO_4 to 5-*thiolacenaphthene* (II), m.p. 51—52° (*Pb* and *Hg* salts; *picrate*, m.p. 133—134°), oxidised by air in NH_3–EtOH to *diacenaphthyl* 5 : 5′-*disulphide*, m.p. 168—169°, which is oxidised by $Na_2Cr_2O_7$ and AcOH to *anhydrodi*-(1 : 8-*dicarboxynaphthyl*) 5 : 5′-*disulphide*, decomp. 300—310°. With 35% NaOH and $CH_2Cl{\cdot}CO_2H$ at 40—50° (II) affords 5-*acenaphthylthiolacetic acid*, m.p. 150—151° (*Na* salt). Oxidation of the amide of (I) with $Na_2Cr_2O_7$ and AcOH gives the *anhydride*, m.p. 249—250° (decomp.), of 5-sulphonamidonaphthalene-1 : 8-dicarboxylic acid. J. W. B.

Syntheses of alkylphenanthrenes. II. Pimanthrene, 1 : 4 : 7-trimethylphenanthrene, retene, and 1 : 4-dimethyl-7-*iso*propylphenanthrene. R. D. Haworth, B. M. Letsky, and C. R. Mavin (J.C.S., 1932, 1784—1792; cf. this vol., 608).—Succinic anhydride, 2-$C_{10}H_7Me$, and $AlCl_3$ in cold $PhNO_2$ give β-(6-*methyl-2-naphthoyl*)*propionic acid* (I), m.p. 162° [*Me* ester (II), b.p. 210—212°/12 mm., m.p. 82—83°], reduced (Clemmensen) to γ-(6-*methyl-2-naphthyl*)-*butyric acid*, m.p. 111—112°, and cyclised by warm H_2SO_4 to 4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 62—63°, which when reduced (Clemmensen) and then dehydrogenated (Se) affords 2-methylphenanthrene. (I) is oxidised by alkaline $K_3Fe(CN)_6$ to 6-*methyl-2-naphthoic acid*, m.p. 225—227° (*Me* ester, m.p. 116—117°), also obtained by hydrolysis of 2-cyano-6-methylnaphthalene [prepared in small yield by distillation of Na 6-methylnaphthalene-2-sulphonate and $K_4Fe(CN)_6$], which is oxidised further to 2 : 6-$C_{10}H_6(CO_2H)_2$. MgMeI and (II) in Et_2O–C_6H_6 give γ-(6-*methyl-2-naphthyl*)-Δ^{β}-*pentenoic acid*, m.p. 143—144°, which when reduced with red P and HI (*d* 1·7) and then treated with H_2SO_4 affords 4-keto-1 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III), b.p. 190—192°/0·4 mm. (*semicarbazone*, m.p. 206—208°). Reduction (Clemmensen) of (III) and subsequent dehydrogenation with Se at 300—340° furnishes 1 : 7-dimethylphenanthrene (pimanthrene). The product from MgMeI and (III) is similarly dehydrogenated to 1 : 4 : 7-*trimethylphenanthrene*, m.p. 72—73° (*picrate*, m.p. 141—142°; *styphnate*, m.p. 129—130°; *quinone*, m.p. 170—171°; *quinoxaline*, m.p. 140—141°), which differs from the methylpimanthrenes obtained from *d*-pimaric acid (Ruzicka and Balas, A., 1924, i, 1311) and *iso*agathicdicarboxylic acid (Ruzicka and Hosking, A., 1931, 359).

Succinic anhydride and 2-$C_{10}H_7Pr^{\beta}$ (by reduction of 2-*iso*propenylnaphthalene or from $C_{10}H_8$, $Pr^{\beta}Br$, and $AlCl_3$) give (as above) β-(6-iso*propyl-2-naphthoyl*)-*propionic acid*, m.p. 159° [*Me* ester (IV), m.p. 81—82°], oxidised to 6-iso*propyl-2-naphthoic acid*, amorphous (*Me* ester, m.p. 109—110°), and thence to 2 : 6-$C_{10}H_6(CO_2H)_2$. MgMeI and (IV) give γ-(6-iso*propyl-2-naphthyl*)-Δ^{β}-*pentenoic acid*, m.p. 144°, convertible into 4-*keto*-1-*methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (V), b.p. 180—185°/0·5 mm., m.p. 71—72°, and thence (by reduction and dehydrogenation) into retene. (V) is converted [as (III)] into 1 : 4-*dimethyl*-7-iso*propylphenanthrene*, m.p. 61—62° (*picrate*, m.p. 115°; *styphnate*, m.p. 142—143°), which is not identical with the methylretene obtained by Ruzicka and Meyer (A., 1922, i, 829) from abietic acid.

The hydrocarbon obtained from $C_{10}H_8$, PrBr, and $AlCl_3$ probably contains a large amount of 2-$C_{10}H_7Pr$; condensation with succinic anhydride gives (probably) β-(6-*propyl-2-naphthoyl*)*propionic acid*, m.p. 147—148°. H. B.

Constitution of rubicene. R. Scholl and K. H. Meyer (Ber., 1932, **65**, [*B*], 926—927).—The formation of 9 : 10-diphenylanthracene and rubicene when 9 : 10-dihydroxy-9 : 10-diphenyldihydroanthracene-1 : 5-dicarboxydilactone is heated with Zn dust in CO_2 at 500° confirms the constitution assigned to rubicene by Schlenk and Karplus (A., 1928, 1235). H. W.

Condensation of formaldehyde with arylamines. N. S. Drosdov (J. Gen. Chem. Russ., 1931, 1, 1170—1176).—CH_2O condenses with NH_2Ph and p-$C_6H_4Me\cdot NH_2$ to compounds of the type $CH_2{:}NAr$ (I) and $CH_2(NHAr)_2$ (II); the type of product formed depends, not on the proportions of the reactants, but on the p_H of the solution, compounds of type (II) being unstable in an acid medium. They are formed almost exclusively at p_H 8 and compounds of type (I) at p_H 7. (I) (Ar=p-C_6H_4Me) passes into (II) on keeping with H_2O at p_H 4. G. A. R. K.

Interaction between thionyl chloride and substances containing the reactive methylene group. K. G. Naik and V. B. Thosar (J. Indian Chem. Soc., 1932, 9, 127—132).—Thionylacetoacetarylamides, $NHR\cdot CO\cdot CAc{:}SO$, and thionylacetonedicarboxylarylamides, $NHR\cdot CO\cdot CH{<}\genfrac{}{}{0pt}{}{SO}{CO}{>}CH\cdot CO\cdot NHR$, are prepared from acetoacet- and acetonedicarboxyl-arylamides and $SOCl_2$ in C_6H_6. The following are described: *thionylacetoacet-anilide*, m.p. (all with decomp.) 90° (shrinks at 69°), -o-*toluidide*, m.p. 110° (shrinks at 87°), -m-*toluidide*, m.p. 93—94° (shrinks at 78°), -p-*toluidide*, m.p. 92—93° (shrinks at 87°), -*α-naphthylamide*, m.p. 112° (shrinks at 92°), -*β-naphthylamide*, m.p. 107° (shrinks at 82°), -1 : 3 : 4-*xylidide*, m.p. 102° (shrinks at 90°), and -1 : 4 : 5-*xylidide*, m.p. 114° (shrinks at 97°); *thionylacetonedicarboxyl-anilide*, m.p. 170° (shrinks at 140°), -o-*toluidide*, m.p. 174° (shrinks at 155—156°), -p-*toluidide*, m.p. 208—210° (shrinks at 185°), -*α-naphthylamide*, m.p. 155° (shrinks at 137°), and -*β-naphthylamide*, m.p. 207° (shrinks at 185°). These sulphoxides are more stable to moisture than the thionylmalonarylamides (A., 1930, 764) and unlike the latter, are not converted into sulphides by $SOCl_2$, HCl, or I. The prep. of *acetoacet-α-*, m.p. 108—109°, and -β-, m.p. 103—104°, -*naphthylamides* and -1 : 3 : 4-, m.p. 92°, and -1 : 4 : 5-, m.p. 96°, -*xylidides*, and *acetonedicarboxyl-α-*, m.p. 165°, and -β-, m.p. 207°, -*naphthylamides* is described. H. B.

Stereochemistry of carbodi-imides. XXII. L. J. Roll and R. Adams (J. Amer. Chem. Soc., 1932, 54, 2494—2498; cf. this vol., 739).—The structural relationship of allenes and diarylcarbodi-imides is pointed out and a method for proving the asymmetry of the carbodi-imide is proposed. If during the conversion of $CS(NHPh)_2$ into $NPh{:}C{:}NPh$, the reaction temp. is much above 80°, NH_2Ph and PhNCS are also formed; NH_2Ph then reacts with $NPh{:}C{:}NPh$ forming triphenylguanidine. Menthyl p-aminobenzoate and PhNCS in C_6H_6 give p-*carbo*-l-*menthoxythiocarbanilide*, m.p. 124—125°, converted by HgO and $CaCl_2$ in C_6H_6 into p-*carbo*-l-*menthoxydiphenylcarbodi-imide*. pp′-*Dicarbethoxydiphenylcarbodi-imide*, m.p. 78—90°, and s-*tri*-(p-*carbethoxyphenyl*)*guanidine*, m.p. 170—171°, are prepared from pp'-dicarbethoxydiphenylthiocarbamide. pp′-*Dibromodiphenylcarbodi-imide* has b.p. 208—212°/4 mm. C. J. W. (*b*)

Formation of diarylthiocarbamides from arylamines and trithiocarbonates. N. S. Drosdov (J. Gen. Chem. Russ., 1931, 1, 1168—1170).—An aq. suspension of $ZnCS_3$ or $NiCS_3$ (prepared by treating aq. $NaCS_3$ with the metal sulphate) gives with primary arylamines the corresponding diarylthiocarbamides; the yield from NH_2Ph is 80%. Complex trithiocarbonates of NH_4 and heavy metals can also be used. G. A. R. K.

Synthesis of 3-iodo-β-naphthylamine. H. Goldstein and E. Cornamusaz (Helv. Chim. Acta, 1932, 15, 935—939).—3-Iodo-β-naphthoyl chloride (I) and N_2H_4,H_2O give 3-*iodo*-β-*naphthoylhydrazine*, m.p. about 250° (decomp.), and NN′-*di*-(3-*iodo*-β-*naphthoyl*)-*hydrazine*, m.p. 318° [sole product if excess of (I) is used]. The former with HNO_2 yields the *azide*, deflagrates at 60—65°, transformed by boiling EtOH into the *urethane*, m.p. 109° (which could not be hydrolysed), and by 90% H_2SO_4 at 0° into 3-*iodo*-β-*naphthylamine*, m.p. 137° (*Ac* derivative, m.p. 198°). The amine with HNO_2 gives 3-*iodo*-β-*naphthol*, m.p. 104°. 3-Acetamido-β-naphthoic acid and $SOCl_2$ give the acid chloride, which with conc. aq. NH_3 affords 3-*acetamido*-β-*naphthamide*, m.p. 237°; this could not be degraded by Hofmann's method. R. S. C.

Trypanocidal activity. II. Derivatives of β-naphthylamine-4 : 6 : 8-trisulphonic acid. G. T. Morgan and J. G. Mitchell (J.C.S., 1932, 1910—1912).—Interaction of β-naphthylamine-4 : 6 : 8-trisulphonic acid (I) (prep. of Na_2 salt described) with 2-nitro-p-toluoyl chloride and 3-nitrobenzoyl chloride in alkaline solution affords the Na_3 salts of 3-*nitro*-4-*methylbenzoyl*- (II) and 3-*nitrobenzoyl*-β-*naphthylamine*-4 : 6 : 8-*trisulphonic acid*, respectively. Reduction of (II) with Fe and HCl, followed by interaction with 3-nitrobenzoyl chloride and 2-nitro-p-toluoyl chloride in alkaline solution, affords the Na_3 salts of 3′-*nitrobenzoyl*- (III) and 3′-*nitro*-4′-*methylbenzoyl*-3-*amino*-4-*methylbenzoyl*-β-*naphthylamine*-4 : 6 : 8-*trisulphonic acid* (IV). Reduction of the 3-nitrotoluoyl derivative of (I) with Fe and HCl and further reaction with 2-nitro-p-toluoyl chloride affords the Na_3 salt of 3′-*nitro*-4′-*methylbenzoyl*-3-*aminobenzoyl*-β-*naphthylamine*-4 : 6 : 8-*trisulphonic acid* (V). (III), (IV), and (V) with $COCl_2$ in alkali (after reduction with Fe and HCl) afford the *Na* salts of *ureido*-3′-*aminobenzoyl*-3-*amino*-4-*methylbenzoyl*-, *ureido*-3′-*amino*-4′-*methylbenzoyl*-3-*amino*-4-*methylbenzoyl*-, and *ureido*-3′-*amino*-4′-*methylbenzoyl*-3-*aminobenzoyl*-β-*naphthylamine*-4 : 6 : 8-*trisulphonic acid*. The therapeutic action of these substances against trypanosomiasis was investigated. J. L. D.

2 : 4-Diamino-1-methylnaphthalene. H. W. Thompson (J.C.S., 1932, 1830—1832).—Interaction of CHPhMe·CN with Et sodiocyanoacetate in boiling EtOH during 15 hr. affords *Et* α-*cyano*-β-*imino*-γ-*phenylvalerate*, m.p. 107° (I), different from the product of methylation of Et α-cyano-β-imino-γ-phenylbutyrate (*ibid.*, 1906, 89, 1906). (I) with H_2SO_4 at 0° affords *Et* 2 : 4-*diamino*-1-*methylnaphthalene*-3-*carboxylate*, m.p. 115° (lit., 74°). Removal of the CO_2Et group followed by acetylation affords 2 : 4-*diacetamido*-1-*methylnaphthalene*, m.p. 303°, identical with the Ac derivative of the *amine*, m.p. 93° (lit., 65°), obtained by reducing 2 : 4-dinitro-1-methylnaphthalene with H_2O and PI_3 during 1 hr. at 100°. J. L. D.

Complex compounds of cobalt with *s*-diphenylethylenediamine. J. V. Dubský and A. Langer (Coll. Czech. Chem. Comm., 1932, 4, 193—199).—A repetition of the work of Gapon (A., 1930, 765) has not yielded the substances described. The products are mixtures of *s*-diphenylethylenediamine hydrochloride with $CoCl_2$ or with the double salt formed by these. E. S. H.

Chromability of azo-dyes from hydroxyquinolines. C. Courtot and H. Hartman (Compt. rend., 1932, **194**, 1949—1952).—The coupling of all possible hydroxyquinolines with diazotised sulphanilic, metanilic, naphthionic, α-naphthylamine-5- and -8-sulphonic, amino-G and -R, and anthranilic acids has been investigated. Only the 5-, 6-, 7-, 8- (*i.e.*, all positions in the Ph nucleus) and 3-OH-derivatives couple, the bathochromic effect of the OH group being greater the closer is its proximity to the N atom, the 8-OH group having the biggest effect. Chromability is generally observed only with dyes from 5- and 8-hydroxyquinoline, but all the hydroxyquinolines give chromable dyes with diazotised anthranilic acid. J. W. B.

Diazo-resins. I. Z. Jolles [with W. Camigliemi] (Atti R. Accad. Lincei, 1932, [vi], **15**, 292—297).—Diazo-resins have been obtained in 70—93% yield in alkaline medium from the normal diazo-compounds from the following amines: NH_2Ph, *m*- and *p*-$C_6H_4Me{\cdot}NH_2$, *o*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$, *o*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}OEt$, *o*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$, and α-$C_{10}H_7{\cdot}NH_2$. Small proportions of the corresponding aromatic hydrocarbons are usually formed in the reaction. In most cases the N content of the products agrees well with the equation (for NH_2Ph) $4Ph{\cdot}N_2{\cdot}OH = C_{24}H_{18}ON_2+H_2O+3N_2$. The resinification seems to be due to internal oxidation of the diazonium hydroxides. T. H. P.

Stability of solutions of diazo-compounds. I, II. P. P. Viktorov (J. Appl. Chem., Russia, 1931, **4**, 777—791, 792—805).—Reducing substances retard the decomp. of solutions of diazo-compounds during the first few hr.; $Na_2S_2O_5$ or $NaHSO_3$ is satisfactory, but not $Na_2S_2O_4$. The effect of NO_3' is catalytic. The rate and degree of decomp. of *p*-nitrodiazobenzene depend on the [OH'] of the neutralising agent. When salts of the same cations are used for neutralisation the decomp. is greatest with the salt having the smallest dissociation const., whilst with salts containing the same anions the decomp. is greatest with the salt which has the most basic cation. HCO_2Na and $CaCO_3$ are exceptions. If $Al(OH)_3$ is used, the quantity taken should be double the calc. amount. Ch. Abs.

Thermal behaviour of phenols at high pressures. A. Hagemann and M. Neuhaus (Braunkohle, 1931, **30**, 949—953, 976—981; Chem. Zentr., 1932, i, 1028—1029).—The tendency of the phenols of tar to produce coke, with elimination of H_2O, CO_2, and CO, increases with increasing mol. wt. The velocity of polymerisation or condensation can be depressed by addition of solvents (*e.g.*, 2·86 mols. of C_6H_6 per mol. of phenol at 410—415°). Solvents which permit dissociation of phenols (*e.g.*, H_2O) or salt formation (*e.g.*, NaOH) considerably increase the reaction velocity. Only by the use of solvents is the catalytic hydrogenation of phenols of high b.p. possible. A. A. E.

Effect of heating of alkali phenoxide solutions under pressure. F. Hofmann, L. Boente, W. Steck, and J. Amende (Naturwiss., 1932, **20**, 403—404).—The reaction products obtained by heating under pressure solutions of PhOH, resorcinol, and α- and β-naphthol in 30—50% aq. NaOH or KOH have been examined. Reaction commences at 415°, 320°, and 390—400°, respectively, the nature of the alkali having no effect; 40—50% of the PhOH, 60% of the resorcinol, and about 20% of the naphthol are converted into CO_2 and H_2O and in all cases H_2, CH_4, and other paraffins are formed. PhOH also yields C_6H_6, PhMe, xanthen, Ph_2O, and coumaran; from the complex reaction products of resorcinol have been isolated 2 : 7-dimethylnaphthalene, COMePr, and higher ketones. α- and β-Naphthol both yield C_6H_6, MePh, *o*-xylene, *o*-ethyltoluene, $C_{10}H_8$, 2-methylnaphthalene, and di-indene; in addition, α-naphthol affords ββ-dinaphthyl and β-naphthol 1 : 2-benzanthracene. AcOH is produced in all cases, salicylic acid from PhOH, *o*-toluic acid from the naphthols, and β-*o*-tolylpropionic acid from β-naphthol. The mechanism of the formation of the various products from naphthol is briefly discussed; the alkali acts as an oxidising agent, removes CO_2H groups, promotes condensation, and, when H_2 is evolved in the early stages, causes hydrogenation of part of the naphthol to $C_{10}H_8$. β-*o*-Tolylacrylic acid is probably an intermediate product from β-naphthol. A. R. P.

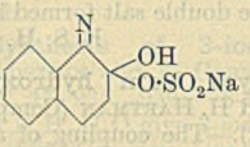
Molecular organic compounds. IV. Molecular organic compounds of phenol, their parachors and refractivities. C. A. Buehler, J. H. Wood, D. C. Hull, and E. C. Erwin (J. Amer. Chem. Soc., 1932, **54**, 2398—2405; cf. this vol., 153).—Mol. compounds (some of which are new) of PhOH and the following substances are isolated; the mol. ratio and m.p. (corr.) are quoted after the second component: NH_2Ph, 1 : 1, 32·6°; *o*-$C_6H_4Me{\cdot}NH_2$, 1 : 1, 35·6°; *m*-$C_6H_4Me{\cdot}NH_2$, 1 : 1, −7°; *p*-$C_6H_4Me{\cdot}NH_2$, 1 : 1, 33°; *m*-4-xylidine, 1 : 1, 16°; α-$C_{10}H_7{\cdot}NH_2$, 1 : 1, 29·1°; β-$C_{10}H_7{\cdot}NH_2$, 1 : 1, 84·4°; benzidine, 1 : 1, 128·4°; *o*-$C_6H_4(NH_2)_2$, 1 : 1, 44·2°; *o*-$C_6H_4(NH_2)_2$, 4 : 1, 29·7°; *m*-$C_6H_4(NH_2)_2$, 3 : 2, 58°; *p*-$C_6H_4(NH_2)_2$, 1 : 1, 98·6°; *p*-$C_6H_4(NH_2)_2$, 2 : 1, 106·5°; $CO(NH_2)_2$, 2 : 1, 61·5°; NH_2Ac, 2 : 1, 42·9°; $NH_2Ac{-}H_2O$, 2 : 1 : 1, 42·1°; NH_2Bz, 2 : 1, 31°; $NHEt_2$, 1 : 1, 12°; pyridine, 1 : 1, −19°; pyridine, 2 : 1, 4°. Vals. of d, γ, and P (parachor) are given for PhOH, NH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$, and *m*-4-xylidine at 25—150°; the observed P are lower than the calc. vals. and increase gradually with rise in temp. (as with alcohols and fatty acids). Vals. are also given for the mol. compounds of PhOH with NH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$, and *m*-4-xylidine at 25—150°; the same relationship exists in these cases, but the temp. coeffs. and the differences between the observed and calc. vals. are greater; it is probable that in both cases association occurs, the amount of which becomes smaller with rise in temp. Vals. of n at 45° for the D, α, and β lines are given for PhOH, NH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$, and *m*-4-xylidine, and for their mol. compounds, and vals. of MR_{D} and EMR_{D} [MR_{D} (obs.)$-MR_{\mathrm{D}}^{20}$ (calc.)] are given for the same series of compounds at 20° (calc.), 45°, 60°, and 80°. A comparison of these vals. indicates that the linking between the components in the mol. compounds has a negative val. C. J. W. (*b*)

Catalytic decomposition of phenol silver salts. VI. Synthesis of 4′-chloro-3 : 5-dibromo-2′ : 6′-di-iodo-4-hydroxydiphenyl ether and the decomposition of its metallic salts. W. H. HUNTER and M. A. DAHLEN (J. Amer. Chem. Soc., 1932, 54, 2456—2463; cf. A., 1921, i, 239).—*4′-Chloro-2′ : 6′-di-iodo-4-methoxydiphenyl ether* (I), m.p. 101—102°, is prepared by the usual method from the 4′-NH_2 derivative; the 4′-*bromo*-2′ : 6′-*di-iodo*-, b.p. 209—219°/2 mm., m.p. 123—123·5°, and 2′ : 4′ : 6′-*tri-iodo*-, b.p. 220—230°/1—2 mm., m.p. 132—133°, analogues are obtained similarly. (I), HI, red P, and AcOH give 82% of 4′-*chloro*-2′ : 6′-*di-iodo-4-hydroxydiphenyl ether* (II), m.p. 154·5°, brominated in AcOH at 75°—b.p. to 4′-*chloro*-3 : 5-*dibromo*-2′ : 6′-*di-iodo-4-hydroxydiphenyl ether*, m.p. 194·5°, the K salt of which decomposes in aq. solution containing a trace of Br, to the amorphous *oxide*, $(C_{12}H_4O_2ClBrI_2)_x$ (also formed by the action of I in KI). The *Ag* salt is decomposed by EtI, I, or by heat to the same oxide. The K and Ag salts of (II) are not decomposed to an amorphous oxide. These results confirm the mechanism previously suggested for the catalytic decomp. of metal salts of halogenophenols. 4-*Bromo*-2′ : 6′-*di-iodo-4-hydroxydiphenyl ether* has m.p. 162—163°. C. J. W. (*b*)

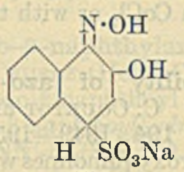
Nitrous acid as a nitrating agent. II. Nitration of dimethyl-*p*-anisidine. H. H. HODGSON and J. H. CROOK (J.C.S., 1932, 1812—1815; cf. A., 1930, 466).—Dimethyl-*p*-anisidine (I) (prep. described) (*picrate*, m.p. 139°) affords with HNO_2 mainly 3-*nitrodimethyl*-p-*anisidine*, m.p. 14° (*hydrochloride*, m.p. 95°; *picrate*, m.p. 143°), also obtained when 4-*chloro*-3-*nitroanisole*, m.p. 45° (prep. from acet-*p*-anisidide), is heated in EtOH with $NHMe_2$, and <1% of *nitroso-monomethyl*-p-*anisidine*, m.p. 47°. Nitration of (I) with conc. HNO_3 in H_2SO_4 at 0° affords 2-*nitrodimethyl*-p-*anisidine*, m.p. 44° (*picrate*, m.p. 175°). These results are discussed in the light of current electronic theory. J. L. D.

Structure of acetone–cresol condensation products. J. B. NIEDERL (Monatsh., 1932, 60, 150—158).—Crit. comparison of analytical results and chemical properties favours the formula $C_{23}H_{28}O_2$ for these products (cf. A., 1929, 551). E. W. W.

Structure of hydrogen sulphite compound of nitroso-β-naphthol (Bucherer's reaction). S. V. BOGDANOV (J. Gen. Chem. Russ., 1932, 2, 9—22).—It is contended that in the reaction between salts of H_2SO_3 and naphthol derivatives, with the formation of a H sulphite compound, the naphthol does not react in the keto-form. This view is corroborated by the stability of the H sulphite compounds towards acids, whereas the corresponding compounds of aldehydes and ketones are rapidly destroyed. By boiling nitroso-β-naphthol with $NaHSO_3$ 1-amino-β-naphthol-7-sulphonic acid is slowly formed. If the conventional formula (I) is assumed for the H sulphite compound, this reaction can be explained only by the sulphonating action of the excess of $NaHSO_3$. By treating the pure H sulphite compound, however, with Zn dust and NH_4Cl or $SnCl_2$ and HCl, the same sulphonic acid is readily formed, indicating that the sulphonating agent is the $O{\cdot}SO_2Na$ group. The constitution (II) is suggested for the H sulphite compound, and its reduction to 1-amino-β-naphthol-4-sulphonic acid follows. The possibility of its reacting in the tautomeric keto-form (III) was investigated by treating it with NH_2OH,HCl in HCl solution, in the hope of obtaining (III) with :O replaced by :N·OH (IV). Instead of the latter, NH_4 2-nitroso-α-naphthol-4-sulphonate (V) was obtained. It is suggested that (IV) is formed as an intermediate stage in the reaction. In the presence of HCl the α-NOH group is hydrolysed and the NH_2OH formed reacts with the sulphonic group to give (V). This reaction gives further proof that the SO_3H of the H sulphite compound is in the 4-position. The bearing of the above conclusions on the structure and reactions of the H sulphite compounds of other naphthol derivatives is discussed. M. Z.



(I.)



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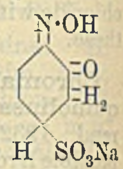
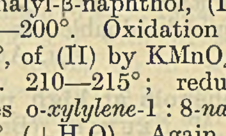
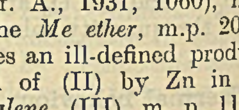


(III.)

Action of *o*-phthaloyl chloride on the methyl ethers of β-naphthol and of β-thionaphthol. W. KNAPP (Monatsh., 1932, 60, 189—204; cf. A., 1929, 186; 1930, 1183, 1296).—The action of *o*-phthaloyl chloride and $AlCl_3$ on β-naphthyl Me sulphide in CS_2 gives, not thionaphtholphthalein Me_2 ether, but o-2-*methylthiol-α-naphthoylbenzoic acid*, m.p. 178—179°; in *s*-$C_2H_2Cl_4$ the product is 2-*methylthiol*-1 : 8-*phthalylnaphthalene*, (I), m.p. 195°, which is oxidised by $KMnO_4$ to unsatisfactory products. Similarly, β-naphthyl Me ether gives in CS_2 o-2-*methoxy-α-naphthoylbenzoic acid*, m.p. 195—196° (severely degraded by HBr in AcOH), and, in *s*-$C_2H_2Cl_4$, 1 : 8-phthalyl-β-naphthol, (II) (cf. A., 1931, 1060), m.p. 199—200°. Oxidation of the *Me ether*, m.p. 206—208°, of (II) by $KMnO_4$ gives an ill-defined product, m.p. 210—215°; reduction of (II) by Zn in H_2 gives o-*xylylene*-1 : 8-*naphthalene* (III), m. p. 113—115° (+H_2O). Again, 4-*bromo-α-naphthyl Me sulphide*, b.p. 200°/13 mm., obtained by the action of Me_2SO_4 on 4-bromo-α-thionaphthol (from 1-bromonaphthalene-4-sulphonyl chloride, reduced by Sn and HCl), gives, in CS_2, o-4-*bromo*-1-*methylthiol-β-naphthoylbenzoic acid*, m.p. 185—186°, whilst 4-bromo-α-naphthyl Me ether gives, in CS_2, *o*-4-bromo-1-hydroxy-β-naphthoylbenzoic acid. E. W. W.

(I.)




(III.)

Preparation of a new ethylnaphthol. G. LÉVY (Compt. rend., 1932, 194, 1952—1954).—α-Benzyl-*n*-butyric acid (*amyl* ester, b.p. 154°/15 mm.) is converted by Braun's synthesis (A., 1927, 258) into

1-keto-3-ethyltetrahydronaphthalene, dehydrogenated by Se (this vol., 266) directly to 3-*ethyl*-α-*naphthol*, m.p. 50·5—51° [*picrate*, m.p. 145° (corr.)].

J. W. B.

Preparation of unsymmetrical diphenyl derivatives. I. R. Sherwood, W. F. Short, and R. Stansfield (J.C.S., 1932, 1832—1835).—An improved method of synthesising unsymmetrical Ph_2 derivatives is described. *cyclo*Hexanones or *cyclo*hexenones and MgAr halides afford *tert.*-alcohols which are dehydrogenated by S (theoretical amount during 3·5—5 hr. at 180—250°), either directly or after dehydration by conc. HCO_2H, to give Ph_2 derivatives. Many aryldiphenyls are prepared in good yield. *cyclo*Hexanone in boiling Et_2O affords with Mg and 3-bromo-*p*-tolyl Me ether during 0·5 hr. 1-(4′-*methoxy*-m-*tolyl*)cyclo*hexanol*, m. p. 77°, dehydrogenated to 2-*methoxy*-5-*methyldiphenyl*, b.p. 170—175°/20 mm., which with HI and red P at 150° for 8 hr. affords 2-*hydroxy*-5-*methyldiphenyl*, m.p. 68°.

J. L. D.

Preparation of β-arylethylamines from α-cyano-β-arylacrylic acids. J. A. McRae and W. H. Vining (Canad. J. Res., 1932, **6**, 409—416).—α-Cyano-β-arylacrylic acids (J.C.S., 1922, **121**, 1699) are reduced by Na–Hg to α-cyano-β-arylpropionic acids, which when heated with Cu powder or (preferably) quinoline give β-arylpropionitriles. These are hydrolysed by cold fuming HCl to β-arylpropionamides, converted by alkaline NaOBr into β-arylethylamines. β-Piperonyl-, β-anisyl-, β-veratryl-, and β-phenyl-ethylamines are prepared. α-*Cyano*-β-4-*hydroxy*-3-*methoxyphenylpropionic acid*, m.p. 80°; β-4-*hydroxy*-3-*methoxyphenylpropionitrile*, b.p. 189—192°/11 mm., m.p. 58°; 3 : 4-*methylenedioxycinnamonitrile*, m.p. 92°, and 4-*hydroxy*-3-*methoxycinnamonitrile*, m.p. 112°, are incidentally described. α-3 : 4-*Methylenedioxyphenylsuccinimide*, m.p. 169° (from the corresponding NH_4 salt at 150—160°), is hydrolysed to the succinic acid by alkaline NaOBr; the NH_2-acid is not produced.

H. B.

Synthesis of pharmacologically important amines. IV. Syntheses of tyramine and epinine. V. Syntheses of hydrastinine, cotarnine, and lodal. K. Kindler and W. Peschke (Arch. Pharm., 1932, **270**, 340—353, 353—362; cf. this vol., 54).—IV. Catalytic reduction (Pd-black) in AcOH of Me *p*-methoxycinnamate, b.p. 182°/13 mm. [prepared in 92% yield from vanillin (I), MeOAc, and Na], gives Me β-*p*-methoxyphenylpropionate, b.p. 284°, m.p. 38°, transformed by 25% aq. NH_3 at room temp. into the amide (II), which yields β-*p*-methoxyphenylethylamine; this with 37% HCl at 150—160° gives tyramine. The yields in the above reactions are nearly quant. *p*-Methoxypropiophenone, $NHMe_2$, and S in C_6H_6 at 130° give β-p-*methoxyphenylthiopropiondimethylamide*, m.p. 70°, hydrolysed by hot aq.-alcoholic KOH to β-*p*-methoxyphenylpropionic acid, which with dry NH_3 at 210° gives a 90% yield of (II).

3 : 4-Dimethoxyacetophenone and NH_2Me at −15° give a product, which, when heated with S, affords 3 : 4-*dimethoxyphenylthioacetmethylamide*, m.p. 130°. This, when reduced electrolytically, affords N-*methyl*-β-3 : 4-*dimethoxyphenylethylamine* (III), b.p. 159°/11 mm. [*picrate*, m.p. 170° (lit. 162—163°)], demethylated to epinine by 37% HCl at 150—155°. By the methods used with (I) methylvanillin affords Me 3 : 4-dimethoxycinnamate, Me β-3 : 4-dimethoxyphenylpropionate (IV), b.p. 181°/13 mm., m.p. 37—38°, β-3 : 4-dimethoxyphenylpropionamide, and β-3 : 4-dimethoxyphenylethylamine (homoveratrylamine) (*Bz* derivative, m.p. 90—91°; *picrate*, m.p. 165°). The last amine and PhCHO give an oily CHPh: compound, which with Me_2SO_4 in dry C_6H_6 at 90° yields an additive compound, transformed by further heating into (III). Veratrole, EtCOCl, and $AlCl_3$ in CS_2 give 3 : 4-dimethoxypropiophenone, which with $NHMe_2$ and S in C_6H_6 at 130° gives β-3 : 4-*dimethoxyphenylthiopropiondimethylamide*, m.p. 94°, transformed by hydrolysis and subsequent esterification into (IV).

V. Benzylidenehomopiperonylamine and Me_2SO_4 in C_6H_6 at 85—90° give an additive compound, which, when further heated in EtOH, yields *N*-methylhomopiperonylamine (I); the formyl derivative of this (prepared by HCO_2H at 210°) with $SOCl_2$ in dry C_6H_6 at 90° gives hydrastinine hydrochloride. β-3 : 4-Methylenedioxy-5-methoxyphenylethylamine (homomyristicylamine) gives similarly the N-*Me* derivative (II), b.p. 173°/13 mm. (*picrate*, m.p. 194°; *hydrochloride*, m.p. 171°), the formyl derivative of which affords cotarnine hydrochloride.

[With R. Schaeffer and H. Christlieb.] Myristicin, $KMnO_4$, Na_2SO_4, and $MgCO_3$ in cold EtOH give myristic and *homomyristic acid*, m.p. 127°; the latter with dry NH_2Me at 210° gives the *methylamide*, m.p. 134°, transformed by K_2S and P_2S_5 in xylene at 150° into the *methylthioamide*, m. p. 152°, which, when reduced electrolytically, gives (II). The formyl derivative of *N*-methylhomoveratrylamine with $SOCl_2$ in hot C_6H_6 gives lodal. The yields in the above syntheses are very good.

R. S. C.

Action of halogens and of alkyl halides on the salts of tribromothiophenol. W. H. Hunter and A. H. Kohlhase (J. Amer. Chem. Soc., 1932, **54**, 2425—2432).—2 : 4 : 6-Tribromothiophenol and its salts react normally with halogens and alkyl halides to give the disulphide or thio-ethers in nearly quant. yield. Products analogous to the amorphous polydihalogenophenylene oxides (obtained from the trihalogenophenols and phenoxides) are not formed. The first stage in the reaction of both phenoxides and thiophenoxides is probably the formation of metal halide and an unstable product containing halogen directly attached to O or S. Details are given for the prep. of 2 : 4 : 6-*tribromophenyl ethylxanthate* [obtained together with a small amount of di(tribromophenyl) dithiolcarbonate], hydrolysed by MeOH–KOH to 2 : 4 : 6-*tribromothiophenol* (I), m.p. 115·5—115·9° (corr.) [*acetate*, m.p. 102·1—102·7° (corr.)]. *Di*-2 : 4 : 6-*tribromophenyl dithiolcarbonate*, m.p. 194·2—194·7° (corr.), is also hydrolysed to (I). The *Ag* salt of (I) and I in C_6H_6 give 92% of 2 : 4 : 6 : 2′ : 4′ : 6′-*hexabromodiphenyl disulphide* (II), m.p. 221·8—222·7° (corr.), reduced by Na and C_6H_6–EtOH to (I). (II) is readily prepared by atm. oxidation of the NH_4 or Na salt of (I), by the action of halogen on (I) (or its salts), and by the reduction of tribromobenzenesulphonic acid with PBr_5. The Ag salt and

EtI give *tribromophenyl Et sulphide*, an oil; with MeI, the *Me sulphide* (2 : 4 : 6-*tribromothioanisole*), m.p. 59·6—60·5°, results. The Na salt of (I) and Br in aq. KBr give about 45% of (II) and about 50% of 2 : 4 : 6-*tribromophenylsulphonyl bromide*, m.p. 74·5—75·7°. The Na salt and liquid Br give as the only definite product (II), also formed from (I) and Br in C_6H_6. PhSH and Br in AcOH afford 4 : 4′-dibromodiphenyl disulphide. C. J. W. (*b*)

Germicidal activity of aromatic sulphides. E. Moness, W. Braker, and W. G. Christiansen (J. Amer. Pharm. Assoc., 1932, **21**, 557—569).—By a modified Hinsberg reaction were prepared 4-hydroxy-(I), b.p. 162—164°/3—4 mm., 4-*hydroxy*-3-*methyl*-(II), m.p. 72°, b.p. 185—190°/4 mm., -2-*methyl*-(III), b.p. 192—197°/5 mm., -3-*carboxy*- (IV), b.p. 162—167°/3—4 mm., cryst., and -3-*ethyl*- (V) (from o-*ethylphenol*) -*diphenyl sulphide*. *p*-Bromophenetole, NaOEt, and Cu powder at 280° give the *Et ether* (VI) of (I) in poor yield. (I), NaOEt, and β-diethylaminoethyl bromide in hot EtOH give the β-*diethylaminoethyl ether* (VII) (*hydrochloride*) of (I); the corresponding *ether* (VIII) of 4-hydroxy-3-methyldiphenyl sulphide was similarly prepared. *o*-Hydroxydiphenyl and SCl_2 in cold CS_2 give 6 : 6′-*dihydroxy*-3 : 3′-*didiphenylyl sulphide* (IX), an oil, and PhOH gives similarly 4 : 4′-dihydroxydiphenyl sulphide (X). *p*-Methoxythiophenol, NaOEt, and *n*-amyl bromide in hot EtOH give p-*anisyl* n-*amyl sulphide*, an oil, hydrolysed (Ac_2O–HBr) to the p-*OH*-compound, b.p. 123—130°. The following were the sole products of the appropriate Hinsberg reaction: 4-*hydroxy*-3-*nitro*- (XI), b.p. 175—181°/5 mm., -3-*bromo*- (XII), b.p. 173—179°/3—4 mm., and -3-*phenyl-diphenyl disulphide*. The toxicity to typhoid bacillus is in the order (I) > (V) and (VIII) > (VII) > (IX) > (X) > (III), (VI), (XI), and (XII) > (II) and (IV), and to staphylococcus (V) > (II) > (III) > (I) > (IX) > (VI), (XI), and (XII) > (IV) > (VII) and (VIII) > (X). Numerous *OAc·Hg* compounds were prepared, but did not show increased toxicity. R. S. C.

2-Amino*cyclo*pentanol and its resolution. M. Godchot and M. Mousseron (Compt. rend., 1932, **194**, 2061—2063).—*cyclo*Pentene oxide and conc. aq. NH_3 at 110° give (trans)-dl-2-*amino*cyclo*pentanol* (I), b.p. 114—115°/13 mm., 205—206°/760 mm. (*hydrochloride*, m.p. 192—193°; *chloroplatinate*; *mercurichloride*; *Ac*, b.p. 194—195°/15 mm., and p-*toluenesulphonyl*, m.p. 142—143°, derivatives; *H* d-*tartrate*, m.p. 69—70°; *H* l-*tartrate*, m.p. 69—70°), converted by PCl_5 in $CHCl_3$ at 0° into 2-*chloro*cyclo*pentylamine*, b.p. 63—64°/12 mm. (*hydrochloride*, m.p. 169—170°). (I) is resolved by *d*- and *l*-tartaric acids into (+)-, α_D +38·25° (*hydrochloride*, m.p. 155—156°, α_D +29·3°; d-*tartrate*, m.p. 77—78°, α_D +29·55°), and (—)-*forms*, α_D —38·25° (*hydrochloride*, m.p. 155—156°, α_D —29·3°; l-*tartrate*, m.p. 77—78°, α_D —29·5°). The former and PCl_5 in $CHCl_3$ give (—)-2-*chloro*cyclo*pentylamine*, b.p. 61—62°/12 mm., α_D —44·9°, converted by $AgNO_3$–Na_2CO_3 into the latter. H. B.

***cis–trans*-Isomerism and steric hindrance. XIII. 2-Methyl*cyclo*hexanols.** G. Vavon, (Mlle.) A. Perlin, and A. Horeau (Bull. Soc. chim., 1932, [iv], **51**, 644—650).—Pure *trans*- (*H succinate*, m.p. 43—44°; 3 : 5-*dinitrobenzoate*, m.p. 115°) and *cis*-2-methyl*cyclo*hexanol (*H succinate*, m.p. 44—44·5°; 3 : 5-*dinitrobenzoate*, m.p. 99—100°; H phthalate, m.p. 104—105°) have been obtained by various methods (cf. this vol., 157). Conditions for the conversion of the *trans*- into the *cis*-alcohol with *p*-toluenesulphonyl chloride are given. The *trans*-H phthalate and succinate are hydrolysed more quickly than the *cis*-, whilst the *cis*-alcohol is more quickly oxidised by CrO_3, and dehydrated by H_2SO_4. A. A. L.

Δ^1-*cyclo*Pentenylalkylcarbinols. Urion (Compt. rend., 1932, **194**, 2311—2313).—Δ^1-cyclo*Pentylmethyl*-, b.p. 165—166°/749 mm., -*ethyl*-, b.p. 179—180°/749 mm., and -n-*propyl*-, b.p. 197—198°/760 mm., -*carbinols*, prepared from Δ^1-*cyclo*pentene-1-aldehyde (A., 1930, 1039) and the requisite Mg alkyl bromide, are dehydrated by Al_2O_3 at about 320° to α-Δ^1-cyclo*pentenyl-ethylene*, b.p. 114—115°/754 mm., -Δ^α-*propene*, b.p. 142—144°/754 mm., and -Δ^α-*butene*, b.p. 59—62°/14 mm., respectively. H. B.

Colour reaction of the sterols. E. Montignie (Bull. Soc. chim., 1932, [iv], **51**, 690).—Cholesterol, phytosterols, stigmasterol, and ergosterol on evaporation with silicotungstic acid in EtOH give a reddish-brown coloration, α- and β-cholesterylene and cholestenone give a reddish-yellow, turpentine, eucalyptus oil, terpine, camphor, and borneol give an orange-yellow, whilst menthol, lemon oil, abietic acid, and aromatic hydrocarbons give negative results. The colour with the sterols may be due to the presence of an indene grouping, since this substance gives a red coloration with the above test. A. A. L.

β-Cholesterol. T. Wagner-Jauregg and L. Werner (Z. physiol. Chem., 1932, **208**, 72—76).—β-Cholesterol, obtained as a by-product in the reduction of cholestenone with Na and EtOH (or preferably MeOH), is a mol. compound of cholesterol and dihydrocholesterol. J. H. B.

Colloidal condition of cholesterol, cholesteryl ester, and lethicin. VII. Tautomerism of cholesterol. I. Remesov (Biochem. Z., 1932, **248**, 256—263; cf. this vol., 632).—The catalytic action of cholesterol is strengthened by ultra-violet radiations and to a much slighter extent by filtered ultra-violet radiations (λ 400—300 mμ). The portion of the irradiated material which is pptd. by digitonin lacks catalytic activity almost entirely, whilst the non-pptd. material is catalytically active, especially if irradiation takes place in an atm. of N_2. Over-irradiated cholesterol (oxycholesterol) is without catalytic properties. It is concluded that ordinary cholesterol is an equilibrium mixture of a catalytically inactive enol form and a keto-form (the " peroxide " form) which is produced by the ultra-violet irradiation and is responsible for the catalytic property. W. M.

Number of carbon atoms in the mol. of sitosterol and other sterols. A. Windaus, F. von Werder, and B. Gschaider (Ber., 1932, **65**, [*B*], 1006—1009).—Elementary analysis of esters and determination of Ac in acetates establishes the following formulæ: cholesterol, $C_{27}H_{46}O$; sitosterol, $C_{29}H_{50}O$; stigmasterol, $C_{29}H_{48}O$; agnosterol, $C_{30}H_{48}O$; lanosterol, $C_{30}H_{50}O$. For ergostanol the data lie between C_{28} and C_{29}, but exclude C_{27}. The following esters of sitosterol are described: 3 : 5-*dinitrobenzoate*, m.p. 203°, $[\alpha]_D^{22}$ −10·6°; 2-*chloro*-3 : 5-*dinitrobenzoate*, m.p. 174—175°, $[\alpha]_D^{22}$ −7°; 3 : 5-*dinitro*-p-*toluate*, m.p. 189°, $[\alpha]_D^{22}$ −6·4°; 4-*bromo*-3-*nitrobenzoate*, m.p. 169°, $[\alpha]_D^{22}$ +0°; *bromoacetate*, m.p. 174—175°, $[\alpha]_D^{20}$ +0·31° in $CHCl_3$. *Ergosteryl* 3 : 5-*dinitro*-p-*toluate*, m.p. 213—214°, $[\alpha]_D^{20}$ −49° in $CHCl_3$, and 2-*chloro*-3 : 5-*dinitrobenzoate*, m.p. 203—204°, $[\alpha]_D^{25}$ −38° in $CHCl_3$, and *vitamin-D_2* 3 : 5-*dinitro*-p-*toluate*, m.p. 115—116°, $[\alpha]_D^{22}$ +91° in $COMe_2$, and 2-*chloro*-3 : 5-*dinitrobenzoate*, m.p. 132°, $[\alpha]_D^{22}$ +60° in $COMe_2$, are described. H. W.

Sterol group. XII. Oxidation of α-ergostenol and derivatives. I. M. Heilbron, J. C. E. Simpson, and D. G. Wilkinson. **XIII. Hydrocarbons of ergosterol series.** I. M. Heilbron, F. S. Spring, and E. T. Webster. **XIV. β-Ergostenol and derivatives.** I. M. Heilbron and D. G. Wilkinson. **XV. Relationship between α- and β-ergostenol and derived hydrocarbons.** A. L. Morrison and J. C. E. Simpson (J.C.S., 1932, 1699—1705, 1705—1707, 1708—1710, 1710—1714).—XII. Oxidation of α-ergostenol (I) with CrO_3–AcOH at 67—70° gives only a little α-ergostenone (II) (cf. Reindel, A., 1929, 61); the main product is a yellow neutral *compound* (III), $C_{21-22}H_{32-34}O_2$, m.p. 185° (*hydroxylamine*, m.p. 196—198°, and *semicarbazide*, m.p. 275°, derivatives), and is accompanied by a minute amount of a cryst. *acid* (IV), $C_{22-23}H_{34-36}O_4$, m.p. 214—216° (?) (isolated as *Me* ester, m.p. 211—213°). Reduction of (III) by Clemmensen's method gives a *hydrocarbon*, $C_{21-22}H_{36-38}$, m.p. 85—86°. Catalytic dehydrogenation of (I) with Cu-bronze at its b.p./0·1 mm. gives (II) in about 60% yield; (II) and (IV) are also formed by oxidation of (I) with the Beckmann reagent. Oxidation of α-ergostenyl acetate with CrO_3–AcOH at 60° gives *α-ergostenonyl acetate* (V), m.p. 170—171° (*semicarbazone*, m.p. 199—200°), two *substances*, $C_{29}H_{44-46}O_4$, m.p. 134—135°, and 214—215°, and a volatile liquid, $C_9H_{18}O$ (*semicarbazone*, m.p. 156—158°) (a dihydrothujaketone; cf. this vol., 611). Hydrolysis of (V) with NaOH in MeOH gives *α-ergostenonol*, $C_{27}H_{44}O_2$, m.p. 155—156°, further oxidised by CrO_3 to *α-ergostendione*, m.p. 183°.

XIII. *α-Ergostadienyl chloride*, m.p. 137°, prepared by interaction of α-dihydroergosterol with $POCl_3$, is reduced by Na and amyl alcohol to *α-ergostadiene*, $C_{27}H_{44}$, m.p. 124—125°, also obtained by reduction of α-ergostadienone by Clemmensen's method. This is converted by HCl in $CHCl_3$ into *β-ergostadiene*, m.p. 66—67°, also prepared by reduction of β-ergostadienyl chloride. *α-Ergostenyl chloride*, m.p. 109—110°, gives on reduction *α-ergostene*, m.p. 77—78°, more readily obtained by reduction of α-ergostenone. Ergostatrienone-*D* (A., 1929, 1065), m.p. 204—205°, is obtained in good yield by dehydrogenation of α-ergostadienone with $Hg(OAc)_2$ in AcOH–EtOH at the b.p., and is reduced by Clemmensen's method to *ergostatriene*-D, m.p. 134—135°, also obtained from α-ergostadiene by the action of $Hg(OAc)_2$.

XIV. *β-Ergostenyl benzoate*, m.p. 158—160°, is prepared from the α-isomeride by the action of HCl in $CHCl_3$, and is hydrolysed by KOH in EtOH to *β-ergostenol* (VI), m.p. 141—142° (*acetate*, m.p. 111—112°), which with H_2–Pd gives ergostanol (*allo-α-ergostanol*; cf. A., 1928, 295). Distillation of (VI) at 0·5 mm. with Cu-bronze gives β-ergostenone (*oxime*, m.p. 220°) (cf. A., 1929, 61); this is reduced by Clemmensen's method to *β-ergostene*, m.p. 87—88°, also obtained by reduction of (crude) β-ergostenyl chloride with Na and amyl alcohol.

XV. Oxidation of α- and β-ergostenol with BzO_2H in $CHCl_3$ at 0° gives α-, m.p. 114—116° (clear at 122°), and *β-ergostenyl oxide*, $C_{27}H_{46}O_2$, m.p. 152—153°, respectively; these with aq. H_2SO_4 in EtOH at its b.p. give dehydroergostenol, also formed by the action of Br (1 mol.) on (VI) (cf. A., 1930, 1178). Both the β-oxide and dehydroergostenol give (I) with H_2 and PtO_2 in AcOH; β-ergostene under the same conditions gives ergostane. α-, m.p. 118—119°, and *β-ergostene oxide*, $C_{27}H_{46}O$, m.p. 122—123°, are similarly prepared, and with H_2SO_4 in EtOH give *dehydroergostene*, $C_{27}H_{44}$, m.p. 71—72°, converted by H_2–PtO_2 into α-ergostene. The similarity of these reactions to those of *apo*cholic and dihydroxycholenic acids (cf. A., 1931, 841, 957) is pointed out, and a similarity of nuclear structure in the two series is suggested. H. A. P.

Esters of dialkylaminomethyl alcohols. E. V. Lynn and F. L. Lofgren (J. Amer. Pharm. Assoc., 1932, 21, 541—548).—The following esters were prepared by condensation of the appropriate *sec.* amine with CH_2O, acylation (Schotten–Baumann), and, when a nitro-acid was used, reduction: *diethylaminomethyl benzoate*, b.p. 157—158°/16 mm., *cinnamate*, m.p. 66—67°, b.p. 190°/17 mm. (*sulphate*, m.p. 121—122°), m- and p-*nitrobenzoate*, m.p. 70—72° and 62—63°, b.p. 200—207°/11 mm. and 200—211°/10 mm., respectively; m- and p-*aminobenzoate*, m.p. 75—76° and 121—122°, b.p. 200—208°/11 mm. and 200—215°/vac. (*hydrochlorides*, m.p. 184—185° and 189—190°), respectively; *di-n-propylaminomethyl benzoate*, b.p. 168—171°/17 mm., *cinnamate*, m.p. 54°, b.p. 200—215°/16 mm. (*sulphate*, m.p. 113—114°); m- and p-*nitrobenzoate*, b.p. 213—218°/11 mm., and m.p. 37—39°, b.p. 210—233°/17 mm., respectively; m- and p-*aminobenzoate*, b.p. 205—210°/9 mm., and m.p. 75—76°, b.p. 215—220°/9 mm. (*hydrochlorides*, m.p. 141—142° and 152—153°), respectively; *di-n-butylaminomethyl benzoate*, b.p. 187—188°/17 mm., *cinnamate*, b.p. 226—227°/14 mm., m- and p-*nitrobenzoate*, b.p. 227—228°/11 mm. and 230—234°/11 mm., respectively, m- and p-*aminobenzoate*, b.p. 215—220°/10 mm. and 210—228°/9 mm. (*hydrochlorides*, m.p. 159—160° and 136—137°), respectively; *diisoamylaminomethyl benzoate*, b.p. 193—194°/16 mm., *cinnamate*, b.p. 227—229°/11 mm., m- and p-*nitrobenzoate*, b.p. 230—233°/11 mm., and m.p. 52—54°, b.p. 232—233°/8 mm., respectively; m- and p-*aminobenzoate*, b.p. 220—233°/10 mm. and 220—235°/10 mm. (*hydrochlorides*, m.p. 178—180° and cryst.), respectively. Some of these compounds have local anæsthetic action, but are irritant. R. S. C.

Natural classification of amines related to adrenaline. Raymond-Hamet (Compt. rend., 1932, 194, 1982—1984).—Adrenaline-like bases are classified as " adrenalinomimetic " or " nicotinic," according as to whether they are vaso-contracting or -dilating in high concn. Bases containing the adrenaline skeleton belong to the first type if (*a*) there are phenolic OH groups in positions 3 and 4, irrespective of the presence of a side-chain OH group [*e.g.*, β-(3 : 4-dihydroxyphenyl)ethylmethylamine, adrenalone, or adrenaline], or (*b*) there is a OH group on the α-C atom of the side-chain and also in the *p*-position [*e.g.*, (β-hydroxy-β-*p*-hydroxyphenyl)ethylmethylamine but not tyramine]. J. W. B.

Enzymic formation and hydrolysis of esters. P. Rona, E. Chain, and R. Ammon.—See this vol., 776.

Manufacture of β-amino-α-phenyl alcohols containing hydroxyl in the phenyl residue. I. G. Farbenind. A.-G.—See B., 1932, 636.

Action of lithium hydride on benzoyl chloride. A. Hodaghian and R. Levaillant (Compt. rend., 1932, **194**, 2059—2060).—LiH and BzCl in petroleum (b.p. 110—130°/15 mm.) and N_2 at 150—210° give benzyl benzoate (I) in 65% yield : $2BzCl+2LiH \longrightarrow 2LiCl+(I)$; LiOBz is a by-product. (I) arises from the intermediate PhCHO under the action of LiH. H. B.

Dynamic isomerism involving mobile hydrocarbon radicals. IV. Rearrangement of 3 : 5-dichloro-substituted triphenylbenzamidines. A. W. Chapman and C. H. Perrott (J.C.S., 1932, 1770—1775).—Extension of the previous investigation (A., 1931, 87) to the cases where R=Ph and $R'=C_6H_3Cl_2$ (3 : 5-), and conversely, gave the expected results. The following were prepared by methods previously described (cf. A., 1929, 1294) : *benz-3 : 5-dichloroanilide*, m.p. 147° (*iminochloride*, m.p. 41°, b.p. 231—232°/16—20 mm.) ; N-3 : 5-*dichlorophenylbenziminophenyl ether*, m.p. 69—70° ; 3 : 5-*dichlorodiphenylamine*, m.p. 41—42°, b.p. 222—224°/25 mm. (*Bz* derivative, m.p. 107—109°) ; N-3 : 5-*dichlorobenzimino*-3 : 5-*dichlorophenyl ether*, m.p. 71° ; 3 : 5 : 3′ : 5′-*tetrachlorodiphenylamine*, m.p. 160—161° (*Bz* derivative, m.p. 135—136°) ; NN′-*diphenyl*-N-3 : 5-*dichlorophenyl*-, m.p. 112°, N-*diphenyl*-N′-3 : 5-*dichlorophenyl*-, m.p. 94—95°, N-*phenyl*-NN′-*bis*-3 : 5-*dichlorophenyl*-, m.p. 95—97°, and N′-*phenyl*-N-*bis*-3 : 5-*dichlorophenylbenzamidine*, m.p. 131—132°. H. A. P.

Ring-closure in triarylamidine series. Source of disecondary *o*-diamines. A. W. Chapman and C. H. Perrott (J.C.S., 1932, 1775—1778).—NN′-*Diphenyl*-N-o-*chlorophenylbenzamidine*, m.p. 171°, gives when heated at 267—269° for 30 min. a water-soluble product, probably 1 : 2 : 3-triphenylbenziminazolium chloride (I), hydrolysed by cold aq. NaOH to *benzoyl*-s-*diphenyl*-o-*phenylenediamine*, m.p. 152° (identified by hydrolysis). Similarly, NN′-*di*-o-*chlorophenyl*-N-*phenylbenzamidine*, m.p. 142°, gives *benzoyl*-N-*phenyl*-N′-o-*chlorophenyl*-o-*phenylenediamine* (position of Bz group not determined), m.p. 124—126°, and N-*diphenyl*-N′-o-*chlorophenylbenzamidine*, m.p. 94°, gives (I) in poor yield at 330°. N-o-*Chlorophenylbenzimino*-o-*chlorophenyl ether*, m.p. 75—76°, and *benzoyl*-2 : 2′-*dichlorodiphenylamine*, m.p. 149°, are described. H. A. P.

Alkamine esters of aromatic acids. Novocaine analogues. II. H. C. Brill (J. Amer. Chem. Soc., 1932, 54, 2484—2487 ; cf. A., 1925, i, 833).—The following b.p. are reported : NHMeEt, 36—37° ; NHEtPr$^{\beta}$, 76° ; NHEtBu, 108—109° ; NPhMeEt, 202° ; NPhEtPr$^{\beta}$, 211° ; NPhEtBu, 247° ; γ-(methylethylamino)propanol, 170° ; γ-(ethyl*iso*propylamino)propanol, 188° ; β-(phenylethylamino)ethanol, 268° ; β-(ethyl*iso*propylamino)ethanol, 175° ; β-(ethylbutylamino)ethanol, 195°. The following alkamine ester *hydrochlorides* are prepared : γ-(methylethylamino)propyl benzoate, m.p. 123° ; β-(phenylethylamino)ethyl propionate, m.p. 171° ; β-(ethyl*iso*propylamino)ethyl benzoate, m.p. 96° ; γ-(ethyl*iso*propylamino)propyl benzoate, m.p. 105° ; β-(ethylbutylamino)ethyl cinnamate, m.p. 151° ; γ-diethylaminopropyl *p*-methoxycinnamate, m.p. 142° ; γ-piperidylpropyl *p*-nitrobenzoate, m.p. 205°, and *p*-aminobenzoate, m.p. 213°. All these compounds (except the *p*-NO_2-derivative) possess anæsthetic properties. C. J. W. (*b*)

Preparation and properties of *tert.*-butyl phenylacetate. D. L. Yabroff and C. W. Porter (J. Amer. Chem. Soc., 1932, 54, 2453—2455).—$CMe_3\cdot OH$ (40 g.) in Et_2O (50 c.c.), slowly added to approx. 0·5 mol. of MgEtBr in Et_2O (300 c.c.), gives $CMe_3\cdot O\cdot MgBr$, which (after refluxing for 15 min.) is then treated with $CH_2Ph\cdot COCl$ (46·1 g.) in Et_2O (50 c.c.) and the mixture boiled for 1 hr. tert.-*Bu phenylacetate*, b.p. 110°/15 mm. (b.p. curve given from about 5 to 30 mm.), m.p. −23° to −21°, is thereby obtained in 65% yield. A prep. of this ester which boils at the same temp. after repeated distillation may show a const. but erroneous val. of *n*. C. J. W. (*b*)

Nitration of the methyl, ethyl, and *tert.*-butyl esters of phenylacetic acid. D. L. Yabroff and C. W. Porter (J. Amer. Chem. Soc., 1932, 54, 2507—2510 ; cf. this vol., 511).—Nitration of the Me, Et, and *tert.*-Bu esters of $CH_2Ph\cdot CO_2H$ gives 12·1, 10·3, and 5·6%, respectively, of the *m*-NO_2-derivative. The effective residual charge in these esters must be slightly more negative than in the free acid, since less of the *m*-derivative is formed. C. J. W. (*b*)

Phenyl-substituted aliphatic acids. J. Harmon and C. S. Marvel (J. Amer. Chem. Soc., 1932, 54, 2515—2526).—Ph-substituted fatty acids are prepared by thermal decomp. of the corresponding malonic acids. The following compounds are described : *phenyloctyl*-, b.p. 124—129°/3 mm., and *phenylnonyl*-, b.p. 121—124°/0·2 mm., -*carbinols* ; *Et α-phenylamyl*-, b.p. 143·5—147°/3·3 mm., *α-phenylnonyl*-, b.p. 186—191°/4 mm., *α-phenyldecyl*-, b.p. 163—166°/0·3 mm., *δ-phenyloctyl*-, b.p. 176—182°/3 mm., *ζ-phenyldecyl*-, b.p. 185—190°/3 mm., *θ-phenyldodecyl*-, b.p. 180—188°/0·13 mm., *δ-phenyltridecyl*-, b.p. 187—194°/0·13 mm., *ζ-phenyltetradecyl*-, b.p. 205—211°/0·25 mm., *η-phenylhexadecyl*-, b.p. 220—225°/0·2 mm., and *θ-phenylhexadecyl*-, b.p. 217—224°/0·15 mm., -*malonates* ; *δ-phenyltridecan-α-ol*, b.p. 158—160°/0·14 mm., formed with a high-boiling acetal from Mg γ-phenyldodecyl bromide and CH_2O ; *δ-phenyloctan-α-ol*, b.p. 125—130°/3 mm., obtained together with an acetal and *γ-phenylheptane*, b.p. 68—71°/3 mm., from Mg γ-phenylheptyl bromide; *ε-phenylnonan-α-ol*, b.p. 137—144°/0·94 mm., from Mg γ-phenylheptyl bromide and $(CH_2)_2O$; *ζ-phenyldecan-α-ol*, b.p. 140—144°/3 mm.; *α-bromo-γ-phenylheptane*, b.p. 118—121°/3 mm. (from the alcohol, HBr, and H_2SO_4); *α-bromo-δ-phenyloctane*, b.p. 124—126°/3 mm.; *α-bromo-ε-phenylnonane*, b.p. 125—127°/2 mm.; *α-bromo-ζ-phenyldecane*, b.p. 135—139°/3 mm.; *α-bromo-γ-phenylundecane*, b.p. 147—150°/3 mm.; *α-bromo-γ-phenyldodecane*, b.p. 141—147°/0·13 mm.; *α-bromo-δ-phenyltridecane*, b.p. 150—155°/0·12 mm.; *α-bromo-θ-phenylhexadecane*, b.p. 169—172°/0·1 mm.; *α-chloro-θ-phenyldodecane*, b.p. 129—136°/0·1 mm.; *α-chloro-ζ-phenyltetradecane*, b.p. 166—173°/3 mm.; *α-chloro-η-phenylhexadecane*, b.p. 160—165°/0·1 mm.; *β-phenylheptoic acid*, b.p. 144—149°/3 mm. (*Et*, b.p. 117—120°/3 mm., and p-*bromophenacyl*, m.p. 47·4—48·2°, esters); *ε-phenyldecoic acid*, b.p. 176—180°/3 mm. (p-*bromophenacyl* ester, m.p. 55·5—56°); *β-phenylundecoic acid*, b.p. 167—172°/2·5 mm. (*Et*, b.p. 154—159°/4 mm., and p-*bromophenacyl*, m.p. 65·5°, esters); *β-phenyldodecoic acid*, b. p. 165—171°/0·3 mm. (*Et*, b.p. 142—148°/0·2 mm., and p-*bromophenacyl*, m. p. 74·5—75·5°, esters); *η-phenyldodecoic acid*, b.p. 184—187°/3 mm. (p-*bromophenacyl* ester, m.p. 89—90°); *ι-phenyltetradecoic acid*, b.p 178—183°/0·1 mm. (p-*bromophenacyl* ester, m.p. 79—80°); *ε-phenylpentadecoic acid*, b.p. 182—185°/0·1 mm. (p-*bromophenacyl* ester, m.p. 73·5—74·5°); *η-phenylhexadecoic acid*, b.p. 190—195°/0·12 mm. (*Et*, b.p. 174—180°/0·13 mm., and p-*bromophenacyl*, m.p. 77—78°, esters); *θ-phenylhexadecoic acid*, b.p. 200—204°/0·09 mm., m.p. 36·5—38° (p-*bromophenacyl* ester, m.p. 83·5—94·5°); *ι-phenyloctadecoic acid*, b.p. 199—205°/0·09 mm., m.p. 40—41·5° (p-*bromophenacyl* ester, m.p. 71—72°). *γ-Phenylheptan-α-ol*, b.p. 116—120°/3 mm., *γ-phenylundecan-α-ol*, b.p. 139—145°/2·5 mm., *γ-phenyldodecan-α-ol*, b.p. 140—142°/0·2 mm., and *θ-phenylhexadecan-α-ol*, b.p. 168—174°/0·1 mm., are prepared by reduction of the above Et esters. The phenylstearic acid prepared from oleic acid, C_6H_6, and $AlCl_3$ contains approx. equal amounts of θ- and ι-phenyloctadecoic acids. C. J. W. (*b*)

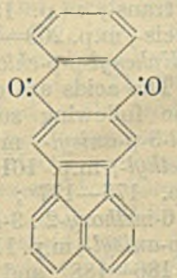
β-Naphthoylhydrazine and 3-hydrazino-β-naphthoic acid. H. Goldstein and E. Cornamusaz (Helv. Chim. Acta, 1932, 15, 939—943).—Et 3-iodo-β-naphthoate and boiling N_2H_4,H_2O (I) give β-*naphthoylhydrazine* (II), m.p. 147·5° (*Ac* derivative, m.p. 138°), also obtained from Me β-naphthoate (modified prep.) and (I) at 100° and, with NN′-*di*-β-*naphthoylhydrazine* (III), m.p. 241°, from β-naphthoyl chloride and (I). The product, m.p. 186°, previously (A., 1897, i, 638) described as (II), must have a different constitution. (III) is also formed from (II) and I in boiling EtOH. Diazotised 3-amino-β-naphthoic acid and $SnCl_2$ afford 3-*hydrazino*-β-*naphthoic acid*, m.p. indef. (*Ac* derivative, m.p. 233°; *benzylidene* derivative, m.p. 241°), changed by heating in vac., finally to 300°, to ββ′-*naphthopyrazolone*, m.p. about 275—280°. R. S. C.

Fluoranthene and its derivatives. IV. J. von Braun and G. Manz (Annalen, 1932, 496, 170—196; cf. A., 1931, 1044).—Acylation (Friedel–Crafts) of fluoranthene, unlike nitration, bromination, and sulphonation (*loc. cit.*), gives mainly the 12-derivative; the 4-isomeride is a by-product.

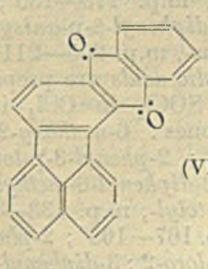
(A.)

[With B. Kratz.] Fluoranthene, $(COCl)_2$, and $AlCl_3$ in CS_2 at 0° give a mixture of mono- (7 pts.) and di- (3 pts.) -carboxylic acids. The former are separated by esterification (EtOH–HCl) and fractionation; *Et fluoranthene*-12-*carboxylate* (I) (*A*, R=OEt), m.p. 90—91°, is separated and the residual ester shown to contain Et fluoranthene-4-carboxylate by its conversion into 4-aminofluoranthene by way of the hydrazide, azide, and urethane. *Fluoranthene*-12-*carboxylic acid* (II), m.p. 283—285° (*chloride*, m.p. 100—103°; *amide*, m.p. 233°; *anilide*, m.p. 233°), is converted through the *hydrazide*, m.p. 213°, *azide*, decomp. 110°, and *urethane*, m.p. 140—142°, into 12-*aminofluoranthene* (III), m.p. 168—169° (*hydrochloride*, decomp. 270—280°; *Ac* derivative, m.p. 191°), which is reduced (Na–Hg) to an oily H_4-derivative (diazotisable), the *Ac* derivative, m.p. 179—180°, of which on oxidation (cf. *loc. cit.*) and hydrolysis, gives an *amino-keto-acid*, $C_{16}H_{13}O_3N$, decomp. from 190°. Oxidation of (II) with CrO_3–AcOH gives fluorenone-1 : 6- and -1 : 7-dicarboxylic acids, whilst reduction (Na–Hg) affords 5 : 6 : 7 : 8-*tetrahydrofluoranthene*-12-*carboxylic acid*, m.p. 237—239°, oxidised to *fluorenone*-1-*carboxylic*-6-*propionic acid*, m.p. 300—305° (*Me*$_2$ ester, m.p. 120°), and thence to *fluorenone*-1 : 6-*dicarboxylic acid*, m.p. 320—325° (decomp.) (*Me* ester, m.p. 163—165°). Fluoranthene, BzCl, and $AlCl_3$ in CS_2 give (mainly) 12-*benzoylfluoranthene* (*A*, R=Ph), m.p. 111—112°, purified through its *oxime*, m.p. 212—213°; rearrangement of the oxime with $PhSO_2Cl$ and pyridine, followed by hydrolysis, affords (III) and BzOH. 4-Benzoylfluoranthene is also produced, since the crude oxime is similarly converted into a little 4-aminofluoranthene. Fluoranthene, o-$C_6H_4(CO)_2O$, and $AlCl_3$ in CS_2 give 12-o-*carboxybenzoylfluoranthene* [*A*, R=·C_6H_4·CO_2H(*o*)], m.p. 212° [*chloride* (IV), m.p. 163—165°; *Me* ester, m.p. 180—181°; *oxime*, m.p. 224—225°, rearranged (as above) to (III)], and some 4-o-*carboxybenzoylfluoranthene* (V), m.p. 230° (*oxime*, m.p. 207—209°, convertible into 4-aminofluoranthene). When (IV) is heated in $C_6H_3Cl_3$ the *quinones* (VI), red (violet vat), m.p. 228°, and (VII), yellow (blue vat), m.p. 332—333°, are produced. Distillation of (VII) with Zn dust gives the corresponding *hydrocarbon*, $C_{24}H_{14}$, m.p. 290—291°, whilst oxidation (CrO_3, AcOH) affords a mixture, m.p. 345—347° (decomp.), of phthaloylfluorenonecarboxylic acids, decarboxylated to a mixture, m.p. 326—337°, of the anthraquinonefluorenone of Schaarschmidt and Herzenberger (A., 1919, i, 26) and an isomeride. Similar

(VI.)



(VII.)



oxidation of (VI) gives an *acid*, $C_{21}H_{10}O_5$, m.p. 290—295° (decomp.), decarboxylated to the anthraquinone-fluorenone of Ullmann and Dasgupta (A., 1914, i, 413). (V) is cyclised and sulphonated by H_2SO_4 at 95°; subsequent hydrolysis with HCl–$BaCl_2$ at 200° gives a *quinone*, $C_{24}H_{12}O_2$, m.p. 328—331°.

5 : 6 : 7 : 8-Tetrahydrofluoranthene (VIII) and $ClSO_3H$ in $CHCl_3$ give, after treatment with NaCl and $POCl_3$, the 4-*sulphonyl chloride*, m.p. 118°; the 4-*sulphonethylamide*, m.p. 156—157°, is dehydrogenated by S at 180—210° to fluoranthene-4-sulphonethylamide (*loc. cit.*). (VIII) and Br (1 mol.) in AcOH give the 4-*Br*-derivative, m.p. 135°, reduced (Na–Hg) to (VIII) and oxidised by $Na_2Cr_2O_7$ in AcOH to 4-bromofluoranthene and 2-*bromofluorenone*-1-*propionic acid*, m.p. 233°, the chloride of which is not cyclised by $AlCl_3$ in CS_2. Fluorenone-1-propionyl chloride is cyclised by this treatment to the *fluorenonehydrindone* (IX), m.p. 236°. (VIII), o-$C_6H_4(CO)_2O$, and $AlCl_3$ in CS_2 give the 4-o-*carboxybenzoyl* derivative, m.p. 220°, since rearrangement of its *oxime*, m.p. 212°, and subsequent hydrolysis affords 4-amino-5 : 6 : 7 : 8-tetrahydrofluoranthene (*loc. cit.*). The formation of small amounts of 12-Br- and 12-NO_2-derivatives during the bromination and nitration of fluoranthene is demonstrated. 4-Bromo- and 4-nitro-fluoranthenes are oxidised by CrO_3–AcOH to 2-*bromo*-, m.p. 252°, and 2-*nitro*-, decomp. 233—235°, -*fluorenone*-1-*carboxylic acids*; fluoranthene-4-carboxylic acid gives fluorenone-1 : 2-dicarboxylic acid [*anhydride* (X), m.p. 318—320°] [also formed by oxidation of (IX) with 20% HNO_3] and a product which is esterified to a *Me* ester, $C_{17}H_{12}O_4$, m.p. 199°, and a *Me H* ester, $C_{16}H_{10}O_4$, m.p. 230—233° (decomp.), re-solidifying at 240°, and thereby passing into (X). H. B.

Syntheses with magnesium triarylvinyl bromides. Triarylacrylic acids and the indones derived from them. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 2487—2493).—The following triarylvinyl bromides are prepared by bromination of triaryl-ethylenes or -ethyl alcohols in AcOH: α-*phenyl*-ββ-*di*-p-*tolyl*-, m.p. 132—133°; α-*phenyl*-ββ-*di*-p-*anisyl*-, m.p. 109—111°; αβ-*diphenyl*-β-p-*tolyl*-, m.p. 114—116°; αβ-*diphenyl*-β-p-*anisyl*-, m.p. 118—120°; cis-, m.p. 156—158°, and trans-, m.p. 103—105°, -αβ-*diphenyl*-β-p-*chlorophenylvinyl bromides*, separable by crystallisation from C_6H_6–MeOH. The Grignard reagents from these bromides are converted by CO_2 into triarylacrylic acids: α-*phenyl*-ββ-*di*-p-*tolyl*-, m.p. 205—206°; α-*phenyl*-ββ-*di*-p-*anisyl*-, m.p. 169—170°; cis-αβ-*diphenyl*-β-p-*tolyl*-, m.p. 185—195°; cis-, m.p. 179—180°, and trans-, m.p. 153—155°, -αβ-*diphenyl*-β-p-*anisyl*-, and cis-, m.p. 203—205°, and trans-, m.p. 205—211°, -αβ-*diphenyl*-β-p-*chlorophenylacrylic acids* are prepared. The acids are converted by $SOCl_2$ in CCl_4 into the following substituted indones: 6-*methoxy*-2-*phenyl*-3-p-*anisyl*-, m.p. 153—154°; 2-*phenyl*-3-p-*tolyl*-6-*methyl*-, m.p. 161—161·5°; 2 : 3-*diphenyl*-6-*methyl*-, m.p. 175—177°; 2-*phenyl*-3-p-*tolyl*-, m.p. 133—134°; 6-*methoxy*-2 : 3-*diphenyl*-, m.p. 167—168°; 2-*phenyl*-3-p-*anisyl*-, m.p. 114—115°; 6-*chloro*-2 : 3-*diphenyl*-, m.p. 186—188°, and 2-*phenyl*-3-p-*chlorophenyl*-, m.p. 162—164°, -*indone*.

αβ-*Diphenyl*-α-p-*tolylethyl alcohol*, m.p. 89°, is prepared from $CO(C_6H_4Me\text{-}p)_2$ and $CH_2Ph{\cdot}MgCl$ (the intermediate must be decomposed with aq. NH_4Cl); αβ-*diphenyl*-α-p-*chlorophenylethyl alcohol* has m.p. 83°. β-*Phenyl*-αα-*di*-p-*tolylethylene*, b.p. 258—259°/24 mm., and αβ-*diphenyl*-α-p-*tolylethylene*, b.p. 245—250°/27 mm., are obtained by distilling the corresponding alcohol with a trace of H_2SO_4 in vac. C. J. W. (*b*).

Decalin series. I. Preparation of 9-substituted decalins. G. R. CLEMO and J. ORMSTON (J.C.S., 1932, 1778—1783).—9-Aminodecalin (prep. described) [*NO*-derivative, m.p. 243° (decomp.)] is converted into $\Delta^{9:10}$-octalin (A., 1929, 921). This with HBr at 0° affords 9-*bromodecalin*, m.p. 29—30°, which regenerates the octalin with Et sodio-(or potassio-)malonate, and does not afford a Grignard reagent. Et Na malonate does not react with $\Delta^{9:10}$-octalin oxide, and with $\Delta^{9:10}$-octalin dibromide affords octalin and Et ethanetetracarboxylate. *cyclo*Hexene oxide with $CH_2Br{\cdot}CO_2Et$ and Zn in boiling C_6H_6 during 4 hr. affords *Et* 2-*hydroxy*cyclo*hexylacetate*, b.p. 114°/13 mm. (probably the *trans*-form) [*hydrazide*, m.p. 154°, not identical with the hydrazide of Et 2-hydroxy*cyclo*hexylacetate described previously (A., 1923, i, 696)]. Similarly, *cyclo*hexanone affords Et 1-hydroxy*cyclo*hexylacetate (*hydrazide*, m.p. 103°) and $\Delta^{9:10}$-octalin oxide during 6—7 hr. affords 2-keto-*cyclo*hexane*spirocyclo*pentane (I) (A., 1899, i, 742) and an ester (II), b.p. 125°/0·1 mm., giving a *hydrazide*, $C_{12}H_{22}O_2N_2$, m.p. 122°. It is probably Et 9-hydroxydecalin-10-acetate. It is not 2-hydroxy*cyclo*hexane-*spirocyclo*pentane-2-acetate, since the latter [from (I) and $CH_2Br{\cdot}CO_2Et$ with Zn in C_6H_6] gives a non-crystallising hydrazide of low m.p. Prolonged dehydrogenation of (II) with Se at a high temp. affords $C_{10}H_8$ and a *compound*, $C_{18}H_{12}$, m. p. 142—143°. J. L. D.

Manufacture of [alkoxy- and alkylthiol] derivatives of 2 : 3-hydroxynaphthoic acid. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 494.

Differing solubilities of optical antipodes in active solvents. E. SCHRÖER (Ber., 1932, 65, [*B*], 966—974).—A solution of *r*-mandelic acid in *d*-carvone is fractionally extracted with H_2O. The successive extracts are diminishingly lævorotatory, then inactive and increasingly dextrorotatory. The activities are not very marked. Similar results are obtained when *l*-carvone is employed, but the sequence of activity is reversed. H. W.

Condensation of butylchloral with gallic acid and the three cresotic acids. (MISS) B. N. KATRAK and A. N. MELDRUM (J. Indian Chem. Soc., 1932, 9, 121—125).—Gallic acid (1 mol.) and butylchloral hydrate (I) (1 mol.) in 95% H_2SO_4 give (after 24 hr.) 3 : 4 : 5-*trihydroxy*-2-ααβ-*trichloropropylphthalide*, m.p. 260° (*triacetate*, m.p. 161—162°, reduced by Zn dust and AcOH to 3 : 4 : 5-*triacetoxy*-2-α-*chloropropenylphthalide*, m.p. 145°); with 2 mols. of (I), a *compound*, $C_{23}H_{20}O_6Cl_{12}$ (structure suggested), m.p. 281—282°, also results. Gallic acid Me_3 ether and (I) in 85% H_2SO_4 afford (after 10 days) 3 : 4 : 5-trimethoxy-2-ααβ-trichloropropylphthalide, m.p. 90—91°, reduced by Zn dust and AcOH to 3 : 4 : 5-*trimethoxy*-2-α-

chloropropenylphthalide, m.p. 110—111°, whilst *4-hydroxy-3 : 5-dimethoxy-2-ααβ-trichloropropylphthalide*, m.p. 154—155° (*acetate*, m.p. 169—170°), is obtained from syringic acid, (I), and 95% H_2SO_4. *o*-Cresotic acid, (I), and H_2SO_4 give *ββγ-trichloro-αα-di-(4-hydroxy-5-carboxy-3-methylphenyl)butane*, m.p. 289°; similar *compounds*, m.p. 277° and 298°, are obtained from *p*- and *m*-cresotic acids, respectively. *m*-Cresotic acid, (I), and a little NaCl in 95% H_2SO_4 afford *3-hydroxy-6-αββγ-tetrachlorobutyl-*p*-toluic acid*, m.p. 210°; corresponding *acids*, m.p. 211—212° and 204—205°, are prepared from *p*- and *o*-cresotic acids, respectively. Similarly, *o*-cresotic acid and $CCl_3{\cdot}CH(OH)_2$ give *2-hydroxy-5-αβββ-tetrachloroethyl-*m*-toluic acid*, m.p. 184—185°. H. B.

Stereoisomerism of 2 : 2′-disubstituted derivatives of diphenyl. A. Corbellini and C. Pizzi (Atti R. Accad. Lincei, 1932, [vi], **15**, 287—291; cf. this vol., 56).—Crystallisation of the brucine salt of 2-(hydroxydiphenylmethyl)diphenyl-2′-carboxylic acid from EtOH yields (1) about 70% of a fraction, m.p. 200°, $[\alpha]_D^{18}$ +41·15°, the rotation of which approaches that of the racemic salt, viz., −14·86°, after a few days, and (2) a residue, m.p. 182°, $[\alpha]_D^{18}$ −7·48°. T. H. P.

Action of hydrogen selenide on acid chlorides. II. *o*-Phthalyl chloride. L. Szperl and J. Böhm (Rocz. Chem., 1932, **12**, 378—380).—*o-Phthalyl monoselenide*, m.p. 126—127°, obtained from *o*-phthalyl chloride and H_2Se at room temp. in the presence of $AlCl_3$, decomposes readily with liberation of Se in the presence of H_2O, acids, and alkalis. R. T.

Electrolytic reduction of alkylphthalimides. IV. Complete reduction. B. Sakurai (Bull. Chem. Soc. Japan, 1932, **7**, 155—157).—When acid solutions of phthalimide and its *N*-Me and -Et derivatives are electrolysed at 80—90° and 30—60 amp./100 sq. cm., both CO groups are reduced at the cathode with formation of the corresponding dihydro*iso*indole. Phenylphthalimide yielded phthalic acid and NH_2Ph. $(NH_4)_2$ phthalate yielded phthalide. D. R. D.

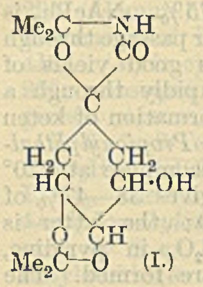
Sulphamide. M. Battegay and L. Denivelle (Compt. rend., 1932, **194**, 2216—2218).—*N*-Chlorosulphonylphthalimide (cf. this vol., 153) in dry C_6H_6 treated with dry NH_3 gives a ppt. which dissolves in H_2O. The solution, freed from NH_3, rapidly deposits phthalimide. The filtrate is evaporated in vac. at 25°, and the sulphamide extracted by EtOAc in 92% yield. The *N*-aminosulphonylphthalimide first formed probably decomposes to phthalimide and trisulphimide, which then hydrolyses: $(SO_2NH)_3+3H_2O=SO_2(NH_2)_2+NH_2SO_3H+H_2SO_4$, an explanation rendered probable by the fact that if NH_3 is replaced by NHPhMe there is formed cryst. $C_6H_4(CO)_2N{\cdot}SO_2NPhMe$, m.p. 160°. C. A. S.

Ketens from acylphthalimides and other substituted amides. C. D. Hurd and M. F. Dull (J. Amer. Chem. Soc., 1932, **54**, 2432—2440).—Both acetylphthalimide and *N*-acetylcarbazole undergo decomp. at refluxing temp. into *cyclo*butane-1 : 3-dione (dimeric keten), in yields of 30—38 and 20—37%, respectively; with the former, careful removal of H_2O increases the yield to 53—75%. $NAcPh_2$ is unchanged after 24 hr. at 290° or after passage through tubes at 500—600°. $NHAc_2$ gives good yields of AcOH and MeCN when passed rapidly through a tube at 635°, but evidence for the formation of keten or its dimeride was not obtained. *Propionylphthalimide*, m.p. 143—144°, begins to decompose at 220° and when heated at 322° for 3 hr. gives 38—47% of $COEt_2$ and 25—29% of $(EtCO)_2O$; the latter is determined by heating with $H_2C_2O_4$ in pyridine, whereby 100% of CO and CO_2 are formed. The gaseous products consist of 81·9% CO_2 and 6·7% CO, with some N_2. Propionylcarbazole gives the same two products. *Butyrylphthalimide*, softens at 70—72° but does not melt until the m.p. of $C_6H_4(CO)_2NH$ is reached, decomposes on keeping for a few hr.; pyrolysis gives $(PrCO)_2O$, $COPr_2$, and CO_2. *Hexoylphthalimide*, m.p. 98·5—99·5°, is pyrolysed to hexoic acid and trimeric *butylketen*, b.p. 213—216°/5 mm.; 12% of the original material is recoverable after 20 min. at 145—150°. iso*Butyrylphthalimide*, m.p. 96—98°, gives a considerable amount of free dimethylketen when heated to 225°. *Diphenylacetylphthalimide*, m.p. 170—171°, is pyrolysed to $C_6H_4(CO)_2NH$ and diphenylketen. These methods are suitable for the prep. of dimeric keten, and dimethyl- and diphenyl-ketens. C. J. W. (*b*)

Bile acids. XXXV. M. Schenck (Z. physiol. Chem., 1932, **208**, 120—124; cf. this vol., 614).—A discussion of the constitution of cholic acid. The formula with :CHMe between C_{11} and C_{12} of ring III is preferred. J. H. B.

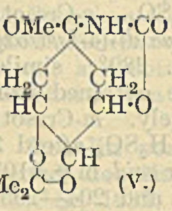
Structure of *apo*cholic acid and the carbon skeleton of the sterols and bile acids. A. R. Todd (Chem. and Ind., 1932, 569—570).—The bridged-ring structure of Borsche and Todd (A., 1931, 841) for *apo*cholic acid affords a more satisfactory explanation of its reactions than does that of Rosenheim and King (this vol., 736). The chrysene structure of the latter authors for cholanic acid is at variance with several of the established facts. H. B.

Quinic acid. II. Constitution and configuration of quinic acid. H. O. L. Fischer and G. Dangschat [with C. Taube, F. Radt, and H. Stettiner] (Ber., 1932, **65**, [*B*], 1009—1031; cf. A., 1921, i, 419).—Since the di*iso*propylidenequinamide, m.p. 155°, $[\alpha]_D^{19}$ −25·1° in EtOH, of Karrer and others (A., 1925, i, 673) does not evolve NH_3 when heated with NaOH and yields *diacetyldi*iso*propylidenequinamide*, m.p. 73—75°, $[\alpha]_D^{18}$ −62·2° in $CHCl_3$, instead of a nitrile, when heated with Ac_2O, it cannot contain the $CO{\cdot}NH_2$ group. The presence of a free OH group is established by the production of 3-p-*toluenesulphonyldi*iso*propylidenequinamide*, m.p. 103°, $[\alpha]_D^{17}$ −92·2° in anhyd. MeOH (converted by hot 80% AcOH into 3-p-*toluenesulphonyl*iso*propylidenequinamide*, m.p. 181° (decomp.), $[\alpha]_D^{20}$ −31·8° in MeOH), *3-acetyldi*iso*propylidenequinamide*, m.p. 157°, $[\alpha]_D^{19}$ −73·7° in $CHCl_3$ (hydrolysed to *3-acetyl*iso*propylidenequinamide*, m.p. 162°), and *dimethoxydi*iso*propylidenequinamide*, b.p. 128—129/1·5 mm. (hydrolysed by 2·5*N*-HCl to


(I.)

3-*methoxyquinic acid*, from which by means of boiling AcOH, 1 : 4 : 5 - *triacetyl* - 3 - *methoxy* - *quinic acid*, m.p. 168—169°, is derived; mixed *anhydride* of acid and AcOH, m.p. 118—120°). The structure (I) is therefore ascribed to di*iso*propylidenequinamide. (I) is transformed by hot 80% AcOH into iso*propylidenequinamide*, m.p. 176—178° after slight softening, $[\alpha]_D^{18}$ −25·0° in H_2O (*Ac*$_4$ derivative, m.p. 163°, $[\alpha]_D^{18}$ −63·1° in $CHCl_3$), converted by Ag_2O and MeI followed by hydrolysis into 3 : 4 : 5-*trimethoxyquinic acid*, identified as the *chloralide*, $C_{12}H_{17}O_6Cl_3$, m.p. 104—106°, $[\alpha]_D^{20}$ −54·2° in anhyd. MeOH. Quinamide, Ac_2O, and pyridine at room temp. afford *tetra-acetylquinamide*, m.p. 186—187° (decomp.), $[\alpha]_D^{21}$ −28·6° in $CHCl_2{\cdot}CHCl_2$, transformed by boiling Ac_2O into *tetra-acetylquinonitrile*, m.p. 161—162°, $[\alpha]_D^{18}$ −29·9° in $CHCl_3$. 1 : 3-*Diacetyl*-4 : 5-iso*propylidenequinonitrile*, m.p. 113° after softening, 1-*methoxy*-4 : 5-iso*propylidenequinamide*, m.p. 158—159°, 1-*methoxy*-3-*acetyl*-4 : 5-iso*propylidenequinamide*, m.p. 148—149° (corresponding *nitrile*, m.p. 107°), 4 : 5-iso*propylidenequin-amide*, m.p. 120° (decomp.), -*anilide*, m.p. 148—149°, $[\alpha]_D^{19}$ −16·4° in $CHCl_3$, and -*methylamide*, m.p. 108—110°, $[\alpha]_D^{19}$ −48·7°, are described.

4 : 5-*iso*Propylidenequinide (II) is transformed by N_2H_4,H_2O into 4 : 5-iso*propylidenequinhydrazide*, m.p. 150—151° (decomp.), $[\alpha]_D^{14}$ −54·0° in H_2O, converted through the corresponding *azide* into 3-*hydroxy*-4 : 5-iso*propylidenedioxy*cyclo*hexanone* (III), m.p. 79°, $[\alpha]_D$ +147° in EtOH. In aq. solution it shows strong mutarotation, from $[\alpha]_D$ +126° to −146° in 20 hr. The ketone is preferably obtained by transforming (II) by a large excess of MgMeI into 1 : 3 : 4 : 5-*tetrahydroxy*-4 : 5-iso*propylidene*cyclo*hexyldimethylcarbinol* (IV), m.p. 151—152°, which is treated with $Pb(OAc)_4$ in C_6H_6 at 40—50°. Treatment of (IV) with AcOH removes $COMe_2$, leaving a *compound*, $C_9H_{18}O_5$, m.p. 115°, which affords an isomeric iso*propylidene* derivative, $C_{12}H_{22}O_5$, m.p. 163°, also derived by treating the Grignard product with $COMe_2$ +1% HCl. The formation of the *iso*propylideneketone establishes the presence of a free OH in the α-position to CO_2H in (II). Since (III) affords a *phenylhydrazone*, $C_{15}H_{20}O_3N_2$, m.p. 150—152° (decomp.), $[\alpha]_D^{14}$ +42·7° in MeOH, under conditions which lead to phenylosazones with *cyclo*hexanolones, it follows that the OH groups are in positions 1, 3, 4, 5 in quinic acid. (III) is characterised by an *Ac* derivative, m.p. 68—69°, not affected by $CH(OEt)_3$ and NH_4Cl, a *semicarbazone*, m.p. 171—172°, $[\alpha]_D^{13}$ +65·2° in H_2O [transformed by $C_6H_4Me{\cdot}SO_2Cl$ and pyridine into a *compound*, $C_{10}H_{15}O_3N_3$, m.p. about 200° (decomp.), and by $COMe_2$–HCl into a *substance*, $C_7H_9O_2N_3$, m.p. 196° (decomp.)], and by conversion by MgMeI into 1 : 3-*dihydroxy*-4 : 5-iso*propylidenedioxy*-1-*methyl*cyclo*hexane*, b.p. 122°/0·2 mm., $[\alpha]_D^{26}$ −35·2° in EtOH [*monohydrate*, m.p. (indef.) 80—83°, $[\alpha]_D^{24}$ −31·12°]. The cryst. ketone (III) probably exists in the oxy*cyclo*-form, since it is inactive towards $CH(OEt)_3$ and cannot be reduced catalytically. Removal of the *iso*propylidene residue causes the ring system to become aromatic.

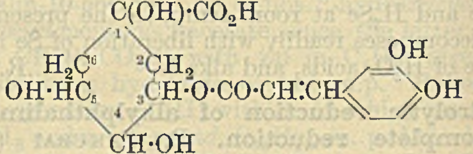

(V.)

Methyl*iso*propylidenequinide and N_2H_4,H_2O give 1 - *methoxy* - 4 : 5 - iso*propylidenequinhydrazide*, m.p. 142—143° (decomp.), $[\alpha]_D^{20}$ −45·6° in H_2O, converted through the azide into the cyclic *urethane* (V), m.p. 144—145°, $[\alpha]_D$ +73·8° in $CHCl_3$, also obtained by the Hofmann degradation of 1-methoxy - 4 : 5 - *iso*propylidenequinamide; hydrolysis with AcOH produces $COMe_2$ and the *substance* $C_8H_{13}O_5N$, m.p. 214—215° (decomp.) (obtained also by the degradation of 1-methoxyquinamide), which is transformed by Br in $CHCl_3$ into a mixture of bromomethoxy- and bromo-quinol.

Quinide is transformed by MeI and Ag_2O in boiling dioxan into 1 : 4 : 5-*trimethoxyquinolactone*, converted by NH_3–MeOH into 1 : 4 : 5-*trimethoxyquinamide*, m.p. 128° after softening, $[\alpha]_D^{18}$ −85·4° in H_2O, which does not yield an *iso*propylidene derivative. With Br and H_2O the lactone yields *iso*vanillic acid. 3-p-*Toluenesulphonyl* - 1 - *methoxy* - 4 : 5 - iso*propylidenequinamide*, m.p. 145°, and 3-p-*toluenesulphonyl*-1-*methoxyquinamide*, m.p. about 108°, have been prepared.

H. W.

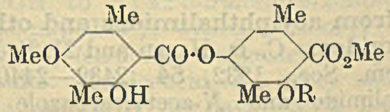
Quinic acid and its derivatives. III. Constitution of chlorogenic acid. H. O. L. Fischer and G. Dangschat (Ber., 1932, 65, [*B*], 1037—1040).—Since chlorogenic acid is not converted by Ac_2O into a lactone it is probable that the 3-OH group is substituted. The constitution (I) is established, since


(I.)

it is transformed by $COMe_2$ and $ZnCl_2$ into di*iso*-*propylidenechlorogenic acid*, m.p. 196—197°, insol. in K_2CO_3, reaction occurring with OH groups at positions 4 and 5, and OH and CO_2H groups at position 1. Treatment with diazomethane methylates the phenolic OH and CO_2H groups and subsequent treatment with Ag_2O and MeI leads to *Me pentamethylchlorogenate*, b.p. 225—232°/0·1 mm., hydrolysed by NaOH–MeOH to 3 : 4-dimethoxycinnamic acid and 1 : 4 : 5-trimethylquinide.

H. W.

Lichen acids. III. Constitution of barbatic acid and syntheses of *iso*rhizonic acid and methyl barbatate. A. Robertson and R. J. Stephenson (J.C.S., 1932, 1675—1681; cf. A., 1930, 472).—*Me*, m.p. 170° (I; R=H) and *Et barbatate*, m.p. 189°, are prepared from the acid (extraction from *Usnea barbata* improved) and the diazoalkane in Et_2O; excess of CH_2N_2 gives *Me O-methylbarbatate* (I; R=Me), m.p. 123°. The Et ester, m.p. 132°, of Hesse (A., 1898, i, 378) and Zopf (A., 1899, i, 716) is probably a degradation product. MeI and Ag_2O in boiling $COMe_2$ give an amorphous product. The structure (I; R=Me) is determined by its synthesis from O-*acetyl*-


(I.)

rhizonoyl chloride, (II), m.p. 84° [from the acid (*loc. cit.*) and PCl_5 in $CHCl_3$] (*anilide*, m.p. 179°), and Me *iso*rhizonate (III) by interaction in pyridine. Similarly, (I; R=H) was synthesised from (II) and Me β-orcincarboxylate. *iso*Rhizonic acid (cf. this vol., 396) was synthesised from the *Ac* derivative, m.p. 67°, of *iso*rhizonaldehyde (A., 1930, 472) by oxidation with neutral aq. $KMnO_4$ and deacetylation of the resulting *acetyl*iso*rhizonic acid*, m.p. 160°. H. A. P.

Syntheses of aromatic acetyl-carboxylic and polycarboxylic acids. F. Feist (Annalen, 1932, 496, 99—122).—Benzenepolycarboxylic acids are prepared by chlorinating acetylpolymethylbenzenes at high temp. and subsequently hydrolysing the trichloroacetylpoly(trichloromethyl)benzenes produced; the Ac group facilitates chlorination of the Me groups. Thus, 4-acetyl-*m*-xylene is chlorinated at 120—130° under intensive irradiation to 2 : 4-*di*(*trichloromethyl*)-*phenyl trichloromethyl ketone*, m.p. 94°, hydrolysed by aq. EtOH–NaOH to trimellitic acid (I) (*Et* ester, b.p. 230°/28 mm.), and converted by boiling MeOH or EtOH into *Me*, b.p. 218°/12 mm., m.p. 129°, or *Et* (II), m.p. 130—131°, 2-*trichloroacetyl*-5-*trichloromethyl*-*benzoates*. Hydrolysis of (II) with 21% H_2SO_4 at 140° gives 4-*trichloroacetyl*iso*phthalic acid*, m.p. 242° (decomp.) (*Et H* ester, m.p. 252—253°, formed as a by-product), converted readily by aq. NaOH into (I) and $CHCl_3$, and reduced (H_2, Pd–$CaCO_3$, 50% EtOH) to 4-*acetyl*iso*phthalic acid*, m.p. 162° (decomp.). Acetyl-*p*-xylene is similarly chlorinated to 2 : 5-*di*(*trichloromethyl*)*phenyl trichloromethyl ketone*, m.p. 144°, convertible by the above methods into *Me*, m.p. 95—96°, and *Et*, m.p. 122—123°, 2-*trichloroacetyl*-4-*trichloromethylbenzoates* (?), *trichloroacetyl*-, m.p. 228° (decomp.), and *acetyl*-, decomp. about 345°, -*terephthalic acids*, and (I). 2 : 4-Diacetyl-*m*-xylene is chlorinated at 210° to a Cl_{12}-derivative, b.p. 240—242°/15 mm., m.p. 225—226°, hydrolysed by 50% NaOH at 190°/16 atm. to pyromellitic acid (III). Acetyl-ψ-cumene is chlorinated at 160° to a mixture (*A*) of a *compound*, $C_{11}H_3OCl_{11}$, m.p. 210°, and a *substance*, m.p. 200—210°, separable through their differing solubilities in AcOH; *A* is hydrolysed by KOH and a little H_2O at 170° to (probably) a *keto-acid*, $C_6H_2(CO_2H)_3\cdot CO\cdot CO_2H,2H_2O$, m.p. 249° (decomp.), m.p. (anhyd.) 270°, whilst hydrolysis with aq. KOH and subsequent treatment of the hydrolysate with Cl_2 gives (III). Diacetylmesitylene is chlorinated to (mainly) 2 : 6-*di*(*trichloroacetyl*)-3 : 5-*di*(*trichloromethyl*)*toluene*, m.p. 182°, hydrolysed by conc. H_2SO_4 or by aq. NaOH at 189°/14 atm. (and subsequent treatment with Cl_2) to *methylpyromellitic acid* ($+3H_2O$), m.p. 233° (decomp.), m.p. (anhyd.) 243° (decomp.) (*Ag* salt; *Me_4* ester, m.p. 103—104°); the latter method of hydrolysis gives also a little $C_6H(CO_2H)_5$.

Aromatic carboxylic acids cannot be acetylated by the Friedel–Crafts reaction. The following are prepared from the requisite bromoaryl Me ketone by Rosenmund and Struck's method (A., 1920, i, 44): acetophenone-4-carboxylic acid; *acetophenone*-3 : 5-*dicarboxylic* (5-*acetyl*iso*phthalic*) *acid*, m.p. 228° [*Ag* salt; *phenylhydrazone*, m.p. 274° (decomp.); *semicarbazone*, decomp. 305°]; 2 : 1-*acetylnaphthoic acid*, m.p. 140° (sinters at 95°) (*Me* ester, m.p. 89°; *phenylhydrazone*, m.p. 165°; *semicarbazone*, m.p. 150°); 2(or 7)-*acetylnaphthalene*-1 : 5-*dicarboxylic acid* (?), m.p. 115°, prepared from 1 : 5-*dibromo*-2(or 7)-*acetylnaphthalene* (?), m.p. 149°, which is formed from 2-$C_{10}H_7Ac$, Br, and Fe powder or from a mixture of 1 : 4- and 1 : 5-$C_{10}H_6Br_2$, AcCl, and $AlCl_3$ in CS_2. Bromination of 2-$C_{10}H_7Ac$ in CCl_4 gives a *Br*-derivative, m.p. 82°; a *Br_4*-derivative, m.p. 120—122°, is also described. H. B.

Lichen substances. XIV. Synthesis of gyrophoric acid. Y. Asahina and F. Fuzikawa (Ber., 1932, 65, [*B*], 983—984).—Orsellinic acid Me_2 ether is converted by $SOCl_2$ into the corresponding chloride, which is condensed in $COMe_2$–C_5H_5N with *Me lecanorate*, m.p. 146°. The neutral product of the reaction when treated with diazomethane in Et_2O affords Me gyrophorate Me_4 ether, m.p. 196—197°, thus confirming the constitution assigned to gyrophoric acid (A., 1931, 221). H. W.

Trinitrobenzaldehyde and its derivatives. A new and convenient method for the preparation of *s*-trinitrobenzene. S. Secareanu (Bull. Soc. chim., 1932, [iv], 51, 591—596; cf. A., 1931, 730).—2 : 4-Dinitro-6-anilinobenzylideneaniline and its $C_6H_4(NO_2)_2$ additive compound give 2 : 4-*dinitro*-6-*anilinobenzaldehydephenylhydrazone*, m.p. 227°, with $NHPh\cdot NH_2$. $C_6H_2(NO_2)_3\cdot CHO$ reacts with amines in cold AcOH to give 2 : 4 : 6-*trinitrobenzylidene*-β-*naphthylamine*, m.p. 206—207° (explodes), -m-*nitroaniline*, m.p. 161—162°, -p-*bromoaniline*, m.p. 184°, -p-*toluidine*, m.p. 177—178°, and -2-*bromo*-p-*toluidine*, m.p. 209°. 2 : 4-*Dinitrobenzylideneaniline*, m.p. 133°, is similarly obtained. 2 : 4 : 6-$C_6H_2(NO_2)_3\cdot CHO$ with alkalis (preferably NH_3) in EtOH gives *s*-$C_6H_3(NO_2)_3$. A. A. L.

α-Keto-aldehydes. W. Madelung and M. E. Oberwegner (Ber., 1932, 65, [*B*], 931—941).—COPhMe in AcOH is converted by Br into ω-bromoacetophenone, which, when shaken with KOAc in MeOH, affords benzoylcarbinyl acetate in 95% yield. The product is transformed by Br in CS_2 into the unstable *benzoylbromocarbinyl acetate* (I), which decomposes when distilled under diminished pressure into AcBr and crude phenylglyoxal, purified by dissolution in MeOH and agitation with $BaCO_3$, followed by distillation; b.p. 108—110°/15 mm. (yield 82%). The hydrate (II) (yield 75%) is prepared by crystallising the crude aldehyde from H_2O or by repeated extraction of the Br-compound with boiling H_2O or 5% H_2SO_4. A *compound*, $C_{24}H_{16}O_4$, m.p. 197—198° (decomp.) (*Ac* derivative, m.p. 169—170°), is obtained as by-product. *Phenylglyoxal dimethylacetal* (III), b.p. 133—134°/16 mm., from (I) and boiling MeOH in 78—80% yield, is converted by Ac_2O containing a trace of conc. H_2SO_4 into ω-*acetoxy*-ω-*methoxyacetophenone*, b.p. 160—162°/14 mm., readily hydrolysed to (II). Treatment of phenylglyoxal with MgPhBr in Et_2O yields ααβ-triphenylethane-αβ-diol, m.p. 164°, converted by conc. H_2SO_4 into triphenylvinyl alcohol, m.p. 135°, whereas (III) gives *hydroxydiphenylacetaldehyde*, b.p. 180—194°/17 mm. (*semicarbazone*, m.p. 238·5°), oxidised by conc. HNO_3 to benzilic acid. (I) and $NPhMe_2$ afford benzoyltetramethyldiaminodiphenylmethane, m.p. 164°, obtained also from phenylglyoxal or $COPh{\cdot}CHBr_2$ and $NPhMe_2$, and converted by MgPhBr into *αα-diphenyl-ββ-tetramethyldiaminodiphenylethyl alcohol*, m.p. 215°, dehydrated by boiling conc. HCl to αα-diphenyl-ββ-tetramethyldiaminodiphenylethylene, m.p. 212°. β-Naphthyl Me ketone yields the Br-derivative, m.p. 82·5°, and thence 2-*naphthoylcarbinyl acetate* (IV), m.p. 80°, hydrolysed by aq. $Ba(OH)_2$ to 2-*naphthoylcarbinol*, m.p. 114° (*hydrate*, m.p. 96°). *Bromo*-2-*naphthylcarbinyl acetate*, m.p. 73°, is transformed into 2-*naphthylglyoxal hydrate*, m.p. 98°, from which are derived 2-*naphthylyoxal* (V) b.p. 183°/20 mm. (partial decomp.), its *dimethylacetal*, b.p. 194°/16 mm., and *Ac*$_2$ derivative, m.p. 150°; evidence of the existence of an isomeric *Ac*$_2$ compound is obtained. Protracted warming of (IV) or (V) with dil. H_2SO_4 gives a *compound*, m.p. 260° (decomp.) (*Na* salt; *Ac* derivative, m.p. 205°). Acetol acetate, prepared from chloroacetone and KOAc in MeOH–$COMe_2$ (evidence of existence of a tautomeric form is obtained), is converted by successive treatment with Br in CS_2 and MeOH into methylglyoxal dimethylacetal, b.p. 56—58°/16 mm.

H. W.

Hydroxy-carbonyl compounds. VIII. Derivatives of 2 : 6-dihydroxytoluene. E. T. Jones and A. Robertson (J.C.S., 1932, 1689—1693).—6-*Nitro*-o-*tolyl* p-*toluenesulphonate*, m.p. 94° (from the nitrocresol and *p*-toluenesulphonyl chloride in pyridine), is reduced by $SnCl_2$–HCl in AcOH to the *NH*$_2$-compound, m.p. 108°, which on diazotisation, decomp., and hydrolysis of the product gives 2 : 6-dihydroxytoluene (I). This is also obtained from 6-methoxy-*o*-cresol (II) or from 2-hydroxy-6-methoxy-*m*-toluic acid by action of aq. HI (*d* 1·7) at its b.p., and gives 2 : 6-*dihydroxy*-m-*tolualdehyde* (III), m.p. 147°, by the Gattermann reaction [$Zn(CN)_2$ as condensing agent]. 2-*Hydroxy*-6-*methoxy*-m-*tolualdehyde*, m.p. 64°, is obtained from (II) by the Gattermann reaction or by partial methylation of (III) (MeI and K_2CO_3 in $COMe_2$); its structure is confirmed by its condensation with *p*-methoxyacetophenone and HCl in EtOAc to 7 : 4′-*dimethoxy*-8-*methylflavylium chloride* (*ferrichloride*, m.p. 177—178°); therefore the acid derived by oxidation with $KMnO_4$ in aq. $COMe_2$, which is identical with *C*-methylated β-resorcylic acid (J.C.S., 1895, 67, 990), is 2-hydroxy-6-methoxy-*m*-toluic acid.

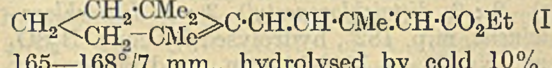
Condensation of (I) with MeCN in Et_2O in presence of HCl and $ZnCl_2$ gives 2-hydroxy-4-methoxy-3-methylacetophenone, m.p. 83° (*C*-methylpæanol; cf. A., 1894, i, 521; 1895, i, 43; J.C.S., 1918, **113**, 868), the orientation of which follows from its conversion into 2-*hydroxy*-4-*methoxy*-3-*methylbenzoylacetone*, m.p. 118°, by interaction with Na and EtOAc, and thence into 7-*methoxy*-2 : 8-*dimethyl*-1 : 4-*benzopyrone* ($+xH_2O$), m.p. 142°, by AcOH containing a little HCl at its b.p.

2-*Hydroxy*-4-*methoxy*-3-*methylbenzophenone*, m.p. 125°, was not obtained by decarboxylation of its carboxylic acid (A., 1930, 1167), but results from partial methylation (MeI and K_2CO_3 in $COMe_2$) of the corresponding (*OH*)$_2$-compound, m.p. 177°, which is prepared by condensation of (I) with PhCN in Et_2O by $ZnCl_2$–HCl, or from (II) by the action of BzCl and $AlCl_3$ in CS_2. It does not undergo ring-closure with Ac_2O and NaOAc. H. A. P.

Formula of fir lignin. P. Klason (Svensk Pappers-Tidn., 1931, **34**, 543—548, 578—581; Chem. Zentr., 1931, ii, 3458—3459).—Concn. of β-lignosulphonic acid must be effected at room temp. or in vac. to avoid the development of a deep brown colour. The brown substance is a polymeride of β-lignosulphonic acid in which the CHO and SO_2H groups are unaffected. The lignin of this compound is named "melanolignin," and the sulphonic acid "melanoligninhydrosulphonic acid." β-Lignin has the formula $2(C_9H_9O_3{\cdot}OH),C_{10}H_{10}O_3$. Oxidation of β-lignosulphonic acid with H_2O_2 and pptn. with $C_{10}H_7{\cdot}NH_2,HCl$ produces the salt $C_{10}H_{10}O_3,C_9H_8O_3,H_2SO_3,C_{10}H_9N,H_2O$; the α-acid is fairly stable towards H_2O_2 at room temp. On the assumption that lignin consists of 2 mols. of α- and 1 mol. of β-lignin, lignin has the formula $C_{92}H_{108}O_{38}$; *M* 1820. Sulphuric acid-lignin is $6C_{10}H_{10}O_3,2C_9H_{10}O_4,C_{10}H_{12}O_4$. α-Lignosulphonic acid is much less sensitive to acid than the β-acid; the former does not pass into the latter during boiling with sulphite. A. A. E.

Chemistry of conifers. P. Klason (Cellulosechem., 1932, **13**, 113—119).—Lignin, which comprises 31·8% of wood, is extracted from it with H_2SO_3 in the form of $\frac{2}{3}$ α- and $\frac{1}{3}$ β-lignin-sulphonic acids. α-Ligninsulphonic acid is a trimeric form of coniferylaldehydehydrosulphonic acid in which the 3 mols. of coniferylaldehyde are linked through the CHO and OH groups. In β-ligninsulphonic acid two of the OMe groups are replaced by OAc. In wood the two forms of lignin appear to be combined with each other and with cellulose. In untreated lignin the side-chains are aldols, $\cdot CH(OH){\cdot}CH_2{\cdot}CHO$, and the sulphonic acids are formed by the displacement of OH by SO_3H. When treated with 66% H_2SO_4 lignin loses its aldol water and also acetic acid from β-lignin. Lignin is simply related to the pentoses, thus $2C_5H_{10}O_5 \longrightarrow C_6H_3(OH)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH + CO_2 + 4H_2O$, the alcohol being then oxidised to the aldehyde and methylated by CH_2O. A. G.

Compounds containing the carbon-ring of β- or α-ionone and several ethylenic linkings. P. Karrer, H. Salomon, R. Morf, and O. Walker (Helv. Chim. Acta, 1932, **15**, 878—889).—Most of the following products were mixtures, probably of stereoisomerides. β-Ionone, $CH_2Br{\cdot}CO_2Et$, and Zn in hot C_6H_6 give *Et* δ-(1 : 1 : 3-*trimethyl*-2-Δ^2-cyclo*hexenyl*)-β-*methylbutadiene*-α-*carboxylate*,



$$CH_2{<}{\begin{matrix}CH_2{\cdot}CMe_2\\CH_2{-}CMe\end{matrix}}{\gg}C{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CO_2Et$$

(I), b.p. 165—168°/7 mm., hydrolysed by cold 10% KOH–EtOH to (?) a mixture of stereoisomerides of the corresponding *acid*, b.p. 150°/0·25 mm., separable into crystals, m.p. 125°, and much oil. By a similar reaction tetrahydroionone gives *Et* β-*hydroxy*-δ-(1 : 1 : 3-*trimethyl*-2-cyclo*hexyl*)-β-*methylvalerate*, b.p. 178—184°/10 mm. (*Ac* derivative, b.p. 182—184°/10 mm.), transformed (not smoothly) by P_2O_5 in hot PhMe into the unsaturated ester. The formation of a OH- or unsaturated ester by the Reformatsky reaction thus depends on the degree of reduction of the ionone ring. *Et* δ-(1 : 1 : 3-*trimethyl*-2-cyclo*hexyl*)-β-*methylvalerate* [prepared by hydrogenation (PtO_2) of (I) in AcOH], b.p. 160°/8 mm. (corresponding *acid*, b.p.

mostly 155—162°/0·2 mm.), with Na and hot EtOH gives ε-(1 : 1 : 3-*trimethyl*-2-cyclo*hexyl*)-*γ-methyl*-n-*amyl alcohol*, b.p. mostly 150—156°/7 mm., whence the *bromide* (II), b.p. mostly 156—160°/8 mm., was best prepared by HBr under certain conditions. The Grignard reagent from (II) with chloromethyl ether gives a mixture containing *Me* ζ-(1 : 1 : 3-*trimethyl*-2-cyclo*hexyl*)-δ-*methylhexyl ether* (not isolated pure), b.p. 157°/9 mm., and ακ-*di*-(1 : 1 : 3-*trimethyl*-2-cyclo*hexyl*)-γθ-*dimethyl*-n-*decane*, b.p. 166—168°/0·025 mm. α-Ionone and Mg allyl bromide give *γ-hydroxy-α*-(1 : 1 : 3-*trimethyl*-2-Δ^3-cyclo*hexenyl*)-*γ-methyl*-$\Delta^{\alpha\epsilon}$-*hexadien-γ-ol*, b.p. 137—140°/9 mm., yielding with hot PhNCO much $CO(NHPh)_2$, a cryst. *substance*, and some α-(1 : 1 : 3-*trimethyl*-2-Δ^3-cyclo*hexenyl*)-*γ-methyl*-$\Delta^{\alpha\gamma\epsilon}$-*hexatriene* (III), b.p. 127—130°/10 mm. The constitution of (III) is proved by oxidation by O_3 to *iso*geronic acid, by CrO_3 to 2 mols. of AcOH, and by $KMnO_4$ to 1 mol. of AcOH. In contrast, Mg allyl bromide adds on to the ethylenic linking of β-ionone. The absorption spectrum of (I) and colours given by several of the above compounds with $SbCl_3$ are recorded. R. S. C.

Benzylideneacetone, cinnamic acid, and bromostyrene. P. P. Schorigin, V. I. Issaguliantz, and A. R. Gusseva (J. Gen. Chem., Russia, 1931, **1**, 506—510).—A modification of Claisen's method for the manufacture of CHPh:CH·COMe (81% yield), an adaptation of Messinger's method for the iodometric determination of this in the crude product, and processes for the prep. of cinnamic acid (71% yield), Me cinnamate (80% yield), and CHPh:CHBr are described. Ch. Abs.

Electrochemical chlorination of some ketones. J. Szper (Bull. Soc. chim., 1932, [iv], **51**, 653—656).—Monochloro-derivatives are obtained in good yield by electrolysis of solutions of $COMe_2$, $COPh_2$, COPhMe, $COPhPr^{\alpha}$ (two products, b.p. 215°, and 225°/760 mm.), and *cyclo*hexanone in HCl or HCl–AcOH. No chloroacetic acid is obtained from the latter mixture. A. A. L.

Preparation of ketochloroimines by the action of chlorine on compounds of the type CR′R″:N·MgX. C. R. Hauser, H. A. Humble, and G. J. Haus (J. Amer. Chem. Soc., 1932, **54**, 2476—2480).—CPh_2:N·MgBr, treated with an equiv. of Cl or *tert.*-alkyl hypochlorite, develops an orange-red colour and gives a red product which apparently contains about 60% of benzophenonechloroimine (as calc. from its active Cl content); the crude product and dry HCl in Et_2O or C_6H_6 afford CPh_2:NH,HCl. The *N*-Mg compound from MgPhBr and *p*-C_6H_4Cl·CN is converted by Cl into p-*chlorobenzophenonechloroimine*, m.p. 104° (32% yield); a stereoisomeride is not isolated. Similarly, the compound from *p*-C_6H_4Cl·MgBr and *p*-C_6H_4Cl·CN affords 35—40% of 4 : 4′-*dichlorobenzophenonechloroimine*, m.p. 74°. C. J. W. (*b*)

Ketone hydrolysis and affinity capacity (electron attraction) of radicals. P. de Ceuster (Natuurwetensch. Tijds., 1932, **14**, 188—202).—The decomp. of asymmetric ketones by $NaNH_2$ and NaOH has been studied with the object of comparing the relative affinities of different radicals. β-*Naphthyl* p-*diphenylyl ketone*, from naphthoyl chloride and Ph_2, has m.p. 132—132·5° (corr.), b.p. 497° without decomp.; its *oxime* has m.p. 170—178°. p-*Anisyl* p-*diphenylyl ketone* has m.p. 167°, and its oxime m.p. 192°. p-*Chlorophenyl* p-*diphenylyl ketone* has m.p. 172°; its *oxime* could be obtained only as a tautomeric mixture of indefinite m.p. p-*Tolyl* p-*diphenylyl ketoxime* has m.p. 198—200°, and *α-naphthyl* p-*diphenylyl ketoxime* m.p. 187—188°. The proportions of the principal products of hydrolysis of these and certain other ketones (12 in all) are in agreement with the theory of the relative affinity capacity of the radicals in only 4 cases; in 5 cases the results are opposed to the theory, and in 3 no definite conclusion could be obtained. Examination of 57 examples of ketone hydrolysis in the lit. shows that 14 accord with the theory, 34 contradict it, and 9 lead to no conclusion. H. F. G.

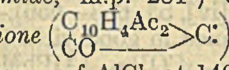
Distribution of partial valencies of methyl- and methoxy-*p*-benzoquinones. H. Erdtman (Svensk Kem. Tidskr., 1932, **44**, 135—148).—Whilst *p*-benzoquinone possesses equiv. cationoid reaction centres at C atoms 2, 3, 5, and 6, the mono-methoxy- and -methyl derivatives show activity at C_5 owing to one of the conjugated systems (·CH:CH·Ċ:O) being neutralised. Thus, methoxy-*p*-benzoquinone (I) is converted by Ac_2O and a little conc. H_2SO_4 into 2 : 4 : 5-*triacetoxyanisole*, m.p. 142°, by dil. H_2SO_4 in AcOH into 2 : 5-*dihydroxy*-4 : 4′-*dimethoxydiphenyl*-2′ : 5′-*quinone* (II), decomp. from 210° [also formed by successive treatment of vanillin with alkaline H_2O_2, dil. HCl, and aq. $FeCl_3$, and when the quinhydrone from equimol. amounts of (I) and methoxyquinol is heated at 95—100°, whereby (I) and (II) result], and by alkali into methoxyquinol and polymeric material. *p*-Toluquinone behaves similarly but is less reactive than (I); the polymeric toluquinone of Spica (A., 1882, 1065) is now formulated as 2 : 5-dihydroxy-4 : 4′-dimethyldiphenyl-2′ : 5′-quinone. Oxidation of (II) with $K_2Cr_2O_7$ and dil. H_2SO_4 gives the 2 : 5 : 2′ : 5′-*diquinone* (III), decomp. 212—214° (slow), 220—230° (rapid heating), which passes when heated into 5-*hydroxy*-4 : 4′-*dimethoxy*-2 : 2′-*diphenylene oxide*-3′ : 6′-*quinone*, m.p. 242—245°, and is converted by dry HCl in $CHCl_3$–AcOH in absence of air into (probably) 2 : 2′-dichloro-3 : 6 : 3′ : 6′-tetrahydroxy-4 : 4′-dimethoxydiphenyl, acetylated by cold Ac_2O–H_2SO_4 to the 3 : 3′(?)-*diacetate*, m.p. 232°, and converted by hot Ac_2O into (mainly) (III) and (probably) 6 : 6′(?)-*dichloro*-5 : 5′-*diacetoxy*-4 : 4′-*dimethoxy*-2 : 2′-*diphenylene oxide*, m.p. 253°.

The nuclear activity of 2 : 6- and (especially) 2 : 5-dimethoxy-*p*-benzoquinones is very small owing to neutralisation of both conjugated systems. The former is affected only by long treatment with alkali (whereby polymerisation occurs), whilst the latter is only hydrolysed by alkali to 2 : 5-dihydroxy-*p*-benzoquinone. 2 : 6-Dimethyl-*p*-benzoquinone possesses some nuclear activity owing to the smaller neutralising power of Me (as against OMe); it is slowly converted by Ac_2O–H_2SO_4 into 2 : 4 : 5-triacetoxy-*m*-xylene, m.p. 103—104° (lit. 99°). 3 : 5 : 3′ : 5′-Tetramethyldiphenoquinone reacts readily with Ac_2O–H_2SO_4 forming 2 : 4 : 4′-*triacetoxy*-

3 : 5 : 3′ : 5′-*tetramethyldiphenyl*, m.p. 141—142°, whilst 4 : 4′-dimethyldiphenyl-2 : 5 : 2′ : 5′-diquinone similarly gives (slowly) 2 : 5 : ? : 2′ : 5′ : ?′-*hexa-acetoxy-4 : 4′-dimethyldiphenyl*, m.p. 202—203°. H. B.

Identification of nitriles. Preparation of 2 : 4 : 6-trihydroxyphenyl alkyl ketones by the Hoesch synthesis on a semi-micro-scale. H. P. Howells and J. G. Little (J. Amer. Chem. Soc., 1932, 54, 2451—2453).—2 : 4 : 6-*Trihydroxyphenyl Bu ketone* (+H_2O), m.p. 87—88° (corr.), m.p. (anhyd.) 149° (corr.), is obtained in 84·7% yield when dry HCl (nearly saturated with Et_2O) is passed through a mixture of *s*-$C_6H_3(OH)_3$ (0·006 mol.), BuCN (0·01 mol.), and $ZnCl_2$ (0·4 g.) in Et_2O (25 c.c.). The method is applicable to MeCN, EtCN, PrCN, and *n*- and *iso*-hexonitriles; the yields of phlorophenones are 37—93%. C. J. W. (*b*)

Degradation of quaternary ammonium salts. VII. Radical migration. T. Thomson and T. S. Stevens (J.C.S., 1932, 1932—1940).—The migration of phenacyl groups from N to C is studied. Diphenacyldimethylammonium bromide affords with NaOH ω-dimethylamino-ω-phenacylacetophenone (*picrate*, m.p. 128—130°), the methosulphate of which with Zn and H_2SO_4 affords diphenacyl. *p*-Bromophenacyl bromide and $NHMe_2$ in EtOH afford *di*-p-*bromophenacyldimethylammonium bromide*, m.p. 215° (decomp.). Diacetonyldimethylammonium chloride [*picrate*, m.p. 198—199° (decomp.)] and *di*-p-*bromobenzyldimethylammonium bromide*, m.p. 193—195° (softening at 170°), are similarly prepared, and with NaOH or MeOH–NaOMe afford only decomp. products. α-Dimethylaminopropiophenone and CH_2PhCl afford an oil, convertible into α-*methylphenacylbenzyldimethylammonium iodide*, m.p. 160—161° (decomp.), which is isomerised by hot NaOH to α-dimethylamino-α-benzylpropiophenone (*picrate*, m.p. 161—162°), converted into α-benzylidenepropiophenone by boiling the methosulphate with NaOH. The corresponding α-Ph and αα-Me_2 compounds could not be prepared. The ease of formation of quaternary salts of the above type is investigated. Bromopropiophenone and excess $NHMe_2$ in EtOH at 100—110° during 2 hr. afford α-dimethylaminopropiophenone (*picrate*, m.p. 128—130°), whilst chlorodeoxybenzoin affords α-*dimethylaminodeoxybenzoin*, m.p. 59—61° [*hydrochloride*, m.p. 222—225° (decomp.)], which does not react further with CH_2PhCl. α-Bromo*iso*butyrophenone and $NHMe_2$ in EtOH at 140—160° during 6 hr. give only traces of α-dimethylamino*iso*butyrophenone (*picrate*, m.p. 153—155°). Benzyldimethylamine and CH_2PhCl in cold C_6H_6 afford *dibenzyldimethylammonium chloride*, m.p. 93—95° (*iodide*, m.p. 192°), unchanged by boiling MeOH–NaOMe, but at 120—140° during 2 hr. decomposed to NMe_2·CH_2Ph and CH_2Ph·OMe. Solid NaOMe at 140° affords some products of decomp. as before, together with αβ-diphenylethyldimethylamine, converted into stilbene by boiling the methosulphate with NaOH. When the N atom has an aryl group attached to it, isomerisation with alkali is accompanied by decomp. NHMe·CH_2Ph and ω-bromoacetophenone afford *phenyldibenzylmethylammonium bromide*, m.p. 144—146°. The iodide is decomposed by boiling MeOH–NaOMe to CH_2Ph·OMe and benzylmethylaniline (*picrate*, m.p. 105—107°) and rearranged by $NaNH_2$ at 160—170° to αβ-*diphenylethylmethylaniline*, m.p. 92—93° (*hydrochloride*, m.p. 230—232°), converted into stilbene by the action of MeOH–NaOH on the methosulphate. The aryl radical attached to N favours the decomp. reaction. Allyl bromide and NMe_2·CH_2Ph in cold C_6H_6 afford *benzyldimethylallylammonium bromide*, m.p. 98—100° (*picrate*, m.p. 108—110°), rearranged by $NaNH_2$ at 80° to β-dimethylamino-α-phenyl-Δ^{γ}-butylene (*picrate*, m.p. 147—149°), reduced by H_2–Pd in AcOH to β-dimethylamino-α-phenylbutane [*hydrobromide*, m.p. 161—163°; p-*bromophenacylobromide*, m.p. 188—190° (decomp.)]. For comparison, α-dimethylamino-α-phenylbutane [*picrate*, m.p. 139—140°; *hydrobromide*, m.p. 162—163°; p-*bromophenacylobromide*, m.p. 208—210° (decomp.)] is prepared. CH_2Ph·MgCl and αγ-bisdimethylaminobutyronitrile afford βδ-bisdimethylamino-α-phenylbutane [*picrate*, m.p. 193—195° (decomp.)]. J. L. D.

Two isomeric (4 : 5- and 2 : 7-)diacetylacenaphthenes. K. Dziewoński and J. Spirer (Bull. Acad. Polonaise, 1931, A, 232—241).—Heated with $AlCl_3$ at 115—120°, α-acetoacenaphthene (I) affords mainly 4 : 5-*diacetylacenaphthene* (II), m.p. 149°, identical with the product obtained by the action of AcCl or Ac_2O on acenaphthene in presence of $AlCl_3$ at 120°. Its *dioxime*, m.p. 196—197°, is converted by the Beckmann change (dry HCl into its solution in Ac_2O) into the *Ac_2 derivative*, m.p. 227—228°, of 4 : 5-diaminoacenaphthene (A., 1931, 82), which is obtained by hydrolysis with 6% HCl. Oxidation of (II) with $Na_2Cr_2O_7$ in AcOH affords the *anhydride*, m.p. 202—203°, of 4 : 5-diacetylnaphthalic acid (*imide*, m.p. 284°) and 4 : 5 : 4′ : 5′-*tetra-acetobiacedione*  $\left(\begin{matrix}C_{10}H_4Ac_2\\ \vert\\ CO\text{———}\end{matrix}\!\!>C:\right)_2$, not melting at 430°. With excess of $AlCl_3$ at 140°, (I) gives mainly 2 : 7-*diacetylacenaphthene* (III), m.p. 195° (*diphenylhydrazone*, m.p. 214°), the *dioxime*, m.p. 223—224°, of which is similarly converted into 2 : 7-diaminoacenaphthene (*loc. cit.*) (*Ac_2* derivative, m.p. 329°). Oxidation of (III) with 3% NaOCl gives *acenaphthene*-2 : 7-*dicarboxylic acid*, m.p. 355° (decomp.). J. W. B

Pinacol–pinacolin rearrangement. o-Substituted benzpinacols. C. H. Beale and H. H. Hatt (J. Amer. Chem. Soc., 1932, 54, 2405—2412; cf. A., 1929, 1175).—Contrary to Bailar (A., 1930, 1438), *s*-2 : 2′-dimethoxybenzpinacol is rearranged by I–AcOH (not successfully with AcCl) to a mixture, m.p. 161°, of two pinacolins [at a faster rate than *s*-2 : 2′-dimethylbenzpinacol (cf. *loc. cit.*)]; the OMe groups are attacked by I in boiling AcOH. The migratory power of the *o*-anisyl group is 0·3 and is greater than that of *m*-anisyl (0·2). Benzpinacol is oxidised by O_2 in AcOH or AcOH–NaOAc, or, better, with I in AcOH–NaOAc, to $COPh_2$. C. J W. (*b*)

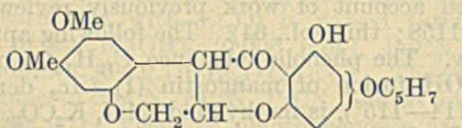
Aurin dimethyl ether and related compounds. A. Bistrzycki and S. von Jabłoński (Helv. Chim. Acta, 1932, 15, 890—906).—Previous work (A., 1908, i, 880) on aurin Me_2 ether is extended and partly corrected, and the prep. of the *o*-, *m*-, and *p*-cresol analogues is investigated. The α- and β-forms of *p*-hydroxytriphenylcarbinol are named the ψ- and normal carbinol, respectively, and similar names are applied to the analogues. Anisilic acid (I), PhOH, and a little conc. H_2SO_4 in AcOH at room temp. give p-*hydroxyphenyldi*-p-*anisylacetic acid*, m.p. indef., 195—211° (decomp.) after softening (*Ag* and *Na* salts; *Ac* derivative, m.p. 172·5—175·5°; gives with MeI–KOH–MeOH at 100° *Me tri*-p-*anisylacetate*, m.p. 136—137°), which with cold, conc. H_2SO_4 gives CO and amorphous, orange ψ-p-*hydroxyphenyldi*-p-*anisylcarbinol* (II), which could not be purified. (II) dissolves in warm *N*-KOH and is pptd. in the colourless normal *form*, m.p. 58—62° [best obtained pure by prolonged washing of the *chloride*, m.p. about 93° (decomp.) after softening from 78°] [*nitrate*, m.p. 117·5°; *sulphate*; *perchlorate*; *Ac* derivative, m.p. 104·5—106°, insol. in cold, dil. KOH, unchanged by hot EtOH (cf. lit.)], previously considered to be aurin Me_2 ether (III). (II) at 120—150° loses H_2O and gives (III), m.p. 186·5—187°, sol. in *N*-KOH only when boiled. The normal form rapidly passes into (II) when kept. Evaporation of a solution of (II) in Et_2O gives the normal form (25%), PhOH, and *pp'*-dimethoxybenzophenone. With Zn and boiling AcOH (II) yields p-*hydroxyphenyldi*-p-*anisylmethane*, m.p. 70·5—73·5° after softening at 52°. (I), *o*-cresol, and H_2SO_4 in cold AcOH give a little anisic acid and 4-*hydroxy*-3-*methylphenyldi*-p-*anisylacetic acid*, m.p. 211° after sintering from 160° (*Ag* salt; *Ac* derivative, m.p. 201·5—203·5°; *Me* ester of *Me ether*, m.p. 134—136°), which in conc. H_2SO_4 gives CO and ψ-4 *hydroxy*-3-*methylphenyldi* p-*anisylcarbinol*, reddish-orange, m.p. 138—140° after softening at about 125° (*chloride*, decomp. 164° after sintering at 155°; *nitrate*; *perchlorate*; *Ac* derivative, m.p. 86—89°), changed by passing CO_2 into its solution in 5% KOH into the unstable normal *form*, colourless; this gives on evaporation of its solution in Et_2O *pp'*-dimethoxybenzophenone and a little anisic acid, yields at 180° *di*-p-*anisyl*-3-*methyl*-1 : 4-*quinomethane*, $(MeO\cdot C_6H_4\cdot)_2C{:}C_6H_3Me{:}O$, m.p. 122—124°, insol. in 5—10% KOH, and is reduced by Zn and boiling AcOH to 4-*hydroxy*-3-*methylphenyldi*-p-*anisylmethane*, m.p. 89—91°. (I) and *m*-cresol give similarly the *lactone* of 2-*hydroxy*-4-*methylphenyldi*-p-*anisylacetic acid*, m.p. 98·5—100·5°, and 4-*hydroxy*-2-*methylphenyldi*-p-*anisylacetic acid*, decomp. 222—223° after sintering at 219° (*Na* and *Ag* salts; *Ac* derivative, m.p. 199·5—202°; *Me* ester of *Me ether*, m.p. 154°); the latter with cold, conc. H_2SO_4 gives *m*-cresol, (I), and a little ψ-4-*hydroxy*-2-*methylphenyldi*-p-*anisylcarbinol* (*Ac* derivative, m.p. 143·5° after sintering at 139·5°). (I) and *p*-cresol give the *lactone* of 6-*hydroxy*-3-*methylphenyldi*-p-*anisylacetic acid*, m.p. 113—115° after sintering at 112°. R. S. C.

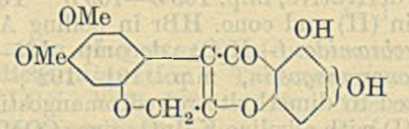
Phenanthrene series. XXXVII. 3-Bromo- and 3 : 6(?)-dibromo-phenanthraquinones. J. Schmidt and M. Eitel (J. pr. Chem., 1932, [ii], **134**, 167—176).—Bromination of phenanthraquinone in $PhNO_2$ gives 3-bromo- [*monosemicarbazone*, m.p. 226—228° (decomp.); *phenazine*, m.p. 249°; *monoxime*, dimorphous, m.p. 179—181°; $(NO_2)_2$-derivative, m.p. 295—296° (*monoxime*, m.p. 199—200° [decomp.])] and 3 : 6(?)-*dibromophenanthraquinone*, dimorphous, yellow, m.p. 283—285°, and orange, m.p. 286—287° [*monosemicarbazone*, m.p. 276° (decomp.); *phenazine*, m.p. 333—334°; *monoxime*, yellow form, m.p. 210—211° (*Cd* salt), green form (nitrosophenanthrol?), m.p. 242°; $(NO_2)_2$-derivative, m.p. 322°]. The 3 : 6-structure is assigned to the Br_2-compound on grounds of symmetry and on account of its formation from the 3-Br-compound; it gives on oxidation with CrO_3–H_2SO_4 5 : 5'-*dibromodiphenic acid*, m.p. 303—304°. H. A. P.

Constitution of mangostin. M. Murakami (Annalen, 1932, **496**, 122—151).—Mainly a more detailed account of work previously reviewed (A., 1931, 1158; this vol., 64). The following appears to be new. The phenolic substance, $C_{19}H_{18}O_6$, obtained by KOH fusion of mangostin (I) (*Ac*$_3$ derivative, m.p. 114—115°), is methylated (MeI, K_2CO_3, $COMe_2$) to a *Me*$_2$ derivative, m.p. 168·5—169·5° Tetrahydromangostin (II) and conc. HBr in boiling AcOH give the *hydrobromide* ($+H_2O$), decomp. 135—138°, of *tetrahydronormangostin*, m.p. 191—192°, which is methylated to dimethyltetrahydromangostin. Oxidation of (I) with alkaline $KMnO_4$ gives $COMe_2$, AcOH, and α-hydroxy*iso*butyric acid; (II) similarly affords *iso*hexoic acid. Dimethylmangostin and $KMnO_4$ in $COMe_2$ give $H_2C_2O_4$, an *acid*, $C_{15}H_{18}O_7$, m.p. 226—228°, and a neutral *compound* (III), $C_{25}H_{30}O_{10}$, m.p. 225°; (III) is converted by $SOCl_2$ into a *compound*, $C_{25}H_{28}O_{10}S$, m.p. 204° (decomp.), and is oxidised by HNO_3 (*d* 1·34) to an *acid*, $C_{10}H_9ON$, m.p. 268°, and a neutral *substance*, $C_{12}H_8O_9N_2$, m.p. 231°. Trimethylmangostin is oxidised ($KMnO_4$–$COMe_2$) to an *acid*, $C_{23}H_{26}O_{10}$, m.p. 240° (*Ba* salt), and a neutral *substance*, $C_{22}H_{18}O_5(OMe)_4$, m.p. 192° (unstable *oxime*, decomp. 100°), whilst acetyldimethylmangostin similarly gives an *acid*, $C_{22}H_{26}O_{11}$, m.p. 122—123° (*lactone*, m.p. 197—199°), and the *Ac* derivative, m.p. 200—201°, of (III). Structural formulæ are suggested for several of the above compounds.

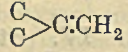
o-Vanillin is nitrated to 5-*nitro*-o-*vanillin*, m.p. 138·5—140°, which with Me_2SO_4 and MeOH–KOH gives the *dimethylacetal*, m.p. 96—97°, of 5-*nitro*-2 : 3-*dimethoxybenzaldehyde*, m.p. 116—117°. 5-*Nitro*-2 : 3-*dimethoxybenzoic acid*, m.p. 176°, is reduced to the 5-*NH*$_2$-*acid*, m.p. 150° [the acid, m.p. 250°, thus described by Rubenstein (A., 1926, 518), is probably 5-amino-2-hydroxy-3-methoxybenzoic acid], converted through the 5-OH-acid into 2 : 3 : 5-trimethoxybenzoic acid. The p-*iododiphenylylurethanes* of methylheptenol and methylheptanol have m.p. 124—125·5° and 140°, respectively. H. B.

Toxicarol. IV. Structure of toxicarol. E. P. Clark (J. Amer. Chem. Soc., 1932, **54**, 2537—2548; cf. this vol., 619).—Toxicarol (I), heated with 5% EtOH–KOH for 3 hr., loses the elements C_5H_6, giving apo*toxicarol* (II), $C_{18}H_{16}O_7$, m.p. 246—247° (*Ac*$_3$ derivative, m.p. 206°; *Me ether*, m.p. 236—237°), which gives a deep reddish-violet colour with $FeCl_3$, and is oxidised by I in hot EtOH–KOAc to *dehydro*apo*toxicarol*, m.p. 298° (after dehalogenation with Zn and AcOH). (I) does not give a Me ether, but is oxidised by alkaline H_2O_2 to *hydroxynetoric acid* (III), $C_{12}H_{14}O_6$, m.p. 189°, or *dehydronetoric acid* (IV), $C_{12}H_{12}O_5$, m.p. 212° (decomp.), according to the concn. of KOH used. (III) and Ac_2O give (IV), reduced to netoric acid. Dehydrodihydrotoxicarol (Ac derivative, m.p. 238°), heated with Zn and EtOH–KOH for 30 min., gives *dihydrotoxicarolic acid*, $C_{23}H_{26}O_9$, m.p. 129° (decomp.) [*Me* ester, m.p. 174° (*Ac_2* derivative, m.p. 143—144°)], oxidised by alkaline H_2O_2 to derric acid. Dehydrotoxicarol is similarly oxidised to *dehydrotoxicarolmonocarboxylic acid*, m.p. 230° (decomp.) (*Ac* derivative, m.p. 163°), oxidised further to rissic acid and reduced (catalytically) to its *dihydro*-derivative, m.p. 211° (decomp.). The following structures are assigned to (I) and (II).


(I.)


(II.)

C. J. W. (*b*)

Ouabain or *g*-strophanthin. W. A. JACOBS and N. M. BIGELOW (J. Biol. Chem., 1932, 96, 647—658).—Ouabain (*g*-strophanthin) (I), $C_{29}H_{44}O_{12}$ (lit. $C_{30}H_{46}O_{12}$), is a rhamnoside of a hexahydroxytetracyclic $\Delta^{\beta\gamma}$-unsaturated lactone, $C_{23}H_{34}O_{18}$. Hepta-acetylanhydro-ouabain (II), $C_{43}H_{56}O_{18}$, m.p. 283—285°, $[\alpha]_D^{21}$ −59·1° in pyridine, −51·7° in 85% EtOH, when reduced catalytically (PtO_2), best in EtOH, gives *hepta-acetyldihydrodeoxyouabain*, m.p. 273—275°, $[\alpha]_D^{22}$ −63·8° in pyridine, yielding with 3% HCl in hot AcOH under certain conditions CH_2O and an *acetyltrianhydrolactone* (III), $C_{24}H_{30}O_4$, m.p. 172—173°, dimorphic, $[\alpha]_D^{22}$ −108·4° in pyridine, which with hot aq. EtOH–NaOH gives the *hydroxytrianhydrolactone*, $C_{22}H_{28}O_3$, m.p. 198—199°, $[\alpha]_D^{20}$ −41·5° in pyridine. Catalytic reduction (PtO_2) of (III) affords α- and β-forms of an *acetylhexahydrolactone*, $C_{24}H_{36}O_4$, m.p. 203—204°, $[\alpha]_D^{20}$ −22·2° in pyridine, and m.p. 167—169°, $[\alpha]_D^{22}$ −21·5° in pyridine, respectively, hydrolysis of which affords α- and β-*hydroxyhexahydrolactones*, $C_{22}H_{34}O_3$, m.p. 94—96°, $[\alpha]_D^{23}$ −8·9° in EtOH, and m.p. 164—166°, $[\alpha]_D^{22}$ +11·2° in EtOH. These are *sec.* alcohols, since the α-isomeride with Kiliani's reagent gives the α-*hexahydroketolactone*, $C_{22}H_{32}O_3$, m.p. 188—191°. Hydrolysis of (I) and (II) under normal conditions gives resins. The loss of a C atom during formation of (III) is considered to be due to hydrolytic fission of a  $\substack{C\\C}\!>\!C{:}CH_2$ group. It is concluded that the rhamnose is attached to the *sec.* OH group, that the four OH groups which are acetylated are *tert.*, and that the OH group removed in formation of (II) corresponds with the *tert.* OH of the strophanthin aglucones. The presence of the last group is confirmed by isomerisation of (I) by KOH–MeOH to iso*ouabain*, $C_{29}H_{44}O_{12}+(?)H_2O$, m.p. 213—215° (decomp.) after softening at 200°, $[\alpha]_D^{19}$ −45·7° in H_2O, which does not give the Legal reaction.

R. S. C.

Amyrilenes. K. H. BAUER and H. J. STARCKE (Arch. Pharm., 1932, 270, 334—338).—With a 0·25*N*-solution of BzO_2H in $CHCl_3$ α-amyrilene gives a monoxide-*A* (I), m.p. 172°, and a monoxide-*B*, m.p. 136—137° (cf. this vol., 517), and with 0·5*N*-solutions gives (I) and a *dioxide*, m.p. 189—190°. β-Amyrilene gives with both solutions a *monoxide*, m.p. 169—170°, and a *dioxide*, m.p. 210—211°. Attempts to prepare derivatives of the oxides failed. R. S. C.

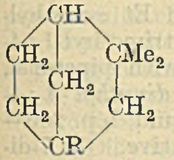
Saponin group. X. Monohydroxytriterpene acids. A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1932, 208, 9—25; cf. this vol., 61).—From *Olibanum* (frankincense), " acetylboswellic acid " (I) was isolated by way of the Ba salt. On acid hydrolysis and fractionation this gave two isomerides: α-*boswellic acid* (II), m.p. 289°, $[\alpha]_D^{19}$ +115° [mixed *anhydride* with AcOH, m.p. 229—232°, resolidifies, decomp. 269—270°; *Ac* derivative (III), m.p. 241—243°, $[\alpha]_D^{19}$ +65°; *Me* ester, m.p. 214—215°, $[\alpha]_D^{19}$ +115°; *Me* ester of (III), m.p. 229—230°, $[\alpha]_D^{19}$ +68°; *formyl* derivative, m.p. 254—257°, $[\alpha]_D^{19}$ +65·5°]; β-*boswellic acid* (IV), m.p. 238—240°, $[\alpha]_D^{19}$ +118° [mixed *anhydride* with AcOH, m.p. 226—228°, decomp. 277—280°; *Ac* derivative (V), m.p. 271—273°, $[\alpha]_D^{19}$ +69°; *Me* ester, m.p. 189—190°, $[\alpha]_D^{19}$ +116°; *Me* ester of (V), m.p. 197·5—198·5°, $[\alpha]_D^{19}$ +74°; *formyl* derivative, m.p. 272—275° (decomp.), $[\alpha]_D^{20}$ +92°]. High vac. distillations of different fractions of the mixture (I) gave *hydrocarbons*, $C_{29}H_{46}$, m.p. 127°, 125°, and 119—121°, $[\alpha]_D^{16}$ +185°, +253°, and +320°, respectively. (III) and (V) gave *hydrocarbons*, m.p. 153—154°, 140—141·5°, $[\alpha]_D^{20}$ +132°, +132°, respectively. All m.p. are corr., all rotations in $CHCl_3$. From equiv. wt. determinations, (II), (IV), oleanolic, ursolic, and elemolic acids have the composition $C_{30}H_{48}O_3$. J. H. B.

Determination of saponins. O. DE A. COSTA (Rev. Soc. Brasil. Chim., 1931, 2, 476—484).—Tests for the detection and determination of saponins are reviewed. The de Campos method (Rev. Chim. e Phys. pur. applic., 1915, No. 3) has been discarded in favour of that of Rosenthaler and Schiller (A., 1913, ii, 354), which can be applied to beers. E. L.

Syntheses of terpenes from isoprene. T. WAGNER-JAUREGG (Annalen, 1932, 496, 52—77).—Isoprene (450 g.), AcOH (1500 c.c.), and conc. H_2SO_4 (5 g.) at room temp. for 3 days give a little caoutchouc and (after hydrolysis) 101 g. of a mixture, b.p. 72—160°/12 mm., of (*a*) primary alcohols [separated by *o*-$C_6H_4(CO)_2O$ in C_6H_6], (*b*) *tert.*-alcohols (removed as borates), and (*c*) hydrocarbons, containing (*a*) geraniol, *cyclo*geraniol, and sesquiterpene alcohols, b.p. (mainly) 114—126°/0·7 mm., of the composition $C_{15}H_{26}O$ and containing three double linkings, (*b*) *dl*-linalool, *dl*-α-terpineol, and sesquiterpene alcohols, b.p. 108—122°/0·43 mm., composition $C_{15}H_{26}O$, and (*c*) a monocyclic hydrocarbon, b.p. 120—125°/12 mm., containing three double linkings, converted by boiling 98% HCO_2H into a dicyclic hydrocarbon of the caryophyllene group. Geranyl acetate and AcOH–conc. H_2SO_4 under the above conditions give hydrocarbons and (after hydrolysis) some *cyclo*geraniol [*naphthylurethane*, m.p. 90—91° (corr.)]. Isoprene shaken with dil. H_2SO_4 in CO_2 for about 5 days gives a mixture of hydrocarbons, alcohols, and ethers (oxides); the last-named are formed by dehydration of polyhydric alcohols. A fraction, b.p. 55—90°/14 mm., is freed from alcohols (as borates), the residue reduced (H_2, PtO_2, AcOH), and the ethers removed as additive compounds with $H_4Fe(CN)_6$. Fractionation of the ethers gives a product, b.p. 170—172°, which with HBr–AcOH affords terpinene dihydrobromide (thus proving the presence of 1 : 4-cineole), and with tetraiodopyrrole gives a little of its additive (1 : 1) *compound*, decomp. 112°, with 1 : 8-cineole. Isoprene is polymerised by $TiCl_4$ in $CHCl_3$ to an amorphous *compound*, *M* 2830, decomp. 190° (softens at 130°). The polymeride obtained using $SnCl_4$ is dehydrogenated by Se at 280—340° to 1 : 2 : 5-trimethylnaphthalene.

The possible mechanisms of formation of some of the above compounds are discussed. H. B.

Hydrocarbons corresponding with particular camphor-like substances. I. Fenchane, *apo*camphane, β-*apo*fenchane, and santenane. G. Komppa and T. Hasselström (Annalen, 1932, 496, 164—170).—dl-iso*Fenchonehydrazone*, m.p. 111—112° (*Ac* derivative, m.p. 193—194°), and EtOH–NaOEt at 180° give fenchane (I, R=Me), b.p. 151—152°/765 mm. The following are similarly prepared: *apo*camphane (α-fenchocamphorane), b.p. 148°/755 mm., from *dl*-α-fenchocamphoronehydrazone, b.p. 120°/11 mm. (*Ac* derivative, m.p. 145—146°); β-*apo*fenchane (β-fenchocamphorane) (I, R=H), b.p. 143·5°, m.p. 17—17·5°, from *dl*-β-fenchocamphoronehydrazone, b.p. 135—138°/14 mm. (*Ac* derivative, m.p. 134—135°), identical with camphenilane, b.p. 142°, m.p. 17° (Nametkin and Chuchrikovaia, A., 1915, i, 701), from camphenilonehydrazone (*Ac* derivative, m.p. 148·5—149·5°); santenane, b.p. 146—148°, m.p. 66—67°, from santenonehydrazone (*Ac* derivative, m.p. 152—153°). H. B.


(I.)

Dependence of optical rotatory power on chemical constitution. XIV. Stereoisomeric aminomethylenecamphors, iminomethylenecamphors, and their derivatives. B. K. Singh and B. Bhaduri (J. Indian Chem. Soc., 1932, 9, 109—119).—The rotatory powers of *d*- and *l*-amino- (I), -imino- (II), and -benzylamino- (III) -methylenecamphors have been measured in various solvents for different wave-lengths at 35°; these decrease in the order EtOH>MeOH>pyridine>$COMe_2$>$CHCl_3$>C_6H_6 for (I) and (II), and in the order MeOH>EtOH>$COMe_2$>pyridine>$CHCl_3$>C_6H_6 for (III). The sp. rotatory power of (II) is nearly twice that of (I); the increase is ascribed to the conjugated system in (II). (I) and (II) obey the one-term simple dispersion formula of Drude.

d-Aminomethylenecamphor (IV), prepared by the method of Bishop *et al.* (A., 1895, i, 62), has m.p. 157°; l-, m.p. 157° (V), and dl-, m.p. 163—164°, -*aminomethylenecamphors* are prepared similarly. *d*-Iminomethylenecamphor, m.p. 216—218° (lit. 221—222°), is best obtained from (IV) and *d*-oxymethylenecamphor in MeOH–AcOH; l-, m.p. 216—218°, dl-, m.p. 216—218°, and meso-, m.p. 217—218° [from (IV) and *l*-oxymethylenecamphor or from (V) and *d*-oxymethylenecamphor], -*iminomethylenecamphors* are described. *d*-Oxymethylenecamphor, $CH_2Ph \cdot NH_2,HCl$, and NaOAc give d-*benzylaminomethylenecamphor*, m.p. 89—91°; the l- and dl-*forms* have m.p. 89—91° and 84—85°, respectively. H. B

Isomerisation of linalolene to dihydromyrcene. V. Longuinov and (Mme.) R. Khasanova (Bull. Soc. chim., 1932, [iv], 51, 636—639; cf. A., 1929, 538).—β-Linalolene, b.p. 158—160°/761 mm., with aq. HBr at 100° gives a *dibromide*, b.p. 125—129°/9 mm., converted by suitable treatment with NMe_3 into β-dihydromyrcene, b.p. 168—170°/760 mm. A. A. L.

Furan reactions. I. Pyrolysis of furan. C. D. Hurd and A. R. Goldsby. **II. Furan from furfuraldehyde.** C. D. Hurd, A. R. Goldsby, and E. N. Osborne. **III. Absorption of furan vapours.** C. D. Hurd and A. R. Goldsby (J. Amer. Chem. Soc., 1932, 54, 2530—2531, 2532—2536, 2558).—I. Furan decomposes at 670—740° in a quartz tube (but at 360° in presence of catalytic Ni); at 670° the gaseous products are approx. 75% of CO, 12% of saturated hydrocarbons and H_2, and the remainder unsaturated hydrocarbons, whilst at 740° less CO and more saturated hydrocarbons and H_2 result. The 11% unsaturated hydrocarbons in the off-gas at 740° and 2·59 sec. consists of 3·1% acetylenes, 5·5% C_2H_4, and 2·4% C_3H_6, with undetermined amounts of allene, *cyclo*propene, and butadiene; the acetylenes consist largely of CH:CMe. C_6H_6 was definitely identified, but no difuryl was observed.

II. Furfuraldehyde decomposes above 550° into furan and its decomp. products; butadiene, C_6H_6, PhMe, PhOH, and a xylenol are also identified. Excellent yields of furan are obtained when furfuraldehyde (vapour) is passed through soda-lime at 350° or through fused NaOH; H_2 and CO_2 are produced. The hot alkali converts a small portion of the furan into gaseous products.

III. Furan (gaseous) is absorbed quantitatively by 82·5% H_2SO_4. A mixture of furan and C_2H_4 can thus be analysed, since C_2H_4 is absorbed only by oleum. This method is not applicable to the quant. analysis of furan admixed with other unsaturated, gaseous hydrocarbons; liquefaction and distillation are necessary for exact analysis. C. J. W. (*b*)

Labile isomeride of 2-methylfuran. N. Kijner (J. Gen. Chem. Russ., 1931, 1, 1212—1228).—The decomp. of furfuraldehydehydrazone with alkali under drastic conditions yields an *isomeride* (I) of 2-methylfuran, b.p. 78—78·5°, d_4^{18} 0·9406, n_D^{18} 1·457, which is probably 2-methylene-Δ^3- or -Δ^4-dihydrofuran or a mixture of the two, possibly an equilibrium mixture. It gives characteristic colour reactions with *p*-diazobenzenesulphonic acid, is readily oxidised by O_2 to furancarboxylic acid, and is hydrated by dil. aq. acids to lævulaldehyde and an unsaturated keto-alcohol $CHAc:CH \cdot CH_2 \cdot OH$, isolated as the *semicarbazidosemicarbazone*, m.p. 187—188° (decomp.) on slow heating (*acetate*, m.p. 120—125°). (I) is isomerised to 2-methylfuran by alkalis, N_2H_4,H_2O, and especially acids. With 10% H_2SO_4 a polymeride $C_{15}H_{18}O_3$ is also formed (*semicarbazone*, m.p. 159—160°); this has one furan ring because it condenses with maleic anhydride to a *compound*, $C_{19}H_{20}O_6$, m.p. 89—90°. (I) reacts exothermically with maleic anhydride giving a *compound* $C_9H_8O_4$, m.p. 71—72°, which is also formed from 2-methylfuran, probably owing to isomerisation of (I) by maleic anhydride; $C_9H_8O_4$ is decomposed by hot H_2O or NaOH into methylfuran. G. A. R. K.

Rearrangement of the α-furfuryl group. II. 5-Methylfurfuryl chloride and 5-methylfurylacetic acid. E. W. Scott and J. R. Johnson (J. Amer. Chem. Soc., 1932, 54, 2549—2556; cf. A., 1930, 783).—Chlorination of Et 2-methyl-3-furoate at 145° and subsequent hydrolysis gives 5-*chloro*-2-*methyl*-3-*furoic acid*, m.p. 122—123°, in 35—50% yields (Cl is not removed by EtOH–NaOH), which with Cu-bronze in coal-tar bases (b.p. 150—200°/16 mm.) at 260—270° affords 50% of 2-*chloro*-5-*methylfuran*, b.p. 48—49°/70—75 mm., 108—110°/740 mm. This is more stable than furfuryl chloride, has no lachrymatory action, and does not undergo rapid spontaneous decomp. on keeping. Details are given for the prep. of 5-methylfurfuraldehyde, its oxime, and 5-methylfuronitrile (by dehydration of the oxime). The nitrile prepared (from furfuryl chloride and aq. NaCN) by Kirner and Richter (A., 1929, 1458) is a mixture of approx. 85% of 5-methylfuronitrile and 15% of furylacetonitrile. 5-Methylfurfuryl alcohol, b.p. 194—196° (slight decomp.)/744 mm., 70—73°/6 mm. (diphenylurethane, m.p. 52—53°), gives an unstable chloride, which with aq. NaCN affords 5-methylfurfuryl cyanide (11% yield), hydrolysed to 5-methyl-2-furylacetic acid, m.p. 57—58°, also prepared from 5-methylfurfuraldehyde. 2 : 5-Dimethylfuroic acid (Et ester, b.p. 83—85°/6 mm., 99—101°/14 mm.) has m.p. 134°. It is suggested that the mechanism of the rearrangement reaction involves 1 : 4-addition of HCN to the furan ring. C. J. W. (*b*)

Coumarins and hydroxycoumarins. T. Pavolini (Riv. Ital. Ess. Prof., 1931, 8, 327—330; Chem. Zentr., 1932, i, 1126).—The origin of coumarin and its derivatives in plants is discussed. Coumarin is detected by boiling with resorcinol (orcinol, or orcein) in 80% H_2SO_4, rendering alkaline, and diluting; a blue (violet) fluorescence, due to the formation of 4-hydroxycoumarin, is obtained. The reaction is not sp. in presence of β-OH- and β-keto-acids. A. A. E.

1 : 2 : 3 : 4-Tetrahydroxybenzene derivatives. Synthesis of 6 : 7 : 8-trihydroxycoumarin and of dimethylfraxetin. F. Wessely and F. Lechner (Monatsh., 1932, 60, 159—164).—1 : 2 : 3 : 4-$C_6H_2(OH)_4$ (A., 1904, i, 240 : improved yield by heating 4-aminopyrogallol hydrochloride with air-free H_2O in sealed tube) (Me_4 ether, new m.p. 87·5°) gives (NaOAc and Ac_2O) a Ac_4 derivative, m.p. 160°. This by $Zn(CN)_2$ and HCl yields 2 : 3 : 4 : 5-*tetrahydroxybenzaldehyde* (decomp. from 170°; sublimes at 160—170° in high vac.) (Ac_4 derivative, m.p. 143°), which by Perkin's synthesis gives 6 : 7 : 8-*triacetoxycoumarin*, m.p. 142·5—145·5° (also obtained from fraxetin and HBr). This with MeOH and HCl gives 6 : 7 : 8-*trihydroxycoumarin*, m.p. 272° (decomp.), subliming at 220°/0·02 mm., of which the 6-methylated derivative (diazomethane) is identical with fraxetin Me_2 ether. E. W. W.

Hydroxy-carbonyl compounds. VII. Coumarins and 1 : 4-benzopyrones derived from *m*-cresol. A. Robertson, T. B. Waters, and (in part) E. T. Jones (J.C.S., 1932, 1681—1688).—*m*-Cresol and Et acetoacetate give 4 : 7-dimethylcoumarin, which is also obtained directly from *m*-tolyl Me ether, Et acetoacetate, and 86% H_2SO_4: this does not exclude the intermediate formation of a cinnamic acid (cf. this vol., 620), since 2-*methoxy*-β : 4-*dimethylcinnamic acid*, m.p. 140—141° [oxidised to 2-methoxy-4-methylacetophenone (*semicarbazone*, m.p. 200—201°)], and 86% H_2SO_4 afford the same coumarin. 2-Hydroxy-4-methylpropiophenone, Ac_2O, and NaOAc yield 2 : 3 : 7-*trimethyl*-, m.p. 86°, which condenses with piperonal to 2-(3′ : 4′-*methylenedioxystyryl*)-3 : 7-*dimethyl*-1 : 4-*benzopyrone*, m.p. 191°. 2-*Methoxy*-6-*methylpropiophenone*, b.p. 137°/16 mm. (*semicarbazone*, m.p. 145°), prepared from 3-methoxy-*o*-toluonitrile and MgEtI, forms, after hydrolysis with Ac_2O and NaOAc, 2 : 3 : 5-*trimethyl*-1 : 4-*benzopyrone*, m.p. 96°. Condensation of *m*-cresol with Et α-methyl- and α-ethyl-acetoacetate in the Simonis reaction gives pairs of isomeric 1 : 4-pyrones. With Et α-methylacetoacetate, a mixture of 2 : 3 : 5-trimethyl-1 : 4-benzopyrone [condensation product with piperonal, 2-(3′ : 4′-*methylenedioxystyryl*)-3 : 5-*dimethyl*-1 : 4-*benzopyrone*, m.p. 166—167°] and a liquid, b.p. 200—220°/15 mm. [corresponding derivative, -3 : 7-dimethyl-], is obtained. 3 : 4 : 7-Trimethylcoumarin is converted into 2-*methoxy*-αβ : 4-*trimethylcinnamic acid*, m.p. 159°. 2-Hydroxy-4-methyl-*n*-butyrophenone, Ac_2O, and NaOAc give mainly 2 : 7-dimethyl-3-ethyl-, since condensation of this with piperonal affords 2-(3′ : 4′-*dimethylenedioxystyryl*)-7-*methyl*-3-*ethyl*-1 : 4-*benzopyrone*, m.p. 160°. Similarly, Et α-ethylacetoacetate and *m*-cresol form a mixture of 2 : 5-*dimethyl*-3-*ethyl*-1 : 4-*benzopyrone*, m.p. 86° [piperonal condensation, 2-(3′ : 4′-*methylenedioxystyryl*)-5-*methyl*-3-*ethyl*-1 : 4-*benzopyrone*, m. p. 180°], and an oil, b.p. 180—190°/20 mm., consisting mainly of 2 : 7-dimethyl-3-ethyl-1 : 4-benzopyrone.

2-*Methoxy*-β : 4-*dimethyl*-α-*ethylcinnamic acid*, from 4 : 7-dimethyl-3-ethylcoumarin, has m.p. 123°. 7-*Methylflavone*, m.p. 120°, is obtained from 2-hydroxy-4-methylacetophenone, Bz_2O, and NaOBz. *m*-Cresol and Et benzoylacetate with P_2O_5 give 5-*methylflavone*, m.p. 129—130°, and with H_2SO_4 yield 4-*phenyl*-7-*methylcoumarin*, m.p. 96°, which cannot be prepared by ring-closure of 2-hydroxy-4-methylbenzophenone (*phenylhydrazone*, m.p. 137—138°), the *acetate*, m.p. 97°, being formed. Condensation of resorcinol Me_2 ether with Et acetoacetate gives 7-methoxy-4-methylcoumarin and with Et α-methylacetoacetate, 7-methoxy-3 : 4-dimethylcoumarin. F. R. S.

Coumarins and chromones from β-naphthol. B. B. Dey and A. K. Lakshminarayanan (J. Indian Chem. Soc., 1932, 9, 149—155).—β-$C_{10}H_7$·OH and $CH_2Ac·CO_2Et$ in cold conc. H_2SO_4 give a mixture of 4-methyl-β-naphthacoumarin (4-methyl-1 : 2-βα-naphthapyrone) (I), m.p. 179°, and 2-methyl-1 : 4-βα-naphthapyrone (II), m.p. 168° (formed when P_2O_5 is the condensing agent), since treatment of the mixture with PhCHO and EtOH–NaOEt affords some 2-*styryl*-1 : 4-β*α-naphthapyrone*, m.p. 198° (*dibromide*, m.p. 175°) [also prepared similarly from (II)]. (I) does not form a condensation product with PhCHO.

H. B.

Preparation of dinaphtho-γ-pyrone (1 : 2 : 7 : 8-dibenzoxanthone). K. Dziewoński and S. Pizoń (Bull. Acad. Polonaise, 1931, **A**, 406—410).—β-Naphthol heated with $CO(NHPh)_2$ or $CS(NHPh)_2$ at 250—265° gives the *anil*, m.p. 263—266°, of 1 : 2 : 7 : 8-dibenzoxanthone (I), which is readily obtained by hydrolysis with AcOH and conc. HCl. A mechanism involving the intermediate formation of β-naphthylurethane is suggested. Fusion of (I) with KOH at 230—260° gives 2 : 2′-*dihydroxy*-1 : 1′-*dinaphthyl ketone*, m.p. 177° (decomp.) (*Ac_2* derivative, m.p. 196°), which is reconverted into (I) at 180°.

J. W. B.

Synthesis of anthocyanins. The four isomeric glucosides of pelargonidin chloride. A. León, A. Robertson, R. Robinson, and T. R. Seshadri (Anal. Fís. Quím., 1932, **30**, 267—301).—Methods similar to that used for the synthesis of 3-β-glucosidylpelargonidin chloride (A., 1928, 895) have now been used for the 4′-, 7-, and 5-glucosides. The last-named is pelargonenin chloride, and pelargonin is probably the 3 : 5-diglucoside. This assumption is in accord with the work of Karrer *et al.* (A., 1927, 1197 ; 1928, 1255).

4 : 6-Dihydroxy-*o*-tolualdehyde and ω-hydroxy-*p*-acetoxyacetophenone condense in EtOAc in presence of dry HCl to give 3 : 7 : 4′-*trihydroxy-5-methylflavylium chloride* (+H_2O). 2 : 6-Dihydroxy-*p*-tolualdehyde yields similarly the 7-*methyl* compound (+$2H_2O$). 4 : 6-Dihydroxy-2-methoxybenzaldehyde with BzCl and K_2CO_3 yields the 4-*benzoyloxy*-compound, m.p. 101—102°, which condenses with ω-hydroxy-*p*-acetoxyacetophenone. The *Bz* derivative obtained yields 3 : 7 : 4′-*trihydroxy-5-methoxyflavylium chloride*. 6-Hydroxy-2-benzoyloxy-4-methoxybenzaldehyde yields similarly 3 : 5 : 4′-*trihydroxy-7-methoxyflavylium chloride* (purified as the *picrate*).

ω-4-Dihydroxyacetophenone [*K* salt (+H_2O) ; *Ag* salt; *osazone*, m.p. 212—214°, with NHPh·NH_2] condenses with 2-*O*-benzoylphloroglucinaldehyde to give 5-*O*-benzoylpelargonidin chloride (A., 1928, 894). ω-*Hydroxy-4-tetra-acetyl*-β-*glucosidylacetophenone*, m.p. 149—150°, and 2-*O*-benzoylphloroglucinaldehyde give 5-O-*benzoyl* - 4′ - *tetra* - *acetyl* - β - *glucosidylpelargonidin chloride* (darkens 182°, softens 193°, decomp. 198°), hydrolysed to 4′-β-*glucosidylpelargonidin chloride* (+2·75H_2O), decomp. 184° (*picrate*, +$3H_2O$, decomp. 146—148°).

2-*O*-Benzoylphloroglucinaldehyde (*K* salt, decomp. 70°), with a little of the 2 : 4-OO′-*Bz_2* derivative, m.p. 139—140°, is prepared by adding BzCl to the aldehyde in ice-cold aq. KOH and pptn. by $NaHCO_3$. The *Ag* salt with ω-acetobromoglucose in C_6H_6 yields 4-*tetra-acetyl*-β-*glucosidyl*-2-O-*benzoylphloroglucinaldehyde* (I), m.p. 144—145°, also obtained from the phenol with α-acetobromoglucose in aq. $COMe_2$. The constitution of (I) is shown by methylation to the 6-O-*Me* derivative, m.p. 95—120°, hydrolysed by acid or alkali to 4-β-*glucosidyl*-2-O-*methylphloroglucinaldehyde*, m.p. 237—239°, which is synthesised by the condensation of 2-*O*-benzoylphloroglucinaldehyde and α-acetobromoglucose, followed by hydrolysis of the 4-*tetra-acetyl*-β-*glucosidyl* derivative, m.p. 149—150°. ω-4-Dihydroxyacetophenone condenses with (I) to give 3 : 4′-*dihydroxy-5-benzoyloxy-7-tetra-acetyl*-β-*glucosidylflavylium chloride* (+0·5H_2O), m.p. 184—186° (softens 177°), hydrolysed to 7-β-*glucosidylpelargonidin chloride* (+$3H_2O$) [isolated first as the *picrate* (+1·5H_2O), m.p. 180° (decomp. ; softens 120°)].

2 : 4-*OO*′-Dibenzoylphloroglucinaldehyde (II) is best prepared by the use of BzCl in C_5H_5N. The 2 : 4 : 6-OO′O″-*Bz_3* derivative, m.p. 121—122° (+0·5MeOH, m.p. 80°), is obtained similarly. Methylation of (II) yields the 6-O″-*Me* derivative, m.p. 133—134°, hydrolysed to 6-*O*-methylphloroglucinaldehyde. Treatment of (II) with α-acetobromoglucose and Ag_2CO_3 in C_6H_6 gave a *substance*, $C_{27}H_{21}O_{11}$, m.p. 110—145° (softens 85°). Treatment of (II) with α-acetobromoglucose and KOH in aq. $COMe_2$ yielded (?) 6-*tetra-acetyl*-β-*glucosidyl*-2 : 4-OO′-*dibenzoylphloroglucinaldehyde* (+3·5H_2O ?), m.p. 144—145°. This substance was also obtained by interaction of (II) with α-acetobromoglucose and Ag_2O in quinoline, accompanied by a *substance*, m.p. 223—224°. The crude material was hydrolysed by KOH–EtOH and condensed with ω-4-dihydroxyacetophenone in alc. HCl, giving 5-β-glucosidylpelargonidin chloride in very small yield.

The colour reactions of the 3-, 4′-, 7-, and 5-glucosides of pelargonidin and the 5- and 7-Me and -MeO analogues in buffer solutions at various values of p_H are recorded (cf. A., 1929, 477). R. K. C.

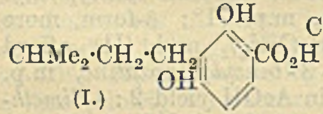
Synthetical experiments in the *iso*flavone group. VI. Reactions of some keto-ethylene oxides. W. Baker and R. Robinson (J.C.S., 1932, 1798—1806).—The oxide of 2 : 4-dimethoxyphenyl styryl ketone (I), obtained by oxidising the ketone with H_2O_2, gives with H_2SO_4 and MeOH, 2 : 4-*dimethoxyphenyl* α-*hydroxy*-β-*methoxy*-β-*phenylethyl ketone*, m.p. 133° (from EtOH corresponding -β-*ethoxy*-compound, m.p. 98°), which forms with AcOH and NaOAc or with aq. EtOH–NaOH, 2 : 4-*dimethoxyphenyl benzyl ketone* (II) (α-form, m.p. 71° ; β-form, more stable, m.p. 86°). *o*-$C_6H_4(NH_2)_2$ and (II) afford 2-(2′ : 4′-*dimethoxyphenyl*)- 3 - *benzylquinoxaline*, m.p. 108—109°. (I) and HCl in AcOH yield 2 : 4-*dimethoxyphenyl* β-*chloro*-α-*hydroxy*-β-*phenylethyl ketone*, m.p. 131°, and (I) with EtOH–NaOH forms 2 : 4-*dimethoxyphenylbenzylglycollic acid*, m.p. 176° (efferv.), which is also similarly obtained from (II), and is oxidised to 2 : 4-dimethoxyphenyl CH_2Ph ketone. With HCO_2H alone, (I) gives 2 : 4-*dimethoxyphenyl* α-*hydroxy*-β-*formoxy*-β-*phenylethyl ketone*, m.p. 154°, but in presence of H_2SO_4, αβ-*diformoxy*-, m.p. 141°, is formed, and when AcOH is used instead of HCO_2H, the α-*hydroxy*-β-*acetoxy*-, m.p. 136°, results; each of the three derivatives yields (II) (β-form) with AcOH and NaOAc.

The *oxide* of 2 : 4-*dimethoxyphenyl* p-*methoxystyryl ketone*, m.p. 108°, similarly forms 2 : 4-*dimethoxyphenyl* α-*hydroxy*-β-*methoxy*-β - p - *methoxyphenylethyl ketone*, m.p. 143—144°, which when boiled with NaOH gives a mixture of the (A), m.p. 102°, and (B) *forms*, m.p. 115°, of 2 : 4-*dimethoxyphenyl* p-*methoxybenzyl ketone*, each transformed by *o*-phenylenediamine into 2-(2′ - 4′-*dimethoxyphenyl*)-3-p - *methoxybenzylquinoxaline*, m.p. 76—79° (these forms are possibly *cis*- and *trans*-

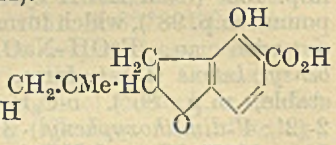
isomerides of the enol form of the diketone). 2 : 4-*Dimethoxyphenyl*-p-*methoxybenzylglycollic acid*, m.p. 177° (efferv.), is oxidised to 2 : 4-*dimethoxyphenyl* p-*methoxybenzyl ketone*, m.p. 84°. F. R. S.

Methoxy-derivatives of xanthone and thioxanthone. K. C. Roberts, L. A. Wiles, and B. A. S. Kent (J.C.S., 1932, 1792—1798).—2-Nitro-, m.p. 180° (cf. A., 1917, i, 336), prepared from the corresponding toluene, is reduced to 2-*amino*-6-*methoxybenzoic acid*, m.p. 87°, which after diazotisation gives the thiocyanate, hydrolysed to 6-*methoxy*-2-*dithiobenzoic acid* (I), m.p. 187°. (I) and quinol Me$_2$ ether form 1 : 4 : 8-*trimethoxythioxanthone*, m.p. 208—209° (*di-* and *mono-chlorostannate*, and *diperchlorate*, in which the O is probably present as O^{IV}), which is hydrolysed to 1 : 8-*dihydroxy*-4-*methoxythioxanthone* (*diacetoborate*). PhOMe and (I) yield 1 : 7-*dimethoxy*-, m.p. 131—132° (*monoperchlorate*; *trihydrochloride*; *chlorostannate*, indicating basic character and a monochelate structure), hydrolysed to 7-*hydroxy*-1-*methoxythioxanthone*, m.p. 246° (decomp.) (*dihydrochloride*). 1-Hydroxy-7-methoxyxanthone forms a *chlorostannate* and a *diacetoborate*. A comparison of the relative effects of oxide O and sulphide S on the basic property has been made by comparing 1 : 7-disubstituted thioxanthones with the Me ethers of euxanthones. F. R. S.

Rotenone, the active constituent of the *Derris* root. IX. Constitution of tetrahydrotubaic acid and rotenone. Synthesis of some products of the degradation of rotenone. S. Takei, S. Miyajima, and M. Ōno (Ber., 1932, 65, [*B*], 1041—1049; cf. this vol., 400).—The recognition of *iso*hexoic acid (p-*iodophenacyl* ester, m.p. 85°) as product of the oxidation of tetrahydrotubaic acid (I) and of 2-γ-*ethyl*-n-*butylresorcinol*, m.p. 85°, as product of its decarboxylation necessitates amended constitutions for (I) and tubaic acid (II).



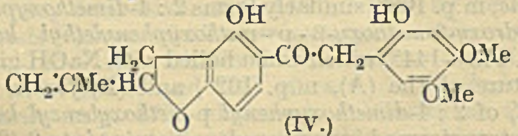
(I.)



(II.)

4-Hydroxyveratrole is converted by CO$_2$ and KHCO$_3$ in glycerol at 160—165° into 2-hydroxy-4 : 5-dimethoxybenzoic acid (III), m.p. 202° (*Me* ester, m.p. 93°), identical with the acid derived from dehydrorotenone. (III) is transformed by successive treatment with NaOH and CH$_2$Cl·CO$_2$Et followed by hydrolysis into 4 : 5-*dimethoxy*-2-*carboxymethoxybenzoic acid*, m.p. 255° (*Me*$_2$ ester, m.p. 86°), identical with rissic acid.

Derritol (amended constitution IV), when successively treated with NaOH, CH$_2$Cl·CO$_2$Et, and hydrolysed, affords derric acid, m.p. 154°, converted by NaOAc and Ac$_2$O at 150° into dehydrorotenone.

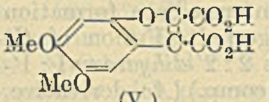


(IV.)

The azlactone of asaraldehyde is converted by H$_2$O$_2$ and KOH into 2 : 4 : 5-trimethoxyphenylacetic acid, m.p. 87°, identical with homoasaronic acid and converted by tetrahydrotubanol and ZnCl$_2$ at 130° into tetrahydromethylderritol, m.p. 159—160°.

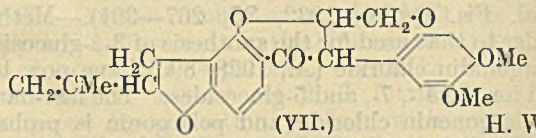
Rotenonone, m.p. 298°, prepared by drastic oxidation of rotenone or dehydrorotenone, is C$_{23}$H$_{18}$O$_7$, and is hydrolysed by 5% KOH to rotenononic acid, C$_{23}$H$_{20}$O$_8$. Both compounds are converted by 20% KOH into derritol and H$_2$C$_2$O$_4$. Rotenonone is obtained in 65% yield from derritol, NaOAc, and Me$_2$C$_2$O$_4$ or Et$_2$C$_2$O$_4$ at 160—170°.

Abutic acid (V) (*Me*$_2$ ester, m.p. 156°), obtained with tubaic acid by action of H$_2$O$_2$ on rotenononic acid (VI), is dibasic, has 2 OMe groups, and hence is assigned the constitution (V). (VI) in dil. acid solution affords β-*rotenonone*, m.p. 275—276° [re-converted into (VI) by 5% KOH–EtOH], whereas with dil. aq. alkali it yields retononone.



(V.)

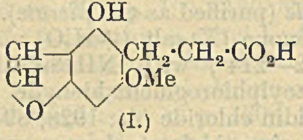
Rotenone receives the amended constitution (VII).



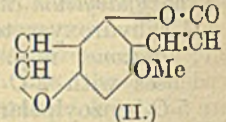
(VII.) H. W.

***iso*Propylidene compound of pyrocatechol.** J. Böeseken and G. Slooff (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 170—172).—Pyrocatechol and COMe$_2$ at room temp. in presence of P$_2$O$_5$ and quartz-sand give o-*isopropylidenedioxybenzene*, b.p. 184°/765 mm., d^{21} 1·063, $n^{21\cdot5}$ 1·5060. E. W. W.

Constituents of root of *Pimpinella saxifraga*. II. F. Wessely and (Frl.) E. Nadler (Monatsh., 1932, 60, 141—144).—The third constituent of this root (cf. this vol., 662), iso*bergapten*, m.p. 222°, a stable lactone, is oxidised by alkaline H$_2$O$_2$ to furan-2 : 3-dicarboxylic acid, and reduced by Na–Hg to 3-*hydroxy*-5-*methoxybenzfuran*-4-*propionic acid* (I), m.p. 147° (decomp.). This distilled at 0·05 mm. and melted gives *dihydro*iso*bergapten* (hydrogenated in the coumarin ring); with diazomethane the acid gives the (OMe)$_2$ compound, new m.p. 132°, also obtainable from bergapten (A., 1892, 71). *iso*Bergapten is therefore (II). E. W. W.

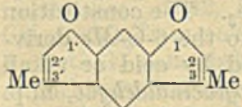


(I.)



(II.)

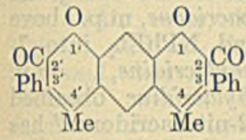
Derivatives of benzodifuran. J. Algar, V. C. Barry, and T. F. Twomey (Proc. Roy. Irish Acad., 1932, 41, *B*, 8—14).—4 : 6-Diacetoresorcinol, CH$_2$Br·CO$_2$Et, and K$_2$CO$_3$ in COMe$_2$ give the *Et*$_2$ *ester*, m.p. 130—131°, of 4 : 6-*diacetyl*-m-*phenylenediglycollic acid* (I), m.p. 246—266° (decomp.). (I), NaOAc, and Ac$_2$O at 150° afford 3 : 3′-*dimethylbenzodifuran* (II), m.p. 107—108°. The (4 : 6)-*dianisylidene*, m.p. 247—248° (decomp.), and *dipiperonylidene*, m.p. 210—211° (decomp.) (softens at 206°), derivatives of (I) are similarly converted into 3 : 3′-*di*-p-*methoxystyryl*-, m.p. 213—214°, and 3 : 3′-



(II.)

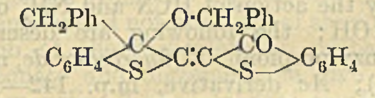
di-(3 : 4-*methylenedioxystyryl*)-, m.p. 199—200°, -*benzodifurans*, respectively. H. B.

Derivatives of dicoumarin. J. ALGAR, A. E. O'REILLY, and M. JOY (Proc. Roy. Irish Acad., 1932, 41, *B*, 1—7).—4 : 6-Diacetoresorcinol (I), $CH_2Ph\cdot CO_2H$, NaOAc, and Ac_2O at 140—150° give 7-*acetoxy*-6-*acetyl*-3-*phenyl*-4-*methylcoumarin*, m.p. 185—187°, whilst (I), $CH_2Ph\cdot CO_2Na$, and Ac_2O at 150° afford 3 : 3′-*diphenyl*-4 : 4′-*dimethyldicoumarin* (II), m.p. 276—277° (slight decomp.). 3 : 3′-*Di*-p-*nitrophenyl*-, not melted at 330°; -*dianisyl*-, m.p. 263—264°, demethylated to the -*di*-p-*hydroxyphenyl*-, not melted at 310°; -*di*-(3 : 4-*methylenedioxyphenyl*)-, m.p. 297°, and -*di*-(3 : 4-*dimethoxyphenyl*)-, m.p. 218—219°, -4 : 4′-*dimethyldicoumarin* are similarly prepared from (I) and the requisite $CH_2Ar\cdot CO_2Na$. H. B.



(II.)

Indigoid dyes. Ethers of leuco-thioindigotin. M. M. TSCHILIKIN and A. F. KARPOVA (J. Gen. Chem. Russ., 1931, 1, 1158—1161).—Leuco-thioindigotin with CH_2PhCl gives the *substance* (I), m.p. 213—214°, hydrolysed by H_2SO_4 to 2-*benzylidene*-1-*ketodihydrothionaphthen*, m.p. 129—130°, 1 mol. of $CH_2Ph\cdot OH$ being eliminated and the thioindigotin mol. at the same time split in two. Madelung's assumption of the wandering of the CH_2Ph group is unnecessary. G. A. R. K.



(I.)

Syntheses of 2-substituted pyrroles. H. FISCHER and M. NEBER (Annalen, 1932, 496, 1—26).—Et 2-formyl-3 : 5-dimethylpyrrole-4-carboxylate and $CH_2(CN)_2$ in EtOH–$NHEt_2$ give *Et* 3 : 5-*dimethyl*-2-ββ-*dicyanovinylpyrrole*-4-*carboxylate*, m.p. 170° (all m.p. are corr.). 3 : 5-*Dimethyl*-4-*ethyl*-2-ββ-*dicyanovinylpyrrole*, m.p. 191·5°, prepared similarly, is hydrolysed by 20% MeOH–KOH to the 2-β-*cyano*-β-*carboxyvinyl* derivative, m.p. 191°, whilst β-3 : 5-*dimethyl*-2-(ββ-*dicyanovinyl*)-4-*pyrrylpropionic acid*, m.p. 235°, is hydrolysed by 10% NaOH to the 2-β-*cyano*-β-*carboxyvinyl* derivative, m.p. 199°; more energetic hydrolysis regenerates the original aldehydes. 2-Formyl-3 : 5-dimethyl-4-ethylpyrrole and $CN\cdot CH_2\cdot CO_2Et$ in EtOH–$NHEt_2$ give 3 : 5-*dimethyl*-4-*ethyl*-2-β-*cyano*-β-*carbethoxyvinylpyrrole*, m.p. 121°; β-3 : 5-*dimethyl*-2-(β-*cyano*-β-*carbethoxyvinyl*)-4-*pyrrylpropionic acid*, m.p. 183°, is similarly prepared. The K salt from Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate, $MeNO_2$, and 25% MeOH–KOH in EtOH is decomposed by dil. HCl to the 2-β-*nitro*-α-*hydroxyethyl* derivative, m.p. 157°, and by 50% H_2SO_4 to *Et* 4-*methyl*-2-β-*nitrovinylpyrrole*-3 : 5-*dicarboxylate*, m.p. 184·5°, which is reduced by Al–Hg in moist Et_2O to 3 : 5-*dicarbethoxy*-4-*methyl*-2-*pyrrylacetaldoxime*, m.p. 183°. 5-*Carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylacetaldoxime*, m.p. 176° (from the 3-β-nitrovinyl derivative), and Ac_2O–KOAc afford 5-*carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylacetonitrile*, m.p. 163°, hydrolysed by 10—15% MeOH–KOH to the 5-*carboxynitrile*, m.p. 178° (decomp.). 5-Carbethoxy-4-methyl-3-β-carboxyethyl-2-pyrrylacetonitrile (from the 2-CH_2Br compound and aq. KCN in Et_2O) is hydrolysed by conc. HCl–AcOH to the -2-*pyrrylacetic acid*, m.p. 215° (decomp.). Et 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate (I) and aq. EtOH–KCN give 3 : 5-*dicarbethoxy*-4-*methyl*-2-*pyrrylacetonitrile*, m.p. 165°; with $CN\cdot CHNa\cdot CO_2Et$ in $COMe_2$, *Et* 4-*methyl*-2-β-*cyano*-β-*carbethoxyethylpyrrole*-3 : 5-*dicarboxylate*, m.p. 118°, results. *Et* 4-*methyl*-3-β-*carboxyethyl*-2-β-*cyano*-β-*carbethoxyethylpyrrole*-5-*carboxylate*, m.p. 178·5°, is similarly prepared. (I) and $CHNa(CO_2Et)_2$ in $COMe_2$ afford *Et* 4-*methyl*-2-ββ-*dicarbethoxyethylpyrrole*-3 : 5-*dicarboxylate* (II), m.p. 95°, hydrolysed by 30% KOH in EtOH to the *tetracarboxylic acid*, m.p. 233°, which is rather stable and is brominated to two Br-compounds, yellow and colourless, both not melted at 280°. Hydrolysis of (II) with 20% MeOH–KOH gives *Et* 4-*methyl*-2-ββ-*dicarboxyethylpyrrole*-3 : 5-*dicarboxylate*, m.p. 179° (decomp.), decarboxylated to the 2-β-carboxyethyl derivative (A., 1931, 101), which is hydrolysed further by 25% MeOH–KOH to *Et* 5-*carboxy*-4-*methyl*-2-β-*carboxyethylpyrrole*-3-*carboxylate* (III), m.p. 203°. Decarboxylation of this affords *Et* 4-*methyl*-2-β-*carboxyethylpyrrole*-3-*carboxylate* (IV), m.p. 150° (*Et*$_2$ ester, m.p. 60°; *lactam*, m.p. 110°). *Et* 5-*formyl*-4-*methyl*-2-β-*carboxyethylpyrrole*-3-*carboxylate*, m.p. 165° (*oxime*, m.p. 196°) [from (IV), HCN, and HCl in Et_2O–$CHCl_3$], with cryptopyrrole and EtOH–conc. HBr gives an unidentified *methene hydrobromide*, m.p. 201°, whilst with opsopyrrole, 4-*carbethoxy*-3 : 3′-*dimethyl*-4′-*ethyl*-5-β-*carboxyethylpyrromethene hydrobromide*, m.p. 184° (*Br*-derivative, darkens at 210°, not melted at 280°), results. (III) or (IV) with conc. HBr in HCO_2H affords 4 : 4′ *dicarbethoxy*-3 : 3′-*dimethyl*-5 : 5′-*di*-β-*carboxyethylpyrromethene hydrobromide*, m.p. 219° (darkens at 210—215°). Et 4-methyl-2-bromomethyl-3-β-carboxyethylpyrrole-5-carboxylate [*compound* (1 : 1) with pyridine, m.p. 197°] and $CHNa(CO_2Et)_2$ in pyridine give *Et* 4-*methyl*-3-β-*carboxyethyl*-2-ββ-*dicarbethoxyethylpyrrole*-5-*carboxylate*, m.p. 111°, hydrolysed by 25% MeOH–KOH to the 2-ββ-*dicarboxyethyl* derivative, m.p. 184°, which is decarboxylated to *Et* 4-*methyl*-2 : 3-*di*-β-*carboxyethylpyrrole*-5-*carboxylate*, m.p. 190° (slight previous sintering). This with conc. HBr and AcOH (?HCO_2H) affords the *hydrobromide*, m.p. 229°, of 3 : 3′-*dimethyl*-4 : 5 : 4′ : 5′-*tetra*-β-*carboxyethylpyrromethene*, m.p. 180°.

Et 4-*methyl*-3-*ethyl*-2-ββ-*dicarboxyvinylpyrrole*-5-*carboxylate*, m.p. 222° (decomp.) [from the 2-CHO compound and $CH_2(CO_2H)_2$ in EtOH–NH_2Ph], is reduced (Na–Hg) to the 2-ββ-*dicarboxyethyl* derivative, m.p. 178°, which is decarboxylated to *Et* 4-*methyl*-3-*ethyl*-2-β-*carboxyethylpyrrole*-5-*carboxylate*, m.p. 169°. Et 4-methyl-3-ethyl-2-bromomethylpyrrole-5-carboxylate and KCNS in aq. $COMe_2$ give the 2-*thiocyanomethyl* derivative, m.p. 127—128°; the *thiocyanomethyl* derivative, m.p. 171°, from (I) is oxidised by 30% HNO_3 to Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate. 3 : 5-Diacetyl-2 : 4-dimethylpyrrole [reduced (Wolff–Kishner) to 2 : 4-dimethyl-3 : 5-diethylpyrrole] and Br in AcOH give the 2-*bromomethyl* derivative, m.p. 149°, m.p. (+C_5H_5N) 286°. β-5-Formyl-2 : 4-dimethyl-3-pyrrylpropionic acid and

SO_2Cl_2 afford a *compound*, $C_9H_{10}O_4NCl_3$, m.p. 191°. 5-*Formyl*-4-*methyl*-3-*propyl*-2-*bromomethylpyrrole* has m.p. 175°. H. B.

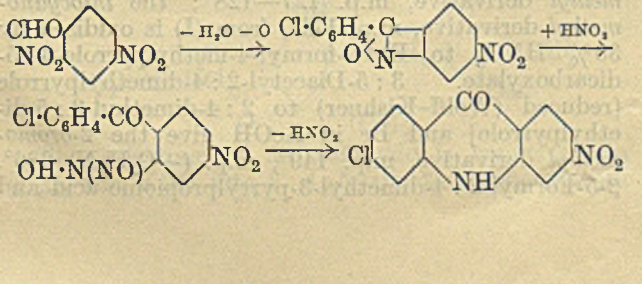
Interaction of magnesium phenyl bromide with 1-chloropiperidine and other *N*-chloro-compounds. R. J. W. Le Fèvre (J.C.S., 1932, 1745—1747).—MgPhBr gives with 1-chloropiperidine, C_6H_6, PhCl, and $C_5H_{11}N$; PhCl is isolated from the reaction with NMe_2Cl, NEt_2Cl, chloramine-*T*, dichloramine-*T*, NCl_3, and NH_2Cl (cf. Coleman and Hauser, A., 1928, 622). F. R. S.

Allyl ethers of heterocyclic enols. B. Mander-Jones and V. M. Trikojus (J. Amer. Chem. Soc., 1932, 54, 2570).—Migration of the allyl group can occur from O to the adjacent β-unsaturated C atom; thus, 4-allyloxy-2-methylquinoline heated at 200° for a short time give 4-hydroxy-2-methyl 3-allylquinoline. C. J. W. (*b*)

6-Hydroxyquinoline-5-aldehyde and derived 5 : 6-disubstituted quinolines. B. Bobrański (J. pr. Chem., 1932, [ii], **134**, 141—152).—Condensation of 6-hydroxyquinoline with excess of $CHCl_3$ and NaOH (not KOH) gives the Na salt of 6-*hydroxyquinoline*-5-*aldehyde*, m.p. 138·5° {NH_4 *salt*; *phenylhydrazone*, m.p. 232—234° (decomp.) [*hydrochloride*, m.p. 221—226° (decomp.), $+1H_2O$]; *azine*, m.p. 351°; *anil*, m.p. 102°}. Its *oxime*, m.p. 235° (rapid heating), is dehydrated by heat or Ac_2O to 6-*hydroxy*-5-*cyanoquinoline*, m.p. 293° (*Na* salt, m.p. >300°, $+1H_2O$); this is hydrolysed only with difficulty, and with conc. H_2SO_4 at 100° gives the *amide*, m.p. 227·5°, not hydrolysed by 20% H_2SO_4 or 25% KOH, but converted by HNO_2 into 6-hydroxyquinoline-5-carboxylic acid, decarboxylated >170° without melting (slow heating). The last-named is also obtained from 6-hydroxyquinoline by the Kolbe synthesis and gives 5-nitro-6-hydroxyquinoline with HNO_3 or HNO_2 in H_2SO_4 (cf. A., 1888, 67). H. A. P.

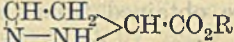
Reaction between quinolinic anhydride and phenylhydrazine. P. R. Sen-Gupta and A. C. Sircar (J. Indian Chem. Soc., 1932, 9, 145—148).—Quinolinic anhydride (I) and $NHPh{\cdot}NH_2$ (II) in cold C_6H_6 for 2 days give *quinolin*-2-*phenylhydrazinic acid*, m.p. 146° (decomp.). *Quinolinphenylhydrazide*, m.p. 201°, is obtained from equimol. amounts of (I) and (II) at 120—130°; with an excess of (II) at 200—230°, *nicotinphenylhydrazide*, m.p. 185°, results. *o*-$C_6H_4(CO)_2O$ and $NPhMe{\cdot}NH_2$ at 130° give N-*methylanilinophthalimide*, m.p. 124°; N-*methylanilinoquinolinimide*, m.p. 155°, and -*naphthalimide*, m.p. 210°, are similarly prepared. H. B.

Acridine. X. Course of the synthesis of 3-nitroacridones according to I. Tanasescu. K. Lehmstedt (Ber., 1932, 65, [*B*], 999—1005).—The course of the synthesis is represented by : PhCl+



(cf. A., 1927, 574; this vol., 169). This view is supported by the observation that HNO_2 is formed by the action of conc. H_2SO_4 on 2 : 4-dinitro- or 4-chloro-2-nitro-benzaldehyde at room temp. 2-Nitroacridone, $NPhMe_2$, and PCl_5 afford 2-*nitro*-5-p-*dimethylaminophenylacridine*, m.p. 255°. 6-Chloro-4-nitrobenzoic acid, *p*-chloroaniline, Na_2CO_3, and Cu powder in boiling amyl alcohol yield 4′-*chloro*-5-*nitrodiphenylamine*-2-*carboxylic acid*, m.p. 242°, which is not greatly affected by conc. H_2SO_4 at 100°, but is converted by successive treatment with PCl_5 and $AlCl_3$ in C_6H_6 into 7-*chloro*-2-*nitroacridone*, m.p. above 380°, transformed by $POCl_3$ and $NPhEt_2$ into 7-*chloro*-2-*nitro*-5-p-*diethylaminophenylacridine*, m.p. 254°. The 5-p-*diethylaminophenylacridine* obtained from Tanasescu's "8(?)-chloro-2-nitroacridone" has m.p. 236°. 2 : 4-Dinitrobenzaldehyde, PhF, and conc. H_2SO_4 give 7-*fluoro*-2-*nitroacridone*, m.p. above 380°, accompanied by HF. H. W.

Hydantoins. L. Synthesis of hydantoins possessing the properties of hypnotics. R. M. Herbst and T. B. Johnson (J. Amer. Chem. Soc., 1932, 54, 2463—2470; cf. A., 1930, 1446).—Amino-acid nitriles (isolated as the hydrochlorides) are prepared by the action of HCN and NH_3 on ketones in abs. EtOH; the following are described: α-amino-α-benzylpropionitrile [*hydrochloride*, m.p. 148—150° (corr.); *Ac* derivative, m.p. 142—143°]; α-amino-α-benzylbutyronitrile [*hydrochloride*, m.p. 135—140°; *Ac* derivative, m.p. 86—87°]; α-amino-γ-phenyl-α-methylbutyronitrile [*hydrochloride*, m.p. 140—141° (corr.)]; α-amino-γ-phenyl-α-ethylbutyronitrile (*hydrochloride*, m.p. 84°; *Ac* derivative, m.p. 116—118°); 1-amino-1-cyano*cyclo*hexane [*hydrochloride*, m.p. 202—204° (corr.)]. α-Carbamido nitriles are prepared from the above hydrochlorides and KCNO in 50% AcOH: α-*carbamido*-α-*benzylpropionitrile*, m.p. 170—171°; α-*carbamido*-α-*benzylbutyronitrile*, m.p. 124—126°; α-*carbamido*-γ-*phenyl*-α-*methylbutyronitrile*, m.p. 138—142°; α-*carbamido*-γ-*phenyl*-α-*ethylbutyronitrile*, m.p. 139°, and 1-*carbamido*-1-*cyano*cyclo*hexane*, m.p. 180—181°, are described. These are converted by warm 20% HCl into 5-*benzyl*-5-*methyl*-, m.p. 227—228° (corr.); 5-*benzyl*-5-*ethyl*-, m.p. 217—218° (corr.); 5-β-*phenylethyl*-5-*methyl*-, m.p. 179—180° (corr.); 5-β-*phenylethyl*-5-*ethyl*-, m.p. 198—199° (corr.), and 5 : 5-cyclo*pentamethylene*-, m.p. 217—218° (corr.), -*hydantoin*, respectively. α-Amino-α-phenylbutyric acid, m.p. 275° (corr.) [*hydrochloride*, m.p. 271° (corr.)]; α-*phenylcarbamido*-α-*phenylbutyric acid*, m.p. 190—190·5° (corr.); and α-*amino*-β-*phenyl*-α-*methylpropionic acid*, m.p. 293—294° (corr.) [*hydrochloride*, m.p. 244—246° (corr.); α-*phenylcarbamido*-derivative, m.p. 187° (corr.)], are described. 5-β-Phenylethyl-5-methyl- and -5-ethyl-hydantoins have marked hypnotic properties. C. J. W. (*b*)

Synthesis of pyrazolinecarboxylic esters. K. von Auwers and F. König (Annalen, 1932, 496, 27—51; cf. A., 1929, 1080).—Diazo-methane (or -ethane) adds (usually readily) to various unsaturated esters to give Δ^1-pyrazoline-5-carboxylates,  $\begin{matrix}CH_2{\cdot}CH_2\\ N{=\!=\!=}N\end{matrix}{>}CH{\cdot}CO_2R$, characterised by their in-difference towards PhNCO, spectrochemically, and by their rearrangement with HCl (1 : 1) to Δ^2-pyrazoline-5-carboxylates,  $\genfrac{}{}{0pt}{}{\mathrm{CH{\cdot}CH_2}}{\mathrm{N{-}NH}}\!>\!\mathrm{CH{\cdot}CO_2R}$, which react with PhNCO and show higher vals. of *d* and *n*. Thus, Et α-methylacrylate (I) and diazomethane in Et_2O give *Et 5-methyl-*Δ^1*-pyrazoline-5-carboxylate*, b.p. 99—100°/11 mm., isomerised to *Et 5-methyl-*Δ^2*-pyrazoline-5-carboxylate*, b.p. 106—107°/15 mm. (1-*phenylcarbamyl* derivative, m.p. 68—69°). Similarly, Et tiglate affords *Et* 4 : 5-*dimethyl*-Δ^1-, b.p. 110°/12 mm. (*Me* ester, b.p. 80—82°/2 mm., from Me tiglate), and -Δ^2-, b.p. 117—118°/16 mm. (1-*phenylcarbamyl* derivative, m.p. 91°), *-pyrazoline-5-carboxylates*, whilst Et Δ^a-propene-αα-dicarboxylate furnishes *Et* 4-*methyl*-Δ^1-, decomp. about 60°/high vac., and -Δ^2-, b.p. 152°/12 mm., m.p. 32·5—33·5°, *-pyrazoline-5 : 5-dicarboxylates*. Diazoethane and (I) give *Et* 3 : 5-*dimethyl*-Δ^1-, b.p. 86—88°/2 mm., and -Δ^2-, b.p. 106—108°/11 mm., *-pyrazoline-5-carboxylates*, whilst Me tiglate similarly affords *Me* 3 : 4 : 5-*trimethyl*-Δ^1-, b.p. 88°/3 mm., and -Δ^2-, b.p. 81°/2 mm. (1-*phenylcarbamyl*, m.p. 97°, and *Ac*, b.p. 146—149°/11·5 mm., derivatives), *-pyrazoline-5-carboxylates*. The pyrazolines from the tiglates are considered to be homogeneous and not mixtures of stereoisomerides; *cis*-addition of the diazomethane probably occurs. Me mesaconate and diazomethane give a little Me 4-methylpyrazoline-3 : 4-dicarboxylate (*loc. cit.*) and (mainly) *Me* trans-5-*methyl*-Δ^1-*pyrazoline*-4 : 5-*dicarboxylate*, b.p. 120—122°/2—2·5 mm., isomerised (as above) to the Δ^2-*ester*, b.p. 150°/12 mm. (corresponding *Et* ester, b.p. 162°/13 mm.), whilst Me dimethylfumarate similarly affords *Me* trans-4 : 5-*dimethyl*-Δ^1-*pyrazoline*-4 : 5-*dicarboxylate*, b.p. 150°/11 mm., isomerised to the Δ^2-*ester*, b.p. 158°/13 mm., m.p. 58·5°—60·5. The last-named esters differ from those obtained from Me dimethylmaleate (*loc. cit.*).

Reaction between Et α-chlorocrotonate and diazomethane in Et_2O is accelerated by moisture; the resulting product is decomposed by HCl or PhNCO and eliminates HCl on distillation, giving Et 4-methylpyrazole-3(5)-carboxylate. Et γγγ-trichlorocrotonate affords *Et* 4-*trichloromethylpyrazoline*-3-*carboxylate*, m.p. 109° (*phenylcarbamyl* derivative, m.p. 138—139°), but Et β-chloro-, -methyl-, and -ethoxy-crotonates do not react. Me fumarate or maleate and diazomethane give Me pyrazoline-3 : 4-dicarboxylate, m.p. 98° [described by von Pechmann (A., 1894, i, 438) as the 4 : 5-derivative] (N-*carbomethoxy*-, m.p. 108—109°, N-*benzenesulphonyl*, m.p. 105°, and N-p-*toluenesulphonyl*, m.p. 106—107°, derivatives); the oily products obtained using $CHN_2{\cdot}CO_2Me$, give *Me* N-*carbomethoxypyrazoline*-3 : 4 : 5-*tricarboxylate*, m.p. 144—145°, when treated with $ClCO_2Me$. The relationship between the isomeric Me tricarbomethoxypyrazolinylacetates, m.p. 104° and 153°, of Buchner and Witter (A., 1894, i, 346) could not be ascertained; the former does not give *N*-derivatives and is converted into the latter by $ClCO_2Et$ (amyl) or MeI, but not by HCl. Spectrochemical data are given for most of the above and some of the previously described (*loc. cit.*) compounds.

H. B.

Some derivatives of anserine, carnosine, and histidine. W. Keil (Z. physiol. Chem., 1932, **208**, 67—71).—Anserine and carnosine with Me_2SO_4 and NaOH add on 4 and 5 Me groups, respectively, the products being identical (*chloroaurate*, m.p. 92—96°). Histidine, when heated with phthalic anhydride, forms α-*phthalylhistidine* (I), m.p. 188° [*picrate*, m.p. 251°; *Me* ester *hydrochloride* (II), m.p. 238—240°; *Me* ester, m.p. 187°; *Et* ester, m.p. 195°]. With BzCl, (II) yields γδ-*dibenzamido*-α-*phthalimido*-Δ^γ-*pentenoic acid*, m.p. 194°. Distillation of (I) with soda-lime gives glyoxaline; on methylation (I) gives β-*methyliminazolyl*-α-*phthalimidopropionate*, β-1 : 4-*methyliminazolyl*-α-*phthalyliminopropionic acid*, and β-1 : 5-*methyliminazolyl*-α-*phthalimidopropionic acid*, isolated as the chloroaurates. J. H. B.

Dihydronaphthopyrazole. I. K. von Auwers and C. Wiegand (J. pr. Chem., 1932, [ii], **134**, 82—96).—α-Tetralone, Et formate, and Na give 1-*keto*-2-*hydroxymethylenetetrahydronaphthalene* (I), b.p. 153·5—154°/10 mm., of which the following derivatives have been prepared: *Et ether*, b.p. 170—170·5°/10 mm.; *Ac*, m.p. 124°; *CO_2Et-*, m.p. 81·5—82·5°; *Bz*, m.p. 112—113°; *anilide*, m.p. 115—116°; *methylanilide*, m.p. 90—91°; *monosemicarbazone* (II), m.p. 200°; *benzoylhydrazone*, m.p. 154—155°; o-*nitrobenzoylhydrazone*, m.p. 196°; and 2-*phenylhydrazone* of 1 : 2-*diketotetrahydronaphthalene*, m.p. 83°. Attempts to prepare hydrazones from the free ketone derivatives result in the formation of *iso*oxazoles. When (II) is heated with H_2SO_4, *dihydronaphthopyrazole* [*dihydro*-α-*naphthisoindazole*] (III), m.p. 123° (*picrate*, m.p. 192—193°), is obtained. (II) and $NHMe{\cdot}NH_2,H_2SO_4$ afford 1-*methyldihydro*-α-*naphthisoindazole*, b.p. 175—175·5°/11 mm. (*picrate*, m.p. 187—188°), and methylation of (III) with MeI and Na gives a mixture of 1- and 2-*Me* derivatives (*picrate*, m.p. 166—167°). (I) and $NHPh{\cdot}NH_2$ form a mixture of 5 parts of 1-*phenyl*-, m.p. 127—128° (*picrate*, m.p. 141—142°), and 1 part of 2-*phenyldihydro*-α-*naphthisoindazole*, m.p. 104—105° (*picrate*, m.p. 123°). (III) yields the following derivatives: 1-*CO_2Me*-, m.p. 116—116·5°; 1-*CO_2Et*-, m.p. 63—64°; 1-*Ac*, m.p. 82·5—83·5°; 1-*Bz*, m.p. 141°; 1-(o-*nitrobenzoyl*), m.p. 157—158°. The results of substitution differ from those obtained with other similar compounds (cf. A., 1925, i, 585; 1927, 1088) and the significance of this is discussed. F. R. S.

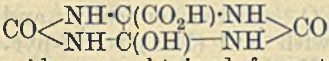
Determination of structure of dihydronaphthopyrazole [dihydro-α-naphth*iso*indazole] derivatives. II. K. von Auwers and F. Enbergs (J. pr. Chem., 1932, [ii], **134**, 97—106).—Condensation of Et 1-ketotetrahydronaphthalene-2-glyoxylate (I) with N_2H_4,H_2O in EtOH gives *Et dihydro*-α-*naphthiso*-*indazole*-3-*carboxylate* (II), m.p. 152° [free *acid*, m.p. 267° (alkaline KOH)]; this with Na and MeI gives (after hydrolysis) 1- (III), m.p. 258°, and 2-*Me* (IV), m.p. 244°, derivatives of the acid, which are separated by heating with 3% alcoholic HCl (which esterifies the 1-derivatives only), and identified by decarboxylation to known methylpyrazoles. Interaction of (I) with $NHMe{\cdot}NH_2,H_2SO_4$ in H_2O in presence or absence of NaOAc gives mainly (III) and a little (IV).

Ethylation of (II) gives 1-, m.p. 231—232°, and 2-*ethyldihydro-α-naphth*iso*indazole-3-carboxylic acid*, m.p. 211°. Interaction of (I) with NH_2·NH·CH_2Ph gives only the 1-*CH_2Ph*, m.p. 155—156° (free *acid*, m.p. 217—218°), and with NHPh·NH_2 the 1-*Ph*, m.p. 155° (free *acid*, m.p. 248°), derivatives of (II) only. The free acid of (II) [but not (II) itself] gives an *Ac* derivative, m.p. 158—159°, with formation of a diketopiperazine derivative, with AcCl; both (II) and the free acid give 1-*CO_2Et* derivatives, m.p. 70—71°, and 139—140°, respectively, with $ClCO_2Et$, the former of which is also formed by esterification of the latter. The *benzoylhydrazone*, m.p. 131—133°, of (I) is unaffected by boiling glacial AcOH or HCO_2H. Interaction of (II) with BzCl gives the *diketopiperazine*, $C_{24}H_{16}O_2N_4$. H. A. P.

Condensation product of *o*-phenylenediamine with quinolinic acid. A. Lecco and V. Ivković (Glasn. hemisk. druš. Kralj. Jugoslav., 1930, 1, 7 pp.; Chem. Zentr., 1932, i, 1100).—Alkaline fission of the condensation product of quinolinic acid and *o*-$C_6H_4(NH_2)_2$ affords a product which, when heated at 260°, loses CO_2 and gives 2-2-pyridylbenziminazole; hence the condensation product is αβ-nicotinoylene-2 : 1-benziminazole. A. A. E.

General method for the preparation of 1-substituted glyoxalines from acetalylthiocarbimide and primary amines. A. P. T. Easson and F. L. Pyman (J.C.S., 1932, 1806—1812).—*Acetalylthiocarbimide* (I), b.p. 133°/40 mm., prepared from CS_2 and aminoacetal, combines with aliphatic, aromatic, and heterocyclic primary amines, yielding thiocarbamides, Q·NH·CS·NH·CH_2·$CH(OEt)_2$. (I) and NH_2Ph give phenyl- and 2-amino-quinoline gives 2-*quinolylacetalylthiocarbamide*, m.p. 139—140°, which is hydrolysed to 2-(2′-*thiolglyoxalinyl*-1′)-*quinoline*, m.p. 263—264° (decomp.), oxidised by HNO_3 to 2-(*glyoxalinyl*-1′)-*quinoline*, m.p. 120—121° (*monohydrochloride*, m.p. 217—218°; picrate, m.p. 206°). 8-Aminoquinoline similarly affords 8-(2′-*thiolglyoxalinyl*-1′)-, m.p. 304° (decomp.) (*hydrochloride*), and 8-(*glyoxalinyl*-1′)-*quinoline*, m.p. 124—125° (*monohydrochloride*, m.p. 247—248°; picrate, m.p. 197—198°); 8-amino-6-methoxyquinoline yields 8-(*thiolglyoxalinyl*-1′)-, m.p. 297° (decomp.), and 8-(*glyoxalinyl*-1′)-6-*methoxyquinoline*, m.p. 139—140° (*monohydrochloride*, m.p. 243—244°; picrate, m.p. 219—220°); NH_2Me forms 2-thiol-1-methylglyoxaline, m.p. 143—144° (lit. 141—142°); NH_2·CH_2·CH_2·OH gives, after hydrolysis, 2-*thiol*-1-β-*hydroxy*-, m.p. 151—152°, oxidised to 1-β-*hydroxyethylglyoxaline*, b.p. 202—206°/20 mm., m.p. 36—40° (picrate, m.p. 142—143°); and Et glycine similarly yields 2-*thiolglyoxaline*-, m.p. 205—206°, and *glyoxaline*-1-*acetic acid*, m.p. 268—269° (decomp.) (*Et glyoxaline*-1-*acetate picrate*, m.p. 124—125°). Some of these compounds were tested for antimalarial activity and found to be inactive. F. R. S.

Oxidation of uric acid in alkaline solution. W. Schuler and W. Reindel (Z. physiol. Chem., 1932, 208, 248—257).—The intermediate product formed by oxidation of uric acid with alkaline $KMnO_4$ was pptd. as the Ag salt and identified as *hydroxyacetylenediureincarboxylic acid* (*Ag_3*, *Ag_2* salts):


$CO<\begin{matrix}NH\cdot C(CO_2H)\cdot NH\\NH-C(OH)—NH\end{matrix}>CO$. Allantoin and uroxanic acid were obtained from the Ag_3 salt. J. H. B.

Porphyrin syntheses. XLIV. Synthesis of 2 : 3 : 6 : 7-tetramethyl-1 : 4 : 5 : 8-tetraethylmalonic acid porphin. H. Fischer and H. J. Riedl (Z. physiol. Chem., 1932, 207, 193—201; cf. this vol., 173).—Condensation of 5-carbethoxy-2-methyl-4-ethylpyrrole with Et methoxymethylmalonate in presence of EtOH and HCl gives 5-*carbethoxy*-2-*methyl*-4-*ethyl*-3-(ββ-*dicarbethoxy*)*ethylpyrrole* (I), m.p. 75°. Br in Et_2O converts (I) into the 2-*bromomethyl* derivative (II), m.p. 86°. On boiling with H_2O, (II) gives 5 : 5′-*dicarbethoxy*-4 : 4′-*diethyl*-3 : 3′-*di*-(ββ-*dicarbethoxy*)*ethyl*-2 : 2′-*pyrromethane* (III), m.p. 106°. Hydrolysis with NaOH in aq. EtOH affords the *Na_6* salt. When heated with HCO_2H and subsequently esterified (III) gives the *Me_8* ester of 1 : 4 : 5 : 8-*tetraethyl*-2 : 3 : 6 : 7-*tetra*-(ββ-*dicarboxy*)*ethylporphin*, m.p. 229° [*Cu*, m.p. 248° (uncorr.), *Fe*, m.p. 174° (uncorr.) and *Zn*, m.p. 264—265° (uncorr.), salts]. The Cu, Fe, and Zn salts are spectroscopically identical with the corresponding complex salts from the Me_8 ester of *iso*uroporphyrin I.

Bromination of 5-carbethoxy-4 : 3′ : 5′-trimethyl-3 : 4′-diethyl-2 : 2′-pyrromethane with 1 mol. of Br gives 5-*carbethoxy*-4 : 3′ : 5′-*trimethyl*-3 : 4′-*diethyl*-2 : 2′-*pyrromethene hydrobromide*, m.p. 169° (decomp.), and with 2 mols. the corresponding 5′-*CH_2Br* derivative, m.p. 142° (decomp.). Et methoxymethylmalonate with 5-carbethoxy-4 : 3′ : 5′-trimethyl-3-ethyl-2 : 2′-pyrromethane gives 5 : 5′-dicarbethoxy-4 : 4′-dimethyl-3 : 3′-diethylpyrromethane, and with 5-carbethoxy-4 : 3′ : 5′-trimethyl-3-(ββ-dicarbethoxy)ethyl-2 : 2′-pyrromethane, 5 : 5′-dicarbethoxy-4 : 4′-dimethyl-3 : 3′-di-(ββ-dicarbethoxy)ethylpyrromethane. J. H. B.

Stereobilin, copromesobiliviolin, and copronigrin. C. J. Watson (Z. physiol. Chem., 1932, 208, 101—119).—Cryst. *stercobilin*, $C_{33}H_{44}O_8N_4$, m.p. 127—140°, was obtained from the pure hydrochloride. Reduction gave a colourless solution which could not be crystallised and HNO_3 oxidation did not yield methylethylmaleimide as with bilirubin. By CrO_3–AcOH oxidation a product resembling hæmatinic acid was obtained. An attempt to obtain ætioporphyrin by way of opsopyrrole failed. The absorption and fluorescence of the Zn salt were measured.

Copromesobiliviolin, m.p. 164—172° (*Cu* compound, m.p. 182—190°), is very similar to mesobiliviolin and closely related to stercobilin, and gives the hydrochloride of the latter on treatment with $FeCl_3$–HCl.

Copronigrin, $C_{42}H_{55}O_{14}N_3$ (*Zn* compound), can be separated into an acid and a basic fraction. Fæces from a case of pernicious anæmia contained deuteroporphyrin Me_2 ester. J. H. B.

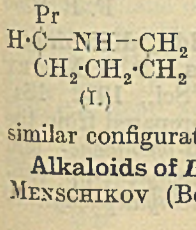
Treatment of the amides of α-hydroxy- or *o*-phenolcarboxylic acids with acetone. H. O. L. Fischer, G. Dangschat, and H. Stettiner (Ber., 1932, 65, [*B*], 1032—1037).—Amides of α-OH-acids are converted into derivatives of tetrahydro-oxazole by $COMe_2$ in presence of HCl but not of $ZnCl_2$. Reaction does not occur if a H atom of the NH_2

group is substituted or if the α-OH-group is protected. The following compounds are described: *4-keto-5-phenyl-2 : 2-dimethyltetrahydro-oxazole* ("*mandelamide-acetone*"), m.p. 127°, converted by Ag_2O and MeI into *4-methoxy-5-phenyl-2 : 2-dimethyl-2 : 5-dihydro-oxazole*, b.p. 126—127°/13 mm., m.p. 49—50°, and by boiling Ac_2O into *4-acetoxy-5-phenyl-2 : 2-dimethyl-2 : 5-dihydro-oxazole*, m.p. 42°; *4-keto-2 : 2-dimethyltetrahydro-oxazole* ("*glycollamide-acetone*"), m.p. 104—105°, *4-methoxy-2 : 2-dimethyl-2 : 5-dihydro-oxazole*, b.p. 31—32°/13 mm., and *4-acetoxy-2 : 2-dimethyl-2 : 5-dihydro-oxazole*, b.p. 79—80°/12 mm.; *4-keto-2 : 2 : 5-trimethyl-3 : 5-dihydro-oxazole* ("*lactamide-acetone*"), m.p. 103—104°, *4-methoxy-2 : 2 : 5-trimethyl-3 : 5-dihydro-oxazole*, b.p. 33°/12 mm., and *4-acetoxy-2 : 2 : 5-trimethyl-3 : 5-dihydro-oxazole*, b.p. 83—84°/12 mm.; *4-keto-2 : 2-dimethyl-3 : 4-dihydro-1 : 3-benzometoxazine* ("*salicylamide-acetone*"), m.p. 137°, *4-methoxy-2 : 2-dimethyl-1 : 3-benzometoxazine*, b.p. 108—110°/13 mm., and 4-acetoxy-2 : 2-dimethyl-1 : 3-benzometoxazine, m.p. 30—32°; *compound* $C_{10}H_{17}O_2N$, m.p. 162—163°, from *cyclo*hexanolcarboxylamide, $COMe_2$, and HCl. H. W.

ψ-1 : 8-*iso*Naphthoxazone. B. Bobrański (J. pr. Chem., 1932, [ii], **134**, 153—157).—The product of condensation of 6-hydroxyquinoline with malic acid in conc. H_2SO_4 is identical with "coumaroquinoline" (A., 1924, i, 87; prep. repeated) and with ψ-1 : 8-*iso*naphthoxazone (J.C.S., 1919, **115**, 536). The constitution previously assigned (*loc. cit.*) is confirmed by its synthesis from 6-hydroxyquinoline-5-aldehyde by the Perkin condensation. H. A. P.

Chemical investigation of *Rauwolfia caffra*. I. Rauwolfine. J. B. Koepfli (J. Amer. Chem. Soc., 1932, **54**, 2412—2418).—Details are given for the separation of *rauwolfine* (I), $C_{20}H_{26}O_3N_2,2{\cdot}5H_2O$, decomp. 235—238° [*chloride*, $C_{20}H_{25}O_2N_2Cl$, m.p. 300—303° (decomp.), $[\alpha]_D^{20}$ +29° in H_2O, m.p. (+H_2O) 297—300°; *bromide* (+H_2O), m.p. 250—253° (decomp.); *iodide* (+H_2O), m.p. 220—225° (decomp.)], from the bark of *R. caffra*, Sonder. Two other cryst. bases (*A*, m.p. 294—295°, and *B*) are also isolated. The pharmacological action of (I) is described. C. J. W. (*b*)

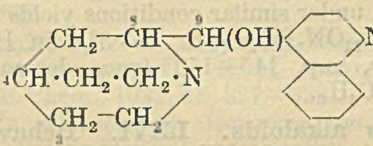
Configuration of optically active coniine and α-pipecoline. W. Leithe (Ber., 1932, **65**, [*B*], 927—931).—*dl*-Pipecolinic acid is resolved by *d*-tartaric acid in EtOH yielding (+)-pipecolinic acid, m.p. 266° (decomp.), $[\alpha]_D^{15}$ +56·2° in H_2O (c=2·93) [H *d*-tartrate, m.p. 192° (decomp.), $[\alpha]_D^{15}$ +29·6° in H_2O; corresponding *hydantoin*, $C_7H_{10}O_2N_2$, m.p. 137—139°, $[\alpha]_D^{15}$ +91·8° in H_2O]. The mode of dependence of [α] of the acid on c and solvent shows the (+)-form to belong to the *d*-series. Since the steric relationship of (+)-conhydrin to (—)-coniine is established (Löffler and Friedrich, A., 1909, i, 180) and (+)-conhydrin can be oxidised to (—)-pipecolinic acid, the configuration of (+)-coniine is expressed by (I). (+)-Coniine, (+)-α-pipecoline, and (+)-α-*cyclo*hexylethylamine have similar configuration. H. W.



(I.)

Alkaloids of *Heliotropium lasiocarpum*. I. G. Menschikov (Ber., 1932, **65**, [*B*], 974—977).—The dried plant is percolated with 95% EtOH containing 1% of NH_3 and the residue after removal of solvent is treated with HCl. The acid solution is made alkaline with NH_3 and the mixed alkaloids are removed by $CHCl_3$. Crystallisation from C_6H_6–light petroleum (1 : 1) affords *heliotrine* (I), $C_{16}H_{27}O_5N$, m.p. 125—126°, $[\alpha]_D$ —75° in $CHCl_3$ (*methiodide*, m.p. 108—111°), which contains two OH and one OMe and a *tert.*-N atom. The residue from (I) when dissolved in HCl and fractionally pptd. with NaOH yields *lasiocarpine*, $C_{21}H_{33}O_7N$, m.p. 94—95·5°, $[\alpha]_D$ —4° in EtOH, which is unsaturated towards $KMnO_4$ and gives the pine-shaving reaction when heated with Zn dust. (I) is hydrolysed by aq. $Ba(OH)_2$ to the saturated, aliphatic *heliotric acid*, $OH{\cdot}C_6H_{11}(OMe){\cdot}CO_2H$, m.p. 92·5—94·5°, $[\alpha]_D$ —12° in H_2O, and *heliotridine*, $C_8H_{13}O_2N$, m.p. 116·5—118°, $[\alpha]_D$ +31° in MeOH (*hydrochloride*, m.p. 122—124°). H. W.

***Cinchona* alkaloids. XXVII. Stereochemical investigations. III. (+)- and (—)-Rubans, the parent substances of the *Cinchona* alkaloids.** P. Rabe and S. Riza (Annalen, 1932, **496**, 151—163).—Rubatoxanone, m.p. about 30° [*dibenzoyl*-d-*tartrate*, m.p. 202—203° (decomp.) (all m.p. are corr.)], is converted as previously described (A., 1922, i, 361) into 9-rubanone, m.p. 85—86° [*dibenzoyl*-d-*tartrate*, m.p. 173—174·5° (decomp.)], which undergoes fission (cf. A., 1909, i, 407; 1910, i, 417) to cinchonic acid and *oximinoquinuclidine*, m.p. 187—188° (decomp.), is reduced (Wolff–Kishner) to a *mixture* of (+)- and (—)-ruban, and is reduced (H_2, Pd-black, dil. HCl) to a mixture of the following four stereoisomeric 9-*rubanols* (I) (the signs denote the configurations of C_8 and C_9, respectively): (++)-, m.p. 229·5—230° (decomp.), $[\alpha]_D^{15}$ +132·5° (all rotations are in EtOH) [*H* l-*tartrate*, m.p. 186—187° (decomp.); *chloride*, m.p. 135—137·5°, $[\alpha]_D^{24}$ +4·9°]; (+—)-, m.p. 118—119°, $[\alpha]_D^{16}$ +14·3° [*dibenzoyl*-d-*tartrate*, m.p. 189—191° (decomp.); *chloride*, m.p. 140—142°, $[\alpha]_D^{21}$ +96·3°]; (—+)-, m.p. 117—118°, $[\alpha]_D^{18}$ —14·9° [*dibenzoyl*-l-*tartrate*, m.p. 189—191° (decomp.); *chloride*, m.p. 141—142°, $[\alpha]_D^{15}$ —96·8°]; and (——)-, m.p. 228·5—230·5° (decomp.), $[\alpha]_D^{15}$ —131·8° [*H* d-*tartrate*, m.p. 186—188° (decomp.); *chloride*, m.p. 136—138°, $[\alpha]_D^{20}$ —4·9°]. The (++)- and (+—)-chlorides are reduced [H_2, Pd–$CaCO_3$, EtOH–KOH) to (+)-*ruban* (I, CH·OH =CH_2), oil, $[\alpha]_D^{16}$ +80·5°, whilst the (—+)- and (——)-chlorides similarly give (—)-*ruban*, an oil, $[\alpha]_D^{16}$ —78·4°. *Dibenzoyl*-l-*tartaric acid hydrate* has m.p. 85°, $[\alpha]_D^{24}$ +103·7°.



(I.)

Comparison of the sp. rotations of the rubanols with those of the 3-ethylrubanols (the isomeric hydrocinchonines and -cinchonidines) (this vol., 289) and those of the rubans with those of deoxyhydrocinchonine and -cinchonidine (*loc. cit.*) indicates that the asymmetric C_3 and C_4 atoms (of the *Cinchona* alkaloids) cause dextrorotation. H. B.

Oxidation of strychnine. B. Alessandro (Nature, 1932, 129, 905).—Oxidation of strychnine with H_2CrO_4 in a carrier acidified with AcOH gives a *compound* $C_{21}H_{20}O_4N_2$ or $C_{42}H_{42}O_8N_4$, m.p. 309—310°, neutral to litmus, and giving colour reactions with strychnine. L. S. T.

***Strychnos* alkaloids. LXV. Oxidation of diketonucidine with bromine. Reaction of this base, of brucine, and of strychnidine with cyanogen bromide.** H. Leuchs and H. S. Overberg (Ber., 1932, 65, [*B*], 961—966; cf. A., 1930, 936).—Improved technique in the oxidation of diketonucidine with Br leads to the isolation of the homogeneous aldehyde, $C_{17}H_{22}O_6N_2$, as *hydrobromide*, $[\alpha]_D^{20}$ +150·8°/*d*, or *perchlorate*, $[\alpha]_D^{20}$ +145°/*d*. The *perchlorate* of the *dioxime* of the anhydride form is described. The hydrobromide is readily oxidised by yellow HgO to 2 : 3-*diketonucic acid hydrate*, $C_{17}H_{22}O_7N_2$, darkening above 260°, $[\alpha]_D^{16}$ +166°/*d* [*semicarbazone perchlorate* (derived from anhydride form)]. Electrolytic reduction of diketonucidine affords ketohydroxynucidine. Treatment of 2 : 3-diketonucidine with CNBr in C_6H_6 affords a non-decomposable quaternary *bromide*, $C_{35}H_{40}O_6N_5Br$, $[\alpha]_D^{23}$ +117·6°/*d* in H_2O, and two isomeric *substances*, $C_{18}H_{20}O_3N_3Br$, prisms, $[\alpha]_D^{23}$ +255·8°/*d* in AcOH, and needles, $[\alpha]_D^{23}$ +28·8°/*d* in AcOH. Hydrolysis and reduction of the prisms leads to a *compound*, $C_{24}H_{26}O_4N_2$, m.p. 280—281° (vac.), $[\alpha]_D^{21}$ +69·4°/*d* in MeOH. Brucine and CNBr in boiling C_6H_6 yield the quaternary bromide, $C_{47}H_{52}O_8N_5Br$, m.p. 209—211° (decomp.), $[\alpha]_D^{20}$ −24·5°/*d* in AcOH, a *substance*, $C_{24}H_{26}O_4N_3Br$, softening and decomp. at 158—163°, $[\alpha]_D^{20}$ +75°/*d* in C_6H_6, and non-homogeneous material. Strychnidine under similar conditions yields the *compounds* $(C_{22}H_{24}ON_3Br)_2$, $[\alpha]_D^{20}$ +43·8°/*d* in H_2O, and $C_{22}H_{24}ON_3Br$, m.p. 145—150° (vac., decomp.), $[\alpha]_D^{20}$ −57·0°/*d* in C_6H_6. H. W.

***Strychnos* alkaloids. LXVI. Behaviour of brucinonic acid towards barium peroxide.** H. Leuchs and F. Kröhnke (Ber., 1932, 65, [*B*], 980—983).—Brucinonic acid is oxidised by H_2O_2 and $Ba(OH)_2$ to glycollic acid and an *NH_2-acid*, $C_{20}H_{22}O_6N_2$, m.p. 254—255° (decomp.), $[\alpha]_D^{15}$ −15°/*d* in H_2O (*perchlorate*, $[\alpha]_D^{20}$ −25·4°/*d*; *hydrochloride*, $[\alpha]_D^{19}$ −33·3°/*d*; *K* salt). The compound is obtained similarly from brucinonic acid hydrate *b*, which evolves CO_2 when boiled with NH_2Ph. H. W.

Narceine : new reactions and interpretation of Wangerin's reaction. J. A. Sanchez (Anal. farm. bioquim., 1931, 2, 68—74).—The presence of the CH_2O_2: group in narceine and narcotine may be shown (1) by heating 0·05 g. with H_2SO_4 (10 drops); the gas collected in H_2O gives a deep red coloration with Schryver's reagent (1% NHPh·NH_2,HCl, 1 c.c.; 5% $K_3Fe(CN)_6$, 2 drops; conc. HCl, 1—2 c.c.), (2) by gently heating a few mg. with about 0·01 g. of carbazole and 10 drops of conc. H_2SO_4, when a deep violet-blue colour gradually develops. The emerald-green colour obtained with tannin and H_2SO_4 is also due to the CH_2O_2 group. Ch. Abs.

Organic compounds of germanium. H. Bauer and K. Burschkies (Ber., 1932, 65, [*B*], 956—960).—Hg di-1-naphthyl and $GeCl_4$ in $C_6H_4Me_2$ at 180° afford *Ge 1-naphthyl trichloride*, hydrolysed by 2*N*-NaOH to *di*-1-*naphthylgermanic anhydride*, $\begin{matrix}C_{10}H_7\cdot GeO\\ C_{10}H_7\cdot GeO\end{matrix}\!\!>\!O$. The sole product of the interaction of $GeCl_4$ with Mg *cyclo*hexyl bromide in Et_2O appears to be *Ge tri*cyclo*hexyl bromide*, m.p. 110°, converted by $AgNO_3$ in boiling EtOH or boiling H_2O or alkali into *Ge tri*cyclo*hexyl hydroxide*, m.p. 176—177°, whence the corresponding *fluoride*, m.p. 92°, *chloride*, m.p. 102°, and *iodide*, m.p. 99—100°, are derived by means of the requisite halogen acid. Successive treatment of $GeCl_4$ with NHPhMe at 100° and NaOH affords *di*-p-*methylanilinogermanic anhydride*, $(NHMe\cdot C_6H_4\cdot GeO)_2O$; *di*-p-*diethylanilinogermanic anhydride* is similarly prepared. The action of H_2S on the requisite substituted germanic anhydride in dil. AcOH leads to the isolation of the following *Ge sesquisulphides*, $(GeRS)_2S$: *diphenyl*; *di*-p-*tolyl*; *di*-p-*diethylanilino*-; *di*-p-*dimethylanilino*-; *di*-1-*naphthyl*. All are colourless powders without definite m.p., very sparingly sol. in H_2O, and slowly evolving H_2S when exposed to moist air: Ge is determined by heating the compounds with conc. H_2SO_4 at 100°, removing the acid, and repeated evaporation of the residue with conc. H_2SO_4 and fuming HNO_3 (1 : 3). H. W.

Halogenomercuribenzoic acids. A. N. Nesmejanov and L. G. Makarova (J. Gen. Chem. Russ., 1931, 1, 1162—1163).—The m.p. of acids of the type $CO_2H\cdot C_6H_4\cdot HgHal$ are: *o*-Cl, 253°, *o*-Br, 249°, *o*-I, stable up to 230°, *m*-Cl, 264°, *m*-Br, 250°, *m*-I, 181—185°, *p*-Cl, 273°, *p*-Br and *p*-I, above 300°. The m.p. of the *o*-Cl-compound (151°; A., 1931, 244) must be due to a misprint. The Me ester of the *o*-Br-acid has m.p. 195°, not 175° (cf. this vol., 70). G. A. R. K.

Organic antimonial compounds. III. (Miss) M. E. Brinnand, W. J. C. Dyke, W. H. Jones, and W. J. Jones (J.C.S., 1932, 1815—1819).—By using the appropriate Grignard reagents the following have been prepared: *ethyldi*-n-*butylstibine*, b.p. 147°/43 mm., -n-*amyl*-, b.p. 167°/51 mm., -cyclo*hexyl*-, b.p. 122—126°/15 mm., -o-, b.p. 196—201°/10 mm., m.p. 102°, -m-, b.p. 211—216°/15 mm., and -p-*tolylethylstibine*, b.p. 226°/5 mm., m.p. 114°. The compounds of tri*iso*butylstibine are described: double *oxide*; *oxide*; *dichloride*, m.p. 91°; *dibromide*, m.p. 88°; *di-iodide*, m.p. 70°; *methiodide*, m.p. above 155°; *methylmercuri-iodide*, m.p. 119°; *methylmercurichloride*, m.p. 117°; *methylchloroplatinate*, m.p. 158°. β-*Naphthylstibinic acid* is obtained from β-naphthylamine with intermediate formation of *NH_4* β-*naphthylchloroantimonate*, and is converted into -*stibinous oxide*, decomp. 160°. *Tetraethyl*- and *tetra*-n-*propylphosphonium*; *dimethyldi*-n-*propyl*-, *methyltriethyl*-, *tetraethyl*-, *methyltri*-n-*propyl*-, and *methyltri*-n-*amylarsonium*; and *methyltri*-n-*propylstibonium antimonyl* d-*tartrates* are described. F. R. S.

Aryl di- and poly-stibinic acids, distibinous oxides, and di-stibino-compounds. S. M. Mistry and P. C. Guha (J. Indian Inst. Sci., 1932, 15A, 25—39).—The following have been prepared from the corresponding amines: m- and p-*phenylene*- and 1 : 4-*naphthylene-distibinic acid*; *diphenylene*-pp- (*pp*-distibinotetraphenylene), 3 : 3-*dimethyldiphenylene*-

4 : 4′-, 3 : 3-*dimethoxydiphenylene*-4 : 4′-, and *diphenylmethane*-pp-*distibinous oxide*; *benzophenone*-pp-*distibinic acid*; *diphenyl*-m-*tolyl-methylcarbinol*-ppp-*tristibinic acid* and *-methane*-ppp-*tristibinous oxide*; *stilbene*-4 : 4′-*distibinic acid* and *-distibinous oxide*; $CO(NH\cdot C_6H_4N_2Cl\cdot SbCl_2,HCl)_2$ gives a *secondary monostibinic acid*, also obtained from *p*-aminodiphenylcarbamide; 4 : 4′-*diacetamidodiphenylmethylenediamine*, m.p. 220°, and *-ethylenediamine*, m.p. 284°; *methylene-* and *ethylene-diaminophenylene*-4 : 4′-*distibinous oxide*; *bis*-p-*aminophenylazomethine*, m.p. 258° (decomp.) [Ac_2 derivative, m.p. 279° (decomp.)]; *bisphenylazomethine*-pp′-*distibinous oxide*; s-*oxal*-, *malon*-, and *succinamido*-, s-*carbohydrazino-diphenylene*-pp-*distibinic acid*; s-pp′-*diaminodiphenylhydrazo*-, m.p. above 370°, and s-pp′-*diacetamidodiphenylazo-dicarbonamide*, m.p. above 370°; *hydrazodicarbonaminodiphenylene*-pp-*distibinic acid*; *hydrazobenzene-* and *benzanilide*-pp′-*distibinous oxide*; p-*nitrobenzoyl*-p′-*acetamidoanilide*, m.p. 293° (decomp.); *triphenyl-phosphine-*, *-arsine-*, and *-stibine*-mmm-*tristibinic acid*. F. R. S.

Derivatives of *cyclo*-2 : 5-dithia-3 : 4-dimethylenestibine. R. E. D. Clark (J.C.S., 1932, 1826—1830).—$(\cdot CH_2\cdot SH)_2$ and $SbCl_3$ give 1-*chloro*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine* (I), m.p. 124° [*oxychloride* ($1H_2O$)], which heated with thiolacetic acid and C_5H_5N affords *pyridine* cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine*-1-*thiolacetate*, m.p. 101°. *m*-Thiolbenzoic acid condenses with (I) to give 1-m-*carboxyphenylthio*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine* (product obtained once only). *p*-Tolyldichlorostibine and $(\cdot CH_2\cdot SH)_2$ yield 1-p-*tolyl*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine*, m.p. 90° (dimorphous). p-*Carboxy*-(or *carbomethoxy*-)*phenyldi-iodostibine*, m.p. 120—132°, obtained from the *stibinic acid*, condenses with $(\cdot CH_2\cdot SH)_2$ to give an *acid*, m.p. 199°, and a *substance*, m.p. 138°. F. R. S.

Cystine. M. Ogawa (Bull. Sci. Fak. Terkult., 1932, 5, 90—102).—The determination of cystine in gelatin by the application of the I method to the acid hydrolysate yields low results when fats, lipins, inorg. salts, or particularly when carbohydrates are present. Hence for the determination of cystine in natural substances a preliminary separation of the proteins is necessary, sulphosalicylic acid, which does not interfere with the I method, being used. HCl and H_2SO_4 are equally suitable for hydrolysis. The solubilities, isoelectric points, and properties of active and inactive cystine are given and the prep. of cystine from hair, depending on crystallisation at the isoelectric point, is described. F. O. H.

Synthesis and degradation of proteins. M. Bergmann (Naturwiss, 1932, 20, 420—422).—The benzylurethane of an NH_2-acid is converted through the acid chloride into a dipeptide-urethane, which is reduced catalytically, giving PhMe, CO_2, and a dipeptide. In this way serylglycine, *d*-α-glutamyl-*d*-glutamic acid, and glycyl-*d*-glucosamine have been obtained. The action of dehydrodipeptidase (cf. this vol., 427) is sp. for dipeptides in which the CO_2H group of the unsaturated NH_2-acid is free. A. C.

Constitution of the keratin molecule. J. B. Speakman and M. C. Hirst (Nature, 1932, 129, 938—939).—A reply to criticism (this vol., 529). L. S. T.

Rapid determination of carbon and hydrogen in organic compounds. III. E. Berl and A. Schmidt (Ber., 1932, 65, [*B*], 978—980; cf. A., 1926, 749; 1928, 312).—Improvements recommended include a new type of flask for preservation and manipulation of $PbCrO_4$, modified H_2SO_4 tube for absorption of H_2O, and modified CO_2 absorption tubes. H. W.

Determination of halogens in organic substances. D. Buttescu (Bul. Chim. pura apl. Bukarest, 1931, 33, 83—92; Chem. Zentr., 1932, i, 710).—Julkowski's method (Monatsh., 1885, 6, 447) is the best for determining halogens. The substance is burnt in O_2 (Pt–quartz catalyst) and the gaseous products are passed through aq. Na_2SO_3–Na_2CO_3. L. S. T.

Organic analysis. Determination of sulphur. D. Buttescu (Bul. Chem. pura apl. Bukarest, 1929, 32, 79—87; Chem. Zentr., 1932, i, 710).—The S oxides after combustion are collected in 2 or 5% aq. H_2O_2. When C and H are to be determined, they are retained by MnO_2 at 150—180°. The MnO_2 is extracted with hot H_2O and the SO_4'' determined gravimetrically. L. S. T.

The Vieböck and Schwappach method for the determination of methoxyl and ethoxyl groups. E. P. Clark (J. Assoc. Off. Agric. Chem., 1932, 15, 136—140).—A modification of the method (H. Meyer, "Analyse und Konstitutionsermittlung," 5 Auf., p. 487) applicable to about 0·005 g. of substance is described. W. J. B.

Determination of reducing sugars (copper-colorimetric method). E. M. Emmert (J. Assoc. Off. Agric. Chem., 1932, 15, 327—329).—The excess of Cu remaining in solution after reduction of Bertrand's reagent is determined colorimetrically. H. R. J.

Microchemical reactions of saccharin. M. Wagenaar (Pharm. Weekblad, 1932, 69, 614—618).—Methods of obtaining characteristic cryst. deposits by sublimation, by pptn., and by reaction with $AgNO_3$, Cd salts, C_5H_5N–Cu salts, $HgCl_2$, and I in KI are described. The most suitable reagents are $HgCl_2$ and I in KI, by means of either of which 0·02 mg. at a dilution of 1 in 300 may be detected. S. I. L.

Isolation of guanidine. J. A. Saunders.—See this vol., 890.

Determination of aldehydes based on the reactions of Cannizzaro and Claisen. L. Palfray, S. Sabetay, and (Mlle.) D. Soutag (Compt. rend., 1932, 194, 1502—1505).—Aromatic aldehydes are determined by heating under a reflux condenser with $0\cdot 5N$-$CH_2Ph\cdot OK$ in $CH_2Ph\cdot OH$ for 2·5 hr., diluting with H_2O, and titrating the excess of alkali in presence of phenolphthalein. J. L. D'S.

Thionylaniline, a reagent for characterising acids as anilides. P. Carré and D. Libermann (Compt. rend., 1932, 194, 2218—2220).—PhN:SO, unlike PhNCO, does not add on to alcohols, being without action on boiling EtOH or PhOH at 185°, but with boiling Bu^aOH affords butylene. In general, aliphatic acids when warmed with PhN:SO afford anilides. The malonic acids and some unsaturated acids, especially those with a double linking near the CO_2H group, react abnormally. Aromatic acids give principally coloured compounds containing S, but phthalic acid gives the anil. J. L. D'S.

Benzylideneacetone, cinnamic acid, and bromostyrene. N. Kislianskia (J. Gen. Chem. Russ., 1932, 2, 103).—In the iodometric determination of benzylideneacetone, Schorigin, Issaguliantz, and Gusseva (this vol., 853) use MeOH as solvent. Since MeOH, even when free from $COMe_2$, reacts with I under the conditions used, it is recommended to use AcOH. M. Z.

Colour reaction of pyrrole and indole derivatives. E. Montignie (Bull. Soc. chim., 1932, [iv], 51, 689—690).—Pyrrole (min., 0·04 mg.) when boiled with 10% H_2SeO_3 and conc. HNO_3 gives a deep violet coloration (reddish-violet when dil.). $CHCl_3$ extracts a blue substance leaving a red solution. Similar treatment of indole (min., 0·05 mg.) gives a violet, tryptophan gives the yellow colour produced by HNO_3 alone, whilst skatole with H_2SeO_3 alone gives a violet changed to red by HNO_3. A. A. L.

Microchemical reactions of atropine. Z. F. Klan (Časopis Českoslov. Lék., 1931, 11, 289—295; Chem. Zentr., 1932, i, 1126).—Identification is best effected with 0·1*N*-I, 10% $AgNO_3$, or saturated aq. picrolonic acid solution. A. A. E.

Colorimetric determination of eserine. M. S. Mokragnatz (Bull. Soc. Chim. Yougoslav., 1931, 2, 175—183).—A solution of 1 g. of benzidine in 30 c.c. of H_2O and 10 c.c. of Ac_2O when diluted to 50 c.c. gives a violet coloration with eserine in the presence of H_2O_2, which can be applied to the colorimetric determination of eserine. R. T.

Biochemistry.

Leucopoietic value of sulphur. T. D. Power (Lancet, 1932, 222, 338—340).—Injections of a 1% S-oil suspension increase the no. of leucocytes in rabbit blood. L. S. T.

Factors in food influencing hæmoglobin regeneration. I. Whole wheat flour, white flour, prepared bran, and oatmeal. M. S. Rose and E. M. Vahlteich (J. Biol. Chem., 1932, 96, 593—608).—The feeding of whole wheat, oatmeal, or prepared bran to rats in which anæmia has been induced by a milk diet results in a regeneration of hæmoglobin approx. proportional to the amount of Fe present in the cereal. Regeneration due to feeding white wheat is less than that due to the same wt. of whole wheat even when the former is supplemented with Cu or Fe or their mixtures. The effect of whole wheat is always superior to that when part is replaced by Cu or Fe, but with oatmeal one half may be replaced by a mixture of Cu and Fe. Also administration of an aq. HCl solution of the ash of whole wheat or of bran does not produce regeneration equal to that shown by the original food material. Hence factors other than Cu and Fe which influence hæmoglobin regeneration are present in greater amounts in oatmeal than in white flour. F. O. H.

Hæmoglobin content of the blood of the hen. H. H. Dukes, L. H. Schwarte, and A. E. Brandt (Science, 1932, 75, 25—26).—The influence of breed and age on hæmoglobin content are discussed, together with the correlation between season, age at maturity and egg production, and hæmoglobin content. L. S. T.

Micro-methods for determining serum-protein fractions. B. Gözsy (Magyar arvosi Archiv., 1931, 32, 369—378; Chem. Zentr., 1932, i, 712).—The Berger–Petschacher–Schretter standard method is compared with that of Darányi which yields satisfactory results and enables several fractions to be determined simultaneously. L. S. T.

Optical density and viscosity of therapeutic sera. C. Achard, A. Boutaric, and M. Gantrot (Compt. rend., 1932, 194, 2249—2253).—The viscosity at 26° of 7 therapeutic sera heated at 55° and 62° for 1 hr. and unheated, varies considerably according to the nature of the serum, but is greater than that of normal horse serum, the effect of heating being to increase the viscosity. There is little difference between the optical density of therapeutic and normal horse serum. A. L.

Effect of sera on the flocculation of colloidal ferric hydroxide. C. Achard, A. Boutaric, and F. Morizot (Compt. rend., 1932, 195, 9—11).—The time of flocculation of colloidal $Fe(OH)_3$ with KNO_3 is considerably shortened by addition of very dil. serum; this accelerating effect is diminished by heating the serum at 55°. Proteins separated by the $COMe_2$ method produce the same effect as the original serum. The sera of syphilitic subjects produce less effect than those of normal or carcinomatous subjects. P. G. M.

Serum-bilirubin. I. Diazo-reaction as quantitative procedure. F. D. White (Brit. J. Exp. Path., 1932, 13, 76—85).—When the diazo-reagent reacts with bilirubin dissolved in blood-serum, the colour produced is proportional to the amount of bilirubin; the bilirubin content of icteric sera can be determined. Van den Bergh's method gives low results, probably owing to adsorption on the proteins pptd. by EtOH. A standard solution is prepared from anhyd. $CoSO_4$ (1·3 g.) in H_2O (50 c.c.), treated gradually, with shaking and cooling, with HCl (*d* 1·19, 40 c.c.) and diluted to 100 c.c. The solution should be prepared 24 hr. before use and kept well stoppered in the dark. Ch. Abs.

Blood-cholesterol. Determination and normal values. J. Castellano and I. Torres (Anal. Fís. Quím., 1932, 30, 384—387).—The methods of Grigaut and of Autenrieth give low vals. owing to incomplete extraction. Correct vals are obtained by the Myers–Wardell method (A., 1918, ii, 461) with slight modifications. Normal vals. are between 140 and 200 mg., mean 175 mg., per 100 c.c. Very high vals. are found in nephritis with œdema. R. K. C.

Antigenic properties of cholesterol, cholesterol derivatives, and synthetic lecithin. A. J. Weil and F. Besser (Klin. Woch., 1931, **10**, 1941—1944; Chem. Zentr., 1932, i, 700).—Pure cholesterol, dihydrocholesterol, and synthetic distearyl-lecithin show antigenic properties of the haptene type. L. S. T.

Blood-sugar and blood-sodium curves. J. Puyal and I. Torres (Anal. Fís. Quím., 1932, **30**, 388—393).—The rise and fall of blood-sugar following oral administration of glucose are accompanied by a small increase and decrease, respectively, of blood-Na. Na and Cl (this vol., 764), as electrolytes of small mol. wt., are eliminated in order to preserve osmotic equilibrium.

A mean val. of 294 mg. blood-Na per 100 c.c. was found in 10 patients by a slight modification of Kahane's method (A., 1930, 726, 880). R. K. C.

Turbidity micro-method for blood-sugar. A. R. Rose, F. Schattner, and W. G. Exton (XL Ann. Mtg. Assoc. Life Insur. Med. Dir. Amer., 1929, 24—25).—The protein is pptd. with $H_3Fe(CN)_6$; the filtrate is rendered alkaline and boiled. The $Fe(CN)_6''''$ is pptd. by addition of ammoniacal Ag solution and the turbidity is measured in a scopometer. The results are lower than those obtained by Folin's method. Ch. Abs.

Influence of glutathione on reduction and rotation of blood-filtrates. J. Groen and J. W. Meyer (Biochem. J., 1932, **26**, 624—632).—In Folin and Wu filtrates of normal human blood the difference between reduction as determined by the Shaffer–Hartmann–Somogyi method and the rotation amounts on the average to 32 mg. per 100 c.c. expressed as glucose. There is no such difference in plasma filtrates and in filtrates of blood prepared by Herbert and Bourne's technique. The reduced glutathione present in the blood is the main cause of the differences between the results of the reduction and rotation methods. The blood of diabetic patients behaves similarly in this respect. S. S. Z.

Isolation of ergothioneine from blood. S. W. Williamson and N. U. Meldrum (Biochem. J., 1932, **26**, 815—816).—The blood is extracted with dil. H_2SO_4, conc. in a vac., and the concentrate aërated. Ergothioneine is then pptd. from it as the Cu compound and decomposed with H_2S. S. S. Z.

Ammonia formation in the blood of the tortoise. W. Mozolovski and T. Mann (Biochem. Z., 1932, **249**, 161—175).—The NH_3 formation after hæmolysis of tortoise blood amounts in 24 hr. to > 10 mg. NH_3-N per 100 c.c. of blood, the NH_3 formation in this case not being inhibited by adjustment with borate to p_H 9·2. For NH_3 formation it is necessary to combine the plasma with either the hæmoglobin solution or the separated stroma and erythrocyte nuclei. On hæmolysis, the urea, uric acid, and amide-N are unchanged. The decomp. of aminopurines explains the formation of only a small portion of the NH_3. P. W. C.

Determination of inorganic sulphate in blood-serum. M. H. Power (Proc. Staff. Meetings Mayo Clinic, 1931, 6, 401—402).—An adaptation of Hubbard and Wakefield's method is described; benzidine sulphate is oxidised with $K_2Cr_2O_7$, the excess being determined iodometrically. 95—100% of 3—5 mg. per 100 c.c. is recoverable. The method has been modified for application to urinary sulphates. Ch. Abs.

Influence of liver damage on the serum-lipase. T. Kameo (J. Biochem. Japan, 1932, **15**, 229—256).—A saline extract of rabbit's liver is injected into dogs. Injection into rabbits of the anti-serum thus obtained produces a decrease followed by an increase in the serum-lipase, whilst in the urine the carbamide decreases and the NH_3 increases. Following exposure of the liver to hard *X*-rays the serum-lipase in the rabbit falls to a min. in 24 hr. and then exhibits a rapid but partial recovery, completely returning to the normal in 15 days. Direct irradiation of the blood or serum has no influence on the lipase val. The variation of serum-lipase with disease in man is investigated. F. O. H.

Parenteral denaturation of foreign proteins. VI. Depolymerisation, homologisation, and retention. H. C. Sox, J. L. Azevedo, and W. H. Manwaring (J. Immunol., 1931, **21**, 409—415).

Parenteral denaturation of foreign proteins. VII. Test-tube synthesis of "hybrid" specificities. H. C. Sox and W. H. Manwaring (J. Immunol., 1932, **22**, 237—243).—Horse serum incubated with dog serum (10—1000 vols.) shows a rapid and consistent destruction, or total denaturation, of proteins of full horse serum specificity, accompanied by an initial increase and subsequent decrease in proteins intermediary in specificity between horse and dog. Ch. Abs.

Precipitinogenic action of minute quantities of ovalbumin. L. Hektoen and A. G. Cole (J. Infect. Dis., 1932, **50**, 171—176).—The sera of rabbits immunised by intravenous injection of approx. 0·00029 and 0·0017 g., respectively, of ovalbumin gave sp. ppts. with the homologous antigen at a dilution of 1 in 10^5. Ch. Abs.

Inception of blood-clotting. E. Armitage, J. W. Pickering, and S. N. Mathur (Biochem. J., 1932, **26**, 853—864).—The disintegration of leucocytes is not an essential occurrence in the inception of blood-clotting. The complete disintegration of blood platelets neither produces intravenous clotting nor hastens the coagulation of normal blood which has been shed in paraffined vessels. The lysis of blood platelets hastens the clotting of blood shed on to glass and also hastens the coagulation of blood shed into paraffined vessels when the blood is contaminated with tissue juices. Fresh blood-serum promptly clots both pure blood and pure blood-plasma which have been shed into paraffined vessels, but the rapid intravascular injection of amounts of fresh sera sufficient to produce extravascular clotting does not produce intravascular coagulation in non-pregnant cats if the amount administered is not lethal. The addition of very small amounts of the fresh juices of testis, muscle, and kidney to blood shed into paraffined vessels rapidly produces complete coagulation, but the rapid intravascular or the rapid intracardiac injection after the isolation of the heart from the general circulation of these juices does not produce clotting *in vivo* in non-pregnant cats. The intravenous injection of the fresh juices of kidney and muscle into pregnant cats produces intravascular clotting. S. S. Z.

Blood-clotting. S. Prakash (Biochem. Z., 1932, 249, 39—47).—The clotting of blood is analogous to gel formation, blood containing a negatively-charged fibrin sol (=fibrinogen) which coagulates as fibrin and shows a strong tendency to absorb similarly charged ions, thus being stabilised in presence of salts and alkaline solutions. The assumption of thrombin and related substances is unnecessary to explain clotting. Spontaneous blood-clotting can be imitated with sufficiently dialysed inorg. sols of $FePO_4$, $Fe_3(WO_4)_2$, Sn and Ce borates, Ce molybdate, the gels in all cases showing a similar syneresis. P. W. C.

Avitaminosis and blood-clotting function. I. N. Kugelmass and E. L. Samuel (Amer. J. Dis. Children, 1932, 43, 53—57).—Withdrawal of vitamin-*A* or -*B* from the diet of rats decreases the blood-fibrinogen. Deficiency of vitamin-*D* may reduce the prothrombin and fibrinogen, but that of -*C* has no effect on the clotting components. Ch. Abs.

Corpuscular volume of blood. I. Prevention of coagulation without effecting change in corpuscular volume. II. Hæmatocrit method. M. Hiraki (J. Biochem. Japan, 1932, 15, 331—337, 339—344).—I. The addition of 2·3% aq. $K_2C_2O_4$ or of 3·6% Na citrate solution to blood in the proportion 1 : 9 effectively prevents coagulation without influencing the corpuscular vol. especially when $\Delta = -0{\cdot}560°$ for the blood sample.

II. A method employing a hæmatocrit tube of 2·0 c.c. capacity is described. The blood (0·20 c.c.) is diluted with a 9 : 1 mixture of isotonic saline and 3·6% aq. Na citrate. F. O. H.

Action of heparin on protein. A. Fischer and A. Schmitz (Naturwiss., 1932, 20, 471—472).—In its action on serum-albumin, heparin shows analogy with the nucleic acids, but the latter have no anticoagulant action. Comparison of the results of electrometric titration of protein and heparin–protein lends support to the view that the combination leads to the formation of complex mol. compounds. Whilst the addition of heparin to blood-serum causes no change in the relative amounts of globulin and albumin as measured by $(NH_4)_2SO_4$ pptn., a change occurs when the blood plasma is used. A. L.

Human skin. I. Skin of the cadaver. A. Nadel (Biochem. Z., 1932, 249, 83—94).—The accuracy of known methods for determination of H_2O, fat, fat-free dry substance, Cl, total N, and residual N when applied to skin after death is determined and tables summarise the results. P. W. C.

Behaviour of native skin against pancreatin. M. Bergmann and G. Pojarlieff (Biochem. Z., 1932, 249, 1—6).—The kneading of skin collagen results in increased digestibility by pancreatin only when the piece of collagen is digested together with the fibres separated in the mechanical treatment. Pancreatic digestion of collagen at 40° in absence of large amounts of salts does not show during 3 days any considerable inhibition by the products of digestion. P. W. C.

Phosphatase and pyrophosphatase of bones and cartilage. T. Yamane (Arb. Anat. Inst. Kais. Univ. Kyoto, 1931, III, C, No. 2, 49—61, 84—99).—The optimal p_H for rabbit's bone phosphatase is 8·9—9·6 and for bone pyrophosphatase is 8·6—9·3. The phosphatolytic effect is parallel with the ossification mechanism. The phosphatase and pyrophosphatase of the bone tissue is intimately connected with the calcification process of bone tissue. The bone tissue of the adult rabbit contains less phosphatase than does that of the young animal. Cartilages in which no calcification occurs contain no phosphatase, and those which calcify later contain but little. Ch. Abs.

Phosphatase in the young rabbit and in the fœtus. I. Horii, M. Morii, and E. Norioka (Arb. Anat. Inst. Kais. Univ. Kyoto, 1931, III, C, No. 2, 37—40).—Organs of newly born rabbits and fœti contain little phosphatase. Ch. Abs.

Cystine content of human hair. II. T. Tadokoro and H. Ugami (J. Biochem. Japan, 1932, 15, 257—260).—The contents of cystine, total S, and total N of pubic and scalp hair were determined. The S content and the cystine/N ratio are greater in scalp hair, whilst the cystine and S contents of the hair of white persons are greater than those of the hair of coloured persons. F. O. H.

Micro-determinations of purine substances in tissues. G. Schmidt. **I. Determination of guanine.** E. Engel (Z. physiol. Chem., 1932, 208, 225—227, 227—236).—I. A micro-method for the determination of guanine is described. The tissue is killed with liquid air and hydrolysed with 2% aq. H_2SO_4. After addition of NaOH and removal of free NH_3 the solution is treated with guanase at p_H 8·8. The NH_3 liberated determines the guanine present. J. H. B.

Hydrolysis of nucleic acid, nucleotides, and nucleosides. Y. Kobayashi (J. Biochem. Japan, 1932, 15, 261—275).—The ease of hydrolysis, as shown by the rate of liberation of PO_4 and ribose, is guanine- > adenine- > uracil- > cytosine-nucleotide. The same order is true for the case of hydrolysis of the corresponding nucleosides. Combination of the two series leads to an explanation of the rate of hydrolysis of nucleic acid. F. O. H.

Wild animal [hedgehog, polecat] fats. A. Pawletta (Pharm. Zentr., 1932, 73, 417—420).—Six samples of the liquid fat (pasty at −15°) of hedgehogs were examined, having: d^{15} 0·9206—0·9259, n^{40} 1·4629—1·4656, sap. val. 195·2—198·2, I val. 89·2—98·4 : the fatty acids had m.p. 33—34°, setting point 22·5—23·4°. Distinction between the fats of hibernating and non-hibernating hedgehogs could not be made. Polecat (*Putorius*) fat (5 samples) had : m.p. 36—39°, f.p. 24·2—24·4°, d^{15} 0·9169—0·9195,

n^{40} 1·4598—1·4621, sap. val. 195—199, I val. 60·6—66·4, the fatty acids had m.p. 38·5—39·0°, setting point 33·5—33·8°. E. L.

Chemical composition of fish. III. Composition of *Pleuronectes* and mackerel. A. J. J. Vande Velde (Natuurwetensch. Tijds., 1932, **14**, 178—187).—*Pleuronectes platessa* contained on the average edible matter 56%, inedible 44%; the composition of the former, as wt.-% of the fresh fish, was: H_2O 45·6%, lipins, 1·06, protein 8·56, ash 0·78, P 0·094, Cl 0·06; that of the inedible fraction was H_2O 33·3, lipins 1·43, protein 6·01, ash 3·26, P 0·4, Cl 0·11. For *Scomber scombrus* the figures were: edible matter 65·5%, composed of H_2O 47·9, lipins 4·0, protein 12·7, ash 0·9, P 0·07, Cl 0·024; the inedible portion contained H_2O 23·9, lipins 3·4, protein 5·6, ash 1·6, P 0·234, Cl 0·056. The composition of individual fish varied widely from the mean. H. F. G.

Crystalline luciferin. S. Kanda (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 1).—A conc. EtOH solution of the substance(s) previously prepared (A., 1930, 1202) is treated with saturated EtOH–$CdCl_2$ until no further pptn. occurs; the ppt. is washed repeatedly with EtOH–$CdCl_2$, the combined filtrates freed from EtOH in a vac., diluted with H_2O, and then extracted with Et_2O or C_6H_6. Slow evaporation of the washed (with much H_2O) Et_2O or C_6H_6 extract gives cryst. *Cypridina* luciferin which still contains P. H. B.

Ash content of insects. E. B. Uvarov (Bull. Entomol. Res., 1931, **22**, 453—457).—The ash of the locust, *Schistocerca gregaria*, contains SiO_2 11·9, Cu 0·13, Fe_2O_3 2·06, Mn 0·16, Na_2O 6·2, K_2O 18·2, CaO 6·2, MgO 4·9, TiO_2 0·16, Ni 0·009, P_2O_5 32·4, SO_3 2·56, Cl 0·40, C 2·4, H_2O 0·54%. Immature, actively feeding locusts contain more SiO_2 than sexually mature locusts. Most of the SiO_2 and Fe_2O_3 is contained in the tissues. Ch. Abs.

Proportion of skeletal tissues in insects. P. A. Buxton (Biochem. J., 1932, **26**, 829—832).—If the dried powdered meal worm is digested with pepsin and pancreatin the reaction stops or becomes very slow when 8·1—8·7% of the original dry material is left. The same proportion of residue is left if the material is exposed to 1% aq. KOH at 100° for 24 hr. With other insects consistent results are also obtained. In the KOH method hæmatin is dissolved in the case of blood-sucking insects. S. S. Z.

Colouring matter of cocoons of green Japanese silkworms. C. Jucci and C. Manunta (Atti R. Accad. Lincei, 1932, [vi], **15**, 473—477).—This colouring matter, *bombichlorin*, is readily sol. in H_2O, and slightly sol. in 95% EtOH, and gives yellow salts with alkalis. T. H. P.

Determination of cholic acid in bile. J. G. Reinhold and D. W. Wilson (J. Biol. Chem., 1932, **96**, 637—646).—Dog or human hepatic bile diluted with H_2O is heated at 70° for 8 min. in presence of $12N$-H_2SO_4 and 1·3 mg. of furfuraldehyde per c.c. The resulting fluid is cooled and compared colorimetrically with a similarly treated standard solution of Na cholate, using monochromatic light of 600—690 mμ (cf. A., 1929, 1114). Human gall-bladder bile must be previously deproteinised with EtOH. Pure conjugated and unconjugated cholic acids in equimol. amounts produce equal intensities of colour. F. O. H.

Solubility of fatty acids in bile under the action of lecithin. E. Szörényi (Biochem. Z., 1932, **249**, 182—188).—Lecithin has no influence on the solubility of oleic acid in solutions of conjugated bile salts. The diffusion of oleic acid dissolved in bile salt solutions is the same in presence or absence of lecithin (0·8%). Lecithin in 1% bile salt solution is not diffusible. P. W. C.

Influence of lecithin on the solubility of oleic acid in bile-salt solutions. A. Müller (Biochem. Z., 1932, **249**, 189—194).—Emulsions obtained by shaking bile-acid solutions with oleic acid and keeping for a long time to separate the undissolved acid, contain 2—3% of oleic acid and can be clarified by addition of a little NaCl. Only 0·5—0·6% of this acid is diffusible and the amount is not materially altered by the presence also of lecithin. P. W. C.

Yield and fat content of human milk. C. Vincent and J. Vial (Compt. rend., 1932, **194**, 2328—2330).—The fat content of human milk given three times daily in the case examined varied considerably within wide limits and was independent of the quantity of milk. The total fat secreted showed, however, the same variations as the quantity of milk given each time. A. L.

Absorption of milk precursors by the mammary gland. III. Relation of amino-acid absorption to protein synthesis. J. H. Blackwood. **IV. Phosphorus metabolism of the mammary gland.** J. H. Blackwood and J. D. Stirling (Biochem. J., 1932, **26**, 772—777, 778—784).—III. In non-lactating cows the NH_2-acid content of the jugular blood is lower than that of the arterial blood. The NH_2-acid content of mammary-venous blood is slightly higher than that of arterial blood. In lactating cows the NH_2-acid content of jugular blood also differs from that of arterial blood. The NH_2 acid content of mammary venous blood is, however, always significantly lower than that of either jugular or arterial blood, thus confirming the view that NH_2-acids are the precursors of milk-protein. The ratio of sugar to N absorbed by the mammary gland is different in different animals, the range of variation being identical with that of the ratio found in milk. The ratio of corpuscular NH_2-acid to that of plasma is approx. 3 : 1 for the dairy cow. The NH_2-acids of the corpuscles play no part in the exchanges between the blood and the mammary gland.

IV. The acid-sol., org. and inorg. P content of the jugular blood of lactating and non-lactating cows is lower than that of the arterial blood 4 hr. after the ingestion of food. The inorg. P content of mammary blood is higher than that of jugular blood and approx. equal to that of arterial blood in lactating and non-lactating cows. The org. acid-sol. P content of mammary venous blood is lower than that of arterial blood in lactating cows but slightly higher in non-lactating cows. The partition of org. acid-sol. P between the corpuscles and the plasma is different for lactating and non-lactating animals. S. S. Z.

Iodometric determination of lactose in milk. J. Fine (Biochem. J., 1932, 26, 569—572).—The milk is clarified with colloidal Fe and the lactose determined iodometrically in the resulting serum.
S. S. Z.

Micro-determination of vacate-oxygen. H. R. Kanitz (Biochem. Z., 1932, 249, 234—238).—The method, depending on HIO_3 oxidation of the urine, is described. P. W. C.

Uric acid in frog's glomerular urine. J. Bordley (3rd) and A. N. Richards (Amer. J. Med. Sci., 1931, 182, 881—882).—Folin's method has been adapted. Ch. Abs.

Classification of products of nitrogen metabolism in the urine of different species of mammals. E. Terroine, (Mlle.) M. Champagne, and (Mlle.) G. Mourot (Compt. rend., 1932, 194, 2235—2237).—The urine of different species of mammals is examined for nitrogenous substances, representative figures being tabulated. The results are discussed.
J. L. D'S.

Tryptophanuria and its significance. A. T. Brice (Arch. Int. Med., 1932, 49, 978—980).—An improved Boltz test (A., 1931, 254) for tryptophan was positive in 33% of 525 specimens of urine from general surgical and medical cases. In some, tryptophan was present without proteinuria, whilst in others proteins were present which apparently contained no tryptophan. W. O. K.

Relation of nutrition to contagious cattle abortion. E. B. Hart, F. B. Hadley, and G. C. Humphrey (Wisconsin Agric. Exp. Sta. Res. Bull., 1932, No. 112, 45 pp.).—A "poor" ration supplemented only with NaCl maintained the condition and milk-producing capacity of cows nearly as well as a high-protein ration supplemented with bone meal, cod-liver oil, and iodised salt, and did not cause any greater susceptibility to infection by *B. abortus*. Use of cod-liver oil as a source of vitamin-*D* depressed milk-fat production. Cows on a "poor" ration adjusted themselves to a low Ca intake, the efficiency of Ca utilisation increasing as the Ca supply in the ration decreased. A. G. P.

Clinical significance of volume and hæmoglobin content of the red blood-cell. R. L. Haden (Arch. Int. Med., 1932, 49, 1032—1057).—In anæmias of all types the investigation of the no., mean vol., and hæmoglobin content of the red blood-cells is important. W. O. K.

Hyperglycæmia of cancer. G. E. Woodward and E. G. Fry (Biochem. J., 1932, 26, 889—897).—The average blood-sugar level in 52 untreated cancer cases as determined by the Hagedorn–Jensen method is 20 mg./100 c.c. above normal. Treated cancer cases and cases of non-malignant growths also show blood-sugar vals. higher than normal, the treated cases being on the whole almost as high as the untreated. Purely medical cases do not in general show an increase in the blood-sugar level. S. S. Z.

Metabolism of thiol compounds in tumour tissue. A. Goerner and M. Goerner (Amer. J. Cancer, 1932, 16, 360—365).—Rats with Flexner–Jobling carcinoma showed a decrease in liver- and tumour-glutathione when on a diet low in cystine. Liver tissue lost glutathione more readily than tumour tissue. On a normal diet the latter varied more widely in glutathione content than the former.
Ch. Abs.

Distribution of blood-cholesterol in cancer. H. R. Downes and G. T. Pack (Amer. J. Cancer, 1932, 16, 290—296).—Blood-cholesterol is normal; the relationship between whole blood and plasma vals. is not const. Ch. Abs.

Blood changes in malignant diseases. C. N. Myers and B. Throne (Amer. J. Cancer, 1932, 16, 297—306).—Cholesterol indices have no val. for the detection of neoplasms. There is evidence of metabolic disturbance involving fats, carbohydrates, and N. Ch. Abs.

Fermentation-accelerating action of tumour extracts and its relationship with Rosenthal's activator. G. Boström (Biochem. Z., 1932, 249, 239—240).—Corrections of the author's paper (this vol., 418). P. W. C.

Blood-sugar in arsphenamine dermatitis. J. Mu (Chinese Med. J., 1932, 46, 449—455).—Of 9 syphilitics suffering from arsphenamine dermatitis 8 gave an abnormally high blood-sugar curve after administration of glucose, whilst in 4 the fasting blood-sugar level was also high. The abnormality in blood-sugar was approx. parallel with the intensity of the dermatitis. W. O. K.

Behaviour of the animal organism in pancreatic diabetes towards certain carbohydrates. III. Effect of sodium hexosediphosphate on diabetic and on normal organisms. V. S. Iljin and J. T. Kusnetzov (Z. ges. exp. Med., 1931, 79, 635—652; Chem. Zentr., 1932, i, 703; cf. A., 1930, 365).—Na hexosediphosphate injected subcutaneously into depancreatised cats produced a pronounced and lasting diminution of blood-sugar frequently down to the normal. The blood-sugar of normal cats is not affected. The inorg. blood-P rises in diabetic animals. Hyperglycæmia often precedes the diminution in blood-sugar. Na glycerophosphate eliminates inorg. P after subcutaneous injection. The blood-sugar content of diabetic animals is lowered neither by small nor by large poisonous doses of Na glycerophosphate, in spite of the rise in blood-inorg. P. L. S. T.

Galactose tolerance of normal and diabetic subjects, and effect of insulin on galactose metabolism. J. H. Roe and A. S. Schwartzman (J. Biol. Chem., 1932, 96, 717—735).—Blood-galactose is determined by removing fermentable sugar with yeast, and applying the Benedict method (A., 1931, 973) to the protein-free filtrate. Blood- and urinary galactose and total blood-sugar vals. after ingestion of galactose (1 g. per kg. body-wt.) show that normal and diabetic persons have approx. the same galactose tolerance. Blood-galactose of rabbits is not influenced by insulin, and the latter is not detoxified by galactose.
A. C.

Clinical significance of the atoxyl-resisting lipase of blood-serum. S. Kunos and A. Gerö (Arch. Verdauungs-Krankh., 1931, 50, 232—246; Chem. Zentr., 1931, ii, 688).—The presence of atoxyl-resisting lipase in blood-serum can be detected with certainty when there is a pathological change in the function of the pancreas. L. S. T.

Excretion of creatine and creatinine. Hourly excretion in normal children and in children with progressive muscular dystrophy. M. C. Magee (Amer. J. Dis. Children, 1932, **43**, 322—326).—The excretion fluctuates; day vals. are higher than night vals. Muscular dystrophy in children is characterised by creatinine coeff. 2 and total creatinine coeff. 6. Ch. Abs.

Sodium chloride and water balance in epilepsy. F. Proescher and W. S. Thomas (J. Nerv. Ment. Dis., 1931, **74**, 577—597).—A tendency towards abnormal NaCl retention is observed. There is no disturbance in the renal H_2O output, but the extra-renal output varies widely. There is no relationship between the no. of convulsions, mental condition, and NaCl storage. Ch. Abs.

Distribution of calcium between blood and [cerebrospinal] fluid and carbon dioxide content of the blood in epilepsy. S. Katzenelbogen (J. Nerv. Ment. Dis., 1931, **74**, 636—643).—The alkali reserve was 57—74; blood-Ca was 8·1—11, and cerebrospinal fluid-Ca 4·3—5·8 mg. per 100 c.c. There was no relation between the Ca vals. and convulsions or mental condition. There appears to be increased permeability to Ca of the barrier between blood and cerebrospinal fluid. Ch. Abs.

Guanidine as a factor in alimentary intoxication in infants. K. Dodd, A. S. Minot, and H. Casparis (Amer. J. Dis. Children, 1932, **43**, 1—9).—The intoxication is characterised by increase in the blood-guanidine and -guanidine-like substances. Intramuscular or intravenous administration of Ca gluconate does not affect the vals. Animals suffering from guanidine poisoning exhibit similar symptoms and show improvement on administration of Ca salts. Ch. Abs.

Blood-urea changes in abnormal mental states after the administration of amino-acid. M. R. Lockwood and D. R. Davies (Biochem. J., 1932, **26**, 745—752).—There is no material difference from the normal in the blood-NH_2-acid changes following the administration of gelatin or glycine to psychotic subjects of varying types. Two characteristic blood-urea curves were observed: one of agitated and simple retarded melancholia which is typified by rapid and uniform changes, the total extent of the changes showing a marked increase of the normal. There is a rapid rise to a high level followed by a rapid fall within the 5-hr. period to the fasting level. In the other curve, which is obtained during recovery from melancholia and in apathetic states generally, whilst the early changes are fluctuating, the max. reading is obtained later than in the normal, the actual changes again being larger than the normal. The rise in urea level is slow, reaching its peak at the 5th hr. of the test period. S. S. Z.

Heart-muscle and experimental myocarditis. H. Wassermeyer and A. Rohrbach (Arch. exp. Path. Pharm., 1932, **166**, 375—391).—Myocarditis in rabbits, induced by injection of caffeine and adrenaline, is accompanied in the heart-muscle by none of the chemical changes typical of fatigue. F. O. H.

Posterior pituitary hormone and toxicosis of pregnancy. E. Fauvet (Klin. Woch., 1931, **10**, 2125—2129; Chem. Zentr., 1932, i, 697).—The toxicosis is attributed to over-production of the hormone. A. A. E.

Nature of urinary protein in eclampsia. N. J. Eastmen (Amer. J. Obstet. Gynecol., 1931, **22**, 756—760).—The globulin is high, urinary albumin : globulin being about 3. Ratios of 6·7 and 13·3 were obtained, respectively, in nephritis and nephrosis complicated by pregnancy. Ch. Abs.

Occurrence and ætiology of rickets. N. R. Dhar (J. Physical Chem., 1932, **36**, 1846—1850).—The disturbance of the acid–base equilibrium, resulting in a change of p_H of blood to the acid side, is the immediate cause of rickets. Vitamin-*D* is essential for the proper oxidation of fats in the body; in its absence acids accumulate, thus preventing normal pptn. of Ca from the blood. Both vitamin-*D* and ultra-violet light aid complete oxidation of fats. It is suggested that thyroid administration should prove useful in curing rickets. R. B. (*b*)

Vitamin therapy in pulmonary tuberculosis. I. Effect of activated ergosterol on calcium and inorganic phosphorus in the blood-serum. P. D. Crimm (Amer. Rev. Tuberculosis, 1931, **23**, 576—592).—The absorption of Ca and inorg. P in the gastro-intestinal tract is increased. The product Ca×P is used as a criterion of the effect of activated ergosterol on the blood-serum-Ca and -P. Ch. Abs.

Serum-calcium in pulmonary tuberculosis. J. Kaminsky and D. I. Davidson (Amer. Rev. Tuberculosis, 1931, **23**, 422—428).—Minimal cases and cases with quiescent lesions gave practically normal serum-Ca vals.; in active cases and cases with extensive lesions the serum-Ca tends to be low. Little difference was observed between the sexes; the age group 37—46 showed the highest and 47—64 the lowest vals. Normal or high vals. were afforded by patients receiving cod-liver oil. Ch. Abs.

Calcification of tuberculous foci in the epididymis by means of calcium diethyl ortho- and pyro-phosphate. R. Tachikawa (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, **C**, No. 2, 29—32).—Calcification was observed when rabbits inoculated with *B. tuberculosis* of the human type were subjected after 3—4 weeks to intravenous injection of 2—3% $Ca(Et_2PO_4)_2$ or $CaEt_2P_2O_7$ (1—2·7 g.). Ch. Abs.

Pulmonary concretions. M. Morii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, **C**, No. 2, 17—18).—The concretions consist chiefly of $Ca_3(PO_4)_2$. Ch. Abs.

Phosphatase in the sputum of tuberculous persons. I. Amount of phosphatase in the sputum and its relation to the number of bacilli found. Y. Imagawa (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, **C**, No. 2, 81—83).—Phosphatase is always present in the sputum of tuberculous persons; the amount is the greater when tubercle bacilli are absent or present only in small quantities. Ch. Abs.

Phosphatase and pyrophosphatase in tubercles. I. I. Horii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 1—12).—A study of the influence of p_H, temp., constituents of the phosphoric ester salts examined, time, and various drugs on the cleavage of the ester salts by phosphatase and pyrophosphatase from tuberculous rabbits. Ch. Abs.

Synthesis of glucosephosphoric acid by tuberculosis phosphatase. M. Morii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 19—20).—Glucosephosphoric acid was produced by an extract of tuberculous lymphomata with Na_2HPO_4, glucose, and NH_4Cl-NH_3 buffer solution at p_H 8·6. Ch. Abs.

Synthesis of phosphoric esters by tuberculosis phosphatase. M. Morii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 33—36).—The velocity of synthesis of glycerophosphoric ester from a mixture of Na_2HPO_4 and glycerol by the extract of tuberculous lymphoma in rabbits increases until the action of the enzyme is nearly exhausted after 96 hr. The optimal p_H is 8·3—8·9. At 60°, but not at 40°, the phosphatase is inactivated. Ch. Abs.

Tuberculosis phosphatase. II. Effect of rays. I. Horii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 62—74).—Sunlight has little effect on the cleavage of the Ca salts of fructosemonophosphate and sucrose- and α-glycero-phosphates by phosphatase from tuberculous lymphomata of rabbits. Ultraviolet light retards it in the first two cases. In the presence of fluorescent substances, *e.g.*, eosin, sunlight diminishes the effect. Hg, Fe, Cu, Au, Al, and Ni salts retard, whilst Mn, Cu, and Mg salts slightly favour, the action. In the presence of K_3AsO_3 the cleavage of the sucrosephosphate is retarded; the others are almost completely hydrolysed. KH_2AsO_4 diminishes the action. Atoxyl slightly increases the cleavage of fructosemonophosphate, but decreases that of the others. Ch. Abs.

Influence of *X*-rays on tuberculous phosphatase. M. Morii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No, 2, 21—22).—*X*-Rays (Mo anticathode) had no essential effect on the phosphatase extracted from tuberculous lymphomata. Ch. Abs.

Tuberculosis pyrophosphatase and taka-pyrophosphatase. M. Morii (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 13—16).—Pyrophosphatase of the tuberculous tissue transforms pyrophosphates into orthophosphates. Takapyrophosphatase ppts. $CaHPO_4,7H_2O$ from solutions of Ca Et_2 pyrophosphate. Injection of $Ca_2P_2O_7$ produces considerable deposition of $CaHPO_4,7H_2O$ in tuberculous lymphomata. Optimal action of pyrophosphatase occurs at p_H 7·4—7·6. Ch. Abs.

Calcium studies. VII. Calcium and inorganic phosphorus content of cerebrospinal fluid and blood-serum in chronic glomerulonephritis with uræmia. A. Cantarow (Arch. Int. Med., 1932, 49, 981—993).—In 10 cases of nephritis the ratio of cerebrospinal fluid-P to serum-P lay within normal limits varying from 0·31 to 0·42 (average 0·38). The degree of hyperphosphatæmia approx. paralleled the creatinine retention and acidosis. The serum-Ca varied from 6·84 to 9·02 mg. per 100 c.c., whilst the cerebrospinal fluid-Ca varied from 3·26 to 5·05. Low cerebrospinal fluid-Ca appeared to be associated with increased nervous irritability. W. O. K.

Oxidation by the brain. J. H. Quastel and A. H. M. Wheatley (Biochem. J., 1932, 26, 725—744).—The rates of oxidation of a no. of substrates in presence of brain-tissue of various animals, after it has become depleted of its oxidisable material, have been studied. The rate of oxidation of added substrates to the brain varies inversely with the size of the animal. Glucose, Na lactate, and Na pyruvate at equiv. concns. are oxidised at approx. the same rate by brain-tissue. Glucose is not appreciably oxidised by brain in Ringer's solution. The addition of phosphate buffer to Ringer's solution restores the rate of oxidation due to glucose. Lactate is probably completely oxidised by brain. The addition of serum increases the O_2 uptake due to brain. Iodoacetic acid inhibits the oxidation by brain of glucose, fructose, and mannose and only partly inhibits the oxidation of lactate, pyruvate, and glutamate. It has no effect on succinate oxidation. The oxidation of succinate by brain tissue varies with its content of oxidisable material. The presence of lactate "spares" the oxidation of succinate by brain, probably due to its competition with succinate for the oxidised form of a carrier. Of all the tissues investigated human grey matter is the least active toward the oxidation of succinate. S. S. Z.

Behaviour of fats during incubation of hen's eggs. K. Kusui (J. Biochem. Japan, 1932, 15, 319—323).—Towards the end of the incubation period there is a marked decrease in the total fats of the egg. The free fatty acids attain a max. after 3 days' incubation. After 14 days the proportion of free fatty acids (to total fatty acids) in the embryo is approx. 5 times that in the remainder of the egg; further incubation results in a decrease of total and free fatty acids in both parts such that the ratio is unchanged. The fatty acids of the hen's egg are mainly unsaturated. F. O. H.

[Physiological] exclusion and utilisation of the liver. G. Rosenfeld (Arch. exp. Path. Pharm., 1932, 166, 205—210).—The blood-sugar-lowering action of diastase resembles that of insulin in being antagonised by adrenaline which, in sufficient amount, inhibits the action of diatase and favours the loss of fat from the liver of P-poisoned dogs (cf. A., 1930, 1209). Introduction of antidiastase-containing serum into P-poisoned dogs prevents fatty degeneration of the liver. The exclusion of diastatic action is equiv. to the recommencement of normal liver carbohydrate metabolism with a concomitant exclusion of fatty infiltration of the liver. F. O. H.

Physiological deposition of fat in the liver and its prevention. G. Rosenfeld (Arch. exp. Path. Pharm., 1932, 166, 211—213).—Dogs fed with sesamé oil experience an increase in the liver-fat, the increase being inhibited by simultaneous administration of glucose or sucrose. F. O. H.

Experimental deposition of fat in the kidney. G. Rosenfeld (Arch. exp. Path. Pharm., 1932, 166, 214—221).—Fatty infiltration of the kidneys of dogs fed on fat occurs only to a limited extent which is not const. with either normal or phloridzinised animals. In both types the increase in fat is inhibited by simultaneous ingestion of sugar. An increase of kidney-fat is not induced by any poison such as P. The deprivation of the kidney-glycogen in the pregnant rabbit and the accumulation of glycogen by the fœtus are investigated and correlated with the related phenomena of carbohydrate deprivation and fat migration. F. O. H.

Lipin excretion. VIII. Lipin content of the intestinal mucosa. W. M. Sperry. **IX. Secretion of lipins into the intestine.** W. M. Sperry and R. W. Angevine (J. Biol. Chem., 1932, 96, 759—768, 769—786).—VIII. The lipin content of the mucosa of the small intestine and colon of normal dogs and dogs with ileostomies does not account for lipin excretion, since this would require a daily desquamation of about 12% of the entire intestinal epithelium.

IX. The lipin excretion of fistulas of the small intestine is greater than that found in the fæces of dogs on a lipin-free diet. Similar excretions from fistulas of the cæcum are found. An appreciable amount of the large secretion of lipins into the small intestine is reabsorbed. The remainder plus a small amount of lipin secreted into the colon comprises the endogenous excretion in the fæces. A. C.

Control of carbohydrate metabolism. J. J. R. Macleod (Lancet, 1932, 222, 1079—1086).—A lecture. L. S. T.

Significance of bile-acids in carbohydrate metabolism. XVII. Influence of bile-acids on lactic acid metabolism. XVIII. Influence of bile-acids on blood-glycolysis and muscle-glycogenolysis. M. Teraoka. **XIX. Influence of cholic acid on the excretion of lactic acid by rabbits poisoned with hydrogen cyanide.** S. Sibuya (Biochem. Z., 1932, 249, 95—117, 118—125, 176—181).—XVII. The mean normal lactic acid vals. for fasting rabbits are for liver 0·0592%, for muscle 0·196%, and for blood 10·558 mg. per 100 g. Subcutaneous administration of small amounts of Na cholate solution to fasting rabbits decreases the liver-lactic acid and of larger amounts of deoxycholic acid solution increases the acid val. of both liver and muscle. The blood val., however, remains unchanged. Small amounts of deoxycholic acid have no effect on any of the vals. Lactic acid formation in ox liver during autolysis is decreased by small and increased by large amounts of cholic acid and is also increased by small amounts of deoxycholic acid. Lactic acid formation in autolysing muscle is always decreased whatever amount of bile-acid is added. Glycogen formation in the livers of fasting rabbits from *dl*-lactic acid, given by mouth, is increased by either subcutaneous or peroral administration of Na cholate.

XVIII.—Blood-glycolysis *in vitro* is not affected by addition of 0·001%, but is inhibited by 0·01—0·04% of bile acid. Glycogenolysis and glycolysis by muscle-enzymes *in vitro* is strongly inhibited by 0·1% of bile acid, deoxycholic having a greater effect than cholic acid.

XIX.—Subcutaneously injected *r*-lactic acid is in part excreted by rabbits after poisoning with HCN. The amount excreted is decreased by administration also of cholic acid. P. W. C.

Sugar assimilation and bile acids. II, III. H. Yuuki (J. Biochem. Japan, 1932, 15, 359—371, 373—379).—II. The absorption of glucose in the intestine and its assimilation in the liver of the rabbit are increased by oral administration of PO_4''' buffer at p_H 7·55. Oral administration of ergosterol increases the assimilation of glucose by the liver and reduces alimentary hyperglycæmia, phenomena probably dependent on increased bile acid formation under the influence of ergosterol.

III. Glycogenesis in the liver of rabbits is increased by oral administration of ergosterol, the effect being more pronounced when Na lactate is simultaneously ingested. Glycogenesis due to Na lactate alone is markedly increased if ergosterol is fed 9 hr. previously. F. O. H.

Determination of pyruvic acid. E. M. Case (Biochem. J., 1932, 26, 753—758).—The principle of the method is based on the determination of the depth of colour produced by dissolving the 2 : 4-dinitrophenylhydrazone in EtOH–KOH. The method is applicable to muscle filtrates. One part in 100,000 parts of $AcCO_2H$ can be determined in abs. amounts at least as low as 0·2 mg. S. S. Z.

Origin of pyruvic acid in muscle. E. M. Case (Biochem. J., 1932, 26, 759—771).—$AcCO_2H$ (I) is produced from starch or glycogen, but little from lactate, in the presence of rabbit muscle extract or of chopped muscle. Amylase or NaF completely suppresses the formation of (I) from starch. No satisfactory evidence can be obtained that the disappearance of (I) from minced muscle is due to the formation of lactic acid. (I) is formed from hexosediphosphate in presence of sulphate, but not from methylglyoxal by muscle extract. Antiglyoxalase increases the production of (I) from starch, Na hexosediphosphate, or methylglyoxal. (I) is not an intermediary in lactic acid formation and is not a product of direct oxidation of lactic acid. S. S. Z.

Determination of lactic acid production without destruction of the muscle. C. A. Mawson and A. D. Ritchie (Biochem. J., 1932, 26, 615—618).—The lactic acid which diffuses into the Ringer's solution surrounding the stimulated muscle is oxidised with freshly-pptd. MnO_2 in presence of $MnSO_4$ and H_3PO_4; the resulting MeCHO is received in $Na_2S_2O_3$ and determined iodometrically. Amounts of lactic acid of the order of 0·1 mg. can be determined. S. S. Z.

Formation of ammonia and decomposition of pyrophosphate in muscle. W. Mozolovski, J. Reis, and B. Sobczuk (Biochem. Z., 1932, 249, 157—160).—The formation of NH_3 and decomp. of pyrophosphate in muscle-pulp proceed side by side, but by adjustment of the p_H to 9·2 (borate buffer) the two processes can be separated, NH_3 formation being inhibited and pyrophosphate decomp. unaffected. P. W. C.

Embryological chemistry of reptiles. IX. Behaviour of the egg-vitellin during incubation of sea-turtle eggs. K. Kusui (J. Biochem. Japan, 1932, 15, 325—330).—The vitellin decreases during the incubation period probably due to its assimilation by the developing embryo. The chemical composition, however, remains const. F. O. H.

(a) Increase of liver-proteins on a diet of amino-acids, butter-fat, and glucose. (b) Increase of liver-proteins on a diet of amino-acids and a minimum of honey. C. Gautier (Bull. Soc. Chim. biol., 1932, 14, 800—803, 804—807).—(*a*) Frogs, fed on a mixed diet containing NH_2-acids as the N constituent, show an increase in liver wt. of $6\frac{1}{2}$ times; the total liver-proteins doubled, whilst the % protein decreased. H. D.

(*b*) The liver wts. of frogs fed on a diet containing only NH_2-acids, salts, vitamins, and a min. of honey are doubled; the protein is lowered, whilst the total protein increased by $>50\%$. H. D.

Feeding experiments with methionine. T. E. Weichselbaum, M. B. Weichselbaum, and C. P. Stewart (Nature, 1932, 129, 795).—*dl*-Methionine, added to the Sherman–Merrill diet, is almost as effective as cystine in producing increased growth in rats (cf. this vol., 83). L. S. T.

Metabolism of tryptophan. III. Availability of kynurenine in supplementing a diet deficient in tryptophan. R. W. Jackson and W. T. Jackson (J. Biol. Chem., 1932, 96, 697—701).—Kynurenine sulphate does not promote growth of rats on a tryptophan-deficient diet when fed in amount 5—10 times greater than the dose of tryptophan which causes sharp increase in wt. The change tryptophan $\longrightarrow$ kynurenine is therefore not reversible in the animal. A. C.

Comparative metabolism of amino-acids. V. Oxidation of phenylalanine and phenylpyruvic acid in the organism of the rabbit. J. P. Chandler and H. B. Lewis (J. Biol. Chem., 1932, 96, 619—636).—Rabbits on a diet of cabbage and oats normally excrete approx. equal amounts of phenaceturic and hippuric acids. Following administration of phenylalanine or of an equiv. amount of phenylpyruvic acid considerable amounts of the latter appear in the urine, the excretion being greater with *dl*-phenylalanine than with the *l*-isomeride. Simultaneously there is an increase in the excretion of phenaceturic but not of hippuric acid. Hence with phenylalanine oxidative deamination is followed by α-oxidation to give products which are not further oxidised, whilst the opening of the Ph ring, which occurs after the oxidative deamination and before further changes in the side-chain, takes place less readily than has previously been assumed. F. O. H.

Digestibility by chickens of the constituents of the nitrogen-free extract of feeds. G. S. Fraps (Texas Agric. Exp. Sta. Bull., 1931, No. 437, 15 pp.).—In numerous trials sugars and starch showed a high and pentosans and residual N-free extract a low digestibility. Pentosans are less digested in roughages than in concentrates. A. G. P.

Productive energy of feeds calculated from feeding experiments with sheep. G. S. Fraps (Texas Agric. Exp. Sta. Bull., 1931, No. 436, 56 pp.).—For 1 lb. gain in wt. of fattening sheep an average of 2·60 therms of productive energy is required. The productive energy of feeding stuffs calc. from experimental data agreed reasonably well with vals. calc. from analyses and the production coeffs. of the individual constituents of rations. Revised vals. for certain production coeffs. are recorded. The productive val. of maize fodder and oat straw was greater in balanced than in unbalanced rations. The effect of a protein concentrate used to correct an unbalanced ration is greater than its actual productive energy. Grinding lucerne to a meal increased its productive energy by about 14%. A. G. P.

Relation of lime and phosphoric acid to growth and bone development of white rats. J. K. Blum (Texas Agric. Exp. Sta. Bull., 1931, No. 441, 18 pp.).—Normal growth was produced by rations having a $CaO : P_2O_5$ ratio of 1 : 1 for CaO contents of 1·0—3·0%. The min. requirements for normal growth were 0·75% CaO and 1·0% P_2O_5 in the ration. Smaller proportions of either constituent reduced growth and lowered the % ash in the femur. With 6·0% CaO and 1·5% P_2O_5, growth was normal. Rations having 6·0% P_2O_5 and 15% CaO reduced growth without an appreciable alteration of the ash content of femurs. A disproportionately high ratio of bone : total wt. was, however, produced. The ratio $CaO : P_2O_5$ in femurs bears no relationship to that in the ration. A. G. P.

Composition of growth. II. Full-term infant. W. M. Swanson (Amer. J. Dis. Children, 1932, 43, 10—18).—The retentions of K, Na, Ca, Mg, Cl, P, and N per kg. gain in wt. are higher for cow's than for human milk diet. Addition of cod-liver oil increases the Ca and P retained. Ch. Abs.

Value of an increased supply of vitamin-B_1 and iron in the diet of children. P. Summerfeldt (Amer. J. Dis. Children, 1932, 43, 284—290).—Addition to normal diet of a cereal mixture containing wheat germ and brewer's yeast (6·8 mg. Fe per day) produces 3·6—4·8 times the expected rate of gain in wt. Ch. Abs.

Utilisation of the iron of protein foods by the albino rat. A. Comparison of growth and iron assimilation as affected by different protein foods. B. Comparison of protein foods supplementary to milk as sources of iron in nutrition. R. C. Miller and E. B. Forbes (J. Nutrition, 1931, 4, 483—505).—A. Fe from pecans, beef muscle, eggs, arachis nuts, and walnuts was well, and from liver and kidney less well, utilised. B. Beef muscle, beef liver, and pecan > kidneys, eggs, and arachis nuts > walnuts and milk powder. The dry body-wt. of rats was not a significant basis of reference for Fe contents. Ch. Abs.

Bromine metabolism. I. Bromine content of blood and the influence of menstruation and of oral administration of bromine. T. Kuranami (J. Biochem. Japan, 1932, 15, 205—218).—The Br' content of whole blood of men and of women during the intermenstrual period varies between 0·51 and 0·67 mg. per 100 c.c. With menstruation the Br′ level falls to a min. at the onset, rises to a val. above normal during the period, and returns to normal at its conclusion. Oral administration of 1 g. of KBr results in an increase of blood-Br′, the return to normal occupying about 5 hr. The urinary Br′ during this period is always less than that of the blood except for the first hr., when it is much higher. The total urinary excretion is much less than the amount ingested, the small amounts of Br′ in the fæces indicating fixation in the organism. F. O. H.

Sulphur metabolism of the dog. X. Effect of *iso*barbituric acid on the excretion of neutral sulphur and ethereal sulphate. N. R. Lawrie and N. W. Pirie (Biochem. J., 1932, **26**, 622—623).—The acid does not cause the disappearance of the neutral S fraction from a dog's urine. It is readily conjugated with sulphate. S. S. Z.

Sulphur assimilation in wool growth. A. T. King (Nature, 1932, **129**, 938).—A discussion. L. S. T.

Determination of sex. III. Masculinisation of *Bonellia viridis* larvæ by traces of copper. C. Herbst (Naturwiss., 1932, **20**, 375—379).—Addition of 0·025 mg. of Cu per 100 c.c. to cultures of these larvæ in natural or artificial sea-water with or without $NaHCO_3$ causes a marked increase in the proportion of males. A. C.

Effect of thiol compounds on regeneration in *Podarke obscura*. S. Morgulis and D. E. Green (Protoplasma, 1931, **14**, 161—169).—Thio-*p*-cresol, thiophenol, thioglycollic acid, and cystine do not accelerate regenerative processes in *P. obscura*. A. G. P.

Biological significance of certain ions. VI. Action of direct current on living nerve-tissue (polarisation effect). W. W. Práwdicz-Neminski (Z. Biol., 1932, **92**, 465—481).—The effect of d.c. on a nerve or cerebrospinal cord prep. of the frog was studied in a closed chamber. A current of 0·30—0·10 milliamp. at 6·6 volts resulted in the cathodic evolution of 0·14—5·9 mg. of NH_3 per 100 g. of nerve, a val. 2—5 times that occurring at the anode. With 0·03—0·05 milliamp. NH_3 was not evolved at the anode, the formation with higher currents being due to damage of the nerve. The surviving cerebrospinal cord prep. also evolved a greater amount of NH_3 at the cathode whether situated at the medulla or sacral end. After polarisation the region at which the cathode was applied contained a diffusible alkaline substance. The mechanism of the formation of NH_3 is discussed. F. O. H.

Permeability of frogs' skin. S. Wowski (Protoplasma, 1931, **14**, 170—178).—The presence of NaCN reduces the permeability of frogs' skin to methylene-blue and this reduction is paralleled by decreased p.d. Exclusion of O_2 increases the permeability. A. G. P.

Behaviour of sodium deoxycholate and saponin towards membranes and tissue constituents. R. Labes and T. Schlenkert (Arch. exp. Path. Pharm., 1932, **166**, 186—204).—Na deoxycholate closely resembles saponin in its effect on membrane permeability. Thus it renders frog's mucous membrane permeable to substances previously not diffusible through it. At slightly acid reactions it passes into the colloidal state and loses the slight power of penetrating membranes which it exhibits at alkaline reactions. The non-toxicity of non-intravenously injected saponin and Na deoxycholate is explicable on these grounds, an additional factor being complex formation with tissue constituents. Saponin is strongly absorbed by charcoal, intestinal cells, and erythrocytes. Na deoxycholate is adsorbed by charcoal and erythrocytes, but only to a small extent by intestinal cells. The adsorption of Na deoxycholate on erythrocytes at the hæmolysis point is almost as great as that for saponin, despite the greater solution concn. of the bile salt necessary for hæmolysis. This is due to its adsorption being less than that of saponin. F. O. H.

"Anomalous osmosis" in animal cells. W. A. Dorfman (Protoplasma, 1931, **14**, 341—359).—Anomalous swelling occurs in frog erythrocytes and in sea-urchin eggs on treatment with small concns. of certain ions, notably Th. The action takes place in iso-, hyper-, or hypo-tonic solutions of electrolytes and non-electrolytes. In hypertonic NaCl solution, Th salts cause anomalous swelling of the erythrocyte nucleus which is more acid ($p_H < 5·8—5·9$) than the cell stroma. The effect is not apparent in hypertonic non-electrolyte solutions nor in iso- or hypo-tonic solutions of electrolytes. A. G. P.

Vanillylethylamine, vanillylmethylamine, and benzylvanillylethylamine: relation of chemical structure to pharmacological action. W. E. Hambourger (J. Pharm. Exp. Ther., 1932, **45**, 163—182).—4-Hydroxy-3-methoxyphenylethylamine (I) has an essentially pressor action which is, however, less than that of tyramine. 4-Benzyloxy-3-methoxyphenylethylamine (II) has a marked depressor action, whilst the effect of 4-hydroxy-3-methoxyphenylmethylamine (III) depends on the dose, being sometimes pressor and sometimes depressor. On isolated smooth muscle, (I) and (III) are predominantly and equally stimulant, whilst (II) is definitely depressant. W. O. K.

Effect of atropine and thyroidectomy on trypaflavine hyperglycæmia. R. Messina (Arch. Farm. sperim., 1932, **54**, 162—175).—Trypaflavine hyperglycæmia in rabbits is intensified by the simultaneous administration of atropine, but is diminished by thyroidectomy. Hyperglycæmia may be induced by direct stimulation of the sympathetic nerve endings as well as by exciting the excretion of adrenaline. R. K. C.

Drugs employed as antidiabetics in Chinese medicine. V. Hypoglycæmic action of phellodendronelactone. I. Action of phellodendronelactone on the normal blood-sugar content of the rabbit. II. Mechanism of the action. N. Sugihara and S. Hirano (Keijo J. Med., 1932, **3**, 160—167, 168—174; cf. A., 1931, 651).—I. Phellodendronelactone administered orally, subcutaneously, or intravenously into rabbits has a marked hypoglycæmic action.

II. It does not antagonise the hyperglycæmic action of adrenaline, but reduces the hyperglycæmia produced by injection of (10%) NaCl solution or of (8·6%) NH_4Cl solution. W. O. K.

Panax Ginseng. IX. Influence on the blood picture of rabbits. K. Kin and N. Sugihara (Keijo J. Med., 1932, 3, 1—14).—" P. Ginseng " (Ginseng extract) administered orally to rabbits increases the nos. of leucocytes and erythrocytes and also the hæmoglobin in the blood. W. O. K.

Hagedorn–Jensen method of blood-sugar determination in phloridzin diabetes. S. Yamada (J. Biochem. Japan, 1932, 15, 311—318).—Phloridzin reduces $K_3Fe(CN)_6$ at room temp. and reacts with I. Hence determinations of the blood-sugar following phloridzin administration are erroneous when the methods employed depend on the use of these reagents. Thus phloridzin apparently effects a hyperglycæmia in rabbits if the blood-sugar is followed by the Hagedorn–Jensen method, but determinations by a Cu method indicate a hypoglycæmia. F. O. H.

Fat transport through the lymph system in fasting and phloridzin poisoning. H. R. Rony, B. Mortimer, and A. C. Ivy (J. Biol. Chem., 1932, **96**, 737—743).—Lymph from the thoracic duct of fasting and phloridzinised dogs contains large amounts of fat; the vals. are greater than the corresponding blood-vals. Since the sugar content of such lymph is far less than that of the blood or of normal lymph, fat is not mobilised and transported as sugar. The findings favour the possibility that fat is transported through the lymph system. A. C.

Examination for narcotic drugs. Coulouma (Ann. Falsif., 1932, 25, 201—204).—The lethal dose of cocaine for guinea-pigs is 0·05 g., and for morphine 0·1 g. per 250 g. body-wt. Heroin and dionine have $[\alpha]_D$ −75° and −97°, respectively. T. McL.

Poisoning by percaine. F. Riechen (Z. Unters. Lebensm., 1932, 63, 557—560).—Symptoms of poisoning, distribution of the drug in the organs, chemical reactions, and distinction from cocaine are described. E. B. H.

Colloid chemistry of nervous systems. IV. W. D. Bancroft, R. S. Gutsell, and J. E. Rutzler, jun. (J. Physical Chem., 1932, **36**, 1521—1548; cf. this vol., 191).—Small increasing amounts of morphine were administered to dogs, and shortly before the abrupt withdrawal of morphine some of the dogs were given NaCNS (a peptising agent). Those receiving NaCNS showed no withdrawal symptoms, whilst those not receiving it showed symptoms. NaCNS may therefore be expected to counteract (in part) the effects of morphine. C. T. S. (*b*)

Disturbance of carbohydrate and acid–base economy and of gaseous exchange in avertin narcosis. H. Fuss and E. Derra (Klin. Woch., 1932, 11, 19—21; Chem. Zentr., 1932, i, 1118).—Experiments in which O_2 or CO_2 were also administered are described. The CO_2 val. of arterial blood is affected in opposite directions by the fall in alkali reserve and the difficulty of breathing. Increase in blood-CO_2 diminishes the blood-lactic acid. A. A. E.

Influence of diet on carbon tetrachloride intoxication in dogs. J. T. Cutler (J. Pharm. Exp. Ther., 1932, **45**, 209—226).—Dogs on various diets, (*a*) poor in carbohydrate and Ca, (*b*) poor in carbohydrate and rich in Ca, (*c*) rich in carbohydrate and Ca, (*d*) rich in carbohydrate but poor in Ca, and (*e*) very rich in fat, were subjected to poisoning with CCl_4, but exhibited no significant differences in the degree of liver damage. The degree of intoxication and the death rate, however, varied markedly according to diet, being very high with diet (*a*), moderate with (*d*) and (*e*), and low with (*b*) and (*c*). Ca and carbohydrate have therefore a protective action, whilst meat protein is deleterious, presumably as the result of its giving rise to guanidine (cf. A., 1931, 651). W. O. K.

Toxicology of the carbonyls. A. J. Amor (J. Ind. Hygiene, 1932, **14**, 216—221).—A review of symptoms, pathology, diagnosis, treatment, and prognosis of poisoning by $Ni(CO)_4$. Safety measures are also discussed. W. O. K.

Antimony salt of sodium β-hydroxy-γ-thiolpropanesulphonate. A. Leulier, M. Juvin, and H. Tête (J. Pharm. Chim., 1932, [viii], 15, 593—597; cf. this vol., 192).—This salt injected into guinea-pigs is excreted mainly in the urine, and to a smaller extent in the fæces. Some is deposited in the liver and kidneys, considerable amounts being found in the former organ if death precedes urination. J. W. B.

[Pharmacology of the] quinoline series. II. W. Heubner. **III. Action of orally administered yatren in diseased animals.** B. Weicker. **IV. Yatren.** H. Nahme and K. Seelkopf. **V. Quinolinesulphonic acids.** K. Seelkopf and H. Nahme. **VI. Benzenesulphonic acids.** H. Nahme. **VII. Carboxylic acids.** F. Grabe and K. Seelkopf. **VIII. Hydroxy- and hydroxyallyl-quinoline.** K. Seelkopf, F. Bender, H. Nahme, and E. Schulze. **IX. Hydroxyquinolinium bases.** F. Grabe, H. Nahme, and K. Seelkopf. **X. Di-iodo-derivatives.** A. Palm (Arch. exp. Path. Pharm., 1932, **166**, 117—122, 123—125, 126—149, 150—156, 157—160, 161—165, 166—171, 172—175, 176—185; cf. A., 1929, 214).—II. The pharmacological action of some quinoline derivatives and allied substances is discussed.

III. Oral administration of yatren to healthy rabbits produces a slight and variable change in the leucocyte count, whereas in rabbits which have previously been subcutaneously injected with turpentine there is a significant increase, the extent of which is dependent on the period between the time of administration of turpentine and that of yatren.

IV. Intravenous injection of yatren into dogs is followed by the excretion of 70—90% of the I injected, the proportions appearing in the urine and fæces being dependent on the amount administered. In the starving dog the excretion of I is slow and mainly in the fæces, the urinary I suddenly increasing on feeding with a protein-free diet. The differences between I-excretion with NaI and that with yatren indicate that with the latter I is excreted as an aromatic compound. The effect of yatren on the basal and protein metabolism, the body temp., and the *R.Q.* of dogs is described.

V. The effect of oral administration of the following compounds on the N-excretion, basal metabolism, and *R.Q.* of dogs was investigated: 5-chloro-8-hydroxyquinoline-7-sulphonic acid; 8-hydroxyquinoline-5-sulphonic acid; 8-hydroxy-7-propylquinoline-5-sulphonic acid; and quinoline-8-sulphonic acid.

VI. The excretion of N, SO_4, and total S following oral administration of the Na or K salts of the following sulphonic acids was determined: benzene-; phenol-*p*-; guaiacol- (a mixture of the 1-hydroxy-2-methoxy-4- and -5-sulphonic acids); and propylguaiacol- (a mixture of 1-hydroxy-2-methoxy-4-propyl-5-sulphonic and -5-propyl-4-sulphonic acids).

VII. The excretion of N following administration of Li 8-hydroxyquinoline-7-carboxylate, Na acetyl-8-hydroxyquinoline-7-carboxylate, and salicylic acid (for which the changes in basal metabolism and *R.Q.* were also followed) was investigated in dogs.

VIII. The changes in urinary urea, basal metabolism, and in the amount and character of the bile, due to oral administration of 8-hydroxyquinoline and its 7-allyl derivative were investigated in dogs with biliary fistulæ.

IX. The N excretion, basal metabolism, and *R.Q.* following oral administration of 8-hydroxyquinoline methochloride were followed in fed and starving dogs. The toxicity of this substance and also that of 8-hydroxy-7-propyl- and -7-allyl-quinoline to rats and mice were determined.

X. Oral administration of 5:7-di-iodo-8-hydroxyquinoline in rabbits is followed by the excretion of up to 90% of the I given. That the excreted I is to a certain extent differently combined in fæces and urine is shown by the difference in the partition of I on C_6H_6 extraction. Examination of the urine indicates that in the organism I is not removed from its quinoline compound, which is excreted in the form of derivatives, of which at least one is a glycuronic ester. With di-iodotyrosine the main excretion of I is in the urine, the organism retaining 10% the distribution of which is determined. With thyroxine, however, the main excretion of I is in the fæces while the body retention is greater. F. O. H.

Physiological properties of neriin and other *Nerium oleander* glucosides. H. Simonnet and G. Tanret (Bull. Soc. Chim. biol., 1932, 14, 724—744).—Neriin is sol. in H_2O and is similar in action to the strophanthin and ouabain groups, being rapid in action and quickly eliminated. A normal dose for the dog is 0·25 mg. per kg. body-wt. The hydrolysis product of neriin, nerigenin, is more toxic. Oleandrin is insol. in H_2O, produces a rise in blood-pressure, and has a weaker diuretic and heart-slowing action. H. D.

Relationships between the Ca and K ion equilibrium and antirheumatic drugs. II. K. In (Keijo J. Med., 1932, 3, 125—137).—After the administration of certain antipyretic drugs to infected rabbits, the Ca content of the blood rises, whilst the K content tends to fall, the original concns. being regained after several hr. W. O. K.

Changes in the blood-sugar due to various degrees of experimental shock. R. Grün and H. Reinwein (Arch. exp. Path. Pharm., 1932, 166, 366—370).—Anaphylactic shock induced in guinea-pigs by injections of Witte's peptone, albumin, or horse-serum is attended by a fall in the blood-sugar, the extent of which, however, is not sufficiently great to permit correlation with that of the shock but appears to depend on the substance producing it. Injection of proteins is followed by a fall in the blood-sugar of a type different from that due to guanidine and its derivatives. F. O. H.

Toxicological detection of hydrogen cyanide. J. A. Klaassen (Pharm. Weekblad, 1932, 69, 655—680).—For the detection of HCN the Prussian-blue reaction is recommended whenever practicable, but the microchemical AgCN reaction provides a valuable preliminary test. For determination of HCN in fresh organs, many methods are satisfactory, but when decomp. has progressed somewhat Schulek's method (BrCN formation) is the best. The reaction between reducing sugars and HCN, the formation of the latter in decaying corpses by the action of bacteria, and the conversion of HCN into CNS derivatives in living and dead organisms are discussed. H. F. G.

Biochemistry of aluminium. III. Effect of aluminium on growth and reproduction of the rat. IV. Occurrence of aluminium in the thyroid. V. Intestinal absorption of aluminium in the rabbit. K. Mackenzie (Biochem. J., 1932, 26, 833—845).—Al additions to the diet have no perceptible influence when the diet is adequate for growth and reproduction in the rat, when the diet is insufficient for growth or maintenance, or when fed to several successive generations of rats. Al absorption from such diets is exceedingly small. Al occurs only in very small quantities in the thyroid and is not correlated with I in normal metabolism. Injection of Al salts into the intestine of rabbits does not cause appreciable absorption of Al into the blood stream. S. S. Z.

Toxicological identification of antimony. C. Palmeri (L'Ind. Chimica, 1932, 7, 567—572).—If HCl and $KClO_3$ are used in the oxidation of org. matter $SbCl_3$ is formed which on diluting and treating with H_2SO_4, to separate Pb and Ba, may be almost completely pptd. as SbOCl, thus escaping identification. Oxidation by HNO_3 and NO_2 is preferred. From the oxidised liquid $PbSO_4$, $BaSO_4$, and H_3SbO_4 are pptd. with dil. H_2SO_4. The ppt. is treated with NH_4OAc and NH_3 which dissolve $PbSO_4$, the residue is washed with NH_4OAc solution, suspended in dil. aq. NH_3, and treated with H_2S, $BaSO_4$ is filtered off, and the filtrate, when acidified with H_2SO_4, gives the characteristic Sb_2S_3 ppt. O. F. L.

Renal threshold for hæmoglobin in dogs uninfluenced by mercury poisoning. W. H. Havill, J. A. Lichty, jun., G. B. Taylor, and G. H. Whipple (J. Exp. Med., 1932, 55, 617—625).—The min. or depression renal threshold for dog hæmoglobin is not modified by moderate doses of $HgCl_2$. Ch. Abs.

Tolerance for mercury poisoning increased by frequent hæmoglobin injections. W. H.

Havill, J. A. Lichty, jun., and G. H. Whipple (J. Exp. Med., 1932, 55, 627—635).—Deposition of pigment in the renal tubular epithelium resulting from injection of superthreshold amounts of dog hæmoglobin permits survival of lethal doses of $HgCl_2$ with little evidence of renal injury. Ch. Abs.

Bile acid metabolism. VII. Bile- and bile acid-secretion in cholecystography with sodium tetraiodophenolphthalein. H. Mikami (J. Biochem. Japan, 1932, 15, 219—228).—Intravenous injection of the substance into dogs with biliary fistulæ produces a small but prolonged increase in bile secretion, whilst the amount of bile acids is decreased. The bilirubin content first decreases and then increases to a level approx. twice that of the normal. The extensive variation in the bile acid/bilirubin ratio indicates that the secretions of the two substances are in no way related. F. O. H.

Absorption of compound solution of iodine from the gastro-intestinal tract: absorption of free iodine. B. N. E. Cohn (Arch. Int. Med., 1932, 49, 950—956).—In anæsthetised dogs the absorption of I from the colon or small intestine is probably preceded by its conversion into iodide. W. O. K.

Graphic correlation of radiation and biological data. F. S. Brackett (Smithsonian Misc. Coll., 1932, 87, No. 8, 1—7).—The transmission curves of H_2O and O_3 for light of different wave-length are correlated with corresponding curves obtained for the emission from heated bodies, from the sun, and from the Hg arc in quartz; also with those of the transmitting power of flesh, relative visibility of the human eye, relative phototropic response of oat seedlings, absorption band for ergosterol, and the erythema response of the human skin. A. L.

Recent advances in the study of enzymes. B. Woolf (Nature, 1932, 129, 928—930).—A summary of a recent discussion. L. S. T.

Determination of enzyme action. A. K. Balls (J. Assoc. Off. Agric. Chem., 1932, 15, 131—136).—Physico-chemical principles are discussed. W. J. B.

Dilatometric studies in enzyme action. II. Contraction constants of enzyme–substrate reactions. M. Sreenivasaya and H. B. Sreerangachar (J. Indian Inst. Sci., 1932, 15A, 17—24; cf. A., 1929, 1488).—A new type of dilatometer in which the substrate and enzyme are mixed within the vessel itself is described. Immediately on mixing enzyme–substrate systems there occurs an increase or a decrease in the total vol. Following the determination of the "contraction const." for urea–urease and arginine–arginase systems, the apparatus may be applied to the determination of urea and arginine in physiological fluids and protein hydrolysates. F. O. H.

Co-enzymes, hydrogen donators, and arsenic poisoning of cell respiration. H. Handovsky (Biochem. Z., 1932, 249, 195).—Criticism of the technique of Banga and Szent-Györgyi (this vol., 537). P. W. C.

Oxidation–reduction potential. Action of anions on succinodehydrogenase. L. Pincussen and J. Görne (Biochem. Z., 1932, 249, 130—140).—An active sample of the enzyme can be prepared from horse flesh without use of phosphate as eluting agent. Halogens in sufficient concn. injure the enzyme, the degree of injury being $Cl<Br<I$. The action of KF cannot be compared, since this substance displaces the p_H into the inactive range. P. W. C.

Kinetics of fumarase. K. P. Jacobsohn, J. Tapadinhas, and F. B. Pereira (Biochem. Z., 1932, 249, 72—74).—An equation is given for determination of the combined velocity coeffs. of a reversible equilibrium, and some preliminary results obtained with rabbit's-liver fumarase indicate its validity. P. W. C.

***o*-Quinones as enzyme models. IV. Catalysts inactive at p_H 6—8.** B. Kisch (Biochem. Z., 1932, 249, 63—71).—Quinol, benzoquinone, protocatechuic acid, pyrogallol, phloroglucinol, and homogentisic acid, although unable to effect oxidative deamination at p_H 6—8, cause a feeble deamination at p_H 9—12. At this p_H, resorcinol is very active and gives 50% of the theoretical amount of NH_3 from glycine. The extent of deamination decreases in the series glycine>serine>phenylglycine>leucine. Little or no deamination occurs with alanine, α-aminobutyric acid, valine, *iso*leucine, nor under the action of orcinol, isatin, alloxan, and ethylene glycol. P. W. C.

Decomposition of hydrogen peroxide by catalase. D. Richter (Nature, 1932, 129, 870).—Comparison with the photochemical decomp. indicates that the enzyme reaction is a chain reaction in which the active centres of the enzyme function only by starting the chains, which then continue in the solution or on other surfaces. The inhibition of enzyme reactions may be due in certain cases to the rupture of the reaction chains by the inhibitors. L. S. T.

Hydrogenlyases. Bacterial enzymes liberating molecular hydrogen. M. Stephenson and L. H. Stickland (Biochem. J., 1932, 26, 712—724).—These enzymes are distinct from formic dehydrogenase and from hydrogenase. In the case of *B. coli* formic hydrogenlyase is formed only when the organism is grown in the presence of formate. Its formation is not due to the partly anaërobic conditions of its production or to the p_H of the medium. Its optimum rate of action is at p_H 7 and it shows a much lower affinity than formic dehydrogenase. The enzyme is very sensitive to poisons and KNO_3 inhibits its production of H_2. In *B. coli* it produces the theoretical amount of H_2 from formate. Formic hydrogenlyase is distinct from the hydrogenlyases liberating H_2 from the sugars. The evolution of H_2 from glucose does not occur through HCO_2H as an intermediate product. S. S. Z.

Reduction of glutathione by a liver-system. P. J. G. Mann (Biochem. J., 1932, 26, 785—790).—It is reduced by glucose in presence of glucose dehydrogenase from liver. The reaction proceeds slowly, and is greatly accelerated by an activator, sol. in H_2O, insol. in EtOH, present in the liver. S. S. Z.

Reduction of glutathione in mammalian erythrocytes. N. U. Meldrum (Biochem. J., 1932, 26, 817—828).—In the intact erythrocyte the glutathione present undergoes a slow oxidation and a much more rapid reduction. *In vitro* the reduction takes place when glucose is added to a suspension of intact corpuscles. Other hexoses as well as maltose possess the power of reduction. Non-reducing sugars and hexahydric alcohols cause no reduction. Pentoses reduce very feebly. S. S. Z.

Structure and enzyme reactions. XI. Action of salts in the systems starch–amylase–proteins. G. Baumgarten (Biochem. J., 1932, 26, 539—542).—In the case of taka-diastase considerable activation takes place with $CaCl_2$ at p_H 8·85. This activation is less at p_H 8·1; at p_H 6·5 there is no increase in the velocity of the reaction and at p_H 4·7 there is a retardation. The accelerating effect of $CaCl_2$ is much smaller in the presence of NaCl or KCl. The augmented production of reducing sugars in the presence of $CaCl_2$ at p_H 8·85 is relatively much greater than the augmented hydrolysis of starch under analogous conditions. NaCl alone accelerates the reaction at various p_H vals., but to a smaller extent than $CaCl_2$. With salivary amylase the action of NaCl may be accelerating or retarding according to its concn. This reaction is retarded by $CaCl_2$ both in the presence or absence of NaCl or KCl and in the presence of either sol. or heat-coagulated egg-white. S. S. Z.

Limit of hydrolysis of starch by malt-amylase. S. Pronin (Biochem. Z., 1932, 249, 7—10).—The limit of hydrolysis of sol. starch by malt-amylase depends on the amount of malt extract added and may amount to 74·9—95·88% (cf. Pringsheim and Schmalz, A., 1924, i, 106). P. W. C.

Influence of guanidine and its derivatives on the action of amylase. E. M. Mystkowski (Biochem. J., 1932, 26, 910—914).—Guanidine and creatine retard and creatinine accelerates enzymic amylolysis, the effect obtained being proportional to concn. of the substance studied. The effects are of the same order in the hydrolysis of starch or glycogen by vegetable or by salivary amylase. When both accelerating and retarding substances (glycine and guanidine) are present together, the resultant velocity of reaction is the mean of the velocities which would be obtained in the presence of each substance separately. S. S. Z.

Exponential analysis applied to the asymmetric hydrolysis of some β-glucosides with emulsin. S. Mitchell and I. MacArthur.—See this vol., 816.

Co-enzyme system of lactic acid formation. O. Meyerhof and K. Lohmann (Naturwiss., 1932, 20, 387—390).—A review (cf. A., 1931, 654, 1184). A. C.

Determination of lipase. B. Umschweif (Biochem. Z., 1932, 249, 75—82).—The usual Willstätter method is critically examined and the stability of pancreatic enzyme preps. on keeping and against acid investigated. P. W. C.

Rennin. I. Purification of rennin and its separation from pepsin. II. Isolation of prorennin. H. Tauber and I. S. Kleiner (J. Biol. Chem., 1932, 96, 745—753, 755—758).—I. A highly-active rennin is obtained from the fourth stomach of the calf by fractional pptn. from feebly acid aq. EtOH. Its isoelectric point is p_H 5·4, Cl and P are absent, and it is irreversibly inactivated by alkali. In these and other respects it differs from cryst. pepsin, although the latter has rennin activity, and appears to be a thioproteose.

II. From the mucosa of the calf's fourth stomach an inactive precursor of rennin is obtained by pptn. from a $CaCO_3$ extract with $MgSO_4$ as a H_2O-sol. substance which is activated by HCl at p_H 1. A. C.

Intracellular enzymes of tissues and glands. I. Desmo-pepsin and desmo-cathepsin. R. Willstätter and M. Rohdewald (Z. physiol. Chem., 1932, 208, 258—272).—The $COMe_2$-dried material (pig's intestinal mucosa) is extracted repeatedly with 100% glycerol below 3°. The residue is washed with 50% glycerol and dried with $COMe_2$, EtOH, and Et_2O after each extraction. This removes the lyo- and leaves the desmo-pepsin. The latter is rendered sol. by 0·1% HCl or by autolysis. Desmo-cathepsin is also present in the fully active condition, no added kinase being required. Active pepsin solutions were obtained showing no reaction for protein. J. H. B.

Non-applicability of the Schütz–Borissow law in the determination of pepsin activity by Mett's method. J. Patterson and J. Adler (Brit. J. Exp. Path., 1932, 13, 72—75).—The tubes (1·5 mm. diameter) should be prepared according to Christiansen's method, and very dil. pepsin solutions should be incubated for several days before the reading is taken. The pepsin concn. is proportional to the cube of the length digested. Ch. Abs.

(*a*) Number and kind of proteolytic enzymes of pancreatic juice. (*b*) Proteolytic enzymes of intestinal and pancreatic juice. F. Mocoroa (Anal. Fís. Quím., 1932, 30, 302—304, 305—306).—(*a*) Pancreatic juice attacks scombrin and chloroacetyltyrosine directly, and caseinogen after addition of kinase, but not di- or tri-peptides. It therefore contains, apart from prokinase, only tryptic enzymes, an inactive proteinase and carboxypolypeptidase, but none of the ereptic enzymes which, although found in extracts of the gland, are endocellular.

(*b*) Contrary to Waldschmidt-Leitz and Waldschmidt-Graser (A., 1927, 698), only abnormal pancreatic juices contain kinase or ereptic enzymes, and intestinal secretion contains enterokinase as well as ereptic enzymes. R. K. C.

Formation of enterokinase from a precursor in the pancreas. J. Pace (Biochem. J., 1932, 26, 640—649).—The separation from pancreas extracts of a pre-stage of enterokinase, which gives rise to an enterokinase resembling that usually obtained from intestinal mucous membrane, is confirmed (Waldschmidt-Leitz and Harteneck, A., 1926, 323). The rate of formation of enterokinase agrees with that of a unimol. reaction. The optimum p_H of formation is about p_H 6·5—7·0. S. S. Z.

Enzymic degradation of guanylic acid in rabbit's liver. G. Schmidt (Z. physiol. Chem., 1932, 208, 185—224).—All the derivatives of guanylic acid containing guanine are deaminated by rabbit's liver; with guanylic acid the NH_2-group of the guanine nucleus is eliminated without previous removal of the H_3PO_4. NH_3 and purine are always formed in equiv. amounts. In the deamination of the guanine nucleus in guanylic acid, guanosine, and guanine at least two enzymes are concerned: guanase (optimum p_H 9·2) and an enzyme attacking guanylic acid (optimum p_H 5·3). The guanase was obtained free from the second enzyme by adsorption methods. The deamination of guanylic acid is inhibited by low concns. (0·0025N), that of guanine only by high concns. (0·1N) of NaF. Both guanase and adenosine-deaminase (optimum p_H 6·2) are highly sp. enzymes; the deamination curves up to 50% fission are linear. Guanylic acid phosphatase was separated from the liver deaminases. It is inhibited by NaF at 0·001N and has two p_H optima, 5—6 and 9. It is affected by an inhibitor in rabbit liver which is most active at about p_H 7. Inosic acid phosphatase has only the alkaline p_H optimum at 9. J. H. B.

Uricolysis. II. W. SCHULER (Z. physiol. Chem., 1932, 208, 237—248; cf. A., 1929, 217).—"Urico-oxidase," the enzyme responsible for the oxidation of uric acid in conversion of the latter into allantoin by the agency of uricase, was extracted from dried liver powder, but could not be further purified by the usual methods. The oxidised product, which was not isolated, is a stronger acid than uric acid, easily loses CO_2 in acid solution, eliminates urea in conc. AcOH solution, and gives the Fosse–Bossuyt reaction for allantoin. Uric acid riboside is not hydrolysed by urico-oxidase. J. H. B.

Is there a co-enzyme for urease? J. B. SUMNER and J. S. KIRK (Biochem. J., 1932, 26, 551—554).—A mixture of active and inactivated urease produces only slightly more NH_3 from urea than active urease alone. If traces of heavy metal are present urease is inactivated less readily in the presence of boiled urease than in its absence. When to cryst. or impure soya-bean urease dialysed urease is added in distilled water, the mixture possesses exactly the sum of the activity of the two components. The slightly higher activity of the second mixture observed by Onodera (A., 1916, i, 228) is due not to the function of a co-enzyme, but probably to the protection of urease against heavy metal impurities. S. S. Z.

Plasma-phosphatase. III. Clinical determination. H. D. JENNER and H. D. KAY (Brit. J. Exp. Path., 1932, 13, 22—27).—A colorimetric method requiring 1—2 c.c. is described. CH. ABS.

Inhibition of kidney-phosphatase by phosphate. E. JACOBSEN (Biochem. Z., 1932, 249, 21—38).—The velocity of hydrolysis in the system glycerophosphate, kidney-phosphatase, and PO_4''' and its dependence on the substrate- and inorg.-PO_4''' concns. are determined. The velocity of hydrolysis is chiefly determined by the separated PO_4'''. P. W. C.

Influence of arsenate on phosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 23—25).—Addition of K_3AsO_4 promotes the cleavage of glucosephosphate and glycerophosphate by takadiastase, but does not activate the synthetic action of the takaphosphatase on solutions of Na_2HPO_4 and glucose or glycerol. CH. ABS.

Behaviour of the phosphorus fractions during autolysis of organs. T. TEORELL and B. NORBERG (Biochem. Z., 1932, 249, 53—62).—The direct P (phosphagen+PO_4'''), residual acid-sol. P (adenosine triphosphate+hexosephosphate), phosphatido-P, and residual P (nucleic acid-P) fractions before and during slow autolysis (at 3—4°) of cat's gastric mucosa, liver, kidney, spleen, pancreas, heart, and striated muscle were determined. The direct P is increased at the expense of the residual acid-sol. P and the lipoid P, but the residual P is scarcely or not affected. The high phosphatase content of the kidney and lecithase content of the pancreas are seen in the very rapid hydrolysis of their corresponding substrates. P. W. C.

Yeast and fermentation. C. R. BOND (Food Tech., 1932, 1, 389—392).—A description of the different yeasts, their requirements for growth, and their various uses is given. E. B. H.

Esterification of arsenic acid by yeast. A. E. BRAUNSTEIN and M. M. LEVITOV (Naturwiss., 1932, 20, 471).—In fermentation experiments in which AsO_4 replaced PO_4, determination of AsO_4, before and after acid hydrolysis, showed that up to 15% of As was in combination as hexosearsenic acid. $CH_2Br·CO_2H$ inhibited the process. A. L.

Osmophilic yeasts. IV. N. KARAMBOLOFF and G. KRUMBHOLZ (Arch. Mikrobiol., 1931, 3, 113—121).—An organism (*Zygosaccharomyces gracilis*) isolated from incompletely fermented Portuguese wine tolerates higher sugar concns. than *Z. variabilis* and ferments glucose, fructose, maltose, and, to a small extent, galactose. Sucrose is fermented only by the crushed cells. A. G. P.

Degradation of aromatic and hydroaromatic compounds by moulds. I. Decomposition of quinic and hydroxybenzoic acids. K. BERNHAUER and H. H. WAELSCH (Biochem. Z., 1932, 249, 223—226).—A series of 28 strains of *A. niger* was grown on a medium containing quinic acid and a mixture of salts in order to follow its conversion by way of protocatechuic acid and pyrocatechol into $H_2C_2O_4$. Three strains on the 4th day gave a green colour with $FeCl_3$ which became red on adding Na_2CO_3. Only one strain gave the reaction on the 6th day and none on the 7th. $H_2C_2O_4$ tests became positive on the 9th—10th day. Inositol, pyrocatechol, quinol, gallic and salicylic acids similarly gave rise to $H_2C_2O_4$. P. W. C.

Relation between [H˙] and citric acid formation by *Aspergillus niger* and *Citromyces glaber*. A. FREY (Arch. Mikrobiol., 1931, 3, 158; cf. A., 1931, 1333).—Differences in optimum p_H for citric acid production recorded by the author and by Virtanen are not wider than might be anticipated for different strains of the fungus. A. G. P.

Influence of aluminium on the development of *Aspergillus niger*. G. LÉVY (Bull. Soc. Chim. biol., 1932, 14, 745—757).—Al is not essential for the growth of *A niger*. Concns. of 0·005—200 mg. per litre of medium have no effect whilst a concn. of 350 mg. per litre completely inhibits growth. H. D.

Effect of associated growth on forms of lactic acid produced by certain bacteria. E. L. Tatum, W. H. Peterson, and E. B. Fred (Biochem. J., 1932, **26**, 846—852).—Lactic acid bacteria which when grown by themselves produce only *d*- or *l*-acid, produce *i*-lactic acid when grown in association with *Cl. acetobutylicum*. This effect is not obtained when the two organisms are separated by a viscose membrane. Closely related butyric acid bacteria or *S. cerevisiæ* do not change the form of lactic acid. S. S. Z.

Physiology and systematics of acetic acid bacteria. M. Krehan (Arch. Mikrobiol., 1932, **3**, 277—321).—In sugar-free asparagine media addition of salts of Na, K, Ca, and Mg markedly affects the oxidation of EtOH by *B. acetigenoideum* and the growth of the organism. By this means AcOH production may be varied from zero to the max. (90% of theoretical), or the acid produced may be further oxidised to CO_2. In general, the ions $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, H_2PO_4', and Cl' favour, and $K^{\cdot}$, $Na^{\cdot}$, and SO_4'' retard AcOH production. At very low concns. all salts show optimum effects between 0·005 and 0·00001*N*. A. G. P.

Ergosterol content of certain species of mycobacterium and the effect of ergosterol on their growth. P. S. Prickett and O. N. Massengale (J. Infect. Dis., 1931, **49**, 297—302).—No ergosterol was found in 9 cultures of 6 species in 5% glycerol nutrient agar. Addition of unactivated ergosterol stimulated growth and pigment production; activated ergosterol in high concn. retarded growth but stimulated pigment production. Pathogenic strains of *M. tuberculosis* were more sensitive to activated ergosterol than non-pathogenic strains. Ch. Abs.

Bacteriological action of certain synthetic organic acids toward *Mycobacterium lepræ* and other acid-fast bacteria. XXI. W. M. Stanley, G. H. Coleman, C. M. Greer, J. Sacks, and R. Adams (J. Pharm. Exp. Ther., 1932, **45**, 121—162).—Of many Na salts of aliphatic monocarboxylic acids tested *in vitro* on *B. lepræ* growing in 5% glycerol broth, the bactericidal action is most marked in those containing 15—18 C atoms. The presence of an ethylenic linking is not advantageous, but a branched chain or ring structure is favourable, rings of 3—6 C atoms being equally effective, provided the total mol. wt. remains approx. const. A Ph group with or without an additional ethylenic linking does not enhance the activity. Aliphatic amines containing 16—18 C atoms including a ring structure are active, but less so than the corresponding carboxylic acids. Some of the Na salts which are active against *B. lepræ* in concns. of 1 in 150,000 to 1 in 200,000 are also bactericidal to *B. tuberculosis*, but only in concns. at least 3 times as great. The bactericidal activity is probably chiefly dependent on the physical properties of the acids and in particular is correlated with the power of the Na salts to lower the surface tension of aq. solutions. W. O. K.

Chemical and biological properties of the phosphatide from the tubercle bacillus. C. H. Boissevain and C. T. Ryder (Amer. Rev. Tuberculosis, 1931, **24**, 751—756).—The separation of Anderson's phosphatide A3 from bacteria and bacterial debris is described. Intraperitoneal injection of the purified phosphatide does not cause the formation of tuberculous tissue or the appearance of cutaneous hypersensitiveness. The tissue reaction to phthioic acid is a foreign-body reaction. Ch. Abs.

Bacterial derivatives. XV. Changes in chemical and biological properties of human tubercle bacillus polysaccharide MB-200 produced by mild acid hydrolysis. K. L. McAlpine and P. Masucci. **XVI. Differential chemical changes accompanying the growth of human tubercle bacillus H 37 and bovine tubercle bacillus 523 grown on Long's synthetic medium.** P. Masucci, K. L. McAlpine, and J. T. Glenn (Amer. Rev. Tuberculosis, 1931, **24**, 729—736, 737—745).—XV. A fraction insol. in EtOH contained much mannose with little free reducing sugar; one sol. in EtOH contained most of the arabinose and much free reducing sugar. Destruction of the precipitin titre is more rapid than the cleavage of the polysaccharide into simple sugars.

XVI. Substances which react with human tubercle bacillus bacillary serum and produce a ppt. appear in the medium. Quant. differences in precipitin titre are discussed. A quant. measure of the pentose radical is an index of the precipitin titre. Some of the pentose in the bovine filtrate is probably free. Ch. Abs.

Oxygen optimum and media for "aërobic" bacteria. H. Zycha (Arch. Mikrobiol., 1932, **3**, 194—204).—In certain media of low nutrient content, nodule bacteria and also *B. prodigiosus* exhibit a growth optimum at O_2 tensions less than atm. For such organisms the term "meso-aërobe" instead of "facultative anaërobe" is suggested. A. G. P.

Metabolic studies of streptococci. M. A. Farrell and S. Thomas (J. Infect. Dis., 1932, **50**, 134—142).—N as NH_4, asparagine, or uric acid did not stimulate or support the growth of *S. rheumaticus*. When rhamnose, fructose, or galactose was added to a non-protein source of N growth was secured to the third transplant. Some NH_2-acids were antagonistic to growth. Glucose lessens the antagonistic action of tyrosine, tryptophan, and phenylalanine. Ch. Abs.

Nitrogen fixation by *Leguminosæ*. I. Nitrogen fixation studies of *Rhizobia* apart from the host plant. P. W. Wilson, E. W. Hopkins, and E. B. Fred (Arch. Mikrobiol., 1932, **3**, 322—340).—No evidence was obtained of the fixation of N by nodule bacteria apart from the host plant, whether grown in pure culture or in association with other organisms or with respiring plant-tissue. Stimulatory effects of Mn on the organism were not confirmed. A. G. P.

Bacteriophage and the root nodule bacteria. D. G. Laird (Arch. Mikrobiol., 1932, **3**, 159—193).—The bacteriophage is not sp. to one strain or species of *Rhizobium*. The optimum p_H is 7·6—8·0. Gum produced by the bacteria inhibits bacteriolysis. Mannitol favours both gum formation and acid production. A. G. P.

Morphology and physiology of the purple and green sulphur bacteria. C. B. van Niel (Arch. Mikrobiol., 1931, 3, 1—112).—In the media used the development of these organisms is dependent on the concn. of H_2S, $NaHCO_3$, and $H^{\cdot}$. In many cases the proportion of undissociated H_2S determines whether or not particular species can develop. The metabolism of the organisms is a true photosynthetic process, probably of the type $CO_2+2H_2S=CH_2O+H_2O+2S$. Green S bacteria produce S only, but the purple species under favourable conditions oxidise H_2S, S, S_2O_3'', and SO_3'' completely to SO_4''. This oxidation is associated with an equiv. reduction of CO_2. In the absence of oxidisable S compounds the purple organism develops under anaërobic conditions in presence of org. matter provided it receives radiant energy. No growth occurs in presence of O_2 or in the dark. A. G. P.

Pigment related to prodigiosin in a pathogenic actinomyces. A. Sartory, R. Sartory, J. Meyer, and M. Antonioli (Compt. rend., 1932, 194, 2339—2340).—The pigment isolated from *A. Allenbachii* by treatment of the cultures with 95% aq. EtOH, pptn. with H_2O, and extraction with Et_2O shows colour changes with aq. NH_3 and 0·1*N*-NaOH identical with those given by prodigiosin, and gives three absorption bands with max. at 5280, 4960, and 4700 Å. A. L.

Production of fluorescence by phytopathogenic bacteria. F. Labrousse (Compt. rend., 1932, 194, 2173—2175).—*B. tabacum* and *B. medicaginis* (var. *phaseolicola*) when grown on a beef extract medium give rise to a definite fluorescence, but only when Mg and phosphate are present. W. O. K.

Significance of accessory nutrients for the typhus-coli group. Sugimoto (Arch. Hyg., 1931, 106, 185—196; Chem. Zentr., 1932, i, 1111).—Growth is favoured by Na citrate, fructose, and EtOH as well as by lemon juice and an Et_2O extract of lemon peel; sp. activity of accessory materials is unlikely. A. A. E.

Quantitative basis of the specific precipitin reaction. T. J. Kurotchkin and C. O. Kratze (Chinese Med. J., 1932, 46, 387—403).—The reaction between the sp. carbohydrate antigen of *Monilia tropicalis* and its antigen (serum of rabbits immunised with killed *M. tropicalis*) has been followed quantitatively by determining the amount of carbohydrate left uncombined when a given concn. of carbohydrate is mixed with a given concn. of antibody. Over a certain range the results are expressed by the usual adsorption formula. W. O. K.

Immunological reactions between dextran polysaccharide and some bacterial antisera. J. Zozaya (J. Exp. Med., 1932, 55, 353—360).—Dextran, produced from sucrose by *Leuconostoc mesenterioides*, reacts immunologically with antisera from pneumococci, some species of *Salmonella*, and some types of *Streptococcus viridans* (Bargen). The existence of a distinct antibody produced by an active group of the sp. bacterial polysaccharide, which is similar to or identical with that of the dextran polysaccharide, is suggested. Ch. Abs.

Carbohydrate and protein fractions of meningococci. J. Zozaya and J. E. Wood (J. Infect. Dis., 1932, 50, 177—184).—The polysaccharide and "nucleoprotein" obtained from meningococci, gonococci, and *N. catarrhalis* have similar immunological properties and are not type sp. There is no parallelism between the agglutination test and the polysaccharide precipitin test. Ch. Abs.

Standardisation of antimeningococcic serum by the polysaccharide precipitin test. J. Zozaya (J. Infect. Dis., 1932, 50, 310—314). Ch. Abs.

Factors affecting the yield of specific enzyme in cultures of the bacillus decomposing the capsular polysaccharide of type III pneumococcus. R. Dubos (J. Exp. Med., 1932, 55, 377—391).—An improved method of prep. and concn. is described. Ch. Abs.

Precipitin reaction. Determination of small quantities of a specific polysaccharide. M. Heidelberger and F. E. Kendall (J. Exp. Med., 1932, 55, 555—561).—A method for the microdetermination of the sp. polysaccharide of type III pneumococcus is based on the precipitin reaction. Ch. Abs.

Carbohydrates adsorbed on colloids as antigens. J. Zozaya (J. Exp. Med., 1932, 55, 325—351).—Polysaccharides of *B. anthracis*, meningococcus, *S. viridans* (Bargen), *B. proteus*, *S. morgani*, *B. dysenteriæ* (Shiga and Hiss), and pneumococcus can be rendered antigenic by adsorption on a colloid carrier. Dextran was also rendered antigenic by the adsorption method. Ch. Abs.

Separation of antibodies from serum-proteins. Protein-free antibody. M. Frankel (Proc. Roy. Soc., 1932, B, 111, 165—174).—The serum is treated with kaolin on which all the antibody and the whole or part of the proteins are adsorbed. The complex is eluted with a 2% solution of glycine in aq. NaCl. From diphtheria antitoxin and antityphoid serum were obtained protein-free solutions containing 12—24% of the antitoxin. Ultrafiltration of antityphoid sera under pressure also yields protein-free, serologically-active fluids which, however, contain only 3—6% of the original flagellar agglutinin titre. With typhoid agglutinin the antibody can be freed from glycine and NaCl by dialysis without loss of activity. The antibody is colloidal, may be dried at room temp. and redissolved without loss of activity, contains traces of Et_2O-sol. material not associated with its serological properties, and is not affected by proteolytic enzymes. F. O. H.

Germicidal activity of aromatic sulphides. E. Moness, W. Braker, and W. G. Christiansen.—See this vol., 844.

Active principle in hog's stomach effective in pernicious anæmia. J. F. Wilkinson and L. Klein (Lancet, 1932, 222, 719—721).—Active extracts were obtained only when fresh stomach tissue was subjected to high pressure. EtOH pptd. from these extracts the whole of the active principle, which appears to be enzymic in nature and is probably not identical with that present in liver. L. S. T.

Does adrenaline affect the diffusion of lactate ions in [frog's] muscles ? W. M. Vesselkina (Z. ges. exp. Med., 1931, 79, 630—634; Chem. Zentr., 1932, i, 698).—Adrenaline increases the amount of lactic acid which separates from muscles immersed in Ringer's solution and decreases that withdrawn by muscles immersed in a similar solution containing Na lactate. It increases the decomp. of glycogen in muscle. L. S. T.

Blood-sugar response to adrenaline in thyroid-fed animals. A. J. Abbott and F. W. Van Buskirk (Amer. J. Med. Sci., 1931, 182, 610—626).—Feeding 2·55 g. of desiccated thyroid to a rabbit resulted in progressive loss of body-wt., decrease in the hyperglycæmic response to adrenaline, and an absence of hyperglycæmic response with fatal hypoglycæmic response to adrenaline when the liver-glycogen was apparently depleted. No decrease in hyperglycæmic response was observed with cats or dogs. Ch. Abs.

Adrenaline blood-sugar curve during fatigue and the potassium : calcium ratio. F. V. Madon and S. Goldberger (Atti R. Accad. Lincei, 1932, [vi], 15, 301—304).—Experiments on four individuals show that fatigue causes an increase of 15—20% in the K content of the blood, whereas the Ca content remains unchanged. The effect of fatigue on the action of adrenaline on blood-pressure varies irregularly and with the individual. Blood-sugar is always less after labour than during rest. T. H. P.

Effect of adrenaline on blood-iodine. A. Schittenhelm and B. Eisler (Klin. Woch., 1931, 11, 9; Chem. Zentr., 1932, i, 698).—Normally, or in myxœdema or vegetative stigmatism the blood-I rises, but in exophthalmic goitre it falls, after injection of adrenaline. A. A. E.

Thyroxine and the central nervous system. A. Schittenhelm and B. Eisler (Klin. Woch., 1931, 11, 9—10; Chem. Zentr., 1932, i, 698).—The I content of the tuber cinereum but not of other parts of the central nervous system is increased by thyroxine injections. Removal of the thyroid lowers the I content of the tuber cinereum, but not of other parts of the brain. L. S. T.

Effect of thyroid preparations on biochemical changes in the muscles and liver of axolotls. S. Vinokurov and S. Epstein (Z. ges. exp. Med., 1931, 79, 747—751; Chem. Zentr., 1932, i, 698).—In muscles the total N, the inorg. and sol. P are unchanged, the non-protein-N is increased, and the P_2O_7'''' markedly decreased by the action of thyroid preps. Liver-glycogen is diminished. L. S. T.

Comparison of the assay of total extracts of posterior pituitary gland by the isolated guinea-pig uterus method with that by the inhibition of diuresis in dogs, rats, and mice. S. Glaubach and H. Molitor (Arch. exp. Path. Pharm., 1932, 166, 243—264).—The assay of preps. of the posterior pituitary lobe can be performed as accurately by the inhibition of diuresis in the dog, rat, or mouse as by the uterus method. Subcutaneous injection of solutions of proteins derived from muscle or thymus gland increases the sensitivity of some animals and decreases that of others. F. O. H.

Metabolism of animals on a carbohydrate-free diet. IV. Effect of pitressin and pitocin on the distribution of fat and glycogen in the liver and muscles of albino rats. A. Hynd and D. L. Rotter (Biochem. J., 1932, 26, 578—585).—There were no significant changes in the case of pitocin whether the animals were on carbohydrate-rich or carbohydrate-free diet. There were changes more striking with carbohydrate-fed rats when pitressin was injected. Slight hyperglycæmia was accompanied by a fall in liver-glycogen, a rise in muscle-glycogen, and a simultaneous infiltration of fat into the liver. As the liver-fat content increased the I val. of the fat fell correspondingly. The liver-fat reached a max. at the 5th—7th hr. when the liver-glycogen was at a min. and the muscle-glycogen increasing. The liver-glycogen reached a max. about the 17th hr., at which time the liver-fat had returned to normal. S. S. Z.

Effect of an acid extract of anterior pituitary on the iodine concentration of blood and thyroid gland. K. Closs, L. Loeb, and E. M. MacKay (J. Biol. Chem., 1932, 96, 585—592).—Injection of acid extracts of the anterior lobe of the pituitary gland into guinea-pigs produces hypertrophy of the thyroid gland and an increased basal metabolism. The distribution of org. I (*i.e.*, EtOH-insol.- or protein-I) in the animals is changed, the org. I of the blood increasing at the expense of that of the thyroid. The bearing of these results on Graves' disease in man is discussed. F. O. H.

Determination of [anterior pituitary] hormone in blood. H. O. Neumann and F. Péter (Klin. Woch., 1931, 10, 2086; Chem. Zentr., 1932, i, 697).—Blood is collected in Na citrate, extracted with Et_2O, the hormone pptd. with EtOH, and the ppt. dissolved in H_2O. L. S. T.

Occurrence of pituitary hormones in the urine in conditions unassociated with pregnancy. T. N. A. Jeffcoate (Lancet, 1932, 222, 662—665).—Prolan *A* has been found at the menopause, after castration, and in some cases of malignant disease. Prolan *B* can occasionally be found in the urine of non-pregnant women, but only when living chorionic elements are present in the body. L. S. T.

Gonadotropic hormones from normal urine and urine of pregnancy. C. Funk and P. Zefirow (Biochem. J., 1932, 26, 619—621).—The hormone is pptd. from the urine with quinine or benzoic acid. The ppt. is then extracted with H_2O and the solution purified by fractionation with EtOH of varying concn. and finally by fractional evaporation and separation of impurities in vac. at low temp. Five doses of 8×10^{-6} g. of the semi-cryst. prep. injected into rats caused a threefold increase in wt. of seminal vesicles and two-fold of the uteri. The simultaneous administration of this hormone and andronin (male sex hormone) to capons evokes less response than that of andronin alone, injections of the gonad-stimulating principle having no effect. Combined administration of the two hormones to infantile rats showed less response than that of each substance separately. S. S. Z.

Metabolically-active extract of the ovary. K. Kaufmann, C. Müller, and O. Mühlbock (Klin. Woch., 1931, 11, 14—18; Chem. Zentr., 1932, i, 696—697).—Extracts from follicular fluid accelerate development and check growth in frog's larva. The extracts were free from sex hormones which have no such effect. Extracts from the whole ovary did not give the metabolically active material. L. S. T.

Chemistry of insulin. J. Jensen (Science, 1932, 75, 614—618).—Mainly a summary of previous work. The actions of acids and alkalis on insulin support the view that the characteristic constituent of the insulin mol. is composed, wholly or partly, of glutamic acid and cystine. L. S. T.

Effect of insulin on the formation of blood-albumin and the influence of administration of carbohydrate and caffeine. M. Taubenhaus and S. Rosenzweig (Z. klin. Med., 1931, 118, 719—735; Chem. Zentr., 1932, i, 699).—Insulin increases the total albumin in human blood resulting from a marked increase in globulin. The ratio albumin : globulin falls markedly. Administration of carbohydrate or injection of caffeine before or at max. hypoglycæmia diminishes this increase in globulin, keeping the blood-sugar unchanged. L. S. T.

International vitamin standards. Medical Research Council (Pharm. J., 1932, 129, 5).—The international standard preps. are described and the international units are defined as (i) the vitamin-*A* activity of 10^{-6} g. of the standard prep. of carotene, (ii) for vitamin-B_1 the antineuritic activity of 10 mg. of the standard prep. adsorbed on kaolin, (iii) for vitamin-*C* the antiscorbutic activity of 0·1 c.c. of fresh lemon juice, and (iv) the vitamin-*D* activity of 1 mg. of the standard solution of irradiated ergosterol. R. K. C.

Stock diet for rats bred for vitamin tests. K. H. Coward, M. R. Cambden, and E. M. Lee (Biochem. J., 1932, 26, 679—690).—Diets suitable in some laboratories were not satisfactory when prepared from the same recipe, but necessarily of materials from different sources. A description of a new diet which is satisfactory for at least 2 generations is given. Reproduction but not the growth of the young rats shows a seasonal variation on this diet. Fluctuations in the degree of rickets appear to be correlated with the source of dried milk. S. S. Z.

Photochemistry of vitamins-*A*, -*B*, -*C*, -*D*. I. M. Heilbron and R. A. Morton (Nature, 1932, 129, 866—867).—A crit. discussion. L. S. T.

Photochemistry of vitamins-*A*, -*B*, -*C*, -*D*. F. P. Bowden and C. P. Snow (Nature, 1932, 129, 943).—A reply to criticism (preceding abstract). L. S. T.

Variations in growth response of rats in vitamin-*A* tests compared with the variation in rats growing normally. K. H. Coward (Biochem. J., 1932, 26, 691—703).—A comparative statistical analysis of the records of many rats in each of the above groups. S. S. Z.

Oxidation of vitamin-*A in vitro*. Influence of the solvent. W. J. Dann (Biochem. J., 1932, 26, 666—678).—Vitamin-*A* in a cod-liver oil concentrate was destroyed by aëration at high temp. more rapidly in some solvents than in others. It is particularly stable in EtOH, EtOH–KOH, and EtOAc. In EtOH it is also stable towards H_2O_2. S. S. Z.

Determination of vitamin-*A*. G. Francke (Biochem. Z., 1932, 249, 48—52).—Standardised rats should be used. P. W. C.

Relative vitamin-*A* and -*D* content of different samples of cod-liver oil. K. H. Coward (Pharm. J., 1932, 129, 4).—Blue vals. and vitamin-*A* and -*D* potencies of 44 samples of cod-liver oil are given. The blue val. is only an approx. measure of vitamin-*A* potency. There is no correlation between vitamin-*A* and -*D* potencies and no estimate of vitamin-*D* potency can be made from blue vals. R. K. C.

Content of vitamin-*A* in commercial preparations. K. Schübel and W. Gehlen (Arch. exp. Path. Pharm., 1932, 166, 354—365). F. O. H.

Chemical methods for determination of vitamins. I. The Bezssonoff reaction. F. V. von Hahn and M. Wieben (Z. Unters. Lebensm., 1932, 63, 481—495).—A historical survey of the reaction is given. The intensity of the colour produced does not necessarily agree with the vitamin content determined by feeding experiments on animals. The same intensity of colour was produced in cases where the vitamin content was negligible and where the activity was high. E. B. H.

Physiology of vitamins. XIX. Acid–base balance of the blood during lack of undifferentiated vitamin-*B*. XX. Glucose tolerance during lack of undifferentiated vitamin-*B*. E. Burack and G. R. Cowgill (J. Biol. Chem., 1932, 96, 673—684, 685—696).—XIX. No marked variations occur in the serum-electrolyte concns. of dogs fed on a diet deficient in the vitamin-*B* complex, if the appetite is maintained. When inanition accompanies *B*-deficiency a slight acidosis occurs. This may be due to increased blood-lactic acid caused by polyneuritic convulsions, but cannot be ascribed definitely to fasting or lack of the vitamin.

XX. The glucose tolerance of dogs was determined by following the blood-sugar curve after glucose injection. Glucose tolerance decreases (increased blood-sugar and delayed removal) in vitamin-*B*-deficient dogs, but this is dependent on the extent of fasting, which was controlled. A sp. influence of vitamin-*B* on carbohydrate metabolism has not been demonstrated. A. C.

Hexuronic acid as the antiscorbutic factor. A. Szent-Györgyi (Nature, 1932, 129, 943).—The results previously described (this vol., 548), and now confirmed, leave no doubt of the antiscorbutic activity and the vitamin nature of the hexuronic acid. L. S. T.

Chemical nature of vitamin-*C*. J. L. Svirbely and A. Szent-Györgyi (Biochem. J., 1932, 26, 865—870).—Guinea-pigs have been completely protected from scurvy for 90 days by the administration of 1 mg. daily of hexuronic acid. Vitamin-*C* is therefore a single substance and identical with hexuronic acid. S. S. Z.

Hexuronic acid as the antiscorbutic factor. S. S. Zilva (Nature, 1932, **129**, 943; cf. this vol., 657).—Guinea-pigs receiving daily 1 mg. of Szent-Györgyi's cryst. hexuronic acid from adrenal glands showed no macroscopic signs of scurvy after 55 days and increased in wt. regularly for the first 40 days. Although the results confirm those of Svirbely and Szent-Györgyi (this vol., 548) and show the presence of the antiscorbutic factor in this prep., they do not afford sufficient evidence of the identity of hexuronic acid with the antiscorbutic factor. L. S. T.

Antiscorbutic fraction of lemon juice. X. S. W. Johnson and S. S. Zilva (Biochem. J., 1932, **26**, 871—888).—The substance (or substances) responsible for the acceleration of the inactivation of the reducing principle and of vitamin-*C* in neutral autoclaved decitrated lemon juice is most probably related to pyrocatechol and is formed from the sugars of the juice during the process of autoclaving. On autoclaving decitrated lemon juice or solutions containing the same concn. of sugars, a substance is produced which is capable of oxidising p-$C_6H_4(NH_2)_2$ but not guaiacum or benzidine. Pyrocatechol and quinol do not destroy the reducing principle of lemon juice in the absence of an enzymic factor, whilst benzoquinone and the ethereal extracts from autoclaved lemon juice or sugars do so unaided. S. S. Z.

Vitamin-*C* content of sheep-liver with observations on the effects of freezing and storage. J. I. Mills (Biochem. J., 1932, **26**, 704—711).—About 3 g. of liver are equiv. to 1 g. of cabbage in antiscorbutic potency. Freezing and thawing of liver diminishes its vitamin-*C* considerably and a further loss is incurred on storage at −19° for 6 months. S. S. Z.

Experimental scurvy. XII. [Total] sulphur metabolism of guinea-pigs on a vitamin-*C*-free diet. XIII. [Detailed] sulphur metabolism of guinea-pigs on a vitamin-*C*-free diet. S. Ohata (J. Biochem. Japan, 1932, **15**, 285—299, 301—310).—XII. The total S contents of various organs, fæces, and urine are not significantly different in normal and scorbutic animals.

XIII. The distribution of S in the urine of normal and scorbutic guinea-pigs is investigated. With scurvy the neutral S fraction is increased, whilst the ethereal-SO_4 fraction is decreased. F. O. H.

Influence of a diet deficient in vitamins-*C* and -*D* on the Ca : PO_4 ratio of serum in rats and guinea-pigs. H. von Euler and M. Rydbom (Biochem. Z., 1932, **249**, 141—156).—The Ca : PO_4 ratio for serum of normal rats (0·28) is somewhat lower than for normal guinea-pigs (0·39—0·43), but in rachitic rats (0·35) corresponds approx. with that for scorbutic guinea-pigs (0·30—0·36). P. W. C.

Production of vitamin-*D* in a glow discharge. F. A. Askew, R. B. Bourdillon, and T. A. Webster (Biochem. J., 1932, **26**, 814).—Vitamin-*D* can be produced in a glow discharge, but the yield per unit of electrical energy is much smaller than that obtained with a Hg-vapour lamp. S. S. Z.

Formation of vitamin-*D* in dried beer-yeast by ultra-violet radiation. K. Schübel and W. Gehlen (Arch. exp. Path. Pharm., 1932, **166**, 348—353).—Ultra-violet irradiation of medicinal yeast (D.A.B. VI) yields a product rich in vitamin-*D*. The optimum wave-length is approx. 300 mμ, when the product may contain 40 clinical units per g. Such preps. retain their activity unchanged for 3 years. F. O. H.

Mode of action of vitamin-*D*. The parathyroid theory; clinical hypervitaminosis. L. J. Harris (Lancet, 1932, **222**, 1031—1038; cf. A., 1931, 659).—Vitamin-*D* acts by permitting increased net absorption of Ca or phosphate from the gut, and tending to raise the level of blood-Ca or phosphate. The latter rise results in increased calcification in sites provided with the calcifying enzyme phosphatase. The parathyroid hormone raises the blood-Ca level by draining mineral matter from bone and not by increased net absorption from the gut. The view that vitamin-*D* acts normally by stimulation of the parathyroid cannot be accepted. The ill-effects on hypervitaminosis are the same in man as in experimental animals, and in the former the toxic overdose of irradiated ergosterol is not far removed from the optimal curative dose. L. S. T.

Vitamin-*D* content of the fat of sea perch, porpoise, and seal. S. N. Matzko and D. A. Vital (Z. Unters. Lebensm., 1932, **63**, 495—498).—The vitamin-*D* contents were 100—150 units per g., <50 per g., and negligible, respectively. E. B. H.

Germination. Evolution of fatty substances and phospholipins in the early stages of development of *Lupinus albus*. A. Hée and L. Bayle (Bull. Soc. Chim. biol., 1932, **14**, 758—782)—The lecithins of the seed grown on H_2O both in the dark and when exposed to light are largely utilised during germination for the building up of the young plant. H. D.

Biocatalysts in germination. H. von Euler, T. Philipson, and D. Burström (Z. physiol. Chem. 1932, **208**, 281—284).—The factor *Z* stimulating fermentation by living yeast is contained in the husks and cotyledons of barley and in leguminous seeds. J. H. B.

Presence of a growth-promoting substance in *Boletus edulis*. N. Nielsen (Biochem. Z., 1932, **249**, 196—198).—The fruit bodies of *B. edulis* do, but of the mushroom, *Psalliota campestris*, do not, contain a substance which promotes the growth of the coleoptile of *Avena*. P. W. C.

Catalase in seeds. J. Stephan (Jahrb. wiss. Bot., 1932, **75**, 771—808).—Determinations of catalase activity by the iodometric and $KMnO_4$ methods give similar vals. both for shaken and unshaken preps. The manometric is preferable to the eudiometric method. The decomp. of H_2O_2 is largely dependent on the rate at which the mixture is shaken. A modification of the Nemec–Duchoň catalasometer is described. In the examination of seed materials admixture with a buffer solution before treatment with H_2O_2 is recommended. A given quantity of the enzyme decomposes a definite amount of H_2O_2. No simple relationship exists between the rate of decomp. of H_2O_2 and the ratio of catalase to H_2O_2 present. The reaction rate corresponds with that of a bimol. reaction only when carried out at 10°. A. G. P.

Comparative variations of some carbohydrates in *Potentilla reptans* and *P. verna*. P. Gillot and H. Wioland (Bull. Soc. Chim. biol., 1932, **14**, 822—831).—The stems and roots were analysed during growth and the initial reducing sugars, the sugars hydrolysable by diastase, the starchy matter, and the glucosides hydrolysable by emulsin were determined. H. D.

Metabolic physiology of green algæ. II. Action of iron, zinc, and copper salts. M. Roberg (Jahrb. wiss. Bot., 1932, **76**, 311—332).—Zn stimulates in concns. up to 0·001 mg. per c.c., and is toxic at 0·05 mg. per 100 c.c. Cu stimulates slightly at very small concns. only. Toxicity is associated particularly with autotrophic and stimulation with heterotrophic and mixotrophic conditions. A. G. P.

Gas content of the cenobia of *Rivularia polyotis* (J. Ag.), Hauck. Z. Danin (Atti R. Accad. Lincei, 1932, [vi], **15**, 317—322).—The gases secreted in these cavities, like those formed in the corresponding cavities of brown and green algæ, contain O_2, which increases with the light intensity to 70%. T. H. P.

Life history of the *Xanthoria* fungi. H. Bartusch (Arch. Mikrobiol., 1931, **3**, 122—157).—Variations in the pigmentation of *X. parietina* are attributed to the extent of pptn. of parietin. This lichen-acid is best detected by the blood-red coloration produced with $Ca(OH)_2$ or $Ba(OH)_2$. The acid is sol. in H_2SO_4, NaOH, or KOH yielding red solutions. Micro-sublimation methods are also applicable. The intensity of coloration of the thallus depends on the no. and size of the crystals formed. A. G. P.

Liberation of hydrogen cyanide by certain fungi. M. Mirande (Compt. rend., 1932, **194**, 2324—2326).—The secretion of HCN by *M. oreades* is localised at points midway up and on both sides of the lamellæ. The carpophores, killed by boiling in H_2O, liberate HCN again on further treatment with boiling H_2O. A. L.

Hydrocyanic acid in sorghum, Sudan grass, and some hybrids. H. Finnemore and C. B. Cox (J. Proc. Roy. Soc. New South Wales, 1931, **65**, 145—152).—In all cases the HCN content is greatest in young seedlings and gradually disappears, but may persist for 130 days. The HCN content of air-dried material varies from 10 to 160 mg. per 100 g. P. G. M.

Biological decomposition of plant materials. VII. Nature of the residual hemicelluloses of rotted straw. A. G. Norman (Biochem. J., 1932, **26**, 573—577).—Only 2 g. of hemicellulose were recovered at the close of 9 months' fermentation from 1 kg. of dry straw containing originally 230 g. of hemicellulose. There was no indication of variation in biological availability of hemicellulose or the accumulation of less available groupings. A H_2O-sol. polysaccharide containing 33% of uronic acid anhydride, 66% of hexosan, and glucose units was isolated from the products of fermentation. S. S. Z.

Lignins from cereal straws. I. Isolation and fractionation of lignin from oat and wheat straw. L. Marion (Canad. J. Res., 1932, **6**, 521—531).—Lignins isolated from oat and wheat straw by means of the Me ether of ethylene glycol (I) and conc. HCl have been fractionated into 5 components by means of various solvents. The main fraction, sol. in $COMe_2$, isolated from oat-straw lignin has the same properties, OMe content, and composition as the corresponding fraction isolated from wheat-straw lignin. The components fractionated are compounds of lignins with (I); lignins isolated by means of unmethylated solvents (*e.g.*, 1 : 4-dioxan) have lower OMe vals. The lignins isolated from other types of plants by the same method have different properties and composition from those of the straw lignins. E. S. H.

Chemical composition of the periwinkle (*Vinca minor*, L.). F. Rutishauser (Compt. rend., 1932, **195**, 75—77).—Addition of $Pb(OAc)_2$ to an extract of periwinkle yields a brown ppt. After removal of Pb from this a yellow lævorotatory product is obtained by fractional pptn. with EtOH. Alkaline hydrolysis of this yields protocatechuic acid; acid hydrolysis gives a product which, on dry distillation or alkali fusion, yields pyrocatechol. An amorphous lævorotatory glucoside (*vincoside*) is also obtained by acid hydrolysis (1·7 g. per kg. fresh tissue). P. G. M.

Toxic constituent of the seeds of *Tephrosia Vogelii*. K. W. Merz (Arch. Pharm., 1932, **270**, 362—363).—Tephrosin, dehydrodeguelin, and deguelin have been isolated. R. S. C.

Chemical constituents of tobacco. II. Glucosides of tobacco leaf. I. K. Yamafuji (Bull. Agric. Chem. Soc. Japan, 1932, **8**, 1—3).—*Tabacinin*, m.p. 227° (decomp.; brown at 175°), and *tabacilin* are isolated from Japanese tobacco leaves by extraction with hot 95% EtOH in presence of $CaCO_3$, and separated by pptn. with $Pb(OAc)_2$. On hydrolysis with dil. aq. H_2SO_4 in EtOH the former gives glycuronic acid and a yellow, cryst. *aglucone*, and the latter glucose, nicotine, and other products. H. A. P.

Essential oil in desert plants. II. Oil of *Chrysothamnus nauseosus*. M. Adams and L. Kehoe (J. Amer. Chem. Soc., 1932, **54**, 2448—2451; cf. B., 1928, 106).—The essential oil of *C. nauseosus* contains about 3% of β-pinene, 30—40% of limonene and dipentene, 2% of cuminaldehyde, and 20% of sesquiterpenes. The occurrence of dipentene and caoutchouc in *Chrysothamnus* suggests that one may be a metabolic product of the other. C. J. W. (*b*)

Phytosterols: sterols of grape-seed oil. C. Antoniani and F. Zanelli (Atti R. Acad. Lincei, 1932, [vi], **15**, 284—286).—Acetylation and bromination by Windaus' method of the crude sterol of grape-seed oil yields only one sol. bromoacetyl derivative, the presence of stigmasterol or analogous sterols being thus excluded. The product is accompanied by a compound which, on fractional crystallisation (and debromination) from EtOH, gives a substance, m.p. 93—94°. The sterol appears to be mostly sitosterol, with a small proportion of a dextrorotatory sterol. T. H. P.

Composition of asarum oil. V. Bruckner and T. Széki (J. pr. Chem., 1932, [ii], **134**, 107—140).—The essential oil of *A. Europæum* contains a terpene, b.p. 62·5°/23 mm. (1—2%; it is doubtful whether this is *l*-pinene as stated in A., 1888, 680), *l*-bornyl acetate (12—15%), a tricyclic (?) sesquiterpene, b.p. 78°/3 mm. (10—12%), methyleugenol (15—20%; or methyl*iso*eugenol ?), asarone (30—35%), asaraldehyde (2—3%), and resins (10—12%). The presence of *l*-bornyl acetate depends on the source of the oil. H. A. P.

Fumaric acid in the micro-sublimate from *Cetraria islandica*. L. Kofler and H. Ratz (Arch. Pharm., 1932, **270**, 338—340).—The sublimate is mainly fumaric and not lichesteric acid (cf. A., 1914, ii, 153). R. S. C.

Proteins of ragweed pollens. C. A. Johnson and B. Z. Rappaport (J. Infect. Dis., 1932, **50**, 290—309).—Giant ragweed pollen contains at least two antigens: possibly a globulin and an albumin. The pollen proteins of the giant and common ragweed and of *Iva xanthifolia*, *Ambrosia bidentata*, *Xanthium canadense*, *Franseria tenuifolia*, *A. psylostachya*, and *F. acanthicarpa* are antigenically related. Dialysis of pollen extracts involves loss of protein, both fractions being active. The carbohydrates and crude fibre were clinically relatively inert; a lipin fraction contained 0·2—0·3% N. The active principle of ragweed pollen is probably of protein nature or clings to a protein moiety. Ch. Abs.

Alkaloids of *Leontica Eversmanii*, Bge. I. A. Orekhov and R. Konovalova (Arch. Pharm., 1932, **270**, 329—334).—The nodules of *L. Eversmanii* contain *leontamine* (I), $C_{14}H_{26}N_2$, b.p. 118—119° [(? *di*)*hydrochloride*; *dichloroplatinate*, m.p. 248° (decomp.); *dipicrate*, m.p. 194—195°; *dimethiodide*, m.p. 265—268°], and *leontidine* (II), m.p. 116—118° [*hydrochloride*, m.p. 293° (decomp.) after sintering at 280°; *chloroplatinate*, m.p. 258—259° (decomp.]. (I) is stable to $KMnO_4$ and is not reduced catalytically; it thus contains four saturated rings. The ratio N : Cl in the hydrochloride of (II) is 1 : 2. R. S. C.

[Constituents of] root-bark of *Plumbago rosea*, L. M. C. T. Katti and V. N. Patwardhan (J. Indian Inst. Sci., 1932, **15A**, 9—15).—Fractional solvation of the material extracted by 90% aq. EtOH from the root-bark of *P. rosea* (chitramul) yields plumbagin, sitosterol (the properties of which support the theory that the sterol exists in three isomeric forms), a fatty alcohol (arachidyl ?), oleic, linoleic, and lignoceric (?) acids, *sitosterol glucoside*, $C_{33}H_{56}O_6$, m.p. 259—260°, a saturated hydrocarbon, m.p. 77—78°, and glucose. Plumbagin, m.p. 75—76°, $C_{11}H_8O_3$ (cf. A., 1928, 1249, 1376), yields a CO_2Et-*derivative*, m.p. 108—109°, and, when treated in EtOH solution with Br, a *Br-derivative*, m.p. 172—173°, containing 44·4% Br. The min. lethal dose of plumbagin for rats is 110—120 mg. per kg. body-wt. when administered subcutaneously and approx. 20 and 35 mg. for guinea-pigs and frogs respectively. F. O. H.

Bog-moss. I. Composition of *Sphagnum fimbriatum*, Wils. M. Shikata and M. Watanabe (Mem. Coll. Agric. Kyoto, 1932, 22, 1—6).—A sample of *S. fimbriatum* from fresh Japanese tundra peat contained H_2O 19·6%, lignin 1·5%, ash 3·2%, pentosans 11·9%, galactosan 1·6%, protein 0·9%, and mannan trace. Vals. for the cellulose content varied from 30·4% (alkali-insol. residue) to 48·5% (chlorination method); the former is regarded as more probable (α-cellulose 8·8%). Both the cellulose and lignin differ in properties from those of wood. H. A. P.

Biochemistry of the autumn fall of the leaf. S. Komatsu and S. Ozawa (Mem. Coll. Sci. Kyoto, 1932, A, **15**, 57—65).—Determinations have been made of the H_2O, ash, Et_2O-sol. matter, N, chlorophyll, carbohydrate, and crude fibre content of the leaves of the *Ginko biloba*, and of the p_H of the sap expressed from the leaves between June and November. At the end of summer the cell-sap becomes more acid and the ratio of H_2O-sol. to H_2O-insol. N decreases, but in autumn the sol. N increases and the acidity falls sharply. The H_2O content of the leaves increases continuously until just before they fall, when it decreases suddenly. As the content of reducing sugars follows the H_2O content it is suggested that the latter plays an important part in the hydrolysis of polysaccharides. The non-reducing sol. sugars are converted into crude fibre during the summer and both the crude fibre and ash contents of the leaves increase with age. It is suggested that the most important function of the autumn leaf-fall is to enable the plant to eliminate inorg. materials the accumulation of which interferes with the metabolic changes of the tissue materials. A. R. P.

Nitrogen compounds of the potato tuber; reaction and f.p. of the juice. S. Popławski (Rocz. Nauk. Roln. Leś., 1931, **25**, 95—126; Chem. Zentr., 1932, i, 1170).—In the vegetation period the total N increases; the amide-N increases more than the NH_2-acid-N. In warm storage the total N falls; cold-stored potatoes contain more N than warm-stored. The embryos, relatively to the tubers, contain more non-protein-N but less NH_2-acid-N. Acidity at first rises after harvesting. On storage the sap attains a characteristic max. f.p. depression. A. A. E.

Isolation of glutathione from potato tubers treated with ethylene chlorohydrin. J. D. Guthrie (J. Amer. Chem. Soc., 1932, **54**, 2566—2567).—Pieces of fresh tubers are treated with 1·6% $CH_2Cl\cdot CH_2\cdot OH$, kept in a closed container for 24 hr., then planted in moist soil for 5 days. They are then washed and ground, and the juice is expressed; 1·5 litres of the starch- and protein-free filtrate give 870 mg. of the $Cu^{\cdot}$ salt of glutathione. Glutathione could not be isolated from the juice of untreated tubers. Potatoes stored for several months gave smaller yields than fresh tubers. C. J. W. (*b*)

Effect of ethylene chlorohydrin treatments on the catalase, peroxidase, p_H, and thiol content of gladiolus corms. J. D. Guthrie, F. E. Denny, and L. P. Miller (Contr. Boyce Thompson Inst., 1932, 4, 131—140).—Treatment of corms with ethylene chlorohydrin (1—3 c.c. of a 40% solution per litre for 1—3 days) increased the catalase and peroxidase activity of the expressed juice and dried tissue, and the SH′ content of the expressed juice and extracts of dried tissue. The simultaneous increase in the p_H of the juice differed with different varieties. The I-reducing power of the corms was not appreciably affected by the treatment except in one case where there was a marked increase. These changes occurred in both dormant and active corms. A. G. P.

Ethylene-induced epinasty of leaves and the relation of gravity to it. W. Crocker, P. W. Zimmerman, and A. E. Hitchcock (Contr. Boyce Thompson Inst., 1932, 4, 177—218).—Of numerous gases examined only C_2H_4, C_2H_2, C_3H_6, CO, and C_4H_8 induced epinasty in plants, their effectiveness in this respect being: 1, 500, 500, 5000, 500,000, in the order named. Activity is associated with the unsaturated linking in the mols. and was not apparent in any saturated derivatives of the above. Acraldehyde, allyl alcohol, and isoprene did not produce epinasty, but were highly toxic to the plants. The action of the gases is not related to their solubility in H_2O, but is probably due to their ability to combine with certain constituents of the protoplasm. The epinastic response of petioles is a sensitive test for small concns. of these gases. The position of the plant in relation to the gravitational pull markedly influenced the epinastic effects. Both excised and attached leaves were affected. The downward pull of leaves following C_2H_4 treatment is 4—8 times their wt. A. G. P.

Conditions affecting nitrate reduction by plants. S. H. Eckerson (Contr. Boyce Thompson Inst., 1932, 4, 119—130).—NO_3' reduction in the plants examined was much reduced by decreasing the light intensity or the period of exposure. Formation of reducase in plants practically ceased if either K or PO_4''' was deficient in the nutrient. When Ca was deficient plant injury occurred first in the roots and later in the stem tips. Decreased reducase activity follows the course of the injury. With SO_4'' deficiency reducase activity diminished slowly to a min. which was maintained for several weeks. No disintegration of the protoplasm was apparent. Reducase activity was not related to the amounts of NO_3' or starch present in the plant. A. G. P.

Influence of potash nutrition on the assimilation rates of wheat leaves. G. Gassner and G. Goeze (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 412—482).—Apparatus is described for determining assimilation rates of cut leaves. Assimilation commences immediately after exposure to light, attains its full rate after 10—15 min., and continues steadily for many hr. Deficiency of H_2O induces a premature retardation. Assimilation vals. of leaves and the susceptibility of the plants to rust vary inversely with the K content of the soil in which they are grown. Possible interrelationships of the K supply and the N economy of plants are discussed. A. G. P.

Accumulation of electrolytes. IV. Internal versus external concentrations of potassium. A. G. Jaques and W. J. V. Osterhout (J. Gen. Physiol., 1932, 15, 537—550).—Lowering of the K˙ content of sea-water from 0·011M to 0·006M, but allowing the total concn. of NaCl+KCl to remain the same, caused a decrease in the K˙ and an increase in the Na˙ content of the cell sap of *Valonia macrophysa*. The cells ceased to grow, although there was no evidence of injury. Increase of K˙ in the sea-water increased the K˙, halide, and total cation content and also the ratio K˙/Na˙ of the cell sap. A. L.

[Properties of] large [vegetable] cells. W. J. V. Osterhout (Austral. J. Exp. Biol., 1932, 9, 135—139).—The protoplasm of large cells (*Nitella*, *Valonia*, *Halicystis*) is probably covered with a liquid film immiscible with H_2O. Electrolytes pass through this film chiefly non-ionised, the curve of penetration being, in general, of the first order. The energy required for the accumulation of electrolytes within the cells is derived from the production of substances by them and the process takes place because an ion may pass inwards in one combination more rapidly than it can pass outwards in another. W. M.

Intake of ions from salt solutions by higher plants. II. K. Pirschle (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 42—60).—The amount of CO_2 evolved by roots of growing plants is large in comparison with the difference between the intake of anions and cations from sterile, neutral-salt solutions. The part played by mol. and dissociated H_2CO_3 and by H˙ and OH′ in maintaining the electrostatic equilibrium between nutrient solutions and plant fluids is discussed in relation to the non-equivalence of the intake of anions and cations. A. G. P.

Rust diseases of cereals. IV. Mechanism of the action of mercury salts on wheat-smut spores [*Tilletia tritici*, Bjerk., Winter]. J. Bodnár and A. Terényi (Z. physiol. Chem., 1932, 207, 78—92; cf. A., 1931, 133).—Rust spores irreversibly adsorb Hg from aq. $HgCl_2$, $HgBr_2$, and $Hg(OAc)_2$, but not from $Hg(CN)_2$. The adsorbed Hg prevents germination on aq. $Ca(NO_3)_2$, but treatment with $Hg(CN)_2$ has no effect on germination. Spores treated with $Hg(OAc)_2$ germinate in moist soil. From $HgCl_2$ and $HgBr_2$ solutions the salts are adsorbed (being lipin-sol.) and kill the spores; $HgBr_2$ has the more powerful effect, as it is less dissociated. From $Hg(OAc)_2$ only metal ions are adsorbed. Germination is prevented by 3·5% Hg˙˙. NaCl depresses the action of $HgCl_2$, but renders $Hg(OAc)_2$ able to kill the spores, owing to the formation of $HgCl_2$. J. H. B.

Isolation of guanidine. J. A. Saunders (Biochem. J., 1932, 26, 801—813).—The guanidine is first adsorbed on charcoal, from which it is removed with acid EtOH, and eventually on "doucil" (Na Al silicate), from which it is eluted with saturated NaCl solution and MeOH. It is finally pptd. as the picrate: 2 mg. of guanidine or dimethylguanidine per 100 c.c. in aq. solution can be detected. For determination in blood the proteins are removed by the method of Folin and Wu. S. S. Z.