

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1934.

General, Physical, and Inorganic Chemistry.

Ground state of the hydrogen molecule. H. M. JAMES and A. S. COOLIDGE (J. Chem. Physics, 1933, 1, 825—835).—Mathematical. The method of Hylleraas for the He atom is extended to the H_2 mol. N. M. B.

Relative intensities of atomic spectral lines from a hydrogen discharge tube. W. W. JACKSON (Phil. Mag., 1934, [vii], 17, 33—53).— H_α varies parabolically and H_β and P_α vary linearly with the discharge current at const. pressure and p.d. across the tube. Relative transition probabilities have been calc. H. J. E.

Negative sections of the cold-cathode glow discharge in helium. K. G. EMBELÉUS, W. L. BROWN, and H. MCN. COWAN (Phil. Mag., 1934, [viii], 17, 146—160).—Discharge characteristics are described. H. J. E.

Stark effect with the helium 5876 line with high resolution. R. RITSCHL (Physikal. Z., 1934, 35, 53).—The Stark effect with the He 5876 line has been investigated with high resolution to discover the behaviour of each component in the electric field. A. J. M.

Measurement of arc temperature from C_2 bands. Transition probability of vibrational transitions. D. T. J. TER HORST and C. KRYGSMAN (Physica, 1933, 1, 114—118).—From the intensities of the C_2 rotation bands the temp. of an arc is calc. as 6000° abs., in agreement with the val. calc. from CN bands. Assuming the same temp. for the vibrational bands, the ratio of transition probabilities agrees with theory (Wurm, Z. Astrophys., 1932, 5, 260). J. W. S.

New terms in the spectra of N III, N IV, N V, O III, O IV, and O V. W. M. CADY (Physical Rev., 1933, [ii], 44, 821—825; cf. Edlén, A., 1933, 991).—Full data and analyses are given for the extreme ultra-violet spectra due to a new type of violent condensed discharge through air at low pressure in a quartz capillary. N. M. B.

Analysis of the N_2^+ bands. A. E. PARKER (Physical Rev., 1933, [ii], 44, 914—918).—Rotational analyses for the (4, 7), (5, 8), (6, 9), and (7, 10) bands, perturbation data for the (5, 8) band, and additional lines in the (5, 8) and (13, 15) bands are tabulated. N. M. B.

Combination relations in the absorption spectrum of liquid oxygen. J. W. ELLIS and H. O. KNESER (Z. Physik, 1933, 86, 583—592).—The absorption spectrum was investigated between 340

and 2750 $m\mu$, and a new band at 1261 $m\mu$ is recorded. The complete spectrum, including infra-red bands, is represented by a linear formula involving the frequencies 793 and 1307 mm^{-1} and the vibrational frequency of O_2 . Certain combination bands are ascribed to $(O_2)_2$. A. B. D. C.

Wave-lengths of the red lines of neon and their use as secondary standards. C. V. JACKSON (Proc. Roy. Soc., 1933, A, 143, 124—135).—Direct comparisons of the wave-lengths of the red lines of Ne with the primary standard show that, for resolving powers $> 250,000$, the Ne lines have const. wave-lengths. With lower resolving powers, however, the wave-lengths become systematically lower, until a min. is reached at about 100,000. This is caused by blending of the weak satellite (due to Ne^{22}) with the main line. A table of corrections to be applied to the standard Ne wave-lengths when used with apparatus of low resolving power is given. L. L. B.

Natural width of neon lines in the visible spectrum. I. W. SCHÜTZ. II. H. SCHILLBACH (Ann. Physik, 1933, [v], 18, 705—720, 721—745).—I. An experimental test of the quantum theory applied to the natural width of Ne lines is proposed and the theory of it discussed. The difference between the results obtained by application of the old and new (Dirac-Weisskopf-Wigner) quantum theories is that according to the latter, within a group of Ne lines with a common initial level the width of the lines due to transition to the unstable s_2 level should be $>$ that of lines due to transition to the metastable s_3 and s_5 levels.

II. An account of the experimental work in connexion with the above is given, involving the determination of the intensity distribution in the Ne lines by an interferometric method, and the density of the dispersion electrons. The results agree with the theory of Weisskopf and Wigner. A. J. M.

Dependence of the intensity of the visible Ne lines of the positive column on the current strength. W. SCHÜTZ (Ann. Physik, 1933, [v], 18, 746—754).—Photographs of the Ne spectrum were taken so that the product of time of exposure and current strength was const. The lines of a group (p_k-s_i) with a common initial term were not of const. intensity under these conditions. A. J. M.

Line absorption of sodium vapour for the two D-lines. W. ZEHDEN (Z. Physik, 1933, 86, 555—582).—Line absorption was measured with an accuracy of 4% for the pressure range 1×10^6 to

4×10^{-5} mm., and the results are compared with those of magnetorotation. A. B. D. C.

Energy balance, electron temperature, and voltage gradient in the positive column in mixtures of Na vapour with Ne, He, and A. M. J. DRUYVESTEYN and N. WARMOLTZ (Phil. Mag., 1934, [vii], 17, 1—27; cf. A., 1933, 1).—Either in pure Na vapour, or in Na + a few mm. of Ne, He, or A, the power input in the discharge equals the output (radiation + wall energy). Discrepancies occur at higher pressures of the rare gas. H. J. E.

Nuclear spin and magnetic moment of sodium from hyperfine structure. L. P. GRANATH and C. M. VAN ATTA (Physical Rev., 1933, [ii], 44, 935—942).—The observed hyperfine structure of the Na *D* lines showed component separations: D_2 (λ 5890), 0.0555, D_1 (λ 5896), 0.0612 cm.⁻¹ Relative intensity measurements indicate a nuclear spin of 3/2. The calc. nuclear magnetic moment is 2.7/1840 Bohr magneton. N. M. B.

Transport of matter in arcs and flames. Optical determination of the radii of alkali atoms. L. A. GINSEL (Arch. Néerland., 1933, [iiiA], 14, 285—333).—The intensity variation of spectral lines due to the metal atom in an arc between the metal and a C electrode was used to examine factors influencing the transport of metal. Line intensity measurements were used to calculate the diffusion consts. of Na, K, Rb, and Cs in a Bunsen flame, and their at. radii. H. J. E.

Remarkable optical properties of the alkali metals. C. ZENER (Nature, 1933, 132, 968).—Treating electrons as moving in no field, Wood's observations (A., 1933, 1096) on the transparency of the alkali metals in ultra-violet light can be qualitatively accounted for; approx. vals. of the crit. wave-length are calc. L. S. T.

Band system of ionised aluminium hydride. W. HOLST (Nature, 1933, 132, 1003).—The new system at 3600 Å. (A., 1933, 991) must be attributed to AlH^+ . New systems at 2700 Å. and 3380 Å. are reported. L. S. T.

Nuclear spin of phosphorus from band spectrum analysis. (Miss) M. F. ASHLEY (Physical Rev., 1933, [ii], 44, 919—926).—Photographs of the emission spectrum of P_2 showed a strong alternation in intensity in successive rotational lines of branches, giving an intensity ratio 3 : 1 from which the nuclear spin of the P atom is $\frac{1}{2}(h/2\pi)$. Fine structure analyses of the (6, 22), (6, 23), (8, 87), (8, 28), and (9, 28) bands are tabulated. N. M. B.

Displacement and unsymmetrical broadening of absorption lines by foreign gases. C. FÜCHTBAUER and F. GÖSSLER (Z. Physik, 1933, 87, 89—104).—Displacement and broadening have been investigated with H_2 as foreign gas in addition to those already given (A., 1933, 1096), and the spectrum of K has been similarly investigated. A. B. D. C.

Zeeman effect and uncoupling phenomena in the CaH bands. W. P. CUNNINGHAM and W. W. WATSON (Physical Rev., 1933, [ii], 44, 815—817; cf. A., 1930, 1074; 1932, 315).—The effect of the

strong *l*-uncoupling in the $^2\Pi$ state on the Zeeman patterns of the lines of the $^2\Pi \rightarrow ^2\Sigma$ CaH band at 7000 Å. is discussed. N. M. B.

Probe measurements for luminous arcs in air at atmospheric pressure. J. L. MYER (Z. Physik, 1933, 87, 1—18).—Potential drop in different regions of the arc was investigated using Fe, Cu, C, Ni, and Zn as electrodes. The cathode fall corresponds with the second ionisation potential of the cathode and is little affected by the anode material; the anode fall was similarly investigated and gave results agreeing with those of Nottingham (J. Franklin Inst., 1928, 206, 43). A. B. D. C.

Standard copper wave-lengths in the region 100—450 Å. P. G. KRUGER and F. S. COOPER (Physical Rev., 1933, [ii], 44, 826—830).—Intensities and 476 standard wave-lengths are tabulated. Possible errors are discussed. N. M. B.

Zeeman separation of infra-red krypton I lines. B. POGÁNY (Z. Physik, 1933, 86, 729—737).—*g*-Coupling is worked out (cf. A., 1933, 1219). A. B. D. C.

Absorption spectra due to excitation of inner electrons. II. Mercury spectrum between 1190 and 600 Å. due to excitation of the ($5d$)¹⁰ shell (HgI^b); III. Cadmium spectrum from 1100 to 600 Å. due to excitation of the ($4d$)¹⁰ shell (CdI^b). H. BEUTLER (Z. Physik, 1933, 86, 710—728; 87, 19—27). A. B. D. C.

Line shape as a function of the mode of spectrograph slit irradiation. D. C. STOCKBARGER and L. BURNS (J. Opt. Soc. Amer., 1933, 23, 379—385).—Non-coherent, coherent, lens, and broad source modes of slit irradiation have been studied and the line shape and its effect on resolution have been investigated for each mode. W. R. A.

Limitations of the theory of complex spectra. H. H. MARVIN (Physical Rev., 1933, [ii], 44, 818—820).—The extension of the theory of two-electron systems to include d^9p and d^9d is discussed. N. M. B.

Measurement of visibility curves for the Michelson interferometer. (Miss) E. J. M. VAN DER SLOOTEN and C. JANSSEN (Z. Physik, 1933, 86, 760—764).—Observed variation of visibility with path difference agrees with the theoretical variation only when polarised light is used. A. B. D. C.

Asymmetries of pressure-broadened spectral lines. H. MARGENAU (Physical Rev., 1933, [ii], 44, 931—934; cf. A., 1933, 879).—Asymmetries in the intensity distribution of pressure-broadened lines are explained by calc. line contours, taking account of repulsive portions of the energy curves. N. M. B.

Determination of spectral intensities applied to problems of atomic and molecular physics. L. S. ORNSTEIN (J. Phys. Radium, 1933, [vii], 4, 613—624).—Methods of determination of spectral intensities are reviewed. The probability of emission, activation, and excitation of atoms by electron collision is discussed. The application of the laws of spectral intensity to the kinetic theory of gases, the theory of the electric arc, and other problems is given. A. J. M.

General conditions for glow discharge without cathode fall and dark space. A. GÜNTHER-SCHULZE and H. FRICKE (Z. Physik, 1933, 86, 821—827).—Various substances are given for the cathode required to produce this glow. Among the best are BeCO_3 , MgO , CaCO_3 , ZrO_2 , ThO_2 , SiO_2 , ZnSiO_3 , Al_2O_3 , Sb_2O_4 , Ta_2O_5 , tale, and glass. A. B. D. C.

Emission of light in gaseous discharges. II. W. DE GROOT (Physica, 1933, 1, 28—34).—Methods of calculation are discussed. F. L. U.

Distribution of radiation in the arc. L. S. ORNSTEIN and H. BRINKMAN (Z. wiss. Phot., 1933, 32, 200).—Attention is directed to papers by the authors to which no reference was made by Brückensteinkuhl (A., 1933, 440). J. L.

Discharge produced by superposing a constant on a high-frequency field. (MLLE.) M. CHENOT (Compt. rend., 1933, 197, 1599—1601).—The effect of superposing a.c. and d.c. on the discharge in a vac. tube with electrodes 30 mm. apart is described, and shown to be largely due to foreign matter in the cathode. C. A. S.

Light of the night sky and active nitrogen. J. KAPLAN (Nature, 1933, 132, 1002—1003). L. S. T.

Simultaneous presence of carbon and titanium oxide bands in [spectra of] sun-spots. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1071—1073; cf. A., 1931, 991).—Stars of spectral type K3 contain sensibly equal nos. of C_2 and TiO mols. The C_2 concn. decreases and the TiO concn. increases in the $S-N$ branch, and vice versa in the $R-N$ branch. J. W. S.

Stellar spectra showing both emission lines of H, He I, He II, C III, O III, and nebulium, and absorption bands of TiO. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1074—1077; cf. Astrophys. J., 1933, 77, 44).—The variable stars AX Persei, RW Hydræ, and CI Cygni, the spectra of which show this phenomenon, probably consist of doublets, a hot star giving rise to the emission spectra, and a cooler star of high Ti concn., the two being so close as to be inseparable spectroscopically. J. W. S.

Scandium oxide bands in the spectra of cold stars. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1078—1095).—The results of Bobrovnikoff (Astrophys. J., 1933, 77, 345) are discussed. J. W. S.

X-Ray K- and L-spectra of aluminium. (A) M. SIEGBAHN and T. MAGNUSSON. (B) M. SIEGBAHN and H. KARLSSON (Nature, 1933, 132, 895, 895—896).—(A) The L-line of Al from Al_2O_3 compared with metallic Al is displaced towards longer wave-lengths and has a different structure without the sharp edge (cf. this vol., 3).

(B) Al metal gives a β -line, corresponding with a transition from the free electron levels to the K-level, with a sharp edge on the short wave-length side, which is not formed by Al_2O_3 , where the corresponding line is more symmetrical. L. S. T.

Dependence of refractive index for X-rays on the angle of incidence. F. JENTZSCH and H. STEPS (Naturwiss., 1933, 21, 883—884).—The dependence of

n of glass for X-rays on the angle of incidence predicted by Orbán (A., 1933, 1233) has been verified. A. J. M.

Atomic constants deduced from secondary cathode-ray measurements. H. R. ROBINSON, J. P. ANDREWS, and E. J. IRONS (Proc. Roy. Soc., 1933, A, 143, 48—60).—The results of new measurements of the energies of the groups of homogeneous secondary cathode rays expelled from Au, W, Ag, and Cu by the K series X-rays of Cu are compared with the vals. predicted by X-ray spectroscopic data. The results are consistent with recent work on electron diffraction, rather than with the accepted vals. of h and e . L. L. B.

Photo-electric yields in the extreme ultraviolet. C. KENTY (Physical Rev., 1933, [ii], 44, 891—897).—Yields for Ni, W, Mg, W-O, and constantan surfaces illuminated by short-wave radiation from positive columns in He, Ne, and A down to 584 Å. varied with the surface and gas (except from Mg). N. M. B.

Determination of Planck's constant from velocity measurements of photo-electrons. S. PRILEŽAEV (Z. Physik, 1933, 87, 28—31).—A reply to Du Bridge (A., 1933, 657). A. B. D. C.

Thermionic constants of platinum. H. L. VAN VELZER (Physical Rev., 1933, [ii], 44, 831—836).—Supersaturation curves for various ageing temp. using cylindrical Pt filaments are given. Stable states were found at 1650° and 1785° abs.; for the latter $A=60$ amp./cm.² deg.², $\phi=5.29$ volts. N. M. B.

Concentration of excited atoms and positive ions of sodium in a low-voltage sodium arc. M. J. DRUYVESTEYN (Physica, 1933, 1, 14—27).—In a Na-vapour lamp containing a small quantity of Ne the no. of Na atoms in the $2p$ condition is about 12% of the no. (Q) of normal atoms, and the no. of positive Na ions is $2Q-5Q$. F. L. U.

Diffusion of positive ions of salts through copper, silver, and gold at high temperatures. Mass-spectrograph analysis of emitted ions. J. CIHOČKI (Ann. Physique, 1933, [x], 20, 478—517).—Investigations previously reported for Cu films (cf. A., 1933, 3) are continued for Ag and Au. The emitted ions undergo an energy loss, indicated by line displacement towards lower magnetic field vals. An approx. explanation of the mechanism is given on the hypothesis of emission of large unstable ions. N. M. B.

Measurement of ionic mobilities in the positive column. S. HARRIS (Phil. Mag., 1934, [viii], 17, 131—145).—Ionic mobilities in air and H_2 were calc. from measurements on the speed of rotation of the positive column around an annular discharge tube with varying magnetic and electric fields, current, and pressure, and from the Hall effect. H. J. E.

Passage of slow positive ions through highly diluted gases. O. BEECK (Physikal. Z., 1934, 35, 36—52).—A summary of work on the effective cross-section of gas mols. towards slow ions, the charge and ionisation cross-sections, excitation and dissociation by collision with positive ions, and the scattering of slow protons. A. J. M.

Emission of electrons from metals by very slow canal rays. G. VALLE (Atti R. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat., 1932, 67, 490—499; Chem. Zentr., 1933, ii, 1309).

Electron-microscopic observations of the movement of emission substances on oxide cathodes. E. F. RICHTER (Z. Physik, 1933, 86, 697—709).—Inversion of images on cathode surfaces is due to evaporation and recondensation of the emitting substance.

A. B. D. C.

Electron velocity in insulators under high field intensities and its relation to the theory of electrical breakdown. A. GÜNTHER-SCHULZE (Z. Physik, 1933, 86, 778—786).

A. B. D. C.

Determination of inner potentials from electron diffraction. V. E. LASCHKAREV (Z. Physik, 1933, 86, 797—801).—Theoretical.

A. B. D. C.

Stationary treatment of elastic scattering of very fast electrons. F. SAUTER (Z. Physik, 1933, 86, 818—820).—This method gives results very simply using relativistic wave mechanics.

A. B. D. C.

Field electron emission from liquid mercury. J. W. BEAMS (Physical Rev., 1933, [ii], 44, 803—807).

N. M. B.

Reflexion of electrons from liquid mercury. R. B. BRODE and E. B. JORDAN (Physical Rev., 1933, [ii], 44, 872—875).—Curves for elastically scattered electrons as a function of electron velocity and angles of incidence and reflexion show a preference for reflexion backwards to the direction of the incident beam.

N. M. B.

Magnetic deflexion method for angular distribution of electrons scattered by gas molecules. A. P. GAGGE (Physical Rev., 1933, [ii], 44, 808—814).—A method is described, applicable to scattering angles up to 180° and to elastic and inelastic collisions of slow electrons, for evaluating the scattering coeff. for electrons colliding with gas mols., if the electrons before and after collision describe circular paths in a uniform magnetic field. Results for 80- and 30-volt electrons in Hg vapour are given.

N. M. B.

Photo-electric investigation of the temperature variation of electron emission potential from a nickel surface with an atomic barium layer. R. SUHRMANN and R. DEPONTE (Z. Physik, 1933, 86, 615—634).—The temp. range was 20—500°.

A. B. D. C.

Measurements of light excitation efficiencies in argon and mercury spectra by electron collision. O. FISCHER (Z. Physik, 1933, 86, 646—666).—Excitation functions were obtained for the violet group of the A arc spectrum and for the blue spark lines with a pressure range of 5—25 × 10⁻³ mm.

A. B. D. C.

Electron scattering in methane, acetylene, and ethylene. A. L. HUGHES and J. H. McMILLEN (Physical Rev., 1933, [ii], 44, 876—882).—Scattering coeffs. for elastic collisions are tabulated for various voltage and temp. ranges. Total absorption coeffs. are calc. For energies > 100 volts scattering coeffs. of electrons by mols. with two C atoms were < those by mols. with one C atom; for 10-volt electrons the reverse was the case. Interference effects between

electron waves scattered by individual atoms were found.

N. M. B.

Electron attachment and negative ion formation in oxygen and oxygen mixtures. N. E. BRADBURY (Physical Rev., 1933, [ii], 44, 883—890).—The probability of electron capture for O₂, air, and O₂-rare gas mixtures was measured by the analysis of a mixed current stream at two points by separating ionic fractions between wire grids. In O₂ and its mixtures an increase in attachment probability occurs at 1.6-volt electronic energy, due to low-energy electrons following inelastic impacts with O₂ mols.

N. M. B.

Electronic flux in problems of several electrons. J. WINTER (J. Phys. Radium, 1933, [vii], 4, 646—649).—Theoretical.

A. J. M.

Polarisation of electrons. G. P. THOMSON (Nature, 1933, 132, 1006).—The asymmetrical scattering of electrons reported by Rupp (A., 1932, 317) could not be confirmed.

L. S. T.

Experimental detection of polarised electrons. E. RUPP (Conv. Fis. Nucl., 1932, 1, 143—151; Chem. Zentr., 1933, i, 1735).

L. S. T.

Complex processes of materialisation. L. GOLDSTEIN (Compt. rend., 1933, 197, 1596—1598).—The probability of the simultaneous creation of pairs of electrons and ionisation by the absorption of a photon by, or the collision of an electron with, an atom, in either case possessed of suitable energy, has a finite val., although < the probability of the creation of pairs of electrons from a heavy nucleus (cf. this vol., 6).

C. A. S.

Annihilation of positrons on contact with matter and the resultant radiation. J. THIBAUD (Compt. rend., 1933, 197, 1629—1632).—Positrons falling on matter are very quickly dematerialised with evolution of photons of energy < 500 kev. Such positrons (average energy 800 kev.) and the photons produced by them give a distinctly different absorption curve from that given by the electrons forming the general radiation, photons X, produced by the positrons among the at. electrons (of average energy 500 kev.). For a thickness of Pt 500 mg. per sq. cm. absorption increases linearly for both positrons and electrons, μ/ρ for electrons being 1.6 times that for positrons; for greater thicknesses the photons due to positrons abandon in the film 1/180 of the intensity of the primary positrons, whilst X yields only 1/7500 of the initial energy of the electrons. Positrons thus produce new radiation 40 times as penetrating as that due to collision of electrons. These results are substantiated by measurement of the energy left in the film. The average quantity of the positrons in Pt is 580 mg. per sq. cm., and average life in ordinary air 1.2 × 10⁻⁸ sec. (cf. A., 1933, 993, 1098; this vol., 4).

C. A. S.

Experimental proof of annihilation of positive electrons. F. JOLIOT (Compt. rend., 1933, 197, 1622—1625).—Positive and negative electrons (from Po) were alternately magnetically directed on a radiator of Pb or Ag, placed above a Geiger-Müller counter, and the results with each compared. Absence of radiation of energies 1 or 0.64 × 10⁶ ev., coupled

with the presence of that of 0.5×10^6 ev. in approx. the required amount, indicates that when the positive electrons are absorbed in matter photons of energy approx. 0.5×10^6 ev., in no. double that of the incident positive electrons, are emitted, as required by Dirac's theory.

C. A. S.

Displacement in an electrostatic field of magneto-electronic cycloids. L. CARTAN (Compt. rend., 1933, 197, 1604—1606; cf. A., 1933, 993; this vol., 4).—The general case (of which Thibaud's method of collecting positrons is a special one) in which the electric field is directed in any direction is dealt with mathematically, and Thibaud's formula deduced.

C. A. S.

Stopping of fast particles with emission of radiation and the birth of positive electrons. W. HEITLER and F. SAUTER (Nature, 1933, 132, 892).—Dirac's theory of the electron has been used to calculate (i) the probability that a fast electron, passing through matter, emits a quantum of radiation (I) with energy comparable with its own, and (ii) the probability that (I), colliding with a nucleus, gives birth to a positive electron.

L. S. T.

Positive electron. P. M. S. BLACKETT (Nature, 1933, 132, 917—919).—A summary.

L. S. T.

Positive electron tracks. D. SKOBELEZYŃ (Nature, 1934, 133, 23—24).

L. S. T.

At. wt. of molybdenum. R. LAUTIÉ (Compt. rend., 1933, 197, 1730—1732).—Commercial MoO_3 was converted into $\text{MoOCl}_2(\text{OH})_2$, and the redistilled product changed back into MoO_3 , and this sublimed at $> 793^\circ$ and reduced to Mo at 800° by H_2 . The mean of seven experiments Mo/MoO_3 gave 96.01 ± 0.01 . Oxidation of Mo to MoO_3 gave 96.02, in good agreement with Aston's 95.97 ± 0.05 (cf. A., 1930, 1338) and the accepted val. 96.0.

C. A. S.

Constitution of neodymium, samarium, europium, gadolinium, and terbium. F. W. ASTON (Nature, 1933, 132, 930—931).—Provisional analyses by accelerated anode rays are Sm, a strong pair 152 and 154, and a triplet 147, 148, and 149; Eu, two odd mass nos. 151 and 153 in approx. equal abundance; Gd, apparently consisting of 155, 156, 157, 158, and 160 with faint effects at 152 and 154 probably due to Sm as impurity; Tb, only one line 159. Nd contains 143 and 145 in addition to 142, 144, and 146 already known, and these are now shown to be in descending order of abundance.

L. S. T.

Abundance ratio of lithium isotopes Li^7 and Li^6 . L. S. ORNSTEIN, J. A. VREESWIJK, jun., and G. WOLFSOHN (Physica, 1933, 1, 53—59).—Measurements of intensity of the Li resonance line 6708 Å. lead to the val. 8.1 ± 0.4 for $\text{Li}^7 : \text{Li}^6$, in agreement with previous optical determinations (A., 1931, 992), and contrary to results given by mass-spectrographic methods.

F. L. U.

Suggested nomenclature for heavy hydrogen and its compounds. R. W. WOOD (Science, 1933, 78, 583).—It is suggested that heavy H_2 (I) be called bar-hydrogen, and written as Hydrogen. Compounds of (I) would be bar-benzene, written Benzene, bar-ammonia, written Ammonia, etc.

L. S. T.

Existence of two new α -radiations and a new definite radiation of unknown origin. G. DIECK (Naturwiss., 1933, 21, 896—897).—From Cu sheet, and Cu and Au wires, two new α -radiations were obtained, of ranges in air 0.9 and 1.5 cm. The radiation could not be connected with the U isotope of Wilkins and Rayton. A corpuscular radiation differing in many ways from α -radiation was also found, being probably \bar{H} -particles, not arising from the walls of the cloud chamber, but set free from the gas in the chamber. The origin of this radiation is discussed. The results of Locher (Physical Rev., 1933, [ii], 44, 779) on the corpuscular radiation produced by the action of neutrons on the gas agree with those now obtained.

A. J. M.

Reversed fine structure of the α -rays. A. POLESSITSKY (Nature, 1933, 132, 969).—Theoretical.

L. S. T.

Excitation of the inner shells of atoms by low-energy protons and α -particles. W. HENNEBERG (Z. Physik, 1933, 86, 592—604).—The probability of ionisation of K-shells is calc. and found to vary as the fourth power of the energy for low-energy vals.

A. B. D. C.

Possibility of emission of neutral particles of nul intrinsic mass in β -radioactivity. F. PERRIN (Compt. rend., 1933, 197, 1625—1627).—Pauli's neutrino is discussed, it being regarded as of zero mass, and consequently has always the velocity of light. It is not pre-existent in the nucleus, but formed like a photon at the instant of emission, and has a spin 1/2.

C. A. S.

Conservation laws and β -emission. G. BECK (Nature, 1933, 132, 967).—Mainly theoretical. The view that U-Z is not a branch product, but a derivative of an unknown isotope of U, is supported.

L. S. T.

Diffusion of hard γ -rays. V. TRKAL (J. Phys. Radium, 1933, [vii], 4, 665—676).—The theory underlying the experimental work of Neukirchen (Z. Physik, 1921, 6, 101) on the absorption of hard γ -rays is developed.

A. J. M.

Investigation of secondary radiation excited by hard γ -rays. T. HEITING (Z. Physik, 1933, 87, 127—138).—Al, Fe, Cu, and Pb when exposed to radiation of 4.7 X all gave a secondary component of wave-length 23.8 X, the intensity of this component varying as the square of the at. no. This secondary radiation is considered to be due to recombination of a positive and a negative electron.

A. B. D. C.

Radioactivity of zinc. H. FESEFELDT (Z. Physik, 1933, 86, 611—614).—The α -particle emission of Zn is $< 1/10$ that observed by Zeigert (A., 1928, 455).

A. B. D. C.

Theory of atomic disintegration. T. SEXL (Z. Physik, 1933, 87, 105—126).—A quant. theory is given for disintegration of nuclei by protons, deuterons, and α -particles.

A. B. D. C.

Half-life period of thorium. H. FESEFELDT (Z. Physik, 1933, 86, 605—610).—The half-life period is 1.3×10^{10} years.

A. B. D. C.

Effective diameters of radioactive nuclei. G. GAMOW and S. ROSENBLUM (Compt. rend., 1933,

197, 1620—1622).—The effective radii of the radioactive elements when plotted against at. wt. for the various α -particles emitted show that elements of the Ra and Th families lie approx. on the same curve; those of the Ac family have comparatively smaller radii (cf. A., 1932, 443).
C. A. S.

Long-range particles from boron liberated on bombardment by protons. F. KIRCHNER and H. NEVERT (Physikal. Z., 1933, 34, 897—898; cf. A., 1933, 551, 1098).—The particles emitted from B of range > 28 mm. have been investigated. The frequency of occurrence of particles with ranges up to 48 mm. has been obtained, the curve showing a very weak max. at 39 mm.
A. J. M.

Excitation of proton emission from boron nuclei by Po α -rays. F. HEIDENREICH (Z. Physik, 1933, 86, 675—693).—Three well-defined groups were observed, and the dependence of their range and intensity on the energy of the primary beam was investigated.
A. B. D. C.

Anomalies in relative amounts of elements and origin of radioactive substances. W. M. ELSASSER and K. GUGGENHEIMER (Compt. rend., 1933, 197, 1627—1629).—The disproportionate rarity of the rare gases is attributed to the action of neutrons (probably from a cosmic cloud) acting on an initial large amount thereof (probably 10^3 to 10^6 kg. per sq. cm.), a neutron being captured by a nucleus with emission of a β -ray, and the process repeated, thus giving rise to other elements. This would be consistent with restriction of radioactive elements to the surface of the earth, and the difference of unity between the masses of radioactive K and Rb and of those of an isotope of A and Kr, respectively.
C. A. S.

Cloud-chamber photographs of the disintegration products of lithium and boron on bombardment with fast protons. F. KIRCHNER (Sitzungsber. bayr. Akad. Wiss., 1933, 129—134; Chem. Zentr., 1933, ii, 1301—1302).

Atomic disintegration by ultra-radiation. W. MESSERSCHMIDT (Physikal. Z., 1933, 34, 896; cf. A., 1933, 551).—The max. of the collision distribution curves (for Pb, Fe, Al, and C) both as regards energy and frequency are displaced towards smaller ion production with increasing at. wt. The collisions observed are identical with the "showers" of Blackett and Occhialini (A., 1933, 441).
A. J. M.

Atomic disintegration by ultra-radiation. E. G. STEINKE, A. GASTELL, and H. NIE (Naturwiss., 1933, 21, 898—899; cf. A., 1933, 995, 1100).—The effect of atm. pressure on disintegration produced by ultra-radiation is surprisingly great, and is probably due to a very soft component of the radiation which is effective in bringing about disintegration, but produces little ionisation. Only the no. of weaker collisions is dependent on atm. pressure. Secondary radiation must also be taken into account. By increasing the thickness of the material through which the radiation must pass the pressure effect is reduced, becoming negligible when a thickness of 30 cm. Fe is interposed.
A. J. M.

New hard component of the cosmic ultra-radiation. A. CORLIN (Nature, 1934, 133, 63).
L. S. T.

Cosmic rays and the new field theory. M. BORN (Nature, 1934, 133, 63—64).—If the assumption of protons be excluded, the high penetrating power observed for cosmic rays supports the new field theory (A., 1933, 1097).
L. S. T.

Experimental evidence for the absence of scattering of light by light. F. L. MOHLER (J. Opt. Soc. Amer., 1933, 23, 386—387).—Certain theoretical relations can be interpreted so that photons will repel and scatter each other at a distance comparable with the wave-length of the radiation. This has been tested experimentally and, if there is any reaction, the scattering radius for photons of visible light is $< 5 \times 10^{-9}$ cm.
W. R. A.

Evidence for the formation of active hydrogen. A. B. VAN CLEAVE and A. C. GRUBB (Nature, 1933, 132, 1001; cf. A., 1931, 805; 1932, 1218).— H_2 , activated by a discharge has properties which do not indicate at. H. With plastic S in the reaction chamber, a definite relation exists between voltage and pressure for the activation of H_2 . Above a crit. pressure, dependent on tube dimensions and proximity of the S, no activity is produced. Coating the tube with syrupy H_3PO_4 gives a less active H_2 , which is contrary to expectations if at. H. is present.
L. S. T.

Electromagnetic mass. M. BORN and L. INFELD (Nature, 1933, 132, 970).—Theoretical.
L. S. T.

Atomic transmutation and stellar temperatures. T. E. STERNE (Nature, 1933, 132, 893).
L. S. T.

Self-forces of elementary particles. II. G. WENTZEL (Z. Physik, 1933, 86, 635—645; cf. this vol., 7).—Theoretical.
A. B. D. C.

Atom factor determinations in the region of anomalous dispersion. II. K. SCHÄFER (Z. Physik, 1933, 86, 738—759).—Powders must consist of particles of size $> 10^{-5}$ cm. for atom factor determinations. These were obtained for Fe and Cr.
A. B. D. C.

Hydrogen-like atoms in the classical quantum theory. P. COPEL (J. Phys. Radium, 1933, [vii], 4, 638—645).—Theoretical.
A. J. M.

Model of the electric field and of the photon. (SIR) J. J. THOMSON (Phil. Mag., 1934, [viii], 17, 197—198).—A note on an earlier paper (A., 1933, 1225).
H. J. E.

Approximate wave function for the normal helium atom. D. R. HARTREE and A. L. INGMAN (Mem. Manchester Phil. Soc., 1932—1933, 77, 69—90).—Mathematical. A simple approximation to the wave function of the neutral He atom in its normal state is proposed, vals. of parameters are determined, and the function is compared with that due to Hylleraas.
N. M. B.

Attribution of wave functions and "eigenwerten" to the separate electrons of an atom. T. KOOPMANS (Physica, 1933, 1, 104—113).—Mathematical.
J. W. S.

Transparency of the atmosphere and absorption by oxygen. J. DUCLAUX (J. Phys. Radium, 1933, [vii], 4, 625—637).—The limit of transparency of the atm. in proximity to the earth is not given exactly by the theory of mol. diffusion. The atm. contains liquids and solids (e.g., NaCl, NaClO₃, NH₄NO₃, and NH₄NO₂), which considerably increase its absorption. Air at a considerable distance from the surface of the earth has not been washed by rain, and may be impure; coeffs. of absorption measured by solar radiation may therefore be too high. It is difficult to prove that the extinction of the solar spectrum between 2500 and 1850 Å. is due to continuous absorption by O₂.
A. J. M.

Infra-red absorption of ozone. G. HETTNER, R. POHLMAN, and H. J. SCHUMACHER (Naturwiss., 1933, 21, 884).—The spectrum of O₃ from the visible to 27 μ has been investigated. No selective absorption was found in addition to that previously discovered (A., 1933, 763). The bands at 7.6, 7.39, and 11.38 μ, respectively, usually assigned to O₃ do not, in fact, belong to it. If NO₂ is introduced into the tube, bands occur at 7.6 and 11.3 μ which probably belong to N₂O₅. It is suggested that the O₃ usually employed would contain some NO giving rise to the above bands.
A. J. M.

Band spectrum of barium oxide. P. C. MAHANTI (Proc. Physical Soc., 1934, 46, 51—61; cf. A., 1933, 444).—Data and vibrational and rotational analyses are given. The band system is due to a ¹Σ⁺ → ¹Σ transition.
N. M. B.

New bands in the electronic band spectrum of neutral OH. (MISS) K. CHAMBERLAIN and H. B. CUTTER (Physical Rev., 1933, [ii], 44, 927—930; cf. Johnston, A., 1933, 445).—Data are given for the lines of the λ 2447 (3,0) and λ 2676 (3,1) bands, excited by a high-frequency discharge in a very rapid flow of H₂O vapour through the tube. Additional faint lines were found in the λ 3064 band, and nine lines, probably of the (4,1) band, in the range λ 2539—2565.
N. M. B.

3240 Å. band of NH. R. W. B. PEARSE (Proc. Roy. Soc., 1933, A, 143, 112—123).—A new band attributed to NH has been observed at 3240 Å. near the 3360 Å. band of NH in the spectrum of a heavy-current discharge tube containing H₂ and a trace of N₂. Considerably greater energy is required to excite the 3240 band than the 3360 band. The new band possesses the intensity distribution and no. of "missing lines" characteristic of a ¹Π → ¹Δ transition. Vals. of the rotational term differences and rotational consts. are given.
L. L. B.

Spectrum of sulphuryl chloride. H. W. THOMPSON (Nature, 1933, 132, 896).—The absorption spectrum of SO₂Cl₂ has been investigated over the range 5000—2000 Å. at 1—100 mm. pressure. It has certain features in common with the spectrum of CrO₂Cl₂ (A., 1933, 997).
L. S. T.

Absorption spectrum of water vapour and carbon dioxide in the region below 2000 Å. G. RATHENAU (Z. Physik, 1933, 87, 32—56).—New regions of continuous absorption by H₂O were observed at 17.8 and 24.5 volts. Interpretations

are given for bands and continua of H₂O and CO₂ down to 270 Å.
A. B. D. C.

Polyatomic molecules. Structure and activation of benzaldehyde. II. Analysis of the absorption spectrum of benzaldehyde vapour. F. ALMASY (J. Chim. phys., 1933, 30, 634—645; cf. A., 1933, 1227).—Vibration frequencies for the normal and three activated states are given. The feeble bands observed in the second portion of the absorption spectrum correspond with a series of Raman frequencies and are attributed to high vibrational levels of the normal mol. Various electronic levels are considered.
R. S.

Vibrational energy levels of hydrogen cyanide. A. ADEL and E. F. BARKER (Nature, 1934, 133, 29).—The bands 4005.6, 4993.9, 5405.0, and 6523.5 cm.⁻¹ have been observed in the infra-red spectrum of HCN vapour.
L. S. T.

Rotational structure of the Raman band (0000) → (020 ± 2) in linear symmetrical molecules YX₂. J. R. NIELSEN (Physical Rev., 1933, [ii], 44, 911—913; cf. A., 1933, 208).—Intensities of rotational lines are calc., confirming the results of Placzek (A., 1933, 446).
N. M. B.

Raman effect in ammonia and some other gases. C. M. LEWIS and W. V. HOUSTON (Physical Rev., 1933, [ii], 44, 903—910).—Interpretation of the Raman rotation spectra of polyat. mols. in terms of the polarisabilities of the mol. allows the calculation of the relative intensities of rotation lines, in good agreement with experimental results, for NH₃, CH₄, C₂H₂, and C₂H₄.
N. M. B.

Raman spectrum of heavy water. R. W. WOOD (Nature, 1933, 132, 970).—Excitation by λ 2536 of 8 c.c. of 18% heavy H₂O gave two Raman bands with an intensity ratio of 1 : 4, the new one having a mean wave-length of 2713 Å. due to H₂O mols. containing one atom of heavy H. The frequency difference is 2577 cm.⁻¹ Slight indication of the band due to mols. containing 2 atoms of heavy H appeared.
L. S. T.

Raman spectra of some cyclanones. L. PIAUX (Compt. rend., 1933, 197, 1647—1648).—The Raman spectra of cyclopentanone, 2- and 3-methylcyclopentanones, cyclohexanone, and 2-, 3-, and 4-methylcyclohexanones from 258 to 2972 cm.⁻¹ all show the ketone lines at 1709—1746 (cf. A., 1933, 1144); the absence of lines between 1600 and 1700 indicates almost complete absence of enolic forms (cf. A., 1931, 465).
C. A. S.

Raman effect. T. G. COUJOUNDZELIS (Praktika, 1932, 7, 242—247; Chem. Zentr., 1933, ii, 669).—New lines in the Raman spectra of C₆H₆, PhMe, PhCHO, PhNO₂, and PhOH are reported. The electrochemical affinity of substituent groups is considered to be an important factor in determining changes in Δν.
A. A. E.

Raman spectrum of fluorobenzene. N. G. PAI (Nature, 1933, 132, 968).—Raman frequencies for PhF are recorded. 1220 cm.⁻¹ appears to be characteristic of the C-F linking. F substitution produces a large shift of the two prominent C₆H₆ frequencies 991 and 3063.
L. S. T.

Raman effect of organic substances. I. Raman effect of a series of esters of benzoic acid and phenyl esters of fatty acids. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1933, 8, 333—365).—Raman data are tabulated for Me, Et, Pr^α, Bu^α, Pr^β, Bu^β, isoamyl, cyclohexyl, *o*-tolyl, and *n*-octyl benzoates, BzCl, PhOAc, PrCO₂Ph, and *o*-tolyl acetate. The constitutive influences on the frequencies of the C₆H₆ ring were observed. The relation among the frequencies in the region 2860—2980 cm.⁻¹ associated with the C-H linking of alkyl radicals was studied for the benzoates. The intensity and breadth of the line corresponding with the shift of 1450 cm.⁻¹, attributed to the transverse vibration of H atoms in the CH₂ group, increases as the no. of C atoms increases. The frequencies 1720, 1270, 670 cm.⁻¹ in benzoates are probably due to the CO₂ group. Shifts due to inner at. vibrations, group linkings, valency frequencies, and rotations are discussed.

N. M. B.

Molecular light scattering by binary mixtures. R. GANS and H. A. STUART [with W. MÜLLER] (Z. Physik, 1933, 86, 765—777).—Degree of depolarisation was measured for the binary mixtures C₆H₆-C₆H₁₄, CCl₄-C₆H₆, PhNO₂-CCl₄, and PhNO₂-C₆H₁₄. Data necessary for calculation of anisotropic factors are available for C₆H₆-CCl₄, and these divided by density do not show a linear variation with concn. as suggested by Rav (Physical Rev., 1923, 22, 78).

A. B. D. C.

Action of light on rubidium iodide vapour. G. H. VISSER and A. C. S. VAN HEEL (Z. Physik, 1933, 86, 694—696).—A criticism of Desai (A., 1933, 1102).

A. B. D. C.

Thermoluminescence spectra of fluorites. II. Division of the bands of the spectrum into two groups. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 22—33; cf. this vol., 10).—The bands emitted are classified into two groups the relative intensities of which vary with different samples of fluorite. After destruction of thermoluminescence by overheating, it is restored by exposure to X-rays.

D. R. D.

Theory of crystal photo-effect. H. TEICHMANN (Physikal. Z., 1933, 34, 897).—Objections to the theory previously put forward (A., 1933, 209) have been studied. It is not now considered that the equations give improbably high vals. of the ratio of the electron concn. in the crystal in the illuminated and dark condition.

A. J. M.

Liberation of ions from glass and rock-crystal surfaces by the action of radiations from radium. A. FERNAU (Physikal. Z., 1933, 34, 899—900).—If conductivity H₂O is irradiated with β- and γ-rays there is an increase in conductivity even in quartz vessels, which is dependent on the material of the vessel. The conductivity of solutions of H₂O₂ of various concns. was determined. The increase in conductivity cannot be due to the formation of H₂O₂, but must arise from the formation of ions from the material of the vessel.

A. J. M.

Effect of temperature on the energy distribution of photo-electrons. I. Normal energies. L. A. DU BRIDGE and R. C. HERGENROTHER. II.

Total energies. W. W. ROEHR (Physical Rev., 1933, [ii], 44, 861—865, 866—871; cf. A., 1933, 657).—I. Current-voltage curves for the temp. range 300—965° abs. are in good agreement with the distribution theory of normal energies.

II. Current-voltage curves for photo-electrons released from Mo at the centre of a large collecting sphere show good agreement with the Du Bridge theory for the total energy in the temp. range 300—1000° abs.

N. M. B.

Photo-cathode and unidirectional effect. P. GÖRLICH (Naturwiss., 1934, 22, 11—12).—Experiments with cells with composite cathodes (Cs₂O layers, with Cs and Ag atoms; A., 1933, 999) indicate that such cathodes show the unidirectional effect well.

A. J. M.

Nature of electrical conductivity of α-silver sulphide. II. C. WAGNER (Z. physikal. Chem., 1933, B, 23, 469—472).—Transport and electrolysis experiments have given further support to the theory (cf. A., 1933, 556) that conduction is preponderantly electronic and that the apparent validity of Faraday's law is due to secondary diffusion effects.

R. C.

Direct determination of number of active centres on a crystalline metallic cathode. N. THON (Compt. rend., 1933, 197, 1606—1608).—The attribution of overvoltage to decrease in resistance along the paths of electrons towards "active centres" leads to the expression $1/2\pi n r \chi$ ($=\eta/i$) for the resistance, where n is the no. of centres, r the radius of one, χ the specific conductivity of the electrolyte, η the overvoltage, and i the c.d. It is shown that n is approx.=the no. of crystals in the deposited metal in the cases of Zn and Cu, and r of the order 10⁻⁸ cm. when the deposit is near equilibrium with i and η both near zero. If this theory holds for larger vals. of i and η , as seems probable, r must increase with i .

C. A. S.

Electron conductivity in alkali halide crystals. I. Stationary currents. R. HILSCH and R. W. POHL (Z. Physik, 1933, 87, 78—88).—The equalisation of the positive charge at the origin of an electron in motion through a crystal was investigated for NaCl and KCl, and is shown to be attained partly by electrons moving in the reverse direction and partly by an electrolytic dark current.

A. B. D. C.

Contact resistance measurements at low temperatures. R. HOLM and W. MEISSNER (Z. Physik, 1933, 86, 787—791).—Contact resistances were measured for Au, Cu, and Ni.

A. B. D. C.

Current measurements in chloroform, with alternating current. H. EISLER (Z. Physik, 1933, 86, 792—796).—Conductivity decreases with increasing purity, and the breakdown strength is the greater the less is the conductivity.

A. B. D. C.

Electrical properties of sea-water for alternating currents. R. L. SMITH-ROSE (Proc. Roy. Soc., 1933, A, 143, 135—146).—The sp. conductivity of sea-H₂O (English Channel) increases from 3.9 × 10¹⁰ e.s.u. at a frequency of 500 cycles per sec. to 5.4 × 10¹⁰ e.s.u. at a frequency of 10,000 kilocycles per sec., at 20°. The part played by the dielectric const., ϵ , in determining the current flowing in the H₂O, in the

above frequency range, is negligible compared with the effect of the conductivity. The val. of ϵ is about 80, as for distilled H_2O , the high apparent vals. obtained at audio- and low radio-frequencies being attributed to the effect of polarisation films at the electrodes. The mean temp. coeff. of the conductivity between 0° and 40° is about $+2.7\%$ per degree. A sudden decrease in the conductivity occurs at -2° .

L. L. B.

Dielectric polarisation of hydrogen chloride in solution. II. Benzene, ethyl bromide, and ethylene dichloride as solvents. F. FAIRBROTHER (J.C.S., 1933, 1541—1543; cf. A., 1932, 322).—The improved technique includes drying the HCl without possible contamination from $POCl_3$, and new data for C_6H_6 solutions confirm previous vals. Electric moments for HCl in EtBr and $(-CH_2Cl)_2$ are 1.02 and 0.97×10^{-18} e.s.u., which accords with Zahn's val. for HCl gas. The applicability of the Debye equation to solutions of which the solvent is more polar than the solute is considered.

J. G. A. G.

Determination of the valency angles of the oxygen and sulphur atoms and the methylene and sulphony-groups, from electric dipole moments. G. C. HAMPSON, R. H. FARMER, and L. E. SUTTON (Proc. Roy. Soc., 1933, A, 143, 147—168).—The electric dipole moments of CH_2Ph_2 , Ph_2O , Ph_2S , and several of their derivatives have been measured, and the angles between the axes of the Ph groups in these compounds have been found to be $115 \pm 5^\circ$, $142 \pm 8^\circ$, and $118 \pm 8^\circ$, respectively. For the anisoles and phenols, the angles have been determined as 150° and 137° , respectively, and the moments of the O-Me and O-H linkings as 2.33 and 2.37. The use of these data gives angles for Me_2O and H_2O of 147° and 134° , respectively. The angle between each pair of valencies in Ph_2SO and its derivatives is about 115° , and the moment of the S \rightarrow O linking 2.63.

L. L. B.

Dielectric constant and absorption of several organic fluids at 1.82 metres. W. T. SZYMANOWSKI (J. Chem. Physics, 1933, 1, 809—816).—Using a resonance method at $\lambda=1.82$ m., dielectric consts. and absorptions were measured for EtOH, Pr^oOH , Pr^pOH , Bu^oOH , Bu^pOH , amyl alcohol, PhCl, $PhNO_2$, and quinoline. For liquids, e.g., ROH and PhCl, the P_∞ of which does not differ from those at normal concn., experimental data are in accord with Debye's theory. For quinoline and $PhNO_2$ Malsch's modification of Debye's formula gives a more satisfactory agreement for the dielectric consts., but not for the absorptions.

W. L. A.

Dipole moments of long-chain molecules. J. W. SMITH (J.C.S., 1933, 1567—1570).—From the dielectric consts. and densities of dil. solutions of palmitic (I) and myristic (II) acids and Me myristate (III) in C_6H_6 at 25° , the dipole moments (I) 1.05, (II) 1.02, and (III) 1.74×10^{-18} e.s.u. are calc., neglecting at. polarisation. Existing data and these results accord with the view that the electric doublet is located almost completely in the head of the mol., and the association of the acids in C_6H_6 decreases with increasing mol. wt.

J. G. A. G.

Dipole moments of the chlorobenzophenone oximes. G. S. PARSONS and C. W. PORTER (J.

Amer. Chem. Soc., 1933, 55, 4745—4746).—The *cis*- and *trans*-o-oximes have identical dipole moments (161×10^{-18} e.s.u.), whilst in the *m*- and *p*-oximes the higher-melting form has the lower dipole moment (*m* 1.50 and 1.61×10^{-18} ; *p* 2.230 and 2.381×10^{-18} e.s.u.). When the low-melting form is subjected to the Beckmann rearrangement the C_6H_4Cl group shifts to the N atom. The unsubstituted Ph migrates when the high-melting form undergoes the Beckmann change.

E. S. H.

Some electrostatic factors which can operate in polar reactions. W. A. WATERS (J.C.S., 1933, 1551—1557; cf. A., 1933, 890, 1124).—Theoretical. Equations are derived for the energy involved in (1) the field or direct effect, which is exerted across space, of ionic charges and permanent dipoles, and (2) the induced effects of these changes and dipoles transmitted through the mol. to the covalent linking which has to be activated. It is suggested that in the experimentally verified equation $E=E_0+C(\mu+a\mu^2)$ (*loc. cit.*) the term $C\mu$ corresponds with (1) and $Ca\mu^2$ with (2). Refractivity data afford linking polarisabilities which show that (2) is $<$ (1), consistent with existing reactivity data. Secondary polarisation and field effects are negligible in org. mols., and hence local electrostatic fields due to mols. will not appreciably alter the frequency of intermol. collisions from that calc. for electrically neutral mols.

J. G. A. G.

Refractive indices and refractions of dilute electrolyte solutions. II. Improvement of interferometric method and measurements with thallium chloride and nitrate. A. E. BRODSKI and N. S. FILIPPOVA. III. Refractive indices and refraction values of potassium chloride, bromide, and nitrate, and sodium chloride. A. E. BRODSKI and J. M. SCHERSCHEVER (Z. physikal. Chem., 1933, B, 23, 399—411, 412—427).—II. The interferometric method of determining n previously described (A., 1931, 122) has been improved and the precision increased. The difference in n between solution and solvent, Δn , and its dispersion and temp. coeff. have been measured for 0.001—0.1N-TlCl and 0.01—0.1N-TlNO₃. For both salts $\Delta n/c$ is a linear function of the concn., c .

III. Δn has been measured for aq. solutions of KCl, KNO₃, NaCl, and KBr over a concn. range of 0.001—0.1N at several temp. For all these salts $\Delta n/c$ decreases with increasing c , the decrease being linear except for NaCl. For KCl, KBr, and NaCl the graph of the apparent mol. refraction, R , of the solute against the concn. in mol. per litre is linear only at the higher concns. It is suggested that over the whole concn. range the electric forces of the ionic atm., and not the mutual deformation of the ions or ionic association, are the factors determining the variation of R .

R. C.

Variation with concentration of molecular refraction of electrolytes. K. FAJANS and W. GEFFCKEN (Z. physikal. Chem., 1933, B, 23, 428—430).—Comments on Brodski's papers (cf. preceding abstract).

R. C.

Dispersion measurements in the infra-red. R. W. POHL (Z. Physik, 1933, 86, 833).—Grundelach

and Korth (cf. A., 1933, 1001) have used interferometers similar to those of Pfund (Z. wiss. Phot., 1913, 12, 341).

A. B. D. C.

Refractometric constant of the CN group. P. BRUYLANTS and R. MERCKX (Bull. Acad. roy. Belg., 1933, [v], 19, 1003—1016).—From the mol. refractivity of hydrocarbons and nitriles the sp. refractivity of the CN group is 5.434 and 5.459 for the H_a and D lines, respectively, the corresponding vals. for H being 1.026 and 1.037, and for CH_2 4.617 and 4.636, respectively.

J. W. S.

Rotatory dispersive power of organic compounds. XXIV. Ascorbic acid. T. M. LOWRY and S. A. PEARMAN (J.C.S., 1933, 1444—1449).—Aq. solutions of ascorbic acid exhibit mutarotation in presence of O_2 and show anomalous dispersion, having a max. in the violet. Dilution or addition of alkali increases the rotatory power of aq. solutions, but the val. for alkaline solutions diminishes after some days, and finally becomes negative on atm. oxidation. Alkaline solutions do not undergo mutarotation in the absence of O_2 , and show simple rotatory dispersion and increased rotatory power.

W. R. A.

Optical rotatory dispersion in the carbohydrate group. II. Ascorbic acid. R. W. HERBERT, E. L. HIRST, and C. E. WOOD (J.C.S., 1933, 1564—1567).—The head of the absorption band, H , of ascorbic acid (I) in dil. aq. and MeOH solutions moves from 260—265 to 240—245 $m\mu$ with rise of concn., c , but in acid solutions H at 240—245 is independent of c . H is at 245 $m\mu$ in dioxan. Although H of Na ascorbate (II) at 265 $m\mu$ is independent of c , it moves to greater λ with increasing alkalinity. The rotatory dispersions, α_1 , of (I) in MeOH and dioxan appear to be simple, but can be represented by two-term equations. Whereas α_1 of (I) in H_2O is very anomalous with a negative term corresponding with λ 2480, α_1 of (II) in H_2O is simple and is controlled by a positive term corresponding with λ 2450. Although the charge on the ion may reverse the sign of circular dichroism without altering the intensity of the observed absorption band, it is likely that the profound change in the dispersion is attributable to instantaneous intermol. change during ionisation.

J. G. A. G.

Mutarotation of α -D-glucose in heavy water. E. PACSU (J. Amer. Chem. Soc., 1933, 55, 5056—5057).—The displaceable H^1 atom of a reducing sugar in $\text{H}^2\text{H}_2\text{O}$ is immediately replaced by H^2 .

E. S. H.

Magnetic birefringence of gaseous oxygen. T. BELLING (Compt. rend., 1933, 197, 1615—1616).—With a field of 45,000 gauss the magnetic birefringence of O_2 is negative and proportional to the pressure from 25 to 100 atm. For 100 kg. per sq. cm. $C_m = -4.8 \times 10^{-14}$, or 0.005 of that deduced from the Langevin-Debye theory, for agreement with which α must = 54° (cf. A., 1933, 663, 765).

C. A. S.

Thermal variation of magnetic birefringence of nitrobenzene, benzene, and carbon disulphide. A. GOLDET (Compt. rend., 1933, 197, 1612—1614).—The variations of the magnetic birefringence with temp. have been determined for PhNO_2 (10—100°), C_6H_6 (10—65°), and CS_2 (0—45°); at 20° they are, respectively, 1/144.6, 1/400, and 1/235. Comparison

with results based on Langevin's theory in the case of CS_2 favour de Malleman's invariant, $(n^2-1)(2n^2+1)/n^2d$; in the other two cases it gives no better agreement than the Lorenz-Lorentz theory (cf. A., 1928, 1310).

C. A. S.

Thermomagnetic study of some nickel salts in the solid state. (MLLE.) A. SERRES (Ann. Physique, 1933, [x], 20, 441—477).—As opposed to Ni salts in solution, the solids gave magnetisation coeffs. diverging from the Weiss law, to which a paramagnetism correction const. must be applied. Full data are tabulated and plotted for the various hydrated states of NiSO_4 , and for $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, NiCl_2 , NiF_2 , NiBr_2 , and $\text{Ni}(\text{CN})_2$. For the last-named no correction is required.

N. M. B.

Ferromagnetism of nickel colloids. S. R. RAO (Physical Rev., 1933, [ii], 44, 850—853).—The intensity of magnetisation of colloidal Ni prepared by an electrical dispersion method, colloid particles being $< 1.5 \mu$ diameter, was $<$ that of the mass metal. The result is discussed with reference to Heisenberg's and Bitter's theories of ferromagnetism.

N. M. B.

Temperature dependence of ferromagnetic saturation. P. S. EPSTEIN (Proc. Nat. Acad. Sci., 1933, 19, 1044—1049; cf. A., 1932, 900).—Theoretical.

R. S.

Magnetic susceptibilities of europium and gadolinium compounds. P. W. SELWOOD (J. Amer. Chem. Soc., 1933, 55, 4869—4875).—Data have been determined from -190° to 70° or 100° for Eu_2O_3 , $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, EuSO_4 , Gd_2O_3 , GdCl_3 , and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The susceptibility and electronic configurations of Eu^{2+} are the same as those of Gd^{3+} .

E. S. H.

Diamagnetic susceptibility of atoms. P. GOMBÁS (Z. Physik, 1933, 87, 57—61).—Theoretical.

A. B. D. C.

Electronic structure of hexafluorides. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1933, 1427—1429).— SF_6 , SeF_6 , and TeF_6 have identical structures according to parachor determinations, viz., two F attached to the central atom by covalent linkings and the remaining four by semipolar singlet linkings.

W. R. A.

Electronic structure of inorganic complexes. W. A. NOYES (J. Amer. Chem. Soc., 1933, 55, 4889—4893).—Theoretical. The ionic charges of complexes are explained on Sidgwick's assumption that the coordinated ions and mols. of the Werner complexes are donors and the central metallic ions acceptors, and that a donor increases its positive valency by 1, whilst an acceptor increases its negative valency by 1. The rearrangement of the negative nitrite and cyanide ions to positive nitro- and carbylamino-groups is discussed.

E. S. H.

"Unshared" electrons and the effects produced by o - p -directive substituents in organic molecules. G. N. BURKHARDT and M. G. EVANS (Mem. Manchester Phil. Soc., 1932—1933, 77, 37—50).—The essentials of the chemical properties ascribed to unshared electrons of N''' , O'' , and halogen atoms, and the interpretation of the origin of o - p -directing power are examined. The cases of Me, NH_2 , and OH

groups, and the ionisation potentials for the various electrons concerned in these linkings are discussed.

N. M. B.

Change from aromatic to metallic electrons in organic compounds. A. R. UBBELOHDE (*Nature*, 1933, 132, 1002).—Theoretical.

L. S. T.

Constitution of liquid substances. P. BOGDAN (*J. Chim. phys.*, 1933, 30, 581—627).—Theoretical. Mol. association and other properties of liquid are discussed.

R. S.

Quantum-mechanical stability of a benzene molecule. M. MARKOV (*J. Chem. Physics*, 1933, 1, 784—788).—The C_6H_6 mol. is considered as consisting of six trivalent N-like CH groups. The Heitler-London-Rumer treatment of valency linking yields a matrix of the 34th order which can be decomposed to six matrices of lower order each corresponding with a definite proper val. of the operator which must be < -9 if the model is to be stable mechanically and thermodynamically. The model chosen is proved mechanically but not thermodynamically stable.

W. R. A.

Molecular symmetry and the reduction of the secular equation. H. EYRING, A. A. FROST, and J. TURKEVICH (*J. Chem. Physics*, 1933, 1, 777—783).—Linking proper functions of any multiplicity may be reduced to a linear independent set; the method of obtaining matrix components for singlet linking proper functions is also extended to all multiplicities. By application of the group theory reduced secular equations are obtained with reference to NH_3 , N_2 , and CH_4 .

W. R. A.

Helium hydride ion. G. GLOCKLER and D. L. FULLER (*J. Chem. Physics*, 1933, 1, 886—887).—The structure of the ion is considered on the basis of wave mechanics.

N. M. B.

Affinity. III. T. DE DONDER (*Bull. Acad. roy. Belg.*, 1933, [v], 19, 1140—1152).—Theoretical.

J. W. S.

Inter-atomic distances and forces. ANON. (*Nature*, 1933, 132, 992—994).—A summary of the British Association discussion.

L. S. T.

Theory of critical phases: generality of properties of zero area. E. JOUGET (*Compt. rend.*, 1933, 197, 1705—1709).—Mathematical. Gibbs' treatment of the phase rule is expanded and generalised in the light of recent work on crit. phenomena.

C. A. S.

Statistics of polyatomic gases. K. SZÉLL (*Z. Physik*, 1933, 86, 810—817).—Fermi-Dirac and Bose-Einstein quantum statistics are applied to translation and rotation of mols. with two or three equal moments of inertia.

A. B. D. C.

Capillary depression of mercury in wide tubes. A. KLEMENC and O. BANKOWSKI (*Naturwiss.*, 1934, 22, 10—11).—The capillary depression of Hg in wide tubes has been investigated by an interferometer method. In a tube 30 mm. in diameter, a depression of 0.002 mm. was found. In a tube 40 mm. in diameter, the depression was $< 0.2 \mu$.

A. J. M.

Fine structure of X-ray absorption by molecular gases. H. PETERSEN (*Arch. Néerland.*, 1933,

[iii], 14, 165—218).—A theory of absorption by polyat. mols. is developed, and that by Cl_2 is discussed.

H. J. E.

Diffuse scattering of X-rays from sodium fluoride. II. Scattering at the temperature of liquid air. G. E. M. JAUNCEY and P. S. WILLIAMS (*Physical Rev.*, 1933, [ii], 44, 794—797; cf. A., 1933, 558).—The ratio of the intensity of X-rays diffusely scattered by a single crystal of NaF at 86° abs. to that at 295° abs. was determined for the angle range $10-42^\circ$. Results are in good agreement with calc. vals.

N. M. B.

Changes in the X-ray diffraction pattern of nitrobenzene produced by an electric field, changes in temperature, and circulation. F. C. TODD (*Physical Rev.*, 1933, [ii], 44, 787—793).—The intensity change in the diffraction pattern due to a field of 10 kv. per cm. was $-0.02 (\pm 0.06\%)$ over the peak. The change produced by temp. increases in the range $16-42^\circ$, and by circulating the $PhNO_2$ past the point of X-ray illumination indicates that the mols. associate in pairs and are dissociated by thermal or mechanical agitation.

N. M. B.

Connexion between chemical constitution and K-X-ray absorption spectra. XII. K-X-Ray absorption spectra of stereoisomerides. I. O. STELLING (*Z. physikal. Chem.*, 1933, B, 23, 338—346; cf. A., 1933, 214).—The X-ray absorption spectra of Cl in compounds of the type $[MA_4YCl]X$, where $A = NH_3$ or $\frac{1}{2}$ en have been studied. For a given cation the position of the soft edge is const., independent of the anion, and the hard edge is affected by the anion only if this is Cl, when it is softened. In the dihalogenotetrammino-salts the long-wave edge of the *trans* form is softer than that of the *cis* form, whilst if Y is NO_2 or NCS both isomerides have the same spectrum. These observations have been applied to the determination of the configurations of the supposed stereoisomerides of $[Co, 3NH_3, H_2O, Cl_2]Cl$ and the corresponding Cr compound.

R. C.

Crystalline structure of the compound MgPr. A. ROSSI and A. LANDELLI (*Atti R. Accad. Lincei*, 1933, [vi], 18, 156—161).—When examined by the powder method MgPr gives a 3.88 \AA . (or an integral multiple thereof), $d^{20} 4.67$, $d_{calc} 4.65$, a calc. from the at. radii 3.95 \AA .

O. J. W.

Energy content, particle dimensions, and lattice formation of active beryllium oxides. R. FRICKE and J. LÜKE (*Z. physikal. Chem.*, 1933, B, 23, 319—329).—BeO prepared from metastable cryst. $Be(OH)_2$ at various temp., from its heat of dissolution in aq. HF, has the higher energy content the lower is the temp. of prep., *T*. X-Ray study shows that the crystallites decrease in size with fall in *T*, and that in the direction of the *c* axis the dimensions lie within the colloidal range. The high energy content of the low-temp. preps. is due, in the main, to imperfect lattice formation.

R. C.

Electron interference experiments with active beryllium oxides. R. FRICKE and J. LÜKE (*Z. physikal. Chem.*, 1933, B, 23, 330—337; cf. preceding abstract).—Cathode-ray interferences of BeO pre-

pared from metastable cryst. $\text{Be}(\text{OH})_2$ at various temp. and supported on fine collodion membranes show that the crystallites are plates perpendicular to the c axis. The intensities of the interferences pass through a max. with rise in the temp. of prep., the suggested explanation being that oxides prepared at a low temp. give weak interferences owing to the imperfectly formed lattice and those ignited at higher temp. give weak interferences owing to their crystallites being too thick. R. C.

Investigation of copper oxide films by electron diffraction. C. A. MURISON (Phil. Mag., 1934, [vii], 17, 96—98).—Surface films on Cu heated in air gave diffraction patterns for Cu_2O and a new form of CuO (I) (cf. Thomson and Fraser, A., 1930, 1082). (I) is formed by heating Cu blocks in an air or O_2 stream at 300—500°. H. J. E.

Alkali alkylarsinates. M. G. GILTZ (Bull. Soc. chim. Belg., 1933, 42, 443—447).—Crystallographic measurements of Cs methylarsinate, and Na ($+2\text{H}_2\text{O}$) and Rb ethylarsinate have been made. F. R. S.

Realgar and benitoite. H. BUTTGENBACH (Bull. Acad. roy. Belg., 1933, [v], 19, 1019—1033).—The crystal forms of these minerals are discussed in detail. J. W. S.

Molecular orientations in p -diphenylbenzene crystal. K. S. KRISHNAN and S. BANERJEE (Nature, 1933, 132, 968—969).—Correlation of the principal diamagnetic susceptibilities of the crystal with those of the mols. of $p\text{-C}_6\text{H}_4\text{Ph}_2$ shows that the lengths of the mols. lie in the (010) plane (I), in the acute angle β , making an angle of 14.3° with the c axis, and that the planes of the two mols. are inclined at $+56.6^\circ$ and -56.6° , respectively, to (I). L. S. T.

Crystal structure of s -triphenylbenzene. K. LONSDALE (Nature, 1934, 133, 67).—The crystal class is orthorhombic pyramidal and not orthorhombic bipyramidal. The crystals show a small piezo-electric effect indicating that the crystallographic a axis is a polar axis. The mols. are asymmetric and the plane of the C_6 rings is not coincident with the (001) plane, but makes a small angle with it (cf. this vol., 17). L. S. T.

X-Ray study of s -triphenylbenzene. B. P. ORELKIN (J. Gen. Chem. Russ., 1933, 3, 643—651).—The distances between the o -, m -, and p -C atoms of $s\text{-C}_6\text{H}_3\text{Ph}_3$ are respectively 0.79, 1.12, and 1.38 Å., and the depth of the C_6 ring is 0.46 Å. R. T.

X-Ray investigation of fatty acid esters of cellulose. J. J. TRILLAT (Compt. rend., 1933, 197, 1616—1618).—Debye-Scherrer photographs of cellulose esters from the triacetate to the tristearate show the same larger outer rings throughout the series, indicating a const. reticular distance, d_2 , whilst the inner ring steadily decreases as the length of the aliphatic chain increases, indicating a regular increase in the reticular distance, d_1 , of 1.3 Å. per C atom. d_2 is therefore due to the cellulosic portion, d_1 to the acyl group. Esters up to the butyrate have a cryst. structure; higher ones are mesomorphic and increasingly plastic. The ester chains are approx. perpendicular to the cellulosic, the distance between the latter increasing with the length of the former (cf. A., 1930, 1352). C. A. S.

X-Ray study of konnjakumanna. III. Orientation of micelles by stretching, freezing, and drying. I. SAKURADA and K. HUTINO (J. Soc. Chem. Ind. Japan, 1933, 36, 662B; cf. A., 1933, 1235).—The micelles in β -konnjakumanna are oriented in films, prepared by drying and in cakes formed by freezing, and not only in stretched material. A. G.

Spontaneous orientation of the micelles in unstretched films of cellulose acetate and nitrate. I. SAKURADA and K. HUTINO (J. Soc. Chem. Ind. Japan, 1933, 36, 659—661B).—X-Ray photographs of films of cellulose acetate or nitrate obtained by drying 5% solutions on glass plates show definite orientation when the rays are parallel to the film surface. A. G.

Dynamics of liquid crystals. P. J. BOUMA (Arch. Néerland., 1933, [iiiA], 14, 219—284).—The dielectric loss for p -azoxyanisole as a function of frequency has a max. corresponding with the crit. frequency observed by Kast (A., 1931, 1116). Below this frequency the swarms are parallel to the field, and above it are at right angles. The val. rises rapidly with temp. In the solid state, the dielectric loss at high frequencies (*e.g.*, 10^6 hertz) is the same as for the liquid crystals. The time for orientation in a steady magnetic field was measured, and factors affecting it are discussed. In absence of disturbing effects, the time may be several min. H. J. E.

Crystal absorption by substrates. G. I. FINCH, A. G. QUARRELL, and J. S. ROEBUCK (Nature, 1934, 133, 28).—Zn vapour condensed on a cool, polished Cu surface gives rise to a well-defined electron diffraction pattern which initially is brilliant but disappears in a few sec. The rate at which the initial cryst. structure disappears becomes slower with each successive deposit. When Zn is deposited under similar conditions but on to a sputtered or etched Cu, or on to a Cu surface which had been oxidised and reduced, a cryst. film of permanent structure is formed. The results are regarded as an experimental proof of the existence of the Beilby layer. L. S. T.

Oscillation figures of piezo-electric crystals. H. STRAUBEL (Physikal. Z., 1933, 34, 894—896).—An arrangement for obtaining oscillation figures of piezo-electric crystals is described. A. J. M.

Magnetic analysis of nickel films deposited by evaporation. H. N. OTIS (Physical Rev., 1933, [ii], 44, 843—849).—Magnetisation curves for films deposited at various temp., under different degrees of annealing, and on metals with coeffs. of expansion $>$ or $<$ that of Ni are given. Results are explained on Becker's strain theory. N. M. B.

Magnetorotation in non-adiabatic change of the magnetic field. E. BRETSCHER and W. DECK (Helv. phys. Acta, 1933, 6, 229—231; Chem. Zentr., 1933, ii, 1314).

Effect of heat-treatment on production of frictional electric charges on metals. P. A. MAINSTONE (Phil. Mag., 1933, [vii], 16, 1083—1096).—Heating Al or Ni at 300—350° in vac. or in N_2 at 1 atm. lowers the normal frictional charge. Partial

recovery occurs on cooling. The effect of de-gassing was studied. The frictional charge on polished Pd changes from positive to negative when it is de-gassed and heated in H_2 to 250° . Results are correlated with adsorption phenomena. H. J. E.

Elliptic reflexion under normal incidence from a transparent anisotropic substance: superficial birefringence of calcspar. R. DE MALLEMANN and H. COURTILOTT (Compt. rend., 1933, 197, 1610—1612).—The possibility previously adumbrated (cf. Bull. Soc. franç. Phys., 1932, 319, 34) of this phenomenon is demonstrated for the case of calcspar. The observations are explicable on the assumption of a passage layer. C. A. S.

Interference of light in metallic films. J. B. NATHANSON (J. Opt. Soc. Amer., 1933, 23, 388—393).—The interference fringes observed when films of Mn and Pt sputtered cathodically on glass are viewed by reflected light have been investigated. The shape of the fringes depends on the shape of the cathode, being circular for a round cathode and straight for a rectangular cathode. The colours arise most probably from interference of light between the front and rear surface of the films, and from this hypothesis the vol. and mass of the film can be computed. For Mn, but not for Pt, the computed mass agrees fairly well with the mass obtained by weighing the film. The discrepancy with Pt may be due to the uncertainty of the optical consts. for thin Pt films or to occlusion of H_2 . W. R. A.

Explanation of a fine structure in the optical absorption bands of metals. R. DE L. KRONIG (Naturwiss., 1934, 22, 11).—Theoretical. An explanation of the results of Smakula (A., 1933, 1226) is based on quantum mechanics. A. J. M.

Flow conditions for crystals. W. BOAS and E. SCHMID (Z. Physik, 1933, 86, 828—830). A. B. D. C.

Plasticity of rock-salt and its dependence on water. R. B. BARNES (Physical Rev., 1933, [ii], 44, 898—902).—Measurements show that H_2O penetrates into the interior of rock-salt when the latter is placed in H_2O . The influence of H_2O on the increased plasticity and tensile strength (Joffé effect) is discussed. N. M. B.

Physical properties of silicon and ferrosilicon. C. BEDEL (Ann. Chim., 1933, [x], 20, 439—519; cf. A., 1929, 756, 997, 1399; 1930, 437; 1931, 674, 1237; 1933, 217; B., 1933, 151).—A full account of work previously published. F. L. U.

Velocity of sound in gases. F. H. VAN DEN DUNGEN (Bull. Acad. roy. Belg., 1933, [v], 19, 1180—1187).—Theoretical. J. W. S.

Acoustical studies. II. Behaviour of a gas with several independent internal energy states. W. T. RICHARDS (J. Chem. Physics, 1933, 1, 863—879; cf. A., 1933, 217).—Mathematical. N. M. B.

Theory of superconductivity. C. J. GORTER (Nature, 1933, 132, 931; cf. this vol., 19).

Superconductivity of zinc. W. H. KEESOM (Physica, 1933, 1, 123—127).—Zn becomes superconducting at 0.79° abs. Cd and Au are not super-

conducting at 0.73° abs., or Pt at 0.77° abs. Phosphor-bronze is not superconducting at 0.75° abs., so Cu is probably not superconductive at that temp. J. W. S.

Change of the resistance of single crystals of gallium in a magnetic field. W. J. DE HAAS and J. W. BLOM (Physica, 1933, 1, 134—144; cf. A., 1930, 675, 985, 1102, 1353).—The resistance of a single Ga crystal at 10 — 20° abs. and in a magnetic field of 5000—22,000 gauss shows similar behaviour to that of a single Bi crystal. The curve of relative change in resistance against inclination of the field to the axis of the crystal is almost sinoidal at low field strengths. The results are in agreement with the rhombic crystal structure of Ga (A., 1932, 987). J. W. S.

Adiabatic cooling of paramagnetic salts in magnetic fields. W. J. DE HAAS, E. C. WIERSMA, and H. A. KRAMERS (Physica, 1933, 1, 1—13; cf. A., 1933, 1026).—By the adiabatic demagnetisation of CeF_3 , $Dy(EtSO_4)_3 \cdot 9H_2O$, $Ce(EtSO_4)_3 \cdot 9H_2O$, and $KCr(SO_4)_2 \cdot 12H_2O$, previously cooled to 1.35° abs., temp. of 0.13° , 0.12° , 0.085° , and 0.05° abs., respectively, have been reached. F. L. U.

Correlation of heat capacity, absolute temperature, and entropy. G. A. LINHART (J. Chem. Physics, 1933, 1, 795—797).—Assuming that at low temp. C is proportional to S , and at high temp. it approaches a limiting val., C_∞ , the following relations connecting C , S , and T are calc.: $C = C_\infty ke^{k \log T} / (1 + ke^{k \log T})$, and $S = 2.3(C_\infty / K) \log C_\infty / (C_\infty - C)$. The validity of these relations is supported by experiment. W. R. A.

Heat capacity and entropy of nitrogen. Heat of vaporisation. Vapour pressures of solid and liquid. Reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ from spectroscopic data. W. F. GIAUQUE and J. O. CLAYTON (J. Amer. Chem. Soc., 1933, 55, 4875—4889).—The heat capacities of N in the two cryst. and liquid forms have been determined from 15° abs. to the b.p. The data recorded are: transition point 35.61° abs.; m.p. 63.14° abs.; b.p. 77.32° abs.; heat of transition 54.71 g.-cal. per mol.; heat of fusion 172.3 g.-cal. per mol.; heat of vaporisation (at 760 mm.) 1332.9 g.-cal. per mol.; entropy at b.p. 36.5 e.u.; abs. entropy at 298.1° abs. 50.154 e.u.; v.p. of solid N (54.78 — 63.14° abs.) $\log_{10} p(\text{cm.}) = -(381.6/T) + 7.41105 - 0.0062372T$; v.p. of liquid N (63.14 — 78.01° abs.) $\log_{10} p(\text{cm.}) = -(339.8/T) + 6.71057 - 0.00562867T$; free energy of formation of NO (298.1° abs.) 20.650 g.-cal. per mol. E. S. H.

Low-temperature specific heats. IV. Heat capacities of potassium chloride, potassium nitrate, and sodium nitrate. J. C. SOUTHARD and R. A. NELSON (J. Amer. Chem. Soc., 1933, 55, 4865—4869; cf. this vol., 20).—The heat capacities (g.-cal. per mol. per degree) at 298.16° abs. are: KCl 19.75 ± 0.06 , KNO_3 31.77 ± 0.10 , $NaNO_3$ 27.87 ± 0.08 . Measurements have been extended over the range 15 — 290° abs. The free energies of formation of the salts from the elements are $-97,700$, $-95,000$, and $-88,300$ g.-cal. per mol., respectively. E. S. H.

Specific heats of metals at higher temperatures. XII. Specific heat of rhenium. F. M. JAEGER

and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 786—788).—The sp. heat c_p for Re at 0—1200° is given by $0.03256 + 0.6625 \times 10^{-5}t$.
J. W. S.

Variation of specific heat of gases with pressure. E. BURLOT (Mém. Poudres, 1933, 25, 314—335).—For the calculation of explosion temp. a correction to the quantity of heat liberated is deduced. This applies only when the Clausius-Sarrau equation of state is applicable, and not when the pressure and temp. are both high, as is usually the case. A. G.

Simple calorimeter for heats of fusion. Data on the fusion of ψ -cumene, mesitylene (α and β), hemimellitene, *o*- and *m*-xylene, and on two transitions of hemimellitene. F. D. ROSSINI (Bur. Stand. J. Res., 1933, 11, 553—559).—Heats of fusion may be measured quickly, with an accuracy of a few %, by using a vac. flask fitted with a thermoelement as a simple calorimeter. The following vals. have been found for f.p. and mol. heat of fusion in kg.-cal., respectively: ψ -cumene, -44.1° , 2.75 ± 0.06 ; hemimellitene (I), -25.5° , 2.00 ± 0.05 ; α -mesitylene, -44.8° , 2.28 ± 0.06 ; β -mesitylene, -51.7° , 1.91 ± 0.05 ; *o*-xylene, -25.3° , 3.33 ± 0.07 ; *m*-xylene, -47.9° , 2.76 ± 0.05 . (I) has two transitions with the following heats of transition: $\gamma \rightarrow \beta$, $-58 \pm 2^\circ$, 0.28 ± 0.04 ; $\beta \rightarrow \alpha$, $-46 \pm 1^\circ$, 0.36 ± 0.04 .
M. S. B.

Butadiene nitriles. G. HEIM (Bull. Soc. chim. Belg., 1933, 42, 461—466).—The b.p., d , n , and mol. dispersion of pure *cis*- and *trans*-crotono- and vinyl-aceto-nitriles have been measured.
F. R. S.

F.p. of organic substances. XIV. Alternation of f.p. in homologous series of symmetrical disubstituted compounds. H. SERWY (Bull. Soc. chim. Belg., 1933, 42, 483—501; cf. A., 1931, 1361).—F.p., b.p., d , coeff. of expansion, viscosity, and n have been determined for a no. of compounds of the type $X \cdot [CH_2]_x \cdot X$ in which $x=1-5$ and $X=Cl, Br, CN, CO_2H$, and CO_2R . The variation of f.p. in homologous series is discussed.
F. L. U.

Thermal expansion of the crystal lattices of silver, platinum, and zinc. E. A. OWEN and E. L. YATES (Phil. Mag., 1934, [vii], 17, 113—131; cf. A., 1933, 1106).—The lattice parameters of Ag and Pt from 0° to 600° have been measured. Vals. for Zn between 20° and 415° along and perpendicular to the hexagonal axis agree with measurements on single-crystal rods of Zn.
H. J. E.

Thermodynamic considerations on a new kind of transition points. O. HALPERN (J. Chem. Physics, 1933, 1, 880—881).—Failure to observe the coexistence of two phases at the new transition point in liquid He (cf. Keesom, A., 1933, 559) can be explained if the two phases do not exhibit a discontinuity in energy.
N. M. B.

Thermodynamic diagrams of liquid helium. W. H. KEESOM and (Miss) A. P. KEESOM (Physica, 1933, 1, 128—133; cf. A., 1933, 894, 1109).—From the data previously recorded, p - T and d - T diagrams are constructed. From these, diagrams have been derived for $(\partial d/\partial p)_T$, $(\partial p/\partial T)_d$, and $(\partial d/\partial T)_p$. Marked discontinuities occur in these differential coeffs.

when passing the transition curve between He I and He II.
J. W. S.

Thermodynamic properties of β -methylpentan- β -ol. F. HOVORKA, H. P. LANDELMA, and C. K. NAUJOKS (J. Amer. Chem. Soc., 1933, 55, 4820—4822).—Data are given for the f.p. ($-103 \pm 1.5^\circ$), surface tension, d , n , viscosity, v.p., parachor, and Eötvös const. of β -methylpentan- β -ol. The b.p. found by interpolation in the v.-p. curve is $121.09 \pm 0.03^\circ$. The calc. heat of vaporisation is about 9700 g.-cal. at the b.p.
E. S. H.

Thermodynamic properties of trichlorotrifluoroethane and tetrachlorodifluoroethane. F. HOVORKA and F. E. GEIGER (J. Amer. Chem. Soc., 1933, 55, 4759—4761).—The d , n , surface tension, v.p., and viscosity have been measured over the range $28.1-90.0^\circ$ for $C_2Cl_4F_2$ and $0.0-40.0^\circ$ for $C_2Cl_3F_3$. The crit. temp., mol. heat of vaporisation, parachor, and v.p.-temp. equation have been calc.
E. S. H.

Vapour pressure of vinyl acetate. J. MARSDEN and A. C. CUTHBERTSON (Canad. J. Res., 1933, 9, 419—423).—The v.p. has been measured by an isoteniscope method between 0° and the normal b.p. (72.5°). The mol. heat of evaporation is 8211 g.-cal., Trouton's const. is 23.8, and the calc. val. of the crit. temp. is 228.3° .
R. S.

Vapour pressures and heats of vaporisation of normal nitriles. G. HEIM (Bull. Soc. chim. Belg., 1933, 42, 467—482; cf. A., 1932, 1197).—V.p. of saturated normal nitriles C_2-C_8 , and of vinylaceto- and *cis*- and *trans*-crotono-nitriles have been determined. Heats of vaporisation have been calc.
F. L. U.

Process of vaporisation. K. SCHREBER (Z. tech. Physik, 1933, 14, 81—85; Chem. Zentr., 1933, i, 1749).—The temp. difference between liquid and vapour is discussed. In pure liquids it depends only on the velocity of vaporisation.
A. A. E.

Relation between viscosity, vapour pressure, and density. F. HOVORKA (J. Amer. Chem. Soc., 1933, 55, 4899—4900).—The empirical equation $S = \eta P^{1/4} d^{1/2}$, where η is the viscosity, P the v.p., d the density, and S a const. characteristic of the substance, is established for many org. liquids.
E. S. H.

Collision areas of 1 : 3 : 5-mesitylene and of the most highly branched heptanes. W. A. EVERHART, W. A. HARE, and E. MACK, jun. (J. Amer. Chem. Soc., 1933, 55, 4894—4897).—The viscosities of the vapours of 1 : 3 : 5-mesitylene ($100.4-200.0^\circ$) and $\beta\beta\gamma$ -trimethylbutane ($70.3-262.1^\circ$) have been determined over the temp. range indicated. The calc. Sutherland consts. are 136.3 and 257, respectively, and the collision areas 42.4 and 31.1 sq. Å.
E. S. H.

Viscosity, heat conductivity, and diffusion in gas mixtures. XXIV. Determination of the "unpaired viscosity" η_{12} ; application, proof, and various methods of explanation of the viscosity law for binary mixtures. M. TRAUTZ (Ann. Physik, 1933, [v], 18, 816—832).—The relations involved in the formulæ of Maxwell, Enskog, Chap-

man, and Trautz for the viscosity of binary gas mixtures are discussed and compared. A. J. M.

F.p. and densities of binary mixtures of alcohol and ether. LALANDE (Mém. Poudres, 1933, 25, 421—435; cf. A., 1933, 345).—The sp. vol. at 0° of mixtures of EtOH and Et₂O is given by $V = V_1N_1 + V_2N_2 + \Phi_{1,2}N_1N_2$ where N_1 and N_2 are mol. fractions and $\Phi_{1,2} = 2.3 \pm 0.3$. The f.-p. diagram shows a eutectic at -125° and 68.3 mol.-% EtOH. A. G.

Fluidity of dioxan-water mixtures. J. A. GEDDES (J. Amer. Chem. Soc., 1933, 55, 4832—4837).—Viscosities have been measured at 20—80°. The fluidity-concn. curves exhibit inflexion at 5% H₂O. The max. deviation from linearity indicates the presence of approx. 5% of C₁H₈O₂.5H₂O. The variation of the fluidity of dioxan with temp. is given by $\phi = [T - 171.97 + (T^2 - 146.58T + 39,264.2)^{1/2}] - 0.51894$. E. S. H.

Specific heat of aqueous solutions of phosphoric acid. M. M. POPOV, S. M. SKURATOV, and N. N. FEODOSSJEV (Z. physikal. Chem., 1933, 167, 42—48).—The true sp. heat of aq. H₃PO₄ for concns. up to 89% has been determined at 20.5—22.0°. The mean sp. heat has been determined for concns. up to 60% at 20—100° and for 60—89% solutions from 20° up to near the b.p. R. C.

Heat of formation of binary liquid solutions from their liquid components. J. J. COLEMAN and F. E. E. GERMANN (J. Chem. Physics, 1933, 1, 847—851).—An empirical equation is given which connects the heat of formation with the temp. and composition of the liquid mixtures. The equation is applied to a large no. of binary mixtures. N. M. B.

Distillation. II. Liquid-vapour equilibria in the systems ethyl alcohol-water, methyl alcohol-water, and acetic acid-water. L. W. CORNELL and R. E. MONTONNA (Ind. Eng. Chem., 1933, 25, 1331—1335).—The data have been obtained by distillation and analysis of successive fractions, the initial and final vapour compositions being obtained by extrapolation. Results are compared with those of other workers. C. I.

Physical properties of mixtures of certain organic liquids. V. C. G. TREW and G. M. C. WATKINS (Trans. Faraday Soc., 1933, 29, 1310—1318; cf. A., 1932, 801).—The density, mass susceptibility, n , sp. heat, heats of mixing, and viscosity of mixtures of Bu^oOH with Pr^oOH, PrⁿOH, BuⁿOH, tert.-amyl alcohol, and of COMe₂ with C₂HCl₃ have been measured at 25°. All give deviations from the mixture law and the max. on the deviation curves vary with the property. H. J. E.

Thermodynamics of mixtures. Ethyl alcohol-water. V. FISCHER (Helv. phys. Acta, 1933, 6, 42—67; Chem. Zentr., 1933, ii, 192).—Accord between theoretical and observed data indicates that for EtOH-H₂O admixture is essentially a physical, and not a chemical, process. A. A. E.

Volume variations of system water-ethyl alcohol-ether. P. BRUN (Compt. rend., 1933, 197, 1637—1638).—The differences between the actual vols. and those derived from the simple mixture rule

are given on a triangular diagram; there is no breach of continuity in the crit. zone (cf. A., 1927, 23).

C. A. S.
Mixed crystals in the sulphate series. I. A. BENRATH and A. BLANKENSTEIN (Z. anorg. Chem., 1933, 216, 41—48).—Data are given for the system MgSO₄-MnSO₄-H₂O. E. S. H.

X-Ray study of the binary alloys of silicon with Ag, Au, Pb, Sn, Zn, Cd, Sb, and Bi. E. R. JETTE and E. B. GEBERT (J. Chem. Physics, 1933, 1, 753—755).—Lattice consts. of the alloys do not differ appreciably from those of the elements, and solid solution formation is therefore very slight. In no case are compounds formed. W. R. A.

Hall effect and some other physical constants of alloys. II. The tin-bismuth series of alloys. W. R. THOMAS and E. J. EVANS (Phil. Mag., 1934, [vii], 17, 65—83; cf. A., 1933, 895).—The Hall coeffs. (I), resistivity, temp. coeff. of resistance, thermoelectric power, and density of annealed Sn-Bi alloys (0—100% Bi) have been measured. A reversal of (I) occurs for some of the alloys at a field strength which depends on the composition. H. J. E.

Surface tension of liquid metals. V. Surface tension of lead-tin alloys. L. L. BIRUMSHAW (Phil. Mag., 1934, [vii], 17, 181—191; cf. A., 1926, 895).—Measurements have been made at 200—800° on alloys with 0—100% Pb. All the alloys show a negative temp. coeff. It is suggested, on the basis of Schofield and Rideal's relation (A., 1925, ii, 960), that the eutectic has a unimol. surface layer of Pb atoms. H. J. E.

Equilibrium diagrams of binary alloys of alkali metals: Na-Rb alloys. E. RINCK (Compt. rend., 1933, 197, 1404—1406; cf. A., 1933, 771).—The diagram of Na-Rb alloys shows a eutectic containing 75 at.-% Rb, m.p. 4.5°. The formation of Na₂Rb is possible. C. A. S.

Alloys of lithium. II. X-Ray analysis of the system lithium-cadmium. A. BARONI (Atti R. Accad. Lincei, 1933, [vi], 18, 41—44; cf. A., 1933, 18).—Thermal analysis of this system confirms the existence of the three compounds LiCd, LiCd₃, and Li₃Cd. The last-named is not revealed by X-ray analysis, which shows that LiCd has a monometric structure of the body-centred CsCl type with a 3.32 Å., Cd (0, 0, 0), Li ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), $d_{\text{calc.}}$ 5.336, and that LiCd₃ is also monometric with 8 mols. per unit cell, a 8.62 Å., $d_{\text{calc.}}$ 7.136. O. J. W.

Cadmium-nickel system. C. E. SWARTZ and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Contrib. No. 55, 1933, 4 pp.).—The eutectic point in the system is at 0.25% Ni and 318°; the Ni is probably in the form of the compound NiCd₇, which appears as hard cubes in hypereutectoidal alloys. A. R. P.

Equilibrium diagram of iron-aluminium system. A. ŌSAWA (Sci. Rep. Tôhoku, 1933, 22, 803—823).—Photomicrographs and X-ray analyses have given the following results: FeAl, cubic, a 5.78 Å.; n (atoms per unit cell) = 16; FeAl₂, rhombohedral, a 6.314, α 74° 9', n 18; Fe₂Al₃, monoclinic, a 9.91, b 10.811, c 8.824, β 124° 59' 53'', n 56; FeAl₃, ortho-

rhombic, a 11.87, b 8.088, c 15.804, n 104. A new phase diagram is constructed. J. G. A. G.

Alloys of gallium with aluminium. N. A. PUSHIN and V. STAJIĆ (Z. anorg. Chem., 1933, 216, 26—28).—Thermal analysis of alloys containing 0—100% Al has established the existence of three compounds: AlGa_2 (m.p. 281°), AlGa (m.p. 374°), and Al_2Ga (m.p. 467°). Al_2Ga exists in a β form at 447—467° and in an α form below 447°. E. S. H.

Structure and origin of the copper-cuprous oxide eutectic. L. W. EASTWOOD (Amer. Inst. Min. Met. Eng., Contrib. No. 59, 1933, 8 pp.).—The Cu— Cu_2O eutectic alloy forms large columnar macrograins when cast in an open mould. The grains etch similarly throughout their individual areas but adjoining grains etch differently according to their orientation. Deep etching produces pits of similar orientation throughout each grain but of different orientation in different grains, and slow deformation produces slip bands which are straight and continuous across a grain but change at the grain boundary. From a micrographical examination of sections through the columnar grains at right angles it appears that the Cu is the directing constituent of the eutectic, axes of growth of the Cu portion of the eutectic dendrite (I) spreading into the melt perpendicular to the mould wall; these axes fill out and branches grow from them until they meet adjacent branches of the same or other dendrites. As (I) grows the Cu_2O is pptd. with a definite orientation; the Cu_2O particles are spheroidal with a rapid rate of solidification and rod-shaped with slower cooling, hence the Cu_2O nearest the central portions of the dendrites is spheroidal, whilst that in the more remote portions forms rods inclined at 45° to the direction of axial growth. The form and structure of the eutectic crystals are generally independent of the existence of primary crystals of Cu or Cu_2O unless the rate of cooling favours surfusion when, since Cu surfuses $>$ Cu_2O , haloes of Cu are formed about the Cu_2O dendrites. Characteristic micro-structures are illustrated.

A. R. P.

Magnesium-zinc-calcium system. R. PARIŠ (Compt. rend., 1933, 197, 1634—1636).—The thermal diagram for the system Ca—Mg indicates the formation of Mg_5Ca_3 (cf. A., 1911, ii, 611), and that for Ca—Zn indicates Ca_5Zn_3 , and not Ca_5Zn (cf. A., 1908, ii, 278). For Mg—Zn the data agree with previous results (cf. A., 1929, 398). The ternary diagram shows the formation of the following: Ca_3Mg_5 , Ca_5Zn_2 , Ca_3Zn_3 , CaZn_4 , CaZn_{10} , MgZn_2 , MgZn_5 , and $\text{Mg}_5\text{Zn}_5\text{Ca}_3$; the last forms large crystals, not attacked by HNO_3 , and melting at 495° without decomp. Alloys with $>$ 30% Ca oxidise and disintegrate in moist air; those with $>$ 40% Zn are not readily oxidisable, but brittle and unworkable; those rich in Mg are also oxidised with difficulty, are very light, and easy to work, but unless both Ca and Zn are $<$ 1%, contain more than one phase.

C. A. S.

Transformations in the solid state of aluminium-magnesium-silicon alloys. A. A. BOCHVAR, K. V. GOREV, and A. M. KOROLKOV (Metallurgist, U.S.S.R., 1933, No. 1, 7—20).—A new constitution

diagram is based on the micro-structures of 47 alloys containing Mg 0—3, Si 0—2.75%. Melts were prepared under a NaCl—KCl—LiCl flux. The alloys were superheated 50—150° for 4—18 hr., then kept for 10 days at 200°, 300°, 400°, 500°, or 550°, and quenched in cold H_2O . Max. ageing was observed with max. Mg_2Si . Excess of Si increases the effect of heat-treating if 0.2—0.4% Fe is present, but decreases it if Fe is present in very small quantity. Max. solubility of Mg_2Si in Al is 1% at 500° and 0.45% at 400°; solubility decreases if excess of Si or Mg is added. CH. ABS.

Iron corner of the system iron-manganese-aluminium. W. KÖSTER and W. TONN (Arch. Eisenhüttenw., 1933—1934, 7, 365—366).—Up to 30% Al and 50% Mn only the α - and γ -phases exist; a narrow ($\alpha+\gamma$) field extends from the Fe corner towards the centre of the triangular diagram and is somewhat broader at lower temp. than at $>$ 1000°. For alloys in the α -field the γ - β Mn transformation begins to be noticeable with $>$ 40% Mn and the alloys become brittle and coarsely crystalline. The ternary α -solid solution is ferromagnetic up to 18% Al.

A. R. P.

The system manganese-tin-mercury. A. N. CAMPBELL and H. D. CARTER (Trans. Faraday Soc., 1933, 29, 1295—1300; cf. A., 1933, 454).—Solubility data for Mn and Sn in Hg at 30°, 55°, and 70° are recorded. The compound Sn_5Mn_2 , stable above 30°, was isolated. Sn, Mn, and Sn_5Mn_2 do not form solid solutions with Hg.

H. J. E.

Interconversion of atomic, weight, and volume percentages in binary and ternary systems. C. S. SMITH (Amer. Inst. Min. Met. Eng., Contrib. No. 60, 1933, 15 pp.).—Tables for facilitating the conversion are given.

A. R. P.

Partly miscible system aniline-water. P. MONDAIN-MONVAL and (MLLE.) H. SCHLEGEL (Compt. rend., 1933, 197, 1632—1634).—The relative densities of the conjugate solutions show inversion at 77°, when the aq. solution becomes the heavier.

C. A. S.

Ternary systems water, pyridine, and salts at 25°. P. M. GINNINGS, B. WEBB, and E. HINOHARA (J. Amer. Chem. Soc., 1933, 55, 4898—4899).—The equilibria can be represented by $y=a+b(10)^{-cx}$, where y is the wt.-% of $\text{C}_5\text{H}_5\text{N}$, x the wt.-% of salt, and a , b , and c are consts. In salt-rich solutions of $(\text{NH}_4)_2\text{SO}_4$ or NaCl the relation $y=a+bx^c$ reproduces the results more satisfactorily.

E. S. H.

Diffusion of gases in liquids under pressure. V. V. IPATIEV, V. P. TEODOROVITSCH, and S. I. DRUSCHINA-ARTEMOVITSCH (Z. anorg. Chem., 1933, 216, 66—74).—A method for determining the diffusion coeff. of gases in liquids under pressure is described, and vals. are determined for the following systems: H_2 in H_2O at 15°, 25°, 35°, and 45° and 40—100 atm., H_2 in liquid NH_3 at 25° and 30° and 35—100 atm., O_2 in H_2O and in 10% and 20% aq. NaOH at 25° and 50 atm. Over the range examined the diffusion coeff. of H_2 is independent of pressure.

E. S. H.

Solubility of inorganic compounds in liquid ammonia. II. M. LINHARD and M. STEPHAN

(Z. physikal. Chem., 1933, 167, 87—102; cf. A., 1933, 456).—The solubility, *s*, of alkali, alkaline-earth, and Ag chlorides, bromides, iodides, and nitrates has been determined at 0°. For the alkali and Ag halides *s* increases with increasing radius of the anion and with decreasing radius of the cation. There is evidence to show that in NH₃ solutions the cations are preferentially solvated, and taking this into account the observed solubilities fit in with Fajans' solubility rule (A., 1923, ii, 750). For the alkali halides *s* generally runs parallel with the tendency to form ammoniates. R. C.

Solubility. XIII. Solubility of iodine in certain solvents. G. R. NORRISI, L. H. DONNALLY, and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1933, 55, 4793—4800).—The solubility of I has been determined in C₂H₄Br₂, SiCl₄, and TiCl₄ at various temp. The relation between solubility and internal pressure is discussed. E. S. H.

Polyiodides. I. Solubility of iodine in potassium iodide solutions and hydration of the iodide ion. S. REICHSTEIN, L. EVENTOV, and I. KASARNOVSKY (Z. anorg. Chem., 1933, 216, 1—9).—The solubility of I in aq. KI (0.055—6.259*M*) has been determined at 25°. At concns. of KI < 2.659*M* addition of sucrose increases the solubility of I, but at higher concns. the reverse effect is observed. In either case the difference of solubility of the I is proportional to the concn. of sucrose added. The *d* of the solutions suggests that I' is hydrated in aq. solution. E. S. H.

Calcium sulphate in sea-water. II. Solubilities of calcium sulphate hemihydrate in sea-waters of various concentrations at 65—150°. T. TORIUMI, T. KUWAHARA, and R. HARA (J. Soc. Chem. Ind. Japan, 1933, 36, 689—690B).—Data for solutions containing 16—97 g. Cl per 1000 g. solution are recorded. The measurements were made with well-formed crystals. J. A. S.

Solubility of the hydrates of nickel chloride in water. E. BOYE (Z. anorg. Chem., 1933, 216, 29—32).—The solubilities of NiCl₂ with 7, 6, 4, and 2H₂O have been determined at temp. up to the b.p. of the saturated solution (117.9°). E. S. H.

Solubilities of amino-acids in water [from 0° to 100°], densities of their solutions at 25°, and calculated heats of dissolution and partial molal volumes. J. B. DALTON and C. L. A. SCHMIDT (J. Biol. Chem., 1933, 103, 549—578).—Data are given for *d*- and *dl*-alanine, *l*- and *dl*-aspartic acid, *d*- and *dl*-glutamic acid, *l*- and *dl*-leucine, di-iodo-*l*-tyrosine, glycine, *dl*-isoleucine, *dl*-norleucine, *dl*-phenylalanine, *l*-tyrosine, and *dl*-valine. It is inferred that *dl*-alanine and *dl*-leucine, and probably also *dl*-aspartic acid, are racemic compounds, whilst *dl*-glutamic acid is probably a racemic mixture. D. R. D.

Solubility of amino-acids in water. M. S. DUNN, F. J. ROSS, and L. S. READ (J. Biol. Chem., 1933, 103, 579—595).—Experimental data at 0°, 25°, 50°, and 75°, and data at 100° (calc. by an extrapolation formula) are given for glycine, *dl*-alanine, *l*-glutamic acid, *l*-valine, *l*-isoleucine, *l*-phenylalanine,

l-norleucine, *l*-leucine, and *l*-aspartic acid, *l*-aspartic acid and *l*-tyrosine, and *d*-glutamic acid. D. R. D.

Solubility law for ideal solutions and its application to a salt-water system. A. W. DAVIDSON (J. Chem. Educ., 1933, 10, 234—237).—The observed solubilities of three modifications of NH₄NO₃ in H₂O over the range 169.6° (m.p.)—70° correspond with those calc. from Schröder's equation for solubility in an ideal solution; at < 70° the observed vals. are < the ideal vals. Compound formation occurs to only a small extent. CH. ABS.

Theory of the distribution of electrolytes between a solid crystalline and a liquid phase. A. P. RATNER (J. Chem. Physics, 1933, 1, 789—794).—Equations showing the influence of the composition of the aq. phase on the distribution ratio, and the dependence of the partition const. on the properties of the pure components are deduced thermodynamically. Results for various systems involving the distribution of radio-elements are shown to agree with the theoretical requirements. W. R. A.

Sorption of hydrogen by reduced nickel. I. Determination of the quantities of hydrogen adsorbed by and diffused in pure and spoiled reduced nickel, and of the isothermal adsorption lines and heat of adsorption. II. Adsorption of hydrogen by reduced nickel at low temperatures. S. IJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 285—300; 23, 34—43).—I. Velocity curves indicate that the sorption of H₂ by Ni is due to adsorption followed by diffusion. Adsorption isotherms at 50—300° with *p* < 15 cm. agree with Freundlich's equation and give 16,350 g.-cal. for the heat of adsorption. The latter is reduced considerably (e.g., to 6479 g.-cal.) if the Ni has been contaminated with air, even if the air is removed as completely as possible by heating in vac. for 1 hr. at 400°.

II. Isotherms are given for —183.5° to 100° and pressures from 0.1 mm. to 1 atm. Even at —183.5° the curve is smooth, provided that temporary overheating due to rapid adsorption is avoided (cf. A., 1930, 990). The isobars pass through a min. at about —80° and a max. at room temp., the temp. varying with *p*. There is no indication of compound formation (cf. A., 1926, 673). D. R. D.

Reversible sorption of gases and vapours by potassium benzenesulphonate. W. LANGE and G. VON KRUEGER (Z. anorg. Chem., 1933, 216, 49—65).—NH₃, H₂S, MeCl, N₂O, CO₂, and C₃H₆ are sorbed by PhSO₃K according to the adsorption isotherm, whilst marked deviations occur with SO₂ and Me₂O. In each case there is a saturation val., at which the mol. ratio of the adsorbent to the adsorbed vapour is a simple, whole no. Capillary condensation plays no part, but the gas mols. probably diffuse through the loose structure of PhSO₃K. E. S. H.

Absorption of carbon monoxide by cuprammonium salts. N. M. SHAVORONKOV and P. M. RESCHTSCHIKOV (J. Chem. Ind. Russ., 1933, 10, No. 8, 41—49).—Max. absorption of CO by aq.-ammoniacal Cu^I formate or lactate is obtained at > 20° and at high pressures. 90% of the absorbed CO is evolved on heating at 80°; at higher temp. loss of NH₃ and

separation of free Cu take place. The absorptive capacity increases with the Cu and NH_3 contents.

R. T.

Reciprocal adsorption. IV, V. E. N. GAPON (J. Gen. Chem. Russ., 1933, 3, 660—666, 667—669).—Theoretical.

R. T.

Heat of adsorption of inert gases and carbon dioxide on ionic crystals. F. V. LENEZ (Z. physikal. Chem., 1933, B, 23, 379—398).—Data for the adsorption of A and Kr at about 90° and of CO_2 at 200 — 240° abs. by powdered alkali halides have been used to derive the heat of adsorption, Q . In the adsorption of inert gases on ionic crystals the attractive effect is the resultant of (1) the London dispersion forces and (2) an effect due to the creation of an electric moment in the adsorbed gas atom by the ions of the lattice. In the adsorption of a polar gas there is in addition a purely electrostatic effect due to interaction between the charged lattice points and the non-uniformly distributed charges of the adsorbed mol. The three effects have been calc. for the adsorbates studied and from them the adsorption potentials derived and compared with those deduced from the experimental data. For A and Kr the agreement is satisfactory. Throughout (1) \gg (2). For the system A-KCl Q is approx. equal to the latent heat of vaporisation of A.

R. C.

Relation between adsorption, solubility, and nature of the solvent. III. N. SATA and K. KURANO (Kolloid-Z., 1933, 65, 283—290; cf. A., 1932, 991).—For picric (I) and benzoic acids in binary mixtures of H_2O , EtOH, CHCl_3 , Et_2O , COMe_2 , PhNO_2 , PhMe, C_6H_6 , and CCl_4 the curves for the solubility and adsorption by C are antibatic. (I) in COMe_2 is anomalous.

E. S. H.

Capillary ascent or depression of liquids in cylindrical tubes. II. Wide tubes. A. W. PORTER (Trans. Faraday Soc., 1933, 29, 1307—1309; cf. A., 1933, 1002).—Theoretical. Capillary corrections for wide tubes are tabulated.

H. J. E.

Theory of electrocapillarity. II. Thermodynamics of capillarity. S. R. CRAXFORD, O. GATTY, and J. ST. L. PHILPOT (Phil. Mag., 1934, [vii], 17, 54—64; cf. A., 1933, 1248).—Theoretical.

H. J. E.

Oil lenses on water and the nature of unimolecular expanded films. I. LANGMUIR (J. Chem. Physics, 1933, 1, 756—776).—Equations are derived which show that the spreading coeff. can be derived from the radii of large lenses of known vol. A method for introducing hydrophilic mols. into the interface between the lens and the H_2O is described, and the resulting changes are examined with reference to the two-dimensional equation of state of adsorbed mols. at the H_2O -oil interface. The presence of a "kink" in the observed F - a curves is attributed to the sudden appearance of micelles. Vals. of F_0 and a_0 for various substances are determined from Adam's data.

W. R. A.

Effect of reduced pressure on the formation of liquid drops on the surface of the same liquid. L. D. MAHAJAN (Kolloid-Z., 1934, 66, 22—23).—The

effect is difficult to reproduce in air at 431 mm. pressure.

E. S. H.

Surface free energy of liquids and liquid mixtures. Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 49—117).—Katayama's equation (A., 1916, ii, 219) and an extension of it to binary mixtures are confirmed by the data for C_6H_6 , PhMe, CCl_4 , PhCl (temp. range 50 — 170°), Et_2O (20 — 110°), EtOAc, MeOH, EtOH, PrOH, and AcOH (20 — 150°), and certain pairs of these. Abnormal results for the alcohols are explained by treating them as binary mixtures of single and triple mols.

D. R. D.

X-Ray spectroscopic experiments on the orientation of palmitic acid at mineral surfaces. E. BERL and B. SCHMITT (Kolloid-Z., 1933, 65, 261—264).—Orientation could not be detected at the surfaces of ZnS, PbS, FeS_2 , CaCO_3 , or PbCO_3 . The existence of a unimol. film is not excluded.

E. S. H.

Structure of surface films. XVIII. Effect of alkalinity in the underlying solution on films of fatty acids. XIX. Influence of alkaline solutions on films with various end groups. N. K. ADAM and J. G. F. MILLER. XX. Surface potential measurements on nitriles. N. K. ADAM and J. B. HARDING (Proc. Roy. Soc., 1933, A, 142, 401—415, 416—422; A, 143, 104—111).—XVIII. Films of the normal fatty acids (12—22 C atoms) on solutions varying from dil. HCl to $2N$ -NaOH have been examined with respect to (a) the lateral adhesion between the mols., indicated either by the temp. at which expansion occurs or by the form of the surface pressure-area relation for the expanded (or gaseous) films; (b) the packing in the condensed films; and (c) the collapse of the films on alkaline solutions.

XIX. Unimol. films of various substances with ionisable end-groups show a marked decrease in lateral adhesion when the alkalinity of the solution is changed so as to ionise the end-groups. This effect is not shown by substances with non-ionisable end-groups. Films of $\text{C}_{15}\text{H}_{31}\text{CO}_2\text{Me}$ are fairly rapidly hydrolysed on $2N$ -NaOH.

XX. Surface potential measurements on unimol. films of long-chain nitriles (14—22 total C atoms in the chain) indicate a max. val. of μ only about $1/7$ of the dipole moment of the CN group as obtained by other methods. The effective "dielectric const." of the surroundings of the film mols. is probably about 7. The transition between condensed and expanded films is heterogeneous.

L. L. B.

Influence of the underlying surface on the cataphoretic mobility of adsorbed proteins. A. DUMMETT and P. BOWDEN (Proc. Roy. Soc., 1933, A, 142, 382—401).—The electrokinetic properties of proteins adsorbed on different surfaces have been studied in aq. solution. For gelatin, the mobility is independent of the nature of the substrate, in agreement with the results of other workers, but in oxy- (I) and carboxy-haemoglobin (II) both the mobility and the isoelectric point vary in a marked degree with the nature of the underlying surface. The surface equilibrium of the protein is attained in a few sec. in conc. solutions, but takes several hr. in dil. solutions. (I) and (II) when adsorbed have identical electro-

kinetic properties, and no evidence is found for two forms of hæmoglobin with different isoelectric points.

L. L. B.

Contact potentials and the effects of unimolecular films on surface potentials. I. Films of acids and alcohols. W. D. HARKINS and E. K. FISCHER (J. Chem. Physics, 1933, 1, 852—862).—Simultaneous measurements of film pressure and surface potential have been made with a form of apparatus which permits the determination of the potential at any point on the surface of the film. Org. substances with homo-heteropolar mols. gave a single smooth curve for surface potential—mol. area at film pressures above that of the gaseous films. For increase of area and reduction of pressure the surface potential becomes variable; it rises rapidly with the no. of C atoms in the hydrocarbon chain, and is higher for alcohols than for acids with the same no. of C atoms. Change of single linking in one film substance to double linking in another lowers the surface potential. Lowering of temp., increase of concn. in the film, or replacement of a basic by an acid solution raises the surface potential. Films in the condensed state show hysteresis with respect to both film pressure and surface potential. The relation between surface potential and mol. moments of mols. constituting the film is discussed.

N. M. B.

Wetting and porosity. Adsorption and total heats of wetting of powders of different particle size. B. ILJIN and A. KISSELEV (Kolloid-Z., 1934, 66, 28—40).—The ordinary calorimeter is unsuitable for determining heats of wetting of powders, as a slow adsorption process is involved. An adiabatic calorimeter has consequently been used to study the heat of wetting of powdered activated wood charcoal of various particle sizes. With decrease in particle size from 0.68 mm. to < 0.15 mm. the amount of adsorbed substance A and the heat of wetting Q (per g. of adsorbent) increase by 4.6% for I and 10% for heptioic acid. The adsorption isotherms are not in accordance with the usual equations, but those for different fractions of adsorbent are related by a simple coeff., which depends on the adsorbed substance. The val. of Q/A_{∞} , where A_{∞} represents max. adsorption, is independent of particle size, indicating that with increasing subdivision the sp. surface of the adsorbent changes, but not its properties. The complete heat of wetting for all fractions of C depends on the wetting liquid; with H_2O it is < with org. liquids and increases with increasing no. of C atoms throughout a homologous series.

E. S. H.

Physical chemistry of wetting phenomena and flotation processes. IX. Influence of adsorption layers of surface-active substances on selective wettability. P. REHBINDER [with M. LIPETZ, M. RIMSKAJA, and A. TAUBMANN]. X. Dependence of wettability on the adsorption of the flotation reagents. Wetting isotherms at the boundary mineral-water-air. P. REHBINDER, M. LIPETZ, and M. RIMSKAJA (Kolloid-Z., 1933, 65, 268—283; 1934, 66, 40—50).—IX. A summary and theoretical treatment of published results.

X. Wetting isotherms have been obtained for the boundary malachite-water-air in presence of various

flotation agents. It is shown that the flotation process depends eventually on the alteration of the wetting conditions by the flotation agents. Flotation activities of several agents (Et, isoamyl, and Bu^x xanthates, aliphatic acids and their Na salts, etc.) towards malachite, ZnS, PbS, FeS_2 , and $CuFeS_2$ are given.

E. S. H.

Passage of gases through porous diaphragms. C. PADOVANI and G. MONTE (Acqua e Gas, 1933, 22, 43—45; Chem. Zentr., 1933, ii, 194).—The relation between the difference in pressure Δp and the vol. Q of gas a transferred in unit time is given by $\Delta p = (128l\eta/\pi D^4N)Q + (16\rho/\pi^2 D^4N^2)Q^2$ (or, simplified, $A\eta Q + B\rho Q^2$), where l is the length, D the diam. of the individual capillaries, N their number, η the coeff. of internal friction, and ρ the d of the gas. A and B depend only on the properties of the diaphragm. The influence on linearity of the various factors concerned has been studied.

A. A. E.

Permeability of dried collodion membranes for amino-acids and for organic non-electrolytes. F. E. SCHMENGLER (Pflüger's Archiv, 1933, 232, 591—603; Chem. Zentr., 1933, ii, 1691).—The behaviour of α - and β -alanine, leucine, lysine, asparagine, aspartic acid, betaine (I), and phenylalanine (II) has been compared with that of polyhydric alcohols. As with cells and tissues, the smaller permeability of NH_2 -acids, except (I) and (II), is attributed to their ampholyte nature (existence as zwitterions). (I) has a small dipole moment, whilst (II) exists as zwitterion only to the extent of 10%.

A. A. E.

Stationary, checked, and other states of osmotic systems. III. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 779—785; cf. A., 1933, 900; this vol., 24).—Theoretical.

J. W. S.

Membrane equilibria and the secondary swelling of protein gels. F. G. DONNAN (J. Soc. Leather Trades Chem., 1933, 17, 136—143).—The Donnan equilibrium is considered in relation to the nature of the solutions concerned. The theory is not easily applicable to a micellar system such as skin or natural fibres. In their application of the theory Procter and Wilson neglected to take account of the effect of inorg. salts on the swelling of isoelectric gelatin gel. The interior of the gelatin micelles is penetrated by ions and H_2O mols.

D. W.

Aphorisms of Liesegang rings. B. KISCH (Kolloid-Z., 1933, 65, 316—319).—Examples of the periodic crystallisation of thin films of aq. inorg. salt solutions and of the formation of secondary Liesegang rings are given.

E. S. H.

Acetethylanilide as a cryoscopic solvent, and the mol. wt. of some cellulose ethers dissolved therein. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1933, [vi], 18, 150—155).—Cellulose nitrate, acetate, and Et ether form true dil. solutions in $NPhEtAc$, and give mol. wts. corresponding approx. with the dimeric formula $(C_6)_2$.

O. J. W.

Individuality of osmotic behaviour of alkali halides. G. DAMKÖHLER and J. WEINZIERL (Z. physikal. Chem., 1933, 167, 71—86).—The mol. f.-p.

depressions of LiBr, NaBr, KBr, and CsBr have been determined. R. C.

Production of disperse systems by explosion of the vapours of the disperse material in the cold liquid dispersion medium. I. P. P. VON WEYMARN and N. SATA (Kolloid-Z., 1934, 66, 1—11).—A small amount of the substance to be dispersed is placed in a closed, thin-walled capsule, which also contains an electric heating element. Several such capsules are lowered into the cooled liquid dispersion medium. When current is passed through the heating element the substance vaporises, breaks the capsule, and is condensed to colloidal disperse particles in the medium. Stable sols of Hg and Se have been prepared in this way. The concn. obtained is about 0.005% and the stability depends on the presence in the medium of a sol. compound having an atom in common with the disperse phase. S gave a coarsely disperse system as may be expected from its greater solubility. E. S. H.

Condensation aerosols; colloidal dispersed arsenic [trioxide] dust. A. WINKEL and G. JANDER (Kolloid-Z., 1933, 65, 290—294).—Aerosols of As_2O_3 have been prepared by rapid cooling of As_2O_3 vapour. The no. of particles per unit vol. decreases rapidly during the first hr., especially in the more conc. sols (150—500 mg. per cu.m.). The variation of mean particle wt. with concn. after a given ageing period is linear. E. S. H.

Measurement of the concentration and density of suspensions with a photo-electric cell. III. M. MATSUI, T. NODA, and S. IWAI (J. Soc. Chem. Ind. Japan, 1933, 36, 691—692B).—Graphs are given showing the relations between the concn., the extinction ($\log I_0/I$), and the fractional scattering $(I'-I'_0)/I_0$, for suspensions of $CaCO_3$, ZnO, PbO, Fe_2O_3 , and C. I' and I'_0 are the intensities of the light scattered by the suspension and by the suspension medium, respectively. A. G.

Colloidal solutions by hydrolysis of cerium sulphate. A. JANEK and A. SCHMIDT (Kolloid-Z., 1933, 65, 295—297).—Sols containing negatively-charged, hydrophobic particles are prepared by pouring sufficiently conc. aq. $Ce(SO_4)_2$ into a large vol. of H_2O . Addition of Na_2SO_4 causes the initially turbid sol to become clear for a time, but later turbidity reappears and is followed by sedimentation. E. S. H.

Action of ethylene oxide on solutions of the halides of the earth and heavy metals. Preparation of sols and reversible gels of hydrated metal oxides. W. ZIESE (Ber., 1933, 66, [B], 1965—1972).—Addition of $(CH_2)_2O$ (I) to $AlCl_3$ in H_2O yields $Al(OH)_3$ and $CH_2Cl \cdot CH_2 \cdot OH$ (II), the former remaining as a sol until about 90% of the theoretical amount of (I) has been added and subsequently solidifying to a clear gel. Removal of by-products from the sol can be effected by extraction with solvents for (II) or by distillation, when H_2O and (II) pass over together at 97°. The sols of Al, Cr, Zn, and Th may be regarded as containing highly basic salts. They are dried without difficulty to reversible gels which give stable sols when brought in contact with

H_2O , conc. EtOH, or glycerol. Excess of (I) ppts. the metal oxide hydrates as gels after passage through the hydrosol phase. Oxides of bivalent metals (Zn, Mn) frequently have a very unstable sol. phase, pptn. occurring with small amounts of (I). Usually the ppts. are very finely divided and, after thorough washing, readily disperse in H_2O . (I) can be replaced by propylene oxide and H_2O by 96% EtOH. Bromide and iodides can be used in place of chlorides. H. W.

Viscosity of colloidal solutions in relation to concentration. G. BERRAZ (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 82—98; Chem. Zentr., 1933, ii, 844).—The viscosity $V=1+KSC/(1000-SC)$, where C is the concn. (g. per litre), S is the vol. of 1 g. of solvatised colloid, and K has different vals. for different systems. When C and S are small Einstein's equation $\mu=\mu_0(1+2.5\phi)$ is approached. A. A. E.

Influence of electric charge on the viscosity of hydrophilic colloids. I. SAKURADA and T. NAKASHIMA (Kolloid-Z., 1934, 66, 62—67, and Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 36, 620—621).—The relation between relative viscosity (η_r) and concn. (c) for systems containing particles of any form can be expressed by $\eta_r=1+a(\phi c/100)$ (I), or $\eta_r=1+a\phi c/(100-\phi c)$ (II), where ϕ is the sp. vol. of the disperse phase, and a a const. which depends on the form and electric charge of the particle (2.5 for uncharged spheres). The validity of (II) has been established for Na celluloseglycollate (III), starch, and gelatin sols. Colloid particles of (III) appear to be spherical and strongly charged in H_2O . The particles are almost completely discharged by adding small amounts of neutral salts or by rise of temp. Starch particles appear to be spherical and not very highly charged. Gelatin particles are apparently either highly charged or non-spherical. E. S. H.

Behaviour of concentrated ferric hydroxide sols in the capillary viscosimeter. A. RABINERSON and G. FUCHS (Kolloid-Z., 1933, 65, 307—316).—The viscosities of conc. (8—20%), stable $Fe(OH)_3$ sols have been determined at pressures of 15—190 cm. H_2O . Structure viscosity is not observed in freshly prepared, dil. sols, but increases with the age and concn. of the sol. It is always < in most lyophilic colloids. The rate of ageing increases with concn. The crit. Reynolds vals. for conc. $Fe(OH)_3$ sols are < those for H_2O , the deviation increasing with increasing concn. E. S. H.

Importance of dialysis in the study of colloids. I. Colloidal ferric hydroxide. B. N. DESAI and S. K. BORKAR (Trans. Faraday Soc., 1933, 29, 1269—1285).—With progressive dialysis of a $Fe(OH)_3$ sol the cataphoretic speed, I , passes through a max. and the viscosity through a min. val. (the two vals. do not correspond), whilst the KCl flocculation val. decreases continuously. The variation of I with the addition of HCl, KCl, $MgCl_2$, H_2SO_4 , K_2SO_4 , and $MgSO_4$, and the effect of dialysis followed by dilution, have been examined. H. J. E.

Elastic properties of collodion during flow. A. PAKSCHVER and M. BUNIN (Kolloid-Z., 1934, 66, 68—75).—Mechanically stressed collodion solutions

(6—20% in EtOH-Et₂O) show thixotropic properties, but regain their original viscosity when kept. Whilst the viscosity is influenced greatly by changes of temp., the elastic limit is unaffected; concn. has a great influence on both properties. The distribution of velocities has been examined for streaming in long and short tubes. E. S. H.

Optics of colourless sols. III. Optical relations in coagulation. T. CASPERSON (Kolloid-Z., 1933, 65, 301—307; cf. this vol., 26).—Mathematical relations are derived. E. S. H.

Action of electric waves on colloids. E. WILKE and R. MÜLLER (Kolloid-Z., 1933, 65, 257—260).—The colour, viscosity, velocity of electrophoresis, and electrical conductivity of As₂S₃ sols are altered by applying a high-frequency electro-magnetic field (wave-length 105—260 m.). E. S. H.

Electric double layer of colloids. II. Double layer and stability of undialysed silver iodide sols. III. Double layer and stability of dialysed silver iodide sols. E. J. W. VERWEY and H. R. KRUYT (Z. physikal. Chem., 1933, 167, 137—148, 149—163; cf. A., 1929, 136).—II. The adsorptive power of a negative AgI sol for I⁻ decreases with increasing age, the decline being especially rapid immediately after pptn. With positive sols there is a similar, but less marked, fall in the amount of adsorbed Ag⁺. These phenomena are not due to a fall in the degree of dispersity. Ageing apparently consists of two phases, the first a rapid structural change in the individual particles, and the second a slow decrease in the degree of dispersity. X-Ray study shows that lattice changes play at most a secondary part in the first phase, which seems to consist in the recrystallisation of the imperfectly constructed particles formed by pptn. to give a more perfect lattice. It is supposed that during this phase the adsorbed ions constituting the double layer are present only at such points as corners and edges of the crystals and loose places. The peptising power of an ion depends, not on its adsorbability, but on its power to take its place in the lattice of the substance to be peptised; AgI is peptised by Cl⁻, but not by OH⁻.

III. By dialysis and electro-decantation of negative AgI sols, very pure and conc. sols of high stability may be obtained. Adsorption measurements indicate that the charge on the double layer is a linear function of the logarithm of the concn. of free I⁻ in the sol. For these sols the first of the above phases of ageing is particularly important. The counter-ion is largely H⁺. The double layer is present only at active points on the surface, such as crystal edges and loose places, and the particle charge is abnormally small. The charge is zero at [Ag⁺]=about 10⁻⁶, i.e., two powers of 10 on the positive side of the equivalence point. This must involve a systematic error in the potentiometric AgI titration. The physico-chemical behaviour of dialysed AgI sols is completely determined by the distribution of I⁻ between AgI and solution. R. C.

Ageing of arsenic trisulphide sols under the influence of light. Variations in stability of sols with respect to electrolytes. V. KRESTINSKAJA (Kolloid-Z., 1934, 66, 58—62).—Ageing of an As₂S₃

sol may cause either an increase or a decrease of stability towards a particular electrolyte, according as the micelles contain excess of As₂O₃ or of H₂S. Ageing results in a decrease of the amount of disperse phase, an increase in the amount of H₃AsO₃ in the dispersion medium, and the production of colloidal S. The influence of these factors on the stability of the sol varies with different electrolytes.

E. S. H.

Oxidation of arsenious sulphide by atmospheric oxygen in alkaline media, under pressure, and at high temperatures. II. E. P. LOPATINA (J. Appl. Chem. Russ., 1933, 6, 803—807).—S hydrosols result from suspensions of As₂S₃ in 4*N*-NaOH on heating for 2 hr. at 150° and 25—50 atm. The S, which is pptd. by aq. CO₂ or H₂SO₄, represents 50—75% of that originally present as As₂S₃.

R. T.

Sodium petroselate as a soap. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1933, 36, 632—633b).—Na petroselate closely resembles Na oleate in viscosity, surface tension, and suspending power. R. S.

Determination of the sign of electric charge and isoelectric point of fine fibres. A. DUMANSKI and O. A. DUMANSKI (Kolloid-Z., 1934, 66, 24—28).—Results obtained by observing the deflexion of the fibre, when placed in H₂O between two oppositely-charged unpolarisable electrodes, are in satisfactory agreement with those given by electro-osmotic or streaming-potential measurements. E. S. H.

Electro-kinetics. XIII. Relation between streaming potential and applied pressure. H. B. BULL (Kolloid-Z., 1934, 66, 20—22; cf. A., 1932, 460, 804).—Repetition of the experiments of Ettisch and Zwanzig (A., 1932, 911) has failed to confirm their results. The streaming potential-pressure curves are straight lines, which pass through the origin.

E. S. H.

Electrophoretic mobilities and the isoelectric point of protein-coated particles. O. HALPERN (J. Chem. Physics, 1933, 1, 882—884).—Theoretical considerations support the observation that the electrophoretic potential of protein-coated quartz or glass particles is independent of their size and shape, and that their isoelectric point coincides with that of the protein ions in the solution. N. M. B.

Behaviour of aqueous solutions of the domestic cocoon. XIII. Velocity of electrophoresis of the sericin particle. XIV. Behaviour in sericin gel. H. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 697—704, 737—740).—XIII. Sericin has a negative charge on the alkaline side of the isoelectric point (*p*_H 4.2; sericin-A, 4.1; -B, 4.3). The velocity of electrophoresis (I) increases in inverse proportion to the concn. and proportionally to the temp. and time of heating. (I) is increased by addition of a small amount of a univalent cation. Sericin has an opposite charge if a small amount of a tervalent cation is added. The electrical behaviour of sericin resembles that of gelatin.

XIV. When an electric current (110 volts) is passed through sericin gel with Pt poles an annular ppt. is formed around the positive pole, due possibly to electrolysis of org. acid adsorbed from sericin-A. If an alkaline-earth or heavy metal is added before gel

formation, a ppt. is formed around the negative pole. The diffusion of org. colouring matters in sericin gel is slower than in gelatin or agar-agar. CH. ABS.

Jellies of zirconium sulphosalicylate. S. PRAKASH (Z. anorg. Chem., 1933, 215, 249—254).—Jellies are obtained when aq. $ZrOCl_2$ and 5-sulphosalicylic acid are mixed in certain proportions. The effect of dilution, temp., Cl^- , and SO_4^{2-} on the time of gelation has been studied. The sols are positively charged and gelation occurs only in acid solution. F. L. U.

(A) Lyophilic colloids. (B) Mechanism of gelation of lyophilic colloids. S. M. LEPATOV (J. Gen. Chem. Russ., 1933, 3, 685—693, 694—697).—A. The solubility of cellulose acetate (I) in $CHCl_3$ falls with diminishing content of low mol. wt. decomp. products (II) of (I), which act as peptisers. At the same time imbibition of solvent by (I) increases as a result of augmented intramolecular osmotic pressure.

B. Gelation of sols of (I) is ascribed to intramolecular solvation, with consequent retardation of Brownian movements of the micelles, and diminution of the distance between the latter. The velocity of gelation falls with increasing content of (II). R. T.

Changes in viscosity of cellulose solutions after various treatments. T. NAKASHIMA and M. NEGISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 621—623B).—The change in viscosity of a cuprammonium solution of the treated cellulose is given by $d\eta/dt = k(\eta - \eta_\infty)^n$. A. G.

Swelling and dissolution of benzylcellulose in organic liquids. I. SAKURADA and I. KIDO (J. Soc. Chem. Ind. Japan, 1933, 36, 656—659B).—The liquids in which benzylcellulose ($2CH_2Ph$ per $C_6H_{10}O_5$) is completely sol. have dipole moments (μ) > 1 and $\mu/V > 12.7(\times 10^{-2})$, V being the mol. vol. The alcohols and the lower esters and ketones satisfy these conditions, but are not solvents on account of their strong association. A. G.

Decomposition of cellulose by hot concentrated aqueous alkalis. N. I. NIKITIN and N. P. NEMTSOVA (J. Appl. Chem. Russ., 1933, 6, 845—849).—The viscosity η of solutions of cotton-wool cellulose which has been immersed for 6 hr. in 20—50% NaOH falls from 9.2—9.4 to 2.0—2.7 when the temp. is raised from 80° to 140°. When the time of immersion is increased to 16 hr. there is little further diminution in η . The Cu val. of the product rises with rising temp. of immersion. R. T.

Measurements of the diffusion of proteins. A. TISELIUS and D. GROSS (Kolloid-Z., 1934, 66, 11—20).—An optical method is described for following the diffusion of high-mol. colloids, which show absorption of visible or ultra-violet light. Diffusion coeffs. thus obtained at 20° are: *R*-phycoerythrin 4.00×10^{-7} , *R*-phycocyan 4.05×10^{-7} , CO-haemoglobin 6.3×10^{-7} , snail haemocyanin 1.05×10^{-7} , ovalbumin 7.7×10^{-7} cm.² per sec. These vals. are in general $<$ those calc. from mol. wts. or sedimentation velocities. E. S. H.

Sedimentation constants, mol. wts., and isoelectric points of respiratory proteins.—See this vol., 92.

Physico-chemical study of flocculation of myxoprotein by resorcinol. A. BOUTARIC, M. PIETTRE, and (MLLE.) M. ROY (Compt. rend., 1933, 197, 1413—1415; cf. A., 1933, 966).—The behaviour indicates that myxoprotein adsorbs resorcinol to form a product of gradually decreasing solubility in aq. NaCl. A small residual portion is not affected in this way, and this is probably globulin present as impurity. C. A. S.

Osmotic pressure of protein solutions. G. S. ADAIR (J. Soc. Leather Trades Chem., 1933, 17, 143—151).—A general consideration of the factors which should be taken into account is the measurement of the osmotic pressure of solutions of proteins. D. W.

Effect of neutral salts on the swelling of gelatin. F. C. THOMPSON (J. Soc. Leather Trades Chem., 1933, 17, 169—178).—Acid-swollen gelatin is repressed osmotically by neutral salts, and this can be adequately explained by the Procter-Wilson theory. There is also a lyotrope effect on non-ionised neutral gelatin, which is a max. at the isoelectric point. Swelling is favoured by I^- and NO_3^- and inhibited by SO_4^{2-} . D. W.

Swelling of proteins in weak acids. W. R. ATKIN (J. Soc. Leather Trades Chem., 1933, 17, 220—228).—The evidence of Kuhn (A., 1922, i, 183) against Procter and Loeb's theories of the swelling of proteins is attributed to the ash content of the gelatin (I) used in the experiments. Small quantities of NaCl increase the swelling of (I) in weak acids. Max. swelling of (I) is always obtained when the p_H of the external solution in equilibrium is 2.4. D. W.

Swelling [of gelatin] in alkaline solutions. R. H. MARRIOTT (J. Soc. Leather Trades Chem., 1933, 17, 178—193).—The first part of the alkaline titration curve p_H 5—8 of gelatin (I) is determined by the lysine and histidine groups, but for $p_H > 8.0$ the curve is due to the arginine groups. The swelling of (I) in alkaline solutions is osmotic and can be explained on the Procter-Wilson theory. A certain amount of H_2O is absorbed owing to the mol. structure of the protein micelles, and this can be calc. for the isoelectric point. Collagen (II) does not swell at $p_H < 9$ and attains a max. about p_H 12. Limed skin, previously dried, shows slight osmotic swelling about p_H 8 and a max. at p_H 12.5. The difference between the swelling of (II) fibres in aq. NaOH and $Ca(OH)_2$ is explained by the Loeb valency law. The greater swelling of (II) fibres by NaOH is attributed to the larger area covered by the Ca^{++} in the protein. The localised osmotic pressure due to the Na^+ causes localised bulging of the protein structure. The resistance of keratin to swelling is explained by the cystine cross-chains linking up the protein mol. "backbones." D. W.

Protein swelling and molecular organisation. D. J. LLOYD (J. Soc. Leather Trades Chem., 1933, 17, 208—220).—The swelling of gelatin (I) jellies varies inversely as the concn. of (I) in the jelly at the time of its coagulation. The swelling of protein (II) fibres varies inversely as the concn. of the (II) in the fibres, i.e., the compactness of the fibrous structure. The diminution in swelling with increased concn. is attributed to a reduction of the space available for the

diffusion of non-colloidal ions leading to a mechanical restraint of their movements, to a reduction of the no. of charged centres on the colloidal ion through the formation of cross-linkings between the (II) mols., and to an increase in the rigidity of the protein caused by the cross-linkings. The unequal distribution of diffusible ions is reduced by these factors and (II) swelling is thereby reduced. D. W.

Formation and constitution of protein salts from the viewpoint of modern theories of valency. H. PHILLIPS (J. Soc. Leather Trades Chem., 1933, 17, 151—169).—The factors which influence the polarities of the basic and acid groups in NH_2 -acids, polypeptides, and proteins, and the interaction of gelatin with acids and bases are discussed from the viewpoint of the electronic theory. A true salt is formed by the free NH_2 groups when gelatin reacts with acids, but the latter then combine through the covalencies with the zwitterions in the mol. Swelling is caused by salt formation and is repressed by the covalent combinations. The free CO_2H groups in gelatin form salts in solutions of $p_{\text{H}} < 10$, and combine with the zwitterions in solutions of $p_{\text{H}} < 11$. The zwitterions are converted into NH_2 groups and CO_2H anions. Alkaline swelling occurs in two stages, first when the CO_2H groups become anionic, and then when they associate with metallic cations; the swelling is suppressed by alkaline covalency combinations. D. W.

Elastic properties of glycerol-gelatin gels hardened with formaldehyde. H. J. POOLE (Trans. Faraday Soc., 1933, 29, 1305—1307).—A discussion of Hatschek's results (A., 1933, 1244), supporting the fibrillary theory of gels. H. J. E.

Swelling peculiarities of gelatin sheets, and conclusions derived therefrom concerning the swelling of emulsoid colloids. J. BOLLHAGEN (Kolloid-Z., 1933, 66, 75—83).—Experiments on the swelling in H_2O of thin gelatin sheets, curved and protected on one side with vaseline so that the swelling surface may be concave or convex to the H_2O , show that the swelling is characterised by two stages: (a) alteration in the form of the particles, involving decrease of one dimension and increase of another, (b) increase in vol. of the particles without further change of form. E. S. H.

Influence of electrolytes on the formation and decomposition of urate gels. E. G. YOUNG, F. F. MUSGRAVE, and H. C. GRAHAM (Canad. J. Res., 1933, 9, 373—385).—In the gelation (I) of supersaturated aq. solutions of the urates of NH_2Me , Li, piperazine, and NMe_4 by electrolytes, the cation is the active agent, the order of efficacy being in general $\text{K} > \text{NH}_4 > \text{Rb} > \text{Cs} > \text{Li} > \text{Na}$. The time of (I) varies inversely, and the rigidity of the gel directly, with the concn. of electrolyte up to the pptn. point. Org. diamines and EtOH may cause (I). The thixotropic effect occurs with gels of piperazine urate containing KCl and Li urate with EtOH. H. S. P.

Action of alkaline copper solution on silk fibroin. IV. Fibroin-copper-amine compounds in the system fibroin-copper-amine. I and II. V. Application of conductometric

titration to the fibroin-copper-amine system. VI. Mechanism of the dissolution of fibroin in copper-amine solution. Y. TAKAMATSU (J. Soc. Chem. Ind. Japan, 1933, 36, 596—604B, 662—668B, 668—672B).—IV. When the fibroin-Cu-en compounds I and II are treated with EtOH-KOH, compounds of the composition fibroin : Cu : K = 1 : 1 : 1 : 5 are obtained, and I and II are therefore formulated [fibroin, Cu][Cu en₂] and [fibroin, Cu]en. If excess of en is added to a fibroin-Cu-en solution, the latter changes from violet to blue, the electrical conductivity is greatly increased, and α diminished. It is probable that $[\text{Cu en}_2](\text{OH})_2$ is formed at the expense of Cu in the fibroin complex.

V. Solutions of $\text{C}_2\text{H}_4(\text{NH}_2)_2$, of $[\text{Cu en}_2](\text{OH})_2$, and complex solutions containing fibroin can be analysed by conductometric titration with H_2SO_4 . Different types of curve are obtained according to whether the solute is [fibroin Cu]en, [fibroin Cu][Cu en₂], or both of these with or without excess of en.

VI. The rate of dissolution of fibroin in cuprammonium or in $\text{Cu}(\text{OH})_2$ -en is given by $x = kt^n$, where k and n are consts. A. G.

State of caoutchouc in solutions. II. Influence of temperature on the viscosity of solutions of different concentrations. B. DOGADKIN and M. LAVRINENKO (J. Gen. Chem. Russ., 1933, 3, 742—746).—The viscosity η of PhMe and xylene solutions of caoutchouc (I) is const. over the interval 3—60° for $\approx 0.3\%$ solutions; at higher concn. η varies inversely with temp. The conclusions are reached that (I) is in mol. dispersion up to 0.3%, and in micellar dispersion at higher concn. (up to 10%). In still higher concn. the continuous phase of the emulsions is (I). R. T.

Physical chemistry of starch and bread-making. XIV. Is the starch in starch paste crystalline or amorphous? J. R. KATZ and J. C. DERKSEN (Z. physikal. Chem., 1933, 167, 129—136; cf. A., 1933, 1117).—Starch paste containing $> 67\%$ H_2O gives an amorphous X-ray diagram which is largely the same as that of liquid H_2O . This suggests that the starch in the warm paste is amorphous. On cooling there is partial crystallisation. With *Gramineae* starches there is between the native starch and the amorphous paste an intermediate form with a V spectrum exhibiting sharp crystal interferences; fresh bread at either 80° or room temp. shows the V spectrum. This intermediate form is not observed with potato starch. Any amorphous starch solution or paste dehydrated in the fresh state with EtOH may under certain conditions give a substance with a V spectrum; the starch then crystallises in an α -modification which is unstable at room temp. if the H_2O content is sufficiently large. R. C.

Thermal dissociation of cyanogen into cyanide radicals. G. B. KISTIAKOWSKY and H. GERSHINOWITZ (J. Chem. Physics, 1933, 1, 885).—Corrections (see this vol., 30). N. M. B.

Water-gas reaction in low-pressure explosions. B. W. BRADFORD (J.C.S., 1933, 1557—1563).—The equilibrium const. has been calc. from analyses of the products of explosion of CO and H_2 with in-

sufficient O_2 for complete combustion. K_p decreases continuously with decreasing initial explosion pressure p for a given mixture, and varies with different mixtures at the same p , according to $K_p = \beta p^a$. The variation of K_p is attributed to changing concn. of OH produced by dissociation of H_2O , the equilibrium being chiefly determined by the rate of the reaction $CO + OH \rightarrow CO_2 + H$. R. S.

Chemical equilibria of reactions between hydrocarbons. V. A. A. VEDENSKI, S. G. VINNIKOVA, V. R. SHARKOVA, and B. M. FUNDILER (J. Gen. Chem. Russ., 1933, 3, 718—728).—The equilibrium consts. for the hydrogenation of PhMe, PhEt, and PhPr at 200—300° are given by $\log K = 10,970/T - A \pm B$, where the respective vals. of A are 20.387, 20.526, and 20.559, and of B 0.053, 0.049, and 0.105.

R. T.

Equilibrium between carbon monoxide, hydrogen, formaldehyde, and methyl alcohol. I. Reactions $CO + H_2 \rightleftharpoons HCOH$ and $H_2 + HCOH \rightleftharpoons CH_3OH$. R. H. NEWTON and B. F. DODGE (J. Amer. Chem. Soc., 1933, 55, 4747—4759).—Reaction (1) in presence of Cu-Zn catalysts yields $K_p = 1.72 \times 10^{-5}$ at 247°. Reaction (2) proceeds readily at 120—200° in presence of Cu-Zn, Cu, Ni, Cu-Ce, Ni-Ce, Cu-Cr, or Zn-Cr, but Os, Pt, or Zn are not active catalysts. Ni tends to promote decomp. of CH_2O into CO and H_2 . Cu tends to give HCO_2Me among the products. For reaction (2) $K_p = 2090$ at 197°. The influence of temp. is given by $\log_{10} K_p = (374/T) - 5.431$ and $\log_{10} K_p = (4600/T) - 6.470$.

E. S. H.

Derivation of equations for regular solutions. J. H. HILDEBRAND and S. E. WOOD (J. Chem. Physics, 1933, 1, 817—822).—Mathematical. Menke's probability function (cf. A., 1932, 986) is used for a statistical treatment of the intermol. potentials in solutions of symmetrical mols. for which the entropy of mixing is the same as for an ideal solution of the same composition. Calc. departures of I solutions from the ideal solution laws agree with experimental vals. N. M. B.

Spectroscopic investigation of dissociation relations of mercuric halides in solution. H. FROMHERZ and K. H. LIH (Z. physikal. Chem., 1933, 167, 103—128).—Extinction curves have been traced between about 180 and 330 $m\mu$. The Hg^{II} halides in aq. solution are practically non-ionised and there is no indication of any polymerisation of the HgX_2 mols. In EtOH solution the band max. are displaced towards the red compared with aq. solutions and are lowered by dilution. The max. of $HgBr_2$ and HgI_2 occupy practically the same position in aq. solution as in the vapour state. In mixed solutions of Hg^{II} and alkali halides there are present complex ions, but with a given pair of halides only one species of complex ion is formed: $HgX_2 + nX' \rightleftharpoons HgX_{n+2}$, where n is probably 1 or 2. The dissociation consts. of the complex ions have been calc. and show the stability to increase in the order $Cl < Br < I$. The ratio of the frequency of the ultra-violet absorption max. of HgX_4^{2-} to that of HgX_2 is approx. the same for all three halides. R. C.

Thermodynamics of aqueous sodium hydroxide solutions from electromotive force measurements. H. S. HARNED and J. C. HECKER (J. Amer. Chem. Soc., 1933, 55, 4838—4849).—Activity coeffs., relative partial mol. heat contents, and heat capacities of NaOH from 0° to 35° have been calc. from the e.m.f. of the cells $H_2 | NaOH(M) | Na_2Hg | NaOH(0.05) | H_2$ at 5° intervals. The results agree well with calorimetric data. An equation for extrapolating the partial mol. heat content has been developed. E. S. H.

Dissociation constants of organic acids. VII. Acetic acid: correction. Solvent correction for salts of weak monobasic acids. G. H. JEFFERY, A. I. VOGEL, and (in part) H. V. LOWRY (J.C.S., 1933, 1637—1643; cf. A., 1933, 125).—A method for the accurate measurement of the conductivities of weak acids is described, involving the addition of sufficient $Ba(OH)_2$ to neutralise all impurity calc. as CO_2 in the solvent H_2O . Applied to NaOAc and KOAc, the method gives 40.54 for the limiting mobility of OAc' at 25°. The corr. vals. for the classical and thermodynamic dissociation consts. of AcOH are 1.824×10^{-5} and 1.764×10^{-5} , respectively.

R. S.

First dissociation constant of carbonic acid in haemoglobin solutions.—See this vol., 92.

Influence of salts on activity of hydrogen ions. V. CUPR and T. KREMPASKÝ (Pub. Fac. Sci. Univ. Masaryk, 1933, No. 182, 3—27).— Li_2SO_4 is pptd. by adding EtOH (66%) to the acid solution; in these conditions Na, K, Be, Mg, Ca, and Al sulphates remain in solution. Corrections for the salt error due to NaCl or KCl in the measurement of the $[H^+]$ of aq. HCl using a quinhydrone electrode (I) have been determined for various concns. When two solutions of the same total mol. concn., containing HCl and different chlorides, are mixed, no change takes place in the $[H^+]$ other than that following from the mixture rule; the same applies to sulphate- H_2SO_4 mixtures. The $[H^+]$ of 0.2N- H_2SO_4 increases in presence of equiv. concns. of $MgSO_4$, $BeSO_4$, $ZnSO_4$, and $CdSO_4$ in the order given, and decreases in the series Li_2SO_4 , Na_2SO_4 , and K_2SO_4 . Chlorides increase the $[H^+]$ of 0.05N-HCl, in the order $KCl < NaCl < LiCl < MgCl_2$. R. T.

Theory of concentrated solutions of strong electrolytes. Calculation of the osmotic coefficients. G. B. BONINO and G. CENTOLA (Atti R. Accad. Lincei, 1933, [vi], 18, 145—149).—Theoretical. The osmotic coeffs. of conc. solutions of NaCl and of KCl are calc. O. J. W.

Strong electrolytes. H. D. CROCKFORD (J. Elisha Mitchell Sci. Soc., 1933, 49, 37).—The activity coeffs. of $PbCl_2$ in aq. $Cd(NO_3)_2$ have been determined for various concns. and used to calculate the mean distance of closest approach of ions in dil. solutions of strong electrolytes. CH. ABS.

Amphoteric hydrated oxides. XXI. Iso- and hetero-polymolybdic acids, especially phosphomolybdic acids. G. JANDER and H. WITZMANN (Z. anorg. Chem., 1933, 215, 310—320; cf. A., 1933, 1118).—Measurement of the diffusion coeff. of

Na_2MoO_4 in solutions of different p_{H} indicates that between p_{H} 14 and 6.5 the only anion present is MoO_4^{--} . Between p_{H} 6.5 and 1.5 $\text{HMo}_6\text{O}_{21}^{--}$, $\text{H}_2\text{Mo}_6\text{O}_{21}^{--}$, and $\text{H}_3\text{Mo}_6\text{O}_{21}^{--}$ are progressively formed, and at about 1.25 $\text{H}_7\text{Mo}_{12}\text{O}_{41}^{--}$. At still higher degrees of acidity there are formed, first the slightly sol. "molybdic acid hydrate," and subsequently sol. compounds in which the Mo forms part of a complex cation. In presence of an equimol. proportion of Na_2HPO_4 the behaviour is the same up to p_{H} 1. When the excess acid (HClO_4) reaches 1*N* the max. proportion of yellow $[\text{H}_2\text{PO}_4(\text{H}_3\text{Mo}_6\text{O}_{21})_2]^{--}$ is formed. The latter remains in equilibrium with amounts of the isopoly-anion and the molybdenyl cation which depend on the p_{H} . A study of the optical absorption of the solutions confirms the conclusions based on the diffusion experiments.

F. L. U.

Equilibrium $\text{H}_2\text{SO}_4 + \text{HF} \rightleftharpoons \text{HSO}_3\text{F} + \text{H}_2\text{O}$ and the influence of strong acids on it. W. LANGE (Z. anorg. Chem., 1933, 215, 321—332; cf. A., 1933, 1014).—If 37% aq. HF is gradually added to H_2SO_4 at 24°, the amount of HSO_3F formed increases at first, reaches a max., and finally = 0. Addition of H_2O to a mixture in equilibrium reduces $[\text{HSO}_3\text{F}]$ more rapidly than the law of mass action would predict. Foreign strong acids displace the equilibrium in favour of HSO_3F , but the action depends on their dehydrating capacity and not on their strength.

F. L. U.

Equilibrium relations in slightly soluble basic salts. VI. W. FEITKNECHT (Helv. Chim. Acta, 1933, 16, 1302—1315).—As previously shown by X-ray analysis (A., 1933, 664) the first pptn. products of bivalent metal salts with aq. NaOH are usually well-defined basic salts. These behave as other slightly sol. compounds and the solubility product (I) can be determined. The calc. (I) of basic ZnSO_4 is shown to be fairly const. over a considerable concn. range, and similarly for basic Bi chloride. Equilibrium conditions are deduced for the coexistence of basic salt and hydroxide in solutions containing a second easily sol. salt with the same anion, and it is shown that the (I) of the hydroxide can be deduced. From the equations the val. 1.6×10^{-17} is obtained for the (I) of $\text{Zn}(\text{OH})_2$. This is confirmed by reference to data for aq. ZnCl_2 . Titration curves actually obtained in the pptn. of basic salts by aq. NaOH do not agree with the theoretical curves, probably because the basic salt is only slowly decomposed in presence of excess of alkali. No conclusion can be reached from the position of the end-point as to the composition of the basic salt. There are indications that in aq. ZnSO_4 containing >75% of alkali basic sulphates of composition $\text{ZnSO}_4 \cdot (6-7)\text{Zn}(\text{OH})_2$ are formed with the layered lattice structure observed in the normal basic salts. Similar conclusions apply to ZnCl_2 .

M. S. B.

Partial pressure of water vapour and oxides of nitrogen over nitrosylsulphuric acid solutions. A. V. TICHONOV (J. Chem. Ind. Russ., 1933, 10, No. 8, 58—60).—The $\text{NO} + \text{NO}_2$ and H_2O pressures of solutions have been determined at 30—90°. R. T.

Direct determination of dissociation pressure of metal oxides. A. KAPUSTINSKI and L. SCHAMOVSKI (Z. anorg. Chem., 1933, 216, 10—16).—The dissociation pressure of NiO has been determined by measuring the electron emission of a superficially oxidised Ni wire at different temp. Between 1420° and 1610° abs. the course of the reaction can be expressed by $\log K_p = -23,250/T + 10,678$. The calc. heat of formation of NiO is +106.3 kg.-cal.

E. S. H.

Dissociation pressure of strontium carbonate. J. CHIPMAN (Trans. Faraday Soc., 1933, 29, 1266—1269).—Becker's data (cf. A., 1931, 41) are used to calculate the dissociation pressure of SrCO_3 between 650° and 1250°. The calc. heat of dissociation is 53,620 g.-cal.

H. J. E.

Temperature-composition relations of the binary system magnesium nitrate-water. W. W. EWING, J. D. BRANDNER, C. B. SLICHTER, and W. K. GRIESINGER (J. Amer. Chem. Soc., 1933, 55, 4822—4824).—The data confirm the existence of the enne-, hexa-, and di-hydrates, and the anhyd. salt.

E. S. H.

Solubility relations of the ternary system magnesium nitrate-nitric acid-water at 25°. W. W. EWING and E. KLINGER (J. Amer. Chem. Soc., 1933, 55, 4825—4827).—The hexa- and di-hydrates and the anhyd. salt can exist as solid phases.

E. S. H.

Temperature-composition relations of the binary system zinc nitrate-water. W. W. EWING, J. J. MCGOVERN, and G. E. MATHEWS, jun. (J. Amer. Chem. Soc., 1933, 55, 4827—4830).—The data confirm the existence of hexa-, tetra-, di-, and mono-hydrates.

E. S. H.

Solubility relations of the ternary system zinc nitrate-nitric acid-water at 25°. W. W. EWING, A. J. RICARDS, W. J. TAYLOR, and D. W. WINKLER (J. Amer. Chem. Soc., 1933, 55, 4830—4832).—The hexa-, tetra-, di-, and mono-hydrates of $\text{Zn}(\text{NO}_3)_2$ can exist in stable equilibrium with HNO_3 at 25°.

E. S. H.

Freezing of solutions. X. Mixtures containing [optically] active alkylsuccinic and α -chlorobutyric acids. J. TIMMERMANS and (MLLE.) J. VAN DER HAEGEN (Bull. Soc. chim. Belg., 1933, 42, 448—460; cf. A., 1932, 1205).—*n*-Hexylsuccinic acid (A) and *n*-propylsuccinic acid (B) have been resolved. *d*-A has m.p. 83.2°, $[\alpha]_D +14.3^\circ$; *d*-B has m.p. 93.9°, $[\alpha]_D +9.6^\circ$. The two *d*-acids give a continuous series of mixed crystals with min. f.p. *d*-B and *l*-A form an equimol. compound. With *d*- α -hydroxybutyric acid PCl_5 gives the *d*-Cl-acid, whereas PBr_5 gives the *l*-Br-acid. A study of the f.-p. curves of mixtures of the K salts of the respective acids shows that the configuration, as well as the rotation, of the OH-acid is changed by PBr_5 .

F. L. U.

System lime-sugar-water. E. SAALMANN (Z. Ver. deut. Zuckerind., 1933, 83, 963—1041).—The conductivity of 0.00023—0.044*N* solutions of $\text{Ca}(\text{OH})_2$ in 0—60% sucrose solutions (I) has been determined. The conductivity of NaCl and BaCl_2 solutions falls linearly as sucrose concn. increases, but for $\text{Ca}(\text{OH})_2$ (and NaOH) the change is parabolic. The difference is due to formation of Ca-sucrose compound, and the

quantity of this in the solutions has been calc. from p_H measurements. The mobility of the saccharate ion lies between 10 and 30. The solubility of $\text{Ca}(\text{OH})_2$ in (I) has been determined when: (a) the $\text{Ca}(\text{OH})_2$ is formed by adding aq. CaCl_2 to (I) containing NaOH ; (b) $\text{Ca}(\text{OH})_2$ is added to (I), and (c) CaO is added to (I). In case (a) colloidal $\text{Ca}(\text{OH})_2$ is formed, and the ppt. consists only of $\text{Ca}(\text{OH})_2$ particles on which sucrose is adsorbed; in (b) mol. dispersion alone occurs, and the Ca concn. in the solution is lower than in (a); in (c) the solubility is much greater, and passes through a max. Viscosity measurements with 10% and 20% (I) containing CaO indicate that colloidal particles are not present. Sucrose is not adsorbed from $\text{C}_5\text{H}_5\text{N}$ by CaO . The theoretical aspects are discussed in reference to van Aken's views. H. F. G.

Equilibrium in the reduction of cobaltous oxide by carbon monoxide. M. WATANABE (Sci. Rep. Tôhoku, 1933, 22, 892—901).—The relation $\log(p_{\text{CO}_2}/p_{\text{CO}}) = 2759/T - 1.0643$ is found for the equilibrium $\text{CoO} + \text{CO} \rightleftharpoons \text{Co} + \text{CO}_2$ in the range 563—861° (cf. A., 1930, 861). Thermodynamic quantities are calc. for CoO and the equilibrium $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ is considered. J. G. A. G.

Oxidation-reduction equilibrium of metallic manganese. S. AOYAMA and Y. OKA (Sci. Rep. Tôhoku, 1933, 22, 824—834).—The relation $\log(p_{\text{H}_2}/p_{\text{H}_2\text{O}})(\text{mm.}) = 8504/T - 2.035$ for the equilibrium $\text{Mn} + \text{H}_2\text{O} \rightleftharpoons \text{MnO} + \text{H}_2$ is derived from dynamic experiments at 1048—1460°. The heat and free energy of formation of MnO are $-\Delta H_{298}$ 96,680 and ΔF_{298} -96,240 g.-cal., respectively. J. G. A. G.

Equilibrium in the reduction of silver sulphide by hydrogen. M. WATANABE (Sci. Rep. Tôhoku, 1933, 22, 902—914).—The relation $\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) = 125.44/T - 0.6449$ is obtained for the equilibrium $\text{Ag}_2\text{S}(\text{cubic}) + \text{H}_2 \rightleftharpoons 2\text{Ag} + \text{H}_2\text{S}$ in the range 453—704°. By calculation, the free energy and heat of formation of Ag_2S (rhombic) are ΔF_{298} -9766 and $-\Delta H_{298}$ 7725 g.-cal., respectively, and the standard electrode potential of S is 0.47 volt. J. G. A. G.

Calcium cyanamide. IV. Nitrogenation equilibria of alkaline earth carbonates with ammonia and of alkaline earth oxides with hydrocyanic acid. H. H. FRANCK and H. BANK (Z. anorg. Chem., 1933, 215, 415—426).—The equilibrium $\text{M}^{\text{II}}\text{CN}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{M}^{\text{II}}\text{CO}_3 + 2\text{NH}_3$ (Ca, Sr, Ba), determined from the nitrogenation side, agrees with that previously found from hydrolysis (A., 1932, 469). Concordant results from both sides have also been obtained for $\text{M}^{\text{II}}\text{O} + 2\text{HCN} \rightleftharpoons \text{M}^{\text{II}}\text{CN}_2 + \text{CO} + \text{H}_2$. The conventional chemical const. of HCN calc. from the latter equilibria is 3.5 (cf. A., 1931, 807).

F. L. U.

Systems liquid iron-carbon oxides and liquid iron-hydrogen-water vapour. H. C. VACHER (Bur. Stand. J. Res., 1933, 11, 541—551).—The val. 0.0025 previously obtained for the product of C and O, in liquid Fe at 1580° in contact with a mixture of CO and CO_2 at 1 atm. has been confirmed. Equilibrium consts. at 1580° have been determined for the following equations: (I) $\text{FeO}(\text{in solution}) + \text{CO}(\text{gas}) \rightleftharpoons \text{Fe}(\text{liq.}) + \text{CO}_2(\text{gas})$; (II) $\text{Fe}_3\text{C}(\text{in solution}) + \text{CO}_2(\text{gas})$

$\rightleftharpoons 3\text{Fe}(\text{liq.}) + 2\text{CO}(\text{gas})$; (III) $\text{Fe}_3\text{C}(\text{in solution}) \rightleftharpoons 3\text{Fe}(\text{liq.}) + \text{C}(\text{in solution})$; (IV) $\text{FeO}(\text{in solution}) + \text{H}_2(\text{gas}) \rightleftharpoons \text{Fe}(\text{liq.}) + \text{H}_2\text{O}(\text{gas})$. They are, respectively, 27.0, 7.9×10^3 , 0.038, and 110. The vals. for (I), (II), and (IV) are reproducible and can be obtained by approaching the equilibrium from > one direction. The ratio of the consts. of (IV) and (I) is 4.07, in good agreement with the val. 3.95 for the equilibrium const. of the water-gas reaction. The C in liquid Fe appears to be due to slightly dissociated Fe_3C . M. S. B.

Double decomposition in the absence of a solvent. XVII. A. G. BERGMAN and N. S. DOMBROVSKAJA. XVIII. N. S. DOMBROVSKAJA (J. Gen. Chem. Russ., 1933, 3, 729—734, 735—741).—XVII. Theoretical.

XVIII. The fusion diagram for the system $\text{AgCl}-\text{NaBr}-\text{AgBr}-\text{NaCl}$ suggests the formation of solid solutions which contain all four components. R. T.

Phase-rule equilibria of acid soaps. IV. Three-component system potassium laurate-lauric acid-water. J. W. MCBAIN and M. C. FIELD (J. Amer. Chem. Soc., 1933, 55, 4776—4793; cf. A., 1933, 901).—Equilibrium diagrams are given for the range 100—370°. At 100° eleven types of 2- or 3-phase equilibria occur; two types have disappeared at 175°, and only three remain at 250°. E. S. H.

Thermodynamic equilibrium in the crystal state. D. BALAREV [with I. JOTZOV] (Kolloid-Z., 1934, 66, 51—57).—Dissolution and growth of large crystals at the expense of the smaller occur with PbI_2 at room temp. in aq. solution if the thickness of the crystals is about 300 μ . PbI_2 crystals have a mosaic substructure. Powdered crystals of sparingly sol. substances (BaSO_4 , SrSO_4 , PbF_2 , PbI_2 , CaF_2), suspended in H_2O , undergo mol. and submicronic dissolution or peptisation and growth. E. S. H.

Heats of formation of cadmium oxide, cadmium hydroxide, and zinc oxide. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1933, 167, 1—15).—The heats of formation of CdO and ZnO , found by combustion of the metals, are 62.36 ± 0.25 and 83.36 ± 0.21 kg.-cal., respectively, at const. pressure and 20°. The vals. deduced from the heats of dissolution of CdO and ZnO in aq. HCl are 61.04 and 83.54 kg.-cal. The heat of formation of $\text{Cd}(\text{OH})_2$ is 133.41 kg.-cal., giving 4.0 kg.-cal. for the heat of hydration of CdO at 20°. Integral heats of dilution of HCl at 20° are recorded. A method for the complete combustion of metals in the bomb calorimeter is described. R. C.

Heats of formation of niobium and tantalum pentoxides. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1933, 167, 16—18).—The heats of formation of Nb_2O_5 and Ta_2O_5 , determined by combustion of the metals, are 463.1 ± 0.7 and 486.0 ± 0.5 kg.-cal., respectively, at 20° and const. pressure. Ta has d 16.64 at 19.6°. R. C.

Thermodynamic study of lithium sulphate. Y. UEDA (Sci. Rep. Tôhoku, 1933, 22, 879—891).—E.m.f. data for $\text{Hg}, 0.035\% \text{Li}|\text{Li}_2\text{SO}_4, \text{H}_2\text{O}(\text{sat.})|\text{PbSO}_4 + \text{LiSO}_4, \text{H}_2\text{O}|\text{Pb}, \text{Hg}$, and $\text{Pb}, \text{Hg}|\text{PbSO}_4 + \text{LiSO}_4, \text{H}_2\text{O}|\text{LiSO}_4, \text{H}_2\text{O} + \text{Hg}_2\text{SO}_4|\text{Hg}$ refer to 20—35°. V.-p. data and heats of dissolution and dilution

of $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ and LiSO_4 at 25° are recorded. The heat of hydration is 3018 g.-cal. The free energy and heat of formation of LiSO_4 are $\Delta F_{298}^\circ -313,614$ and $-\Delta H_{298}^\circ 338,099$ g.-cal., respectively. J. G. A. G.

Heats of dilution of aqueous solutions of zinc, cadmium, and copper sulphates and sulphuric acid at 25° . E. LANGE, J. MONHEIM, and A. L. ROBINSON (J. Amer. Chem. Soc., 1933, 55, 4733—4744).—Data for CdSO_4 , CuSO_4 , and ZnSO_4 (1.0—0.00005*M*) and H_2SO_4 (0.05—0.00005*M*) lead to the following integral heats of dilution: *M*- ZnSO_4 -1314, *M*- CdSO_4 -1973, *M*- CuSO_4 -1590, 0.1*M*- H_2SO_4 -2960 g.-cal. per mol. Relative partial mol. heat contents have been calc. for the concn. range indicated. E. S. H.

Heats of dissolution and dilution of potassium and ammonium phosphates. K. CHOMIAKOV, S. JAVOROVSKAJA, and P. SCHIROKICH (Z. physikal. Chem., 1933, 167, 35—41).—Integral and differential heats of dissolution and differential heats of dilution of KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ over the complete concn. range are recorded. R. C.

Determination of heat of dehydration of kaolin at 450° . H. E. VON GRONOW and H. E. SCHWIETE (Z. anorg. Chem., 1933, 216, 109—112).—Earlier work is criticised. The val. obtained, 213 g.-cal. per g., is considerably higher than former vals. E. S. H.

Kohlrausch's theory of moving boundaries. J. MUKHERJEE (Kolloid-Z., 1933, 65, 297—301).—Theoretical. E. S. H.

Conductivity of potassium and sodium hydroxide solutions at high temperatures. P. M. KOROTKOV and N. K. SOKOLOV (J. Gen. Chem. Russ., 1933, 3, 670—678).—The sp. conductivity κ of aq. NaOH is greatest at 50° and 55° in 20%, at 60 — 75° in 22.5%, and at 80° in 25% solutions; for aq. KOH κ is greatest at 50 — 55° in 30%, and at 60 — 80° in 32.5% solutions. R. T.

Activity coefficient and transference numbers of potassium iodide. R. W. GELBACH (J. Amer. Chem. Soc., 1933, 55, 4857—4860).—E.m.f. of cells of the types (a) $\text{KHg}|\text{KI}(m_1), \text{AgI}|\text{Ag}-\text{Ag}|\text{AgI}, \text{KI}(m_2)|\text{KHg}$, (b) $\text{KHg}|\text{KI}(m_1)|\text{KI}(m_2)|\text{KHg}$, and (c) $\text{Ag}|\text{AgI}, \text{KI}(m_1)|\text{KI}(m_2), \text{AgI}|\text{Ag}$ have been measured at $25 \pm 0.02^\circ$. The Debye-Hückel consts. and transference nos. have been determined for KI and the activity coeffs. calc. E. S. H.

Dichromic acid. E. CARRIÈRE and H. SENDRAS (J. Chim. phys., 1933, 30, 628—633).—The equiv. conductivities of K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ between 20° and 30° have been measured and the mobilities of 0.5CrO_4^{2-} and $0.5\text{Cr}_2\text{O}_7^{2-}$ at 20° calc. as 66.9 and 51.8, respectively. The % of H ions formed by dissociation of $\text{H}_2\text{Cr}_2\text{O}_7$ between *M*/60 and *M*/300 has been obtained from these vals. in conjunction with conductivity measurements of the mixtures (a) $2\text{K}_2\text{CrO}_4 + 4\text{HCl} = 4\text{KCl} + \text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$, and (b) $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{HCl} = 2\text{KCl} + \text{H}_2\text{Cr}_2\text{O}_7$, at different dilutions. Results from (a) and (b) are in good agreement and indicate that $\text{H}_2\text{Cr}_2\text{O}_7$ is largely ionised. R. S.

Electrochemical and cryoscopic investigation of the ternary systems aluminium bromide-

lithium, copper, and silver bromides-benzene, toluene, or xylene. V. A. PLOTNIKOV, I. A. SCHEKA, and V. A. JANKELEVITSCH (J. Gen. Chem. Russ., 1933, 3, 481—499).—The conductivity of the systems $\text{AlBr}_3\text{-MBr}(M=\text{Li}, \text{Ag}, \text{Cu})\text{-C}_6\text{H}_6$ or PhMe increases rapidly with concn. of MBr to a max. val. which corresponds with $\text{MBr}, 2\text{AlBr}_3$. The conductivity increases in the order $\text{Cu}, \text{Li}, \text{Ag}$. Cu and Ag are deposited on the cathode from the corresponding solutions, and Al from that containing LiBr; the cohesion of the deposits increases in the series $\text{C}_6\text{H}_6 < \text{PhMe} < \text{xylene}$. The decomp. potentials in C_6H_6 are CuBr 1.13, AgBr 1.35, and LiBr 1.60 volts; in PhMe the vals. are 1.40, 1.14, and 2.00 volts. The compounds $\text{MBr}, 2\text{AlBr}_3$ are shown cryoscopically to be highly associated in C_6H_6 to an extent which increases with concn. R. T.

Calomel electrode. K. NOMURA (J. Biochem. Japan, 1933, 18, 301—309).—The potential of a 3.5*M*- $\text{KCl-Hg}_2\text{Cl}_2$ electrode attains a const. val. within 2 days, the vals. for the single electrode being approx. $0.28382t^{-0.03983}$ (13— 25°) and $0.30249t^{-0.05967}$ (25 — 43°). F. O. H.

Antimony electrode. I. Stability of electrode potential and its effect on the relation between p_{H} and electromotive force. T. TOMIYAMA (J. Biochem. Japan, 1933, 18, 285—299).—The prep. of Sb electrodes and the variations of their potential with temp. etc. have been investigated. Before the attainment of equilibrium and when the potential change is 1 mv. per 30 min., the potential against a *N*- Hg_2Cl_2 electrode is given by $E = 0.022 + 0.0567p_{\text{H}}$ at 20° . F. O. H.

Mechanism of the oxygen electrode. T. P. HOAR (Proc. Roy. Soc., 1933, A, 142, 628—646).—The kinetics of the processes which occur at the so-called "O₂ electrode" are consistent with the hypothesis that the total electrode process can be represented by the reversible reaction $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightleftharpoons 4\text{OH}'$, which takes place in stages on the surface of the oxide film with which the inert electrode is covered. Cathodic and anodic polarisation curves have been obtained for O₂ electrodes formed by Pt and Au in various O₂-saturated electrolytes, and the log c.d. bears a linear relation to the electrode potential except at very low c.d. Extrapolation of the anodic and cathodic curves gives a val. of $+1.20 \pm 0.03$ volts at 25° for the reversible O₂ potential referred to H₂ in the same solution, agreeing with the val. $+1.227$ volts calc. from thermal data by Lewis and others. L. L. B.

The cell $\text{Pt}|\text{quinhydrone}, \text{HCl}(0.01\text{M})|\text{AgCl}|\text{Ag}$, and the normal electrode potential of the quinhydrone electrode from 0° to 40° . H. S. HARNED and D. D. WRIGHT (J. Amer. Chem. Soc., 1933, 55, 4849—4857).—The e.m.f. of the cell is reproducible to 0.1 mv. from 0° to 40° , although side reactions destroy the equilibrium after a short time above 30° . Vals. are also given for the cell $\text{Pt}|\text{quinhydrone}, \text{HCl}|\text{H}_2$ with an accuracy of ± 0.1 mv. from 0° to 25° and ± 0.15 mv. from 30° to 40° . E. S. H.

Diffusion potentials. I. V. ČUPR and J. ŠPAČEK (Pub. Fac. Sci. Univ. Masaryk, 1933, No. 183, 3—25).—Apparatus for measuring diffusion potential, *E*, and conductivity, *c*, is described. The results ob-

tained with various pairs of solutions agree with Henderson's formula (A., 1907, ii, 426). Büchi's statement that the E between two electrolytes of equal c can be eliminated by interposing a third electrolyte (I) of any concn. (A., 1924, ii, 744) applies only when the concn. of (I) is relatively much $>$ that of the other two. For two solutions $E=0$ when the equiv. c are equal; for mixtures of electrolytes $E=0$ when the ratios of sp. c to ionic strength are equal. R. T.

Liquid junction potentials. I. J. B. CHLOUPEK, V. Z. DANEŠ, and B. A. DANEŠOVA (Coll. Czech. Chem. Comm., 1933, 5, 469—478).—The e.m.f. of the cells Hg|HgCl, 0.1*N*-KCl|junction solution|0.1*N*-HCl|Hg with "free diffusion" type of junction have been determined at 25° and 32°. The junction liquids are 0.001—*S**N* solutions of twelve salts of several valency types, and in all cases the e.m.f. increases with decreasing concn. J. G. A. G.

Physico-chemical studies of complex formation involving weak acids. VII. Hydroferrocyanic acid, and precipitation of ferrocyanides of silver, lead, copper, zinc, cobalt, nickel, and manganese. H. T. S. BRITTON and E. N. DODD (J.C.S., 1933, 1543—1546).—Titration by the glass electrode method shows $H_4Fe(CN)_6$ to be slightly weaker than H_2SO_4 . The pptn. of ferrocyanides from salt solutions has been investigated conductometrically by direct titration and by measurements of solutions in equilibrium with solid phases of known composition. $K_4Fe(CN)_6$ ppts. $Pb_2Fe(CN)_6$ from $Pb(NO_3)_2$, and double ferrocyanides from $CuSO_4$, $ZnSO_4$, $CoSO_4$, $NiSO_4$, and $MnSO_4$. The first ppt. in $AgNO_3$ is $Ag_4Fe(CN)_6$, which is at once converted into $KAg_3Fe(CN)_6$. R. S.

Studies of complex salts by e.m.f. measurement. I. Silver. K. MASAKI (J. Electrochem. Assoc., Japan, 1933, 1, 25—28).—The e.m.f. at 25° of the cell $Ag|AgNO_3(c), alkali\ or\ NH_3(C)|KCl(c')|AgCl|Ag$ is given by the formula $[0.0591 \log Kc / (C - nc)^n]c'/S$, where K is the dissociation const., S the solubility product, and n the no. of radicals combined with Ag. The formation of $Ag(CN)_3$, $Ag(CNS)_4$, AgI_4 , $Ag(S_2O_3)_2$, and $Ag(NH_3)_2$ is confirmed. CH. ABS.

Effect of iron on the establishment of the oxidation-reduction potential of alloxantin. E. S. HILL and L. MICHAELIS (Science, 1933, 78, 485—486).—The p.d. for alloxantin (I) at a Pt or Au electrode becomes erratic when the saturated solution of (I) is somewhat diluted. On addition of $FeSO_4$ (0.1—1.0 mg. per 25 c.c. of solution) the p.d. becomes reproducible and is quickly established even in very dil. solutions of (I) (1 in 10^4). (I) can be reduced to dialuric acid in the electrode vessel by H_2 and colloidal Pt, and after replacement of H_2 by N_2 can be titrated with Br yielding alloxan, but the establishment of a p.d. is sluggish and erratic unless a small quantity of $FeSO_4$ is added. The titration curve is that of an ordinary dyestuff system with no indication of an intermediate step in the oxidation. The effect of Fe is most marked between p_H 4 and 6, and disappears at p_H 1. Fe cannot be replaced by Cu, Mn, Co, Ni, or org. dyes. An explanation of the effect is discussed. L. S. T.

Current density-potential curves. V. SIHVONEN and O. ENWALD (Suomen Kem., 1933, 6,

74B).—Simultaneous measurements of c.d. and p.d. at electrodes of Fe and Ni in aq. NaOH have led to a formula connecting these vals. E. S. H.

Catalytic hydrogen replacement and the nature of overvoltage. J. A. V. BUTLER (Nature, 1934, 133, 26).—A criticism (cf. this vol., 37). L. S. T.

Rate of decay of hydrogen and oxygen overvoltages. G. ARMSTRONG and J. A. V. BUTLER (Trans. Faraday Soc., 1933, 29, 1261—1266; cf. A., 1932, 700).—An expression is derived for the rate of decay of H and O overvoltages when these are not affected by the electromotive activity of any product of electrolysis. This agrees with the H overvoltage at Hg cathodes when the initial electrode potential is not more negative than -1.0 volt. For the O overvoltage at Pt electrodes agreement is obtained after a period of 100 sec. Deviations under other electrode conditions are discussed. H. J. E.

Decomposition voltages of fused salts. I. Method of determination and decomposition voltage of zinc chloride. Y. KONISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 677B).—A graphite anode, cathode, and neutral electrode were used and the e.m.f. between each pair was measured. The decomp. potentials of fused $ZnCl_2$ at 408°, 459°, and 498° are 1.94, 1.89, and 1.83 volts, respectively, the vals. calc. from the heat of formation (97.21 kg.-cal.) and the sp. heat (0.1362) being 1.902, 1.880, and 1.843 volts, respectively. A. G.

Reaction rates of the hydrogen isotopes. M. POLANYI (Nature, 1934, 133, 26—27).—The assumption that diplogen (H_2^2) will invariably react more slowly than H_2 is not justified. L. S. T.

Determination of velocity of gas reactions of atomic hydrogen. E. CREMER, J. CURRY, and M. POLANYI (Z. physikal. Chem., 1933, B, 23, 445—468).—The method used consists in allowing an inert gas with which at. H is mixed to issue from a jet in a vessel containing the other reactant, X. The reaction velocity, k , is ascertained by determining in the stationary state the no. of H atoms in the reacting mixture, N , the concn. of X, and the no. of H atoms entering the reaction vessel per sec. N is found by observing the power of the H atoms to transform admixed para- H_2 into normal H_2 . It has not yet been possible to determine k , but only upper or lower limits for the energy of activation, E . CH_2Cl_2 , $CHCl_3$, and CCl_4 react much more rapidly than $MeCl$. Multiple substitution apparently loosens the mol. structure so that both H and C react more readily and H reacts as readily as Cl attached to the same C atom. $MeBr$ reacts more rapidly than $MeCl$. The reactions with EtI and HBr have also been studied. Comparison with the reactions of the above substances with Na vapour shows that the order of reaction velocity is the same in both reactions, and probably the vals. of E do not differ greatly. R. C.

Combustion of hydrocarbons. W. A. BONE (J.C.S., 1933, 1599—1617).—A lecture. H. S. P.

Combustion pressures. A. PIGNOT (J. Usines Gaz, 1932, 56, 594—599; Chem. Zentr., 1933, i, 1749).—The spontaneous combustion of hydrocarbon-

air mixtures under adiabatic compression has been studied. With increasing compression ratio (3—8) the max. pressure P increases (35—52 kg. per sq. cm.), the ratio P/p (p = pressure at end of compression) and retardation of inflammation diminish, whilst the duration of the reaction is const. (air: cyclohexane = 12.04 : 1 by wt.). With fall in original temp. (100—63°) and const. compression ratio (8.28) the duration of retardation and of the total reaction increase. With increasing hydrocarbon content the max. pressure rises. On addition of 5% of an anti-knock to air- C_6H_{12} mixtures (ratio 17.5 : 1 by wt.) the duration of the reaction falls in the order (in 0.004 sec.) $PbEt_4$ 2.82, $C_6H_4Me \cdot NH_2$ 2.50, Et_2O 1.96, $MeOH$ 1.47, Et_2S 1.36, no anti-knock 1.06.

A. A. E.

Influence of pressure on the spontaneous ignition of inflammable gas-air mixtures. II. Pentane-air mixtures. D. T. A. TOWNEND and M. R. MANDLEBAR (Proc. Roy. Soc., 1933, A, 143, 168—176; cf. A., 1933, 1016).—By increasing the pressure from 1 to 10 atm., the ignition temp. of C_5H_{12} -air mixtures are shown to fall into two groups, one above 490° for pressures < 3 atm., and one below 350° for higher pressures. Transference of an ignition point from the lower to the higher group occurs at a crit. pressure dependent on the composition of the mixture. The presence of $PbEt_4$ raises the ignition points from the lower to the higher group at pressures near the crit. transition pressure, but small amounts of $MeCHO$ at all pressures > 1 atm. produce a transference to the lower group.

L. L. B.

Flame speeds during the "inflammation" of moist carbon monoxide-oxygen mixtures. W. A. BONE and J. BELL (Proc. Roy. Soc., 1933, A, 143, 1—15).—When successive $CO-O_2$ media within the range 55CO : 45 O_2 and 80CO : 20 O_2 are ignited by a small flame at atm. pressure at the open end of a horizontal glass tube, the other end being closed, the max. initial uniform flame speed is reached at the 3CO + O_2 composition with moist media, saturated at 15°. Partial drying of such media moves the max. flame speed point towards the 2CO + O_2 composition, until with media containing 4.8 mm. H_2O it is at the composition 70CO : 30 O_2 , approx. Almost complete drying with $CaCl_2$ produces a nearly const. initial uniform flame speed of about 35 cm. per sec. throughout the whole composition range. The initial uniform flame speed observed when an explosive medium is ignited at the open end of a horizontal tube, the other end of which is closed, is shown to have no fundamental significance.

L. L. B.

Slow combustion of ethylene. W. A. BONE, A. E. HAFNER, and H. F. RANCE (Proc. Roy. Soc., 1933, A, 143, 16—37).—The reaction between C_2H_4 and O_2 at 300° and atm. pressure is homogeneous and preceded by an induction period, during which a small amount of aldehyde (but no peroxide) appears. The addition of 1% of NO or $MeCHO$ practically eliminates the induction period and accelerates the subsequent reaction; CH_2O shortens the induction without affecting the reaction period, whilst C_2H_4O scarcely affects the former, but retards the latter. The presence of H_2O vapour has no influence on the

reaction. Of all $C_2H_4+O_2$ media, the most reactive is $2C_2H_4+O_2$, C_2H_4O being the initial oxidation product. All the evidence points to the normal course of oxidation being a series of hydroxylations. $CH_2 \cdot CH \cdot OH$ is first formed, any accumulation of this in the medium being transformed rapidly into an equilibrium mixture of the three C_2H_4O isomerides.

L. L. B.

Kinetics and mechanism of decomposition of hydrocarbons. I. Thermal decomposition of hexane at atmospheric pressure. A. I. DINTZES and A. V. FROST (J. Gen. Chem. Russ., 1933, 3, 747—758).—The reaction commences at 520°, and consists of the primary reactions: C_6H_{14} (I) \rightarrow C_6H_{12} (II) + H_2 ; (I) \rightarrow $C_5H_{10} + CH_4$; (I) \rightarrow $C_4H_8 + C_2H_6$; (I) \rightarrow $C_3H_6 + C_3H_8$, and the secondary reactions (II) \rightarrow $C_5H_4 + C_4H_6$; (II) \rightarrow $2C_3H_6$; $C_5H_{10} \rightarrow C_2H_4 + C_3H_6$; $C_4H_8 \rightarrow 2C_2H_4$. The heat of activation of the primary reactions for the interval 525—565° is 64.5 ± 1.5 kg.-cal., and the velocity coeff. is given by $\log K = 14.22 - 14,105/T \pm 0.031$.

R. T.

Dynamics and mechanism of aliphatic substitutions. E. D. HUGHES and C. K. INGOLD (Nature, 1933, 132, 933—934).—Dynamical evidence relative to previous theoretical views (A., 1933, 701) is summarised.

L. S. T.

Decomposition of formic acid by sulphuric acid. R. E. DE RIGHT (J. Amer. Chem. Soc., 1933, 55, 4761—4764).—Decomp. of HCO_2H by small quantities of H_2SO_4 is apparently unimol. and is inhibited by H_2O . Experiments have also been conducted in excess of H_2SO_4 containing various amounts of SO_3 , but the discussion of results is reserved.

E. S. H.

Thermal decomposition of propyl mercaptan. H. A. TAYLOR and E. T. LAYNG (J. Chem. Physics, 1933, 1, 798—808).—The v.-p. curve of $PrSH$ between 12° and 68° is represented by $\log p = -1647/T - 7.7190$. The thermal decomp. of $PrSH$ was investigated between 405° and 435°/100—350 mm. by a static and a dynamic method. It is homogeneous on a poisoned glass surface. An induction period is found and the reactions before and after the point of inflexion are different, the respective energies of activation being 40,000 and 39,000 g.-cal. The induction period is due to the bimol. reaction $2PrSH \rightarrow Pr_2S + H_2S$ without vol. change. Experiments with Pr_2S showed that $PrSH$ and H_2S remove the induction period. Intermediate additive compounds $SPr_3 \cdot SH$ (I) and $SHPr_2 \cdot SH$ (II) are postulated. Analogues of (I) have been synthesised; they have a very marked instability suggesting the immediate decomp. of (I) to $3C_3H_6 + 2H_2S$, whilst (II) gives $2C_3H_6 + 2H_2S$. Subsequently the reaction proceeds thus: $C_3H_6 + H_2S \rightleftharpoons Pr^2SH$ (finally in pseudo-equilibrium) and polymerisation of C_3H_6 .

W. R. A.

Rates of thermal decomposition of triphenylmethyl alkyl ethers. J. F. NORRIS and A. CRESSWELL (J. Amer. Chem. Soc., 1933, 55, 4946—4951; cf. A., 1930, 470).—The rates of decomp. of $CPh_3 \cdot OMe$ (I), $CPh_3 \cdot OEt$ (II), and $CPh_3 \cdot OPr^i$ (III) at 259—298° in sealed tubes have been studied. At 259° and

269°, the decomp. (up to about 11%) of (II) is unimol.; the rate is doubled for an increase of 10°. Similar results are found for (III) up to about 28% decomp. For (I), the calc. unimol. velocity coeffs. increase rapidly with time; CHPh_2 has a marked accelerating effect on the decomp. The rate of decomp. in air is much $>$ in N_2 . H. B.

Reaction kinetics in films. Hydrolysis of γ -stearolactone. R. J. FOSBINDER and E. K. RIDEAL (Proc. Roy. Soc., 1933, A, 143, 61—75).—Films of γ -hydroxystearic acid and γ -stearolactone (I) have been examined by the surface potential and surface pressure methods. The variation of the electric moment of the acid with compression and temp. indicates that the CH-OH group is probably removed from the surface when under compression. Complexes formed between (I) and substrate are indicated by the vals. obtained for the surface potential equilibrium spreading vals. Information relative to the kinetics of mechanism of the hydrolysis of (I) has been obtained by the method of phase boundary potentials. L. L. B.

Rate of oxidation of hydrogen peroxide by chlorine in presence of hydrochloric acid. B. MACKOWER and W. C. BRAY (J. Amer. Chem. Soc., 1933, 55, 4765—4776).—The rate of the rapid reaction $\text{H}_2\text{O}_2 + \text{Cl}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{Cl}^-$ over the $[\text{HCl}]$ range 0.4—5.2 M agrees with $-d[\text{H}_2\text{O}_2]/dt = \gamma_2 \cdot [\text{H}_2\text{O}_2] a_{\text{Cl}} a_{\text{H}^+} / a_{\text{H}_2\text{O}}$. When the activity of HCl is $> 2M$, γ_2 is nearly const. at 5×10^3 at 25°. The step determining the rate involves the bimol. reaction $\text{H}_2\text{O}_2 + \text{HOCl} \xrightarrow{\kappa_2} \text{O}_2 + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^-$, where $-d[\text{H}_2\text{O}_2]/dt = \kappa_2 [\text{H}_2\text{O}_2][\text{HOCl}]$. This reaction is discussed from the electronic point of view. The bimol. reaction has the max. sp. rate 10^7 at 25°, when $[\text{HOCl}]$ is $> 10^{-7}$. At other temp. the coeff. is approx. represented by $10^{10 \pm 1.5} e^{(-4000 \pm 2000)/RT}$. At low $[\text{HCl}]$ and correspondingly high $[\text{HOCl}]$ the law is not obeyed and the coeff. is much smaller. E. S. H.

Conversion of ammonium cyanate into carbamide. Mechanism and kinetic salt effect. J. C. WARNER and F. B. STITT (J. Amer. Chem. Soc., 1933, 55, 4807—4812).—Determination of the rate at different concns. of NH_4CNO with and without addition of other salts support the view that the conversion depends on collisions between NH_4^+ and CNO^- , and not on collisions between undissociated mols. of NH_4CNO . A method for calculating the limiting velocity coeff. when activity coeffs. are known is devised. The coeff. thus obtained is in good agreement with that obtained by extrapolating the ordinary bimol. coeff. to zero ionic concn. E. S. H.

Kinetics of certain reactions of alkyl iodides in hydroxylic solvents. E. A. MOELWYN-HUGHES (J.C.S., 1933, 1576—1580).—The rate of reaction between EtI and $\text{S}_2\text{O}_3^{2-}$ in aq. solution is approx. that calc. for a bimol. reaction if it is assumed that one internal degree of freedom contributes to the energy of activation. A side reaction between EtI and H_2O also takes place. Comparison with analogous reactions indicates that the energy of activation is associated chiefly with the linking between the alkyl radical and the halogen atom. H. S. P.

Influence of poles and polar linkings on the course pursued by elimination reactions. XXI. Dynamics of elimination of the *tert.*-butyl group from sulphonium compounds. E. D. HUGHES and C. K. INGOLD (J.C.S., 1933, 1571—1576; cf. A., 1933, 701).— $\text{SMe}_2\text{Bu}^+\text{OH}$ in aq. solution may decompose to give an olefine or an alcohol. The first reaction is bimol. and the second unimol., depending only on the concn. of the cation. The speed of the second reaction is therefore independent of added OH^- and is identical with that of the analogous decomp. of salts. The effect of replacing H_2O by EtOH as solvent is studied. *Dimethyltert. butylsulphonium iodide*, decomp. 160°, *picrate*, decomp. 132°, and *hydroxide* (obtained in solution, decomp. below b.p.) were prepared. H. S. P.

Preparation and quaternary ammonium decomposition of formocholine. T. D. STEWART and H. P. KUNG (J. Amer. Chem. Soc., 1933, 55, 4813—4819).—The prep. of $\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ (I) and $\text{NEt}_3\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ (II) is described. The rates of decomp. in dil. acid are in accordance with the equations $\text{R}_3\text{N}^+\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{R}_3\text{N}^+\cdot\text{CH}_2\text{O}^- + \text{H}^+ \rightarrow \text{R}_3\text{NH}^+ + \text{CH}_2\text{O}$. The first part is fast and the second slow. At const. p_{H} the reaction is of the first order and the rate is inversely proportional to $[\text{H}^+]$. The sp. reaction rates at 25° are given by $\log K = a + p_{\text{H}}$, where a is -4.017 for (I) and -3.213 for (II). E. S. H.

Rate of decomposition of creatine in acid and in alkaline solution. A. T. CAMERON and J. S. GUTHRIE (Canad. J. Res., 1933, 9, 360—372).—The rate of decomp. of creatine (I) in acid and alkaline solution at 37.5° and 50° has been studied. The rate of transformation shows a min. in approx. 0.1 N - HCl and a max. in 0.01 N - HCl , due probably to the catalysis of (I) and its hydrochloride at different rates. The results with alkali support the view that (I) is first transformed into $\text{CO}(\text{NH}_2)_2$ and sarcosine, which reunite to form NH_3 and methylhydantoic acid. H. S. P.

Unimolecular film in heterogeneous reactions. E. E. AYNSLEY and P. L. ROBINSON (Nature, 1933, 132, 894—895).—The reaction between H_2 and S at 343° remains homogeneous down to pressures of H_2 of approx. 40 mm. At lower pressures the velocities are $>$ correspond with the homogeneous gaseous reaction (I). At 3 mm. pressure there occur the ordinary (I) and a new reaction (II) on the Pyrex surface (III). (II) has an initial velocity independent of $[\text{S}]$ over a wide range, but proportional to the H_2 pressure and to the area of (III). The velocity falls rapidly, however, and (II) ceases when an amount of H_2S sufficient to cover (III) with a unimol. layer has been formed. A unimol. layer of H_2S thus appears to prevent (III) from promoting further union either at low pressures or at pressures up to 760 mm. The contribution of H_2S from (II) is very small compared with that from (I) and is revealed only at low pressures. The results indicate that (i) (I) and (II) proceed independently, (ii) a unimol. film of S is present on (III), and (iii) the mols. in this film and in the liquid S surface are definitely oriented. L. S. T.

Speed of dissolution of potassium minerals. V. E. VILNYANSKI and E. M. MENSHIKOVA (Kali,

U.S.S.R., 1933, No. 1, 17—26).—Vals. of K in $dc/dt = K(S/v)(C-c)$, where S is the surface of the dissolving salt, v is the vol. of solvent, C is the concn. of the saturated solution, t is the time, and c is the concn. of the solution at the given instant, decrease for rock-salt as the concn. of $MgCl_2$ in brine increases; in a concn. solution of $MgCl_2$ \bar{K} (carnallite) is $> K$ (rock-salt).

CH. ABS.

Crystallisation velocity and number of [crystallisation] centres of tin, bismuth, and lead. G. TAMMANN and H. J. ROCHA (Z. anorg. Chem., 1933, 216, 17—25).—The linear velocity of crystallisation increases with the degree of supercooling and is greater in a thermally conducting tube than in a non-conducting tube. In a tube of Al the max. crystallisation velocity is attained at 2° supercooling. The max. vals. obtained are: Sn 200, Bi, 2, Pb 5 cm. per min. Vals. were also determined for Sn-Cd and Sn-Pb alloys, although max. vals. were not reached. The no. of crystallisation nuclei formed in a given time depends also on the degree of supercooling, but is in order $Pb > Sn > Bi$.

E. S. H.

Inhibitors in the decomposition of hydrogen peroxide by catalase. H. N. ALYEA and J. PACE (J. Amer. Chem. Soc., 1933, 55, 4801—4806).—The decomp. of H_2O_2 by catalase from sheep's liver is inhibited by nineteen org. substances, of which twelve do not appear to deactivate the catalyst, although the remaining seven apparently do so. The relative efficiencies of the inhibitors differ from those for the same substances in the photolysis of H_2O_2 at 75°.

E. S. H.

Enolisation as directed by acid and basic catalysts. I. Acid-catalysed enolisation of menthone. P. D. BARTLETT and J. R. VINCENT (J. Amer. Chem. Soc., 1933, 55, 4992—4997).—The rates of catalytic "inversion" and iodination of *l*-menthone (I) in AcOH containing a little HNO_3 (catalyst) are determined at 30.9°. The results show that (I) gives $79 \pm 5\%$ of Δ^3 -menthen-3-ol.

H. B.

Physico-chemical investigation of the colloidal condition of cholesterol, cholesteryl ester, and lecithin. VIII. Catalytic properties of cholesterol. I. REMESOV and O. SEPALOVA (Biochem. Z., 1933, 266, 330—336).—The catalytic properties of colloidal cholesterol (I) are seen not only in reactions with diamines, but also in the usual reactions for phenolases (pyrogallol, phenol, and naphthol reactions). In N_2 the dehydrogenation reactions of (I) do not occur and atm. O_2 participates in the reaction. The addition of an acceptor to (I) enables its dehydrogenating action to occur in N_2 . Alcohols inhibit the catalytic action of (I). (I) catalyses also the decomp. of H_2O_2 .

P. W. C.

Sulphonation reaction.—See this vol., 178.

Para-hydrogen transformation on carbon surfaces at low temperatures. K. W. RUMMEL (Z. physikal. Chem., 1933, 167, 221—239).—The catalysis is not, in general, due to impurities in the C. Charging with gases which attack the surface atoms; e.g., O_2 at room temp. or above, reduces the catalytic power of the C, whereas molecularly adsorbed gases, e.g., N_2 , have no effect. O_2 at liquid air temp. seems to be

molecularly adsorbed. A large proportion of the C surface is catalytically active, but the activity varies from point to point. A small fraction consists of particularly active centres and is susceptible to poisoning; a part of this has an especially high adsorbent power for H_2 . The transformation follows the unimol. law and is probably brought about by the residual magnetism of surface C atoms. Between -167° and -210° the temp. coeff. of the para-ortho change is small and positive, and that of the ortho-para change negative. The period of half conversion in the ortho-para change is independent of the pressure between 7 and 760 mm., but falls with the pressure below 7 mm. The effect of activation of the adsorbent has been studied.

R. C.

Catalysed reaction of hydrogen with water and the nature of overvoltage. J. HORIUTI and M. POLANYI (Nature, 1933, 132, 931).—Previous observations (this vol., 37) indicate that the rate at which H is ionised depends on the composition of the aq. solution with which the Pt electrode is in contact. This cannot be explained if the inertia (I) of the process is attributed to the reaction of H with Pt, but is readily explicable if (I) is attributed to the transition of the H atoms into the solution. The rate of ionisation of H on Pt-black in different solutions is (H_2O unity) $N-HCl$ 0.7, $N-H_2SO_4$ 0.2, $0.25N-KOH$ 0.4, $EtOH + 2\% H_2O$ 0.4, $EtOH + 2\% H_2O + 0.25N-KOH$ < 0.02 .

L. S. T.

Catalytic oxidation of carbon monoxide. (MME.) L. S. MATHIEU-LÉVY and M. GELOSO (Bull. Soc. chim., 1933, [iv], 53, 1039—1050).—The activity of MnO_2 catalysts (I) promoted with Cu, Fe, and Ni is deduced from the differentially determined rise of temp. of the mass during the passage of air-CO (1—7%) mixtures. For a given gas mixture, the activity of (I), previously exposed to air or mixtures containing lower % CO, rises to a max. and falls to a const. val., Δ , finally decreasing very slowly. In general, Δ increases and decreases with the corresponding changes of % CO, but only during the middle portion, M , of the life of (I) are the vals. of Δ reproducible and linearly proportional to % CO. With a new catalyst, the % CO_2 in the effluent gas is $<$ that produced, whilst with an old catalyst, the reverse obtains. During M , the % CO_2 is linearly proportional to the vals. of Δ . These results are related to adsorption phenomena.

J. G. A. G.

Oxidation of phosphorus with water at high pressures and temperatures. V. N. IPATIEV and FREITAG (Z. anorg. Chem., 1933, 215, 388—414).—The reaction $P_4 + 10H_2O \rightarrow P_4O_{10} + 10H_2$ has been studied at 175—420° and at 20—530 atm. The primary reaction products are PH_3 and H_3PO_3 , each of which then reacts with H_2O to give the end products. The primary reaction is rapid compared with either of the others. All the reactions are accelerated by increase of pressure and rise of temp. Excess of H_2O retards all three; excess of H_2 accelerates the secondary reactions, also the primary reaction if direct contact of H_2 with P is avoided. Free alkali, alkali salts, and free acids have no influence, but H_3PO_3 and H_3PO_4 exercise a retarding effect. Compounds of Co, Ni, Ag, Cu, and Fe have marked catalytic activity, $Ni(NO_3)_2$ in

particular enabling the reaction to reach completion rapidly at 200°. F. L. U.

Poisoning by arsenic of a tin-barium-vanadium catalyst.—See B., 1934, 59.

Poisoning of catalysts for ammonia synthesis.—See B., 1934, 15.

Hydrogenation of naphthalene.—See this vol., 178.

Conversion of acetylene and acetaldehyde into acetone.—See B., 1934, 52.

Catalytic reduction of phenol and *o*-cresol.—See B., 1934, 53.

Hydrogenation of carboxylic acids.—See B., 1934, 53.

Electrolytic production of H²H²O. H. S. TAYLOR, H. EYRING, and A. A. FROST (J. Chem. Physics, 1933, 1, 823—824).—The prep. is described in detail. N. M. B.

Electrolytic concentration of diplogen. R. P. BELL and J. H. WOLFENDEN (Naturc, 1934, 133, 25—26).—A preliminary investigation of the effect of various factors on the efficiency of the concn. of H² by electrolysis in alkaline solution has been made. Neither temp. nor nature of the cathodic metal, nor, possibly, c.d. appears to have any effect on the efficiency of separation. L. S. T.

Electrolytic separation of hydrogen isotopes and the mechanism of the process. B. TOPLEY and H. EYRING (J. Amer. Chem. Soc., 1933, 55, 5058—5059).—The relative rates of separation of H¹ and H² in the electrolysis of H₂O containing 7% H²H²O and 0.5*N*-KOH or H₂SO₄ have been determined, using a Pt anode and cathodes of Pb, Fe, Pt, Cu, Ni, or Ag. Evidence is adduced that the slow cathodic process is not the combination of atoms to mols. E. S. H.

Polarographic studies with the dropping mercury cathode. XXXVI. Catalysis of the electro-deposition of hydrogen due to the presence of the platinum metals. P. HERASYMENKO and I. ŠLENDYK (Coll. Czech. Chem. Comm., 1933, 5, 479—496; cf. A., 1933, 29).—The total catalytic current of H deposition at the dropping Hg cathode from 0.01*N*-HCl increases linearly with concn. of the catalysts, of which the order of increasing efficiency is Pd, Os, Pt, Ir, Rh, Ru. The limiting current increases rapidly with increasing [H⁺] < 0.05*N* and then rises slowly to a max. The current-voltage curves exhibit, in general, three stages which become more clearly defined at high [H⁺] and high concn. of catalyst and are attributed to three types of centres of different activity formed successively by aggregation of the catalyst atoms into polyat. complexes at the Hg surface. The catalytic effects of the several stages can be enhanced or suppressed by varying the rate of dropping of the Hg. The inactivity of Cu, Ag, and Au and the very low val. for Pd are attributed to the strong affinity of these atoms for Hg. J. G. A. G.

Kinetics of electrode processes. III. Behaviour of platinum and gold electrodes in sulphuric acid and alkaline solutions containing oxygen. G. ARMSTRONG, F. R. HIMSWORTH, and

J. A. V. BUTLER (Proc. Roy. Soc., 1933, A, 143, 89—103).—In the anodic polarisation of Pt electrodes a single layer of adsorbed O is formed. Cathodic polarisation effects the reduction of the adsorbed layer simultaneously with depolarisation by dissolved O₂ in the solution. In alkaline solutions Au behaves similarly to Pt, and after long-continued electrolysis the oxidation corresponds with a single layer of O at the surface. In dil. H₂SO₄, however, a Au electrode on polarisation forms a definite oxide when the potential reaches +1.27 volts. The efficiency of oxide formation (100% in the earliest stages) steadily decreases as electrolysis proceeds and reaches a const. val. of about 0.9%. L. L. B.

Electrolysis of sodium sulphide. W. BOHN-HOLTZER and F. HEINRICH (Z. Elektrochem., 1933, 39, 939—947).—The anode phenomena in electrolysis of Na₂S solutions in a U-tube between Pt wire electrodes were studied from the c.d.—anode potential curves. With increasing applied e.m.f., the anode passes through the following states: (I) bright, with low c.d. and anode potential, when the only reaction is the formation of polysulphides; (II), dull owing to an insulating layer, possibly monoclinic S, resulting in the nearly complete suppression of the current; (III), the coating becomes porous, possibly rhombic S; anode potential rises, but is still small and almost independent of c.d., which may rise to considerable vals. Polysulphides are formed; (IV) anode bright again, low c.d., and formation of sulphate and some dithionate, but no S or polysulphides; (V) coated with S and gas bubbles. High c.d. and production of all possible products; (VI) anode nearly free from S, some O₂ evolution, and notable production of thiosulphate. Periodic electrolysis cannot be explained as due simply to an insulating film, but appears to consist of a cyclic recurrence of stages I, II, IV, and III. D. R. D.

Electrolysis of methyl alcohol solution of cupric chloride. E. GUILLERMET (Compt. rend., 1933, 197, 1608—1610).—When a MeOH solution of CuCl₂ (5 wt.-%) is electrolysed with Pt cathode and Pt or Cu anode, c.d. 1.3—5 amp. per sq. dm., the primary reaction is CuCl₂ = CuCl + Cl; some HCl is formed by the interaction of Cl and MeOH, which on electrolysis produces H₂, thus accounting for formation of Cu at the cathode, the amount of which may vary from nil to 80% of the cathode deposit. The poor yield (sometimes only 8%) is due to direct recombination of CuCl and dissolved Cl₂ (cf. A., 1901, ii, 157). C. A. S.

Electrodeposition of rhodium. G. GRUBE and E. KESTING (Z. Elektrochem., 1933, 39, 948—958).—Rh may be deposited in highly reflecting form from solutions of Rh sulphate, silicofluoride, perchlorate, borofluoride, or oxalate, and the bath may be regenerated by the addition of freshly pptd. Rh(OH)₃. The c.d.—potential curves and the effects of temp. and free acid were studied in the above solutions (except borofluoride) and in solutions of Na₃RhCl₆ and phosphate. Metal deposition is always accompanied by H₂ evolution even at low c.d. D. R. D.

Validity of Faraday's law for electrode processes in electrical discharges in dilute gases. V. SIHVONEN (Suomen Kem., 1933, 6, 71—74B).—A

discussion of the reactions occurring at a graphite anode under electrical discharge in O_2 at very low pressure. Faraday's law holds for short time periods. E. S. H.

Photochemical combination of hydrogen and chlorine in strong light. V. KOKOTSCHASCHVILI (Z. physikal. Chem., 1933, B, 23, 431—444).—By means of an apparatus incorporating a new type of glass-membrane manometer the reaction in the light from Mg flash powder of intensities almost sufficient to cause explosion has been studied. During the flash the velocity, v , first rises rapidly to a max., then falls at first rapidly, and then increasingly slowly. With increasing intensity of illumination the max. v first increases linearly, but after a short period of less rapid increase ultimately increases more rapidly than corresponds with linearity. This last phase is probably the result of chain branching, perhaps through the reaction $HCl^* + HCl^* + Cl_2 = 2HCl + Cl + Cl$. The duration of the chains in the present experiments is ≈ 0.01 sec. R. C.

Photographic properties of silver sulphide. II. Print-out effect: chemical aspect. K. HICKMAN and W. WEYERTS (J. Franklin Inst., 1933, 216, 683—706; cf. B., 1934, 123).— Ag_2S , in contact with certain reducing solutions containing free Ag ions, particularly solutions of (I) Ag_2SO_3 with excess of Na_2SO_3 , and (II) $AgNO_3$ with excess of $NaNNO_2$, is sensitive to light and darkens on exposure. This darkening is caused by the deposition of Ag. The yield of Ag is not stoichiometrically related to the amount of Ag_2S or to the loss of S (which is very slight, and of a secondary nature). The spectral sensitivity extends from the violet to 1.4μ , with an apparent max. at 1.1μ . (I) shows a positive, but (II) shows an apparent negative, thermal coeff., probably due to dissolution of Ag by the HNO_3 simultaneously formed. In analogous manner, marked reciprocity failure is found, differing in direction and degree in the two solutions. These experiments have been made on Ag_2S suspensions; the addition of gelatin (III) greatly depresses the intensification process. Any reagent having affinity for Ag ions (e.g., NH_3 , $Na_2S_2O_3$, etc.) practically banishes the sensitivity. Changes in p_H (from 10 to 5) scarcely affect the pure suspensions, but profoundly modify the restraining effect of (III), which is almost removed at p_H 4.8 [the isoelectric point of (III)]. In more acid solutions the Na_2SO_3 decomposes and Ag_2SO_3 is deposited. The mechanism of the reactions in (II) is considered to be relatively simple; in (I) it is known to be complex. J. L.

Photographic summation law and its range of validity. A. VAN KREVELD (Physica, 1933, 1, 60—77).—If three photographic plates are respectively exposed for equal times to two different monochromatic lights and to a mixture of these, the intensities being such that equal photographic densities are produced in each plate, and if the energies associated with the three lights are, respectively, E_a , E_b , and E_m , then ${}_aE_m/E_a + {}_bE_m/E_b = 1$ (in which ${}_aE_m$ and ${}_bE_m$ are the respective contributions of E_a and E_b to E_m) is valid for a range of different emulsions, for different (equal) times of illumination, for any wave-length in the visible spectrum, for any ratio of the monochromatic components, for any selected density, and for different

developers provided single-grain layers are compared. The law is also extended to mixtures of any no. of monochromatic components, i.e., the effects produced by the components of a heterochromatic light are additive. A further corollary is that the Schwarzschild exponent is independent of the wave-length for all densities. F. L. U.

Photochemical action of complex light. M. PADOA and N. VITA (Z. wiss. Phot., 1933, 32, 185—195; cf. A., 1930, 1136; 1933, 791; Winther, *ibid.*, 238).—Winther's criticisms are refuted. From thermoelectric and photographic measurements the transparency of a saturated $NiSO_4$ solution 8.2 cm. thick (diam. of a spherical flask) for the green region in question is about 9.0%, as found before. Reproducible results for the titration of I with $Na_2S_2O_3$, in either neutral or acid solution, are easily obtained if the I solution is sufficiently diluted before titration. The authors' margin of error is much $<$ that of Winther. Several errors in Winther's experiments are pointed out; the passage of a continuous stream of O_2 through the reaction mixture will remove I from the solution. J. L.

Photographic effect of ultra-soft X-rays. M. RENNINGER (Z. Physik, 1933, 86, 382—386; cf. A., 1932, 1184; Prins, A., 1933, 548).—The width of the $K\alpha$ line of C (graphite) is directly proportional to the D_{max} obtained. This confirms the accuracy of the previous results (*loc. cit.*). In the ultra-soft region, a linear relation between exposure time and D_{max} of the line was obtained (on Schleussner "Doneo" film). J. L.

Nomography in photography. G. MAASS (Z. wiss. Phot., 1933, 32, 196—199).—The advantages of graphical representations over tabulated figures are described, with special examples. J. L.

Action of light on iodine in the atmosphere and in the organism. H. KOEPE (Monatsh. Kinderheilk., 1933, 56, 149—155; Chem. Zentr., 1933, ii, 1645).—Irradiation of aq. I with sun- or Hg-light forms I' and eventually H' and IO_3' , the catalytic power for decomp. of H_2O_2 diminishing. The catalytic activity of KI solutions also diminishes on irradiation in air. Administration of KI increases the blood-catalase. A. A. E.

Catalytic oxidations. IV. **Photochemical oxidation of some ethylenic double linkings.** V. Oxidation of ergosterol. K. MEYER (J. Biol. Chem., 1933, 103, 597—606, 607—616).—IV. Chlorophyll (I) and cosin catalyse the photo-oxidation of olive oil, oleic acid, and undecenoic acid by O_2 . *iso*-Chlorophyllin is less active. The autoxidation of bixin and lycopene (II) is accelerated by light in presence of eosin; (I) is active with (II) only. Citronellal, linalool, pulegone, and terpineol all photo-oxidise in presence of (I).

V. Ergosterol (III) autoxidises in the dark, taking up 3 mols. O_2 (approx.); the reaction is slower with highly purified materials and is inhibited by HCN. The rate is markedly affected by solvents and p_H . (III) also photo-oxidises slowly, but in presence of eosin or (I) different reactions occur, the end-point depending on the dye; HCN does not inhibit in this case. D. R. D.

Formation of formaldehyde by the action of ultra-violet light on carbon dioxide and water: application of the Allison magneto-optic apparatus. J. H. YOE and R. E. WINGARD (J. Chem. Physics, 1933, 1, 886).—The formation of CH_2O with a uniform increase in concn. with the time of irradiation was detected. N. M. B.

Reaction between potassium oxalate and iodine and the relation between intensity [of light] and velocity. W. V. BHAGWAT (J. Indian Chem. Soc., 1933, 10, 649—654).—The temp. coeff. of the "dark" reaction is 6.86. Velocities of the photochemical reaction have been measured for different intensities and wave-lengths. F. L. U.

Primary photochemical processes. III. Absorption spectrum and photochemical decomposition of keten. R. G. W. NORRISH, H. G. CRONE, and O. SALTMARSH (J.C.S., 1933, 1533—1539).—Monomeric keten vapour is decomposed by light from a Hg lamp into 2 vols. of CO and 1 vol. of C_2H_4 . The absorption spectrum shows a series of bands between 3700 and 2600 Å. with a max. at 3100 Å. due to the CO group and a region of continuous absorption beginning at 2200 Å. due to the double linking. Energy is probably absorbed by the CO group and transferred to the CH_2 group, causing rupture of the mol. The stages of the decomp. are considered to be $\text{CH}_2:\text{CO} + h\nu = \text{CH}_2 + \text{CO}$, followed by $\text{CH}_2:\text{CO} + \text{CH}_2 = \text{C}_2\text{H}_4 + \text{CO}$. H. S. P.

Chemical reactions brought about by X-rays and their determination. N. WATERMAN and H. LIMBURG (Biochem. Z., 1933, 266, 329).—A table omitted from the author's paper (A., 1933, 1020) is supplied. P. W. C.

Effect of ultra-violet rays on nicotine.—See this vol., 196.

Mitogenetic radiation of gas reactions. E. RUYSSSEN (Acta brev. néerl. Physiol., 1933, 3, 51—52; Chem. Zentr., 1933, ii, 1371—1372).—Emission of mitogenetic radiation has been observed in simple reactions (e.g., $\text{HCl} + \text{NaOH}$) in the liquid phase and in the flames of coal gas- and $\text{H}_2 - \text{O}_2$. A. A. E.

Heavy hydrogen. (LORD) RUTHERFORD (Nature, 1933, 132, 955—956).—An address. L. S. T.

Separation and properties of the isotopes of hydrogen. H. C. ÜREY (Science, 1933, 78, 566—571).—A lecture. L. S. T.

Heavy hydrogen. A. FARKAS and L. FARKAS (Nature, 1933, 132, 894).—The formation of HH^2 from mixtures of H_2 and H_2^2 ($\leq 95\%$) in contact with a hot Ni wire has been studied. For the reaction $\text{H}_2 + \text{H}_2^2 \rightleftharpoons 2\text{HH}^2$ at temp. $>$ room temp. K is approx. $\frac{1}{3}$ and independent of temp. Calc. and experimental vals. for the equilibrium consns. of HH^2 in samples of H_2 of known H_2^2 content are compared. In the diffusion of H_2 through Pd, the gas diffusing at lower temp. has a higher H: H^2 ratio than the original, but at higher temp. the ratio becomes lower. The residual gas is conc. and the recovered gases contain the equilibrium mixture of the three mols. Some separation of the two isotopes occurs when

they diffuse through a small nozzle at low pressures, e.g., when pumped through a valve. Above 600° , the formation of the equilibrium mixture from H_2 and H_2^2 proceeds in the homogeneous gas phase: $\text{H} + \text{H}_2^2 \rightleftharpoons \text{HH}^2 + \text{H}^2$, $\text{H}^2 + \text{H}_2 \rightleftharpoons \text{HH}^2 + \text{H}$, and possibly $\text{H}_2 + \text{H}_2^2 \rightarrow 2\text{HH}^2$. The energy of activation of this reaction must be > 60 kg.-cal. The formation of HH^2 does not occur at -195° on charcoal. L. S. T.

Separation of hydrogen isotopes by diffusion through palladium. L. HARRIS, W. JOST, and R. W. B. PEARSE (Proc. Nat. Acad. Sci., 1933, 19, 991—994).—A hundredfold decrease in pressure by diffusion is accompanied by a tenfold increase in concn. of H^2 . The rate of pressure decrease is in agreement with the theory of diffusion by atoms. R. S.

Preparation of the pure heavy hydrogen isotope by diffusion. G. HERTZ (Naturwiss., 1933, 21, 884—885).—It is possible to separate Ne^{22} from Ne^{20} by diffusion so completely that the latter can no longer be detected spectroscopically. The same method can be used to separate the H isotopes. H_2O from an electrolysis apparatus was reduced by Mg. The H_2 thus obtained consisted of a mixture of H_2^1 and H^1H^2 with only a small proportion of H_2^2 . By passing the electric discharge through the mixture H^1H^2 was broken up into H_2^1 and H_2^2 , which, after diffusion, gave H_2^2 spectroscopically pure. Photographs of the line spectra of H_2 mixtures of various compositions are given. A. J. M.

Isotopic fractionation of water. E. W. WASHBURN, E. R. SMITH, and M. FRANDBEN (Bur. Stand. J. Res., 1933, 11, 453—462).—The variation in d previously observed (this vol., 40) in the residual H_2O on electrolysis has been plotted against change in vol. 0.01N- H_2SO_4 was used. When d 1.001376 was reached for the residual H_2O its physical properties were determined. The temp. of max. d is approx. the same for heavy and for normal H_2O . F.p. for heavy H_2O is 0.053° , b.p. $100.02 \pm 0.002^\circ$, and n for λ 5876 Å. is $<$ for normal H_2O by $(59 \pm 1) \times 10^{-6}$. By continuing the electrolysis using $\text{Ba}(\text{OH})_2$, H_2O of d 1.0153 was ultimately obtained. The O_2 and H_2 evolved during this stage were dried and separately combined with normal H_2 and O_2 , respectively. The resulting samples of H_2O contained in one case an increased concn. of O^{18} and perhaps O^{17} and in the other an increased concn. of H^2 . H_2 collected at the end had at. wt. 1.012. The method of d determination is described and the relationship between d and isotopic composition calc. The min. val. of the at. fraction of H^2 in normal H_2O is probably 3×10^{-5} . H_2O can be fractionated isotopically by distillation (cf. *ibid.*, 41) and by adsorption on charcoal. M. S. B.

Deuteroammonias. H. S. TAYLOR and J. C. JUNGERS (J. Amer. Chem. Soc., 1933, 55, 5057—5058).— NH_3^2 (68, 90, and 99%) has been prepared by reaction of H_2^2O with Mg_3N_2 . The physical properties show a progressive change with increasing concn. of H^2 . The 99% product has m.p. 199° abs., b.p. 242.3° abs.; v.p. have been determined between 202.3° abs. and 238.6° abs. The calc. latent heat

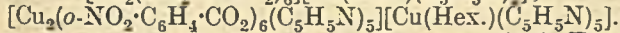
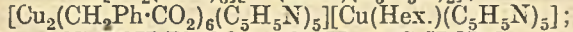
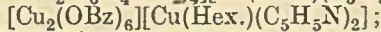
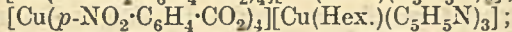
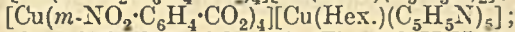
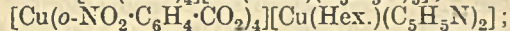
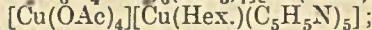
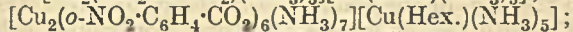
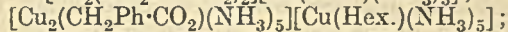
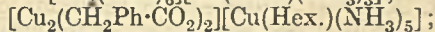
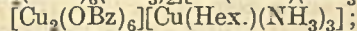
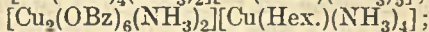
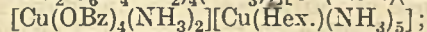
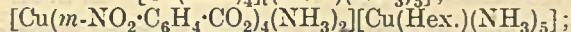
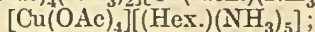
of vaporisation is 5990 g.-cal. per mol. The ultra-violet absorption spectrum has been investigated.

E. S. H.

Additive reactions with H and O atoms at low temperatures. K. H. GEIB and P. HARTECK (Ber., 1933, 66, [B], 1815—1825; cf. A., 1933, 1257).—Additive reactions appear to occur with difficulty when a stable compound can arise from another stable compound by increase in valency of an atom. Addition takes place readily at low temp. in the case of compounds in which a subsidiary valency is chemically active; the union is so feeble that the compounds are not known at room temp. Thus H and HCN at -190° give a product which effervesces at -60° and ultimately affords NH_2Me , HCN, NH_3 , and a yellow oil. C_2N_2 gives products similar to those derived from HCN and, mainly, a substance resembling hydrazalamine. SO_2 yields (?) H_2SO_2 and finally H_2S , SO_2 , S, and H_2O . NH_3 , N_2O , and NH_2Me do not react. C_6H_6 appears to be hydrogenated immediately. C_3H_4 is reduced to C_2H_6 . The intermediate production of C_2H_4 from C_2H_2 is slight. The additive product from C_2H_4 and O decomposes at about -110° , giving finally $(\text{CH}_2)_2\text{O}$, CH_2O , MeCHO , CO_2 , and liquid materials. The product from C_3H_2 yields CO, $(\text{CHO})_2$, HCO_2H , CO_2 , and H_2O . CO yields about 1.3% of CO_2 , SO_2 slowly produces SO_3 , whilst it remains uncertain whether the production of NO_2 from NO is due to at. O. HCN, N_2O , and H do not appear to yield additive compounds. HCl gives mainly Cl_2 and H_2O with a small proportion of ClO_2 . NH_3 , NH_2Me , and NMe_3 readily add at. O. At -80° , C_6H_6 gives a colourless, glassy material which decomposes into CO_2 , CO, HCO_2H , and H_2O ; quinones appear to be formed. Interaction between Xe and at. O was not observed. H. W.

Formation of amines in aqueous solution.

XI. R. RIŞAN (Bul. Soc. Ştiinţe Cluj, 1932, 7, 60—78; Chem. Zentr., 1933, ii, 1003—1004).—The following compounds have been prepared [$\text{Hex.}=(\text{CH}_2)_6\text{N}_4$]:



A. A. E.

Magnesium sulphite. H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 63).—The salt forms a hexa- and a tri-hydrate with a transition point at 40° .

A. R. P.

Solid reaction between calcium oxide and silicic acid. K. HILD and G. TRÖMEL (Z. anorg.

Chem., 1933, 215, 333—344).—The reaction has been studied at 1000° , using equimol. quantities. The time required for completion varies from 5 min. to 400 hr., and is determined by the nature of the reactants and the intimacy of mixing. For reaction times > 20 min. the initial product is $\beta\text{-Ca}_2\text{SiO}_4$, which then reacts with SiO_2 to give $\beta\text{-CaSiO}_3$ (wollastonite). In the most rapid reaction (5 min.) the main product is $\alpha\text{-CaSiO}_3$. In experiments in which quartz was used, the latter was frequently converted into cristobalite in presence of CaCO_3 , but never in presence of CaO. F. L. U.

Calcium oxide-phosphoric acid compounds.

II. M. A. BREDIG, H. H. FRANCK, and H. FÜLDNER (Z. Elektrochem., 1933, 39, 959—969; cf. A., 1932, 469).—Mixed apatites have been prepared containing the following bivalent groups in place of F: aluminate, ferrite, and cyanamide. Carbonate-mixed-apatite has been characterised by its X-radiogram, and most naturally occurring Ca phosphates consist of it. The materials of bones and teeth are hydroxyoxyapatites. The transformation of the two forms of $\text{Ca}_3\text{P}_2\text{O}_8$ is very sensitive to CaO and H_2O , and this is explained on the basis of the stability of hydroxyoxyapatites.

D. R. D.

Amphoteric behaviour of metal hydroxides.

II. Zincates. R. SCHOLDER and H. WEBER (Z. anorg. Chem., 1933, 215, 355—368; cf. A., 1933, 474).—Conditions of formation and the composition of Na zincates are described. The salt $\text{Na}_2[\text{Zn}(\text{OH})_4]$, the dihydrate of which is known, has been prepared. It forms mixed crystals with $\text{NaOH}\cdot\text{H}_2\text{O}$. Mixed crystals are also formed from $\text{Na}[\text{Zn}(\text{OH})_3]\cdot 3\text{H}_2\text{O}$ and $\text{H}[\text{Zn}(\text{OH})_3]\cdot 3\text{H}_2\text{O}$. Both Na_1 and Na_2 zincates are decomposed by EtOH at room temp., NaOH being abstracted. The following salts are described: $\text{Ba}[\text{Zn}(\text{OH})_4]$, with 1 and 5 H_2O ; $\text{Sr}[\text{Zn}(\text{OH})_4]\cdot\text{H}_2\text{O}$; $\text{Ba}_2[\text{Zn}(\text{OH})_6]$; $\text{Sr}_2[\text{Zn}(\text{OH})_6]$. Constitutional formulæ based on results of experiments on dehydration are proposed. F. L. U.

Chemistry of finely-divided matter. E. BERL and B. SCHMITT (Kolloid-Z., 1934, 66, 87—91).—The superior reactivity of finely-divided substances is illustrated by many examples, which include the flotation of powdered Zn blende by NaCN solutions.

E. S. H.

Halides of the rare earths. VIII. Action of hydrogen on the chlorides of the rare earths.

G. JANTSCH, N. SKALLA, and H. GRUBITSCH (Z. anorg. Chem., 1933, 216, 75—79; cf. A., 1933, 579).— H_2 reduces the trichlorides of the following metals to the free metal at the temp. given: Y 880° , La 880° , Nd 840° , Gd 820° , Tu 650° , Lu 750° ; trichlorides of the following are reduced to dichlorides: Sm 400° , Eu 270° , Yb 560° . In the first series the dichlorides are unstable. E. S. H.

Existence of lower valencies in the halides of the rare earths. G. JANTSCH and W. KLEMM (Z. anorg. Chem., 1933, 216, 80—84).—Theoretical (cf. preceding abstract). E. S. H.

Quantitative study of the lanthanum-neodymium separation. P. W. SELWOOD (J. Amer. Chem. Soc., 1933, 55, 4900—4901).—Analysis of the efficiency

of various methods of separation shows that Prandtl's basic NH_3 separation gives the highest efficiency and is followed by the NH_4 double nitrate procedure.

E. S. H.

Mechanism of formation of silane. III. R. SCHWARZ and P. ROYEN (*Z. anorg. Chem.*, 1933, 215, 288—294).—The mechanism previously suggested (A., 1925, ii, 418) is supported by recent observations on unsaturated Ge hydrides (see following abstract).

F. L. U.

Germanium. XIV. Properties of polygermene (GeH_2)_x. P. ROYEN and R. SCHWARZ (*Z. anorg. Chem.*, 1933, 215, 295—309; cf. A., 1933, 579).—By the action of aq. NaOH stepwise replacement of H by OH occurs, the colour of the product changing from yellow to brownish-red with increasing O content. Halogen acids convert the hydroxylated products reversibly into halogen derivatives. HX and NaOH give rise finally to GeX_2 and Na_2GeO_2 , respectively, and the H formed during the change hydrogenates the still intact $\text{GeH}_2 \cdots \text{GeH}_2$ residues to give a mixture of saturated hydrides, GeH_4 predominating. Pyrolysis of $(\text{GeH}_2)_x$ at 120—220° gives a mixture of GeH_4 , Ge_2H_6 , Ge_3H_8 , and H_2 , with a residue of Ge. The chemical behaviour of $(\text{GeH}_2)_x$ indicates an open-chain structure of high mol. wt., analogous to that of the polyoxymethylenes.

F. L. U.

Preparation and constitution of the thio-stannates. I. Sodium ortho- and meta-thio-stannate. E. E. JELLEY (*J.C.S.*, 1933, 1580—1582).—Monoclinic crystals of $\text{Na}_4\text{SnS}_4 \cdot 18\text{H}_2\text{O}$ have been prepared from aq. $\text{Na}_2\text{Sn}(\text{OH})_6$ and Na_2S . After heating at 200° or drying over P_2O_5 , only $2\text{H}_2\text{O}$ remains, and is considered to form part of a complex anion in which Sn is 6-covalent. When SnS_2 is dissolved in aq. Na_4SnS_4 , tetragonal crystals of $\text{Na}_2\text{SnS}_3 \cdot 3\text{H}_2\text{O}$ are deposited from the hot solution and prismatic crystals of $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$ at room temp. Constitutions for these hydrates in which Sn is 6-covalent are advanced.

H. S. P.

Interaction of phosphorus bromide and chloride. III. A. RENC (*Rocz. Chem.*, 1933, 13, 569—577; cf. A., 1932, 1258).—Br and PCl_3 yield yellow crystals of a limiting composition PCl_3Br , whilst Cl_2 and PBr_3 yield a liquid, PClBr_2 , and yellow crystals, PClBr_4 . PCl_3Br is converted at 135° into a cryst. phase, $\text{PCl}_{4.5}\text{Br}_{0.5}$, a deep red liquid, $\text{PCl}_{3.4}\text{Br}_{3.6}$, and a light red liquid, $\text{PCl}_{2.87}\text{Br}_{0.27}$.

R. T.

Ammonia and phosphorus pentachloride. H. MOUREU and P. ROCQUET (*Compt. rend.*, 1933, 197, 1643—1645).—If NH_3 is passed over PCl_5 at -50° and NH_4Cl is removed by washing with liquid NH_3 , PN_2H_4 , probably $\text{P}(\text{NH})_2\text{NH}_2$, is obtained as an intensely hygroscopic white amorphous powder. It begins to evolve NH_3 at 50°, but must be heated for 100 hr. at 350—400° to complete the transformation $\text{P}(\text{NH})_2\text{NH}_2 = \text{PN}_2\text{H} + \text{NH}_3$. At 480° PN_2H begins to evolve NH_3 , $3\text{PN}_2\text{H} = \text{P}_3\text{N}_5 + \text{NH}_3$, but the evolution is completed only at 700°, when dissociation to P and N_2 begins (cf. A., 1907, ii, 541).

C. A. S.

Action of vanadium tetrachloride on anhydrous chlorides. A. MORETTE (*Compt. rend.*, 1933, 197, 1641—1643).— VCl_4 and Cl_2 were passed over various

chlorides at 300—600°; NaCl , LiCl , AgCl , CaCl_2 , SrCl_2 , BaCl_2 , MgCl_2 , ZnCl_2 , MnCl_2 , PbCl_2 , and CrCl_3 were unacted on. KCl , RbCl , and CsCl absorb varying quantities of V and Cl, the max. (at 400—500°) being represented by KCl , 0.315 $\text{VCl}_{3.14}$, RbCl , 0.330 $\text{VCl}_{3.10}$ and CsCl , 0.613 $\text{VCl}_{3.13}$. These alkali chlorides appear to catalyse the reaction $\text{VCl}_4 \rightleftharpoons \text{VCl}_3 + \text{Cl}$ (cf. A., 1911, ii, 291).

C. A. S.

Existence of pyro- and meta-arsenic acids. V. AUGER (*Compt. rend.*, 1933, 197, 1639—1640).—Repetition of the author's previous work (cf. A., 1908, ii, 489) has confirmed that the only hydrate of As_2O_5 is $\text{H}_5\text{As}_2\text{O}_{10}$, which when heated passes into As_2O_5 without forming any intermediate hydrate (cf. A., 1930, 558).

C. A. S.

Action of solutions of potassium hydroxide on bismuth iodide. F. FRANÇOIS and (Mlle.) M. L. DELWAULLE (*Bull. Soc. chim.*, 1933, [iv], 53, 1104—1106).—The proportion of Bi_2O_3 produced relative to BiOI increases with increased concn. of KOH , but pure BiOI is obtained with excess of BiI_3 . BiI_3 is found in the residual solution of KI only if the liquid is no longer basic.

J. G. A. G.

Properties of the chlorides of sulphur. A. H. SPONG (*J.C.S.*, 1933, 1547—1551).—An iodometric method of determining the total Cl in S chloride mixtures dissolved in CCl_4 has been found to give approx. accurate results. Free Cl_2 in the mixture may be removed by $\beta\text{-C}_{10}\text{H}_7\text{-OEt}$ and so measured by difference. The composition of the mixture is determined mainly by the equilibrium $2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$, but also probably by $3\text{S}_2\text{Cl}_2 \rightleftharpoons \text{S}_3\text{Cl}_2 + \text{S}_3\text{Cl}_4$.

H. S. P.

Intermediate states of reduction of chromic acid. T. R. BALL and K. D. CRANE (*J. Amer. Chem. Soc.*, 1933, 55, 4860—4864).—Investigation by the magneto-optical method has shown that when H_2CrO_4 is partly reduced by FeSO_4 , Hg_2SO_4 , SnCl_2 , or $\text{H}_2\text{C}_2\text{O}_4$, Cr^{IV} is produced as an intermediate product. No evidence of Cr^{IV} has been found. When SnCl_2 is partly oxidised by H_2CrO_4 , evidence has been obtained for the existence of Sn^{III} .

E. S. H.

Influence of temperature on chemical inertia. Action of chlorine on metals. M. LEMARCHANDS and M. JACOB (*Bull. Soc. chim.*, 1933, [iv], 53, 1139—1144; cf. A., 1931, 1016).—The reactions of gases with solids are discussed with reference to surface films and the v.p. of the solids. Min. temp. of interaction of Cl_2 with twelve metals and three non-metals calc. from the b.p. of the elements and their chlorides are, in general, consistent with the data.

J. G. A. G.

Salts of perrhenic acid. E. WILKE-DÖRFURT and T. GUNZERT (*Z. anorg. Chem.*, 1933, 215, 369—387; cf. A., 1927, 128, 238; 1930, 308).—*Perrhenates* of Ca, Sr, Zn, Cd, $\text{Ag}(\text{NH}_3)_2$, $\text{Zn}(\text{NH}_3)_2$, $\text{Cd}(\text{NH}_3)_4$, $\text{Co}^{\text{II}}(\text{NH}_3)_4$, $\text{Co}^{\text{III}}(\text{NH}_3)_6$, $\text{Cr}(\text{NH}_3)_6$, $\text{Cr}([\text{CO}(\text{NH}_2)_2]_6)$, $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4$, and $\text{Cu}(\text{C}_5\text{H}_5\text{N})_4$, also $(\text{NO})\text{ReO}_4$, are described. Comparison of perrhenates with corresponding salts of HMnO_4 , HClO_4 , and HBF_4 reveals striking differences in solubility, crystal form, and content of H_2O of crystallisation.

F. L. U.

Cementite. P. PINGAULT (*Ann. Chim.*, 1933, [x], 20, 371—438).—Cementite (I) (6.65—6.70% C), con-

taining 0.05% of free C, has been prepared by heating Fe with NaCN at 600—650°; it may also be prepared by electrolysis of fused NaCN with Fe electrodes or by passing coal gas or CH₄ over Fe at 850—975° (in which case much free C is deposited on the surface of the metal). (I) has *d*⁰ 7.30, is not attacked by H₂ at 425°, and begins to decompose at about 1000°. The equilibria in the system Fe—(I)—O₂ at 830—1000° have been studied. When Cr is heated at 650° with NaCN an impervious surface film of carbide is formed which prevents further reaction. Mn treated with CH₄ at 950—975° yielded a product containing total C 7.5%, free C 3.55%, but a pure compound could not be obtained. H. F. G.

Internal complex salts of bivalent iron. B. EMMERT and H. G. SOTTSCHEIDER (Ber., 1933, 66, [B], 1871—1874; cf. A., 1931, 825).—The following complex salts are obtained from CH₂Bz₂ and FeSO₄ and the requisite bases, usually in absence of air: C₃₀H₂₂O₄Fe, 2C₅H₅N (I), C₃₀H₂₂O₄Fe, 2C₅H₁₁N (piperidine); C₃₀H₂₂O₄Fe, 2C₁₀H₁₄N₂ (nicotine); C₃₀H₂₂O₄Fe, 2NH₃ which yields C₃₀H₂₂O₄Fe when heated at 120°/0.5 mm. (oxidised to C₄₅H₃₃O₆Fe); C₃₀H₂₂O₄Fe, C₂H₄(NH₂)₂. The dry salts do not absorb NO. In C₆H₆ or PhMe, NO is absorbed by Fe^{II} acetylacetonate with or without presence of C₅H₅N, by Fe^{II} benzoylacetonate (+2C₅H₅N) or by (I). CH₃Ac₂, FeSO₄, and *o*-C₆H₄(NH₂)₂ in MeOH—H₂O yield $o\text{-C}_6\text{H}_4\left\langle\begin{array}{c} \text{N:C:CMc} \\ \text{N:C:CMc} \end{array}\right\rangle\text{CH}_2, \text{FeSO}_4, 1.5\text{H}_2\text{O}$, whence dimethylbenzoheptadiazine, m.p. 132°. H. W.

Salts of iron carbonyl hydride. F. FEIGL and P. KRUMHOLZ (Z. anorg. Chem., 1933, 215, 242—248; cf. A., 1932, 485).—By the action of certain metal ammine salts on Fe(CO)₅ in aq. NH₃ cryst. compounds which are regarded as salts of Fe(CO)₄H₂ are formed. The following compounds are described: Fe(CO)₄Cd(NH₃)₂, Fe(CO)₄Cd(C₅H₅N)₂, [Fe(CO)₄H]₂Ni(NH₃)₆, [Fe(CO)₄H]₂Fe(α'-phen)₃ (phen=phenanthroline), Fe(CO)₄Cd. Dil. mineral acids in all cases liberate Fe(CO)₄H₂. F. L. U.

Formation of amines in aqueous solution. X. Double thiocyanates. R. RIPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1932, 7, 25—36; Chem. Zentr., 1933, ii, 1003).—The following compounds are described: [M(SCN)₄(C₅H₅N)₂][Fe(Hex.)₂(C₅H₅N)₄]_xH₂O, where M and *x* are Ni (10, 4) and Co (10, 6); Hex.=(CH₂)₆H₄. M(SCN)₂Fe(SCN)₂2Hex., 8H₂O (M=Ni, Co). [Mn(SCN)₆][Fe(Hex.)₃(H₂O)₃]₂6H₂O; [Mn(SCN)₆][Fe(Hex.)₃(C₅H₅N)₅]₂12 or 6H₂O. A. A. E.

Decomposition of thiosulphatopentacyanocobaltic acid and isomerism of thiosulphuric acid. P. R. RAY (J. Indian Chem. Soc., 1933, 10, 631—635).—A quant. study of the hydrolysis of the "normal" and "iso" complex acids supports the view put forward previously (A., 1931, 1140) regarding their constitution. The results further indicate that H₂S₂O₃ is capable of existing in two forms, one of which decomposes into H₂S and H₂SO₄. F. L. U.

Dithiosulphato-diethylenediamine cobaltates. P. R. RAY and S. N. MAULIK (J. Indian Chem. Soc., 1933, 10, 655—658; cf. A., 1931, 1140).—The salts

M[Co(S₂O₃)₂en₂] (M=Na, K, Tl) have been prepared in the *cis* and *trans* forms. The former are red, the latter green and more stable. F. L. U.

Thiosulphato-tetramminocobaltic series. II. Constitution of Duff's salt. B. C. RAY and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 625—630; cf. A., 1931, 184).—A new structural formula for Duff's salt is proposed. The following compounds are described: thiosulphatoaquo-diethylenediaminocobaltic iodide, nitrate, thiocyanate, and sulphate; [Co(S₂O₃)₂en₂]Na (*cis* and *trans*). F. L. U.

Basic nickel sulphate. G. GIRE (Compt. rend., 1933, 197, 1646).—On adding powdered Mg to 0.25—0.05N-NiSO₄ dissolution proceeds slowly with deposition of a bright green, highly hydrated, efflorescent cryst. salt, which, dried at 100°, contains NiSO₄·4NiO·10H₂O, is non-magnetic, almost insol. in H₂O, but sol. in hot acid. Co behaves similarly (cf. A., 1893, ii, 528). C. A. S.

Non-existence of a higher nickel carbide. J. SCHMIDT [with E. OSSWALD] (Z. anorg. Chem., 1933, 216, 85—98).—Chemical and X-ray analysis fail to reveal a carbide higher than Ni₃C in the products of reaction of Ni with CO at 240—250° or with C₂H₂ at 180—200°. At 260° CH₄ is decomposed by Ni, giving C, but no carbide is formed. E. S. H.

Complex dipyriddy and phenanthroline salts of bivalent metals. P. PFEIFFER and F. TAPPERMANN (Z. anorg. Chem., 1933, 215, 273—287; cf. A., 1933, 400).—The following compounds are described (dipy=dipyriddy, phen=*o*-phenanthroline): Ni phen₂X₂·10H₂O (X=Cl, Br); M phen₂Cl₂ (M=Mn, Ni); Ni phen₂SO₄·14H₂O; Ni phen₂SO₄; Ni dipy₂Cl₂; Co phen₂Cl₂·4H₂O; Mn phen₂SO₄·8H₂O; M phen₂(O·SO₂·C₁₀H₇-β)₂·6H₂O (M=Co, Ni, Fe, Zn, Cd); Ni dipy₂(O·SO₂·C₁₀H₇-β)₂; M phen₂(O·SO₂·C₁₀H₇-β)₂ with 1 H₂O (Cu) and 2 H₂O (Mn); Mn phen₂(O·SO₂·C₁₀H₁₄OBr)₂ (α-bromocamphor-π-sulphonate). F. L. U.

Analogy of ruthenium to iron. Nitric oxide compounds of bivalent ruthenium. W. MANCHOT and H. SCHMID (Z. anorg. Chem., 1933, 216, 99—103).—The prep. and properties of Ru₂NO and RuBr₂NO are described. These compounds undergo a reversible reaction with CO, forming corresponding carbonyls. E. S. H.

Preparation and autoxidation of blue ruthenous solution. W. MANCHOT and H. SCHMID (Z. anorg. Chem., 1933, 216, 104—108).—Solutions of Ru^{II} are prepared by cathodic reduction of RuCl₃ in 4N-HCl, using a Pt cathode. The solution oxidises slowly in presence of air. Addition of NaOH ppts. Ru(OH)₃ immediately, although in absence of O₂ Ru(OH)₂ is pptd. E. S. H.

Factors in sedimentation analysis. E. W. GALLIHER (Amer. J. Sci., 1933, [v], 26, 564—568).—Na oxalate and citrate are more efficient dispersing agents than aq. NH₃. Flocculation is sometimes caused by micro-organisms; it can be prevented by sterilising with PhMe. R. P. B.

Interferences of metal ions in the detection of acids. L. J. CURTMAN and S. M. EDMONDS (J. Chem. Educ., 1933, 10, 567—570). CH. ABS.

Spectrum analysis for traces of elements in ore and rock minerals. H. MORITZ (Chem. Erde, 1933, 8, 321—338).—Tables are given of the sensitive lines for a no. of elements when present in small measured amounts. L. J. S.

Silver electrodes of the "second kind" as comparison electrodes. F. L. HAHN (Z. anal. Chem., 1933, 95, 337; cf. A., 1933, 1027).—A claim for priority (cf. A., 1932, 471). J. S. A.

Micro-quinhydrone electrode.—See this vol., 230.

Eupittone [as indicator]. K. BRAND and E. PERUCHE (Pharm. Zentr., 1934, 75, 8—13).—Eupittone (3 : 5 : 3' : 5' : 3'' : 5''-hexamethoxyaurin) gives a sharp colour change from orange to pure blue at p_H 6.6—7.4, but except in the case of picric acid it offers no advantage over other indicators. S. C.

Indicator properties of *p*-, 2 : 4-di-, and 2 : 4 : 6-tri-nitrophenylacetylhydrazides. A. BLOOM and A. OSOL (Amer. J. Pharm., 1933, 105, 551—553).—The three substances [denoted (1), (2), or (3) according to the no. of NO₂-groups] give good results in titrating strong acids (pale green) with strong bases (brown to orange-brown), but the colours, particularly of (3), are unstable in alkaline solution. The p_H ranges and apparent dissociation consts. (Salm), both determined colorimetrically by means of buffer solutions, are respectively as follows: (1) 6.6—8.0; 7.6, (2) 7.6—9.6; 9.1, (3) 9.0—10.6 approx. The colour of (3) fades too rapidly to permit a measurement of pK_1 . W. S.

System mercuric cyanide-chromithiocyanate as a turbid indicator [in acidimetry and alkalimetry]. R. UZEL (Coll. Czech. Chem. Comm., 1933, 5, 457—465).—0.06 g. of Hg(CN)₂ + 0.01 g. of NH₄NO₃ + 0.002 g. of K₃Cr(CNS)₆ in 1 c.c. added to 25 c.c. of liquid affords at $p_H < 4.0$ a turbidity due to Hg₃[Cr(CNS)₆]₂ which redissolves at higher p_H . This indicator fails in the presence of I', S₂O₃'', and large quantities of Br' and CNS', but is satisfactory in coloured solutions where other indicators are inapplicable and permits the titration of H₂CrO₄ as a strong monobasic acid. Small quantities of free H₂CrO₄ have been determined in commercial K₂Cr₂O₇. J. G. A. G.

Acid-base titrations in alcohol-water mixtures. II. Indicators in alcohol-water mixtures. H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Dansk Tidsskr. Farm., 1933, 7, 225—272; cf. A., 1933, 1015).—The dissociation exponents and regions of colour change of eleven indicators were determined colorimetrically in 20—85% EtOH. The variation of dissociation exponent with EtOH concn. leads to the conclusion that the azo-indicators are uncharged bases and the sulphonephthaleins uncharged acids. Me-red behaves like the latter, and its isoelectric form must therefore be chiefly uncharged NH₂-acid and not zwitterion. The results are discussed in terms of different theories of colour and structure. The carbinol indicators behave anomalously; a special mechanism is proposed involving reaction with H₂O. The absorption curves of four indicators were measured in acids, bases,

and buffer mixtures. In all cases the absorption curves change with changing EtOH concn.

R. P. B.

Isotopic analysis of water. R. H. CRIST, G. M. MURPHY, and H. C. UREY (J. Amer. Chem. Soc., 1933, 55, 5060—5061).—Determination of *n* is recommended. E. S. H.

Refractive index of H₂O¹⁸ and the complete isotopic analysis of water. G. N. LEWIS and D. B. LUTEN, jun. (J. Amer. Chem. Soc., 1933, 55, 5061—5062).—By determining *n* and *d* the complete isotopic constitution of H₂O can be ascertained from the formulæ $x = 1.370\Delta d - 190.5\Delta n$ and $y = 7.692\Delta d + 180.9\Delta n$, where *x* is the mol. fraction of H₂O, *y* the mol. fraction of H₂O¹⁸, Δd and Δn are the differences in *d* and *n* of the sample and ordinary H₂O at 25°. E. S. H.

Determination of chlorine in potassium iodide.—See B., 1934, 15.

Determination of bromine in presence of chlorine in mineral waters.—See B., 1934, 59.

Micro-titration of iodides alone or in presence of other halogens. V. STANEK and T. NEMES (Z. anal. Chem., 1933, 95, 240—244; cf. A., 1932, 529, 631).—I' can be accurately titrated with Hg(NO₃)₂, using Na nitroprusside as indicator, provided the solution contains ≥ 30 mg. of I in 200 c.c. In presence of Cl' or Br', the I' may be determined by Winkler's method (A., 1932, 487), and the other halogen with Hg(NO₃)₂. F. L. U.

Determination of fluorine. I. Precipitation of fluoride ion as lead chlorofluoride. J. FISCHER and H. PEISKER (Z. anal. Chem., 1933, 95, 225—235).—The influence of degree of acidity, concn., mode of pptn., and the presence of foreign substances on the determination of F' as PbClF has been studied. Procedure is described whereby results accurate within 0.5% may be obtained rapidly and conveniently. F. L. U.

Detection and determination of fluorides. I. M. KORENMAN (Z. anorg. Chem., 1933, 216, 33—40).—Greeff's method (A., 1913, ii, 975) gives low results. A modification of Steiger's procedure (A., 1908, ii, 426) gives good results for 0.05—0.5 mg. HF. Smaller amounts of HF in air (0.002 mg. per litre) can be detected by a reagent paper containing Zr(NO₃)₄ and alizarin. E. S. H.

"Fluorinated" methæmoglobin. Spectrophotometric determination of fluorides.—See this vol., 92.

Conversion of thiosulphuric acid into polythionic acids with the help of catalysts. III. Regularities in the precipitation of arsenic or antimony sulphides. A. KURTENACKER and E. FÜRSTENAU (Z. anorg. Chem., 1933, 215, 257—270; cf. A., 1930, 302).—The pptn. of As or Sb as sulphide by Na₂S₂O₃ is controlled chiefly by the nature and concn. of the acid present. With HCl, H₂SO₄, or HClO₄ the pptn. reaches a max. at about 0.1*N*-acid, being quant. for Sb and 50—80% for As. Above this concn. the pptn. falls to zero with HCl, whereas it passes through a min. with H₂SO₄ (2—3*N*) and HClO₄ (1*N*), and becomes almost quant. at still higher

condens. The observations are interpreted in terms of the conversion of $S_2O_3^{2-}$ into polythionic acids under the influence of mineral acids. F. L. U.

Oxidation of nitric oxide in low concentrations, and its determination. V. PIANKOV (J. Gen. Chem. Russ., 1933, 3, 652—659).—Griess' method is applicable to the determination of 0.1 mg. NO per litre of air. The process of oxidation takes place in two stages: $2NO + O \rightarrow N_2O_3$; $N_2O_3 + O \rightarrow N_2O_4$; the former reaction is practically instantaneous, whilst the velocity of the latter varies with concn. of NO, 95% of 0.06 mg.-% NO being oxidised to N_2O_4 after 2.5 hr., and only 84% of 0.04 mg.-% NO after 20 hr. at 16° . R. T.

Use of diphenylamine azo-dyes as indicators for nitrous acid. A. E. PORAT-KOCHITZ and L. V. TSCHERVINSKAJA (Anilinokras. Prom., 1933, 3, 339—351).—Metanil-yellow, tropæolin OO, and a no. of other similar dyes prepared from diphenylnitrosoamine or its mono- or di-*p*-sulphonic acids and *o*- $NH_2 \cdot C_6H_4 \cdot SO_3H$, *m*- and *p*- $NH_2 \cdot C_6H_4 \cdot NO_2$, NH_2Ph , *m*- and *p*- $C_6H_4(NH_2)_2$, *o*- and *p*- $C_6H_4Me \cdot NH_2$, and *p*- $C_6H_4Cl \cdot NH_2$ give violet colorations in acid solution, changing to yellow in presence of HNO_2 , and again becoming violet on removal of HNO_3 . The above dyes can be used as indicators in the titration of primary amines by aq. $NaNO_2$. R. T.

Micro-determination of phosphorus as phosphomolybdate. R. H. A. PLIMMER (Biochem. J., 1933, 27, 1810—1813).—The method is adapted to the determination of 0.01—0.1 mg. P by pptn. with a purified MoO_4^{2-} reagent in the presence of 20 c.c. of 10% NH_4NO_3 solution per 1 c.c. of conc. H_2SO_4 added, filtration with a Bertrand asbestos filter, and washing with 50% EtOH. H. D.

Determination of phosphorus in titaniferous material. G. HØRGÅRD (Z. anal. Chem., 1933, 95, 329—336).—The effect of Ti in hindering the quant. pptn. of PO_4^{3-} as phosphomolybdate may be avoided by addition of 10 c.c. of conc. HCl or $HNO_3 + 10$ g. NH_4Cl or NH_4NO_3 , respectively, for 2 g. of material of low P and Ti content. With $>$ approx. 1% Ti, quant. pptn. is not possible. J. S. A.

Osmium tetroxide as catalyst for the oxidation of arsenious acid by permanganate and ceric sulphate. K. GLEU (Z. anal. Chem., 1933, 95, 305—310).—Oxidation of As_2O_3 in dil. H_2SO_4 solution by $KMnO_4$ or $Ce(SO_4)_2$ is catalysed by the addition of a few drops of 0.01*M*- OsO_4 solution, enabling As_2O_3 to be determined by titration with these reagents in the cold. With $Ce(SO_4)_2$, a $Fe(o\text{-phenanthroline})_3^{3+}$ salt is used as oxidation-reduction indicator. J. S. A.

Use of Bougault's reagent for the gravimetric determination of arsenic in presence of tin and antimony. J. P. PLUCHON (Bull. Trav. Soc. Pharm. Bordeaux, 1932, 70, 140—144; Chem. Zentr., 1933, i, 1816).—25 c.c. of the solution containing approx. 0.1 g. As are mixed with 50 c.c. of Bougault's reagent, heated at $120\text{--}125^\circ$ for 30 min., quickly cooled, filtered on a 1G3 Jena glass filter, and washed with cold boiled-out H_2O . Residues containing As are then dissolved by successive treatments with HNO_3 and 5% KOH and the united extracts evaporated to

dryness in porcelain, extracted with 4 c.c. of HNO_3 , and taken to dryness again. Finally, the residue is dissolved in hot H_2O and the As determined as $Mg_2As_2O_7$. L. S. T.

Microchemical determination of carbonic acid in carbonates. W. REICH-ROHRWIG (Z. anal. Chem., 1933, 95, 315—323).— CO_2 is liberated by the action of 2—3*N*-HCl, in an apparatus described, and swept over in a purified air stream at const. pressure. The gas is freed from H_2S and H_2O by $CuSO_4$ -pumice and P_2O_5 , and the CO_2 absorbed in "ascarite" followed by P_2O_5 . Vals. so obtained are given for Morogoro pitchblendes, showing difference in composition between inner and outer layers. J. S. A.

Errors in determination of carbonate in boiler waters.—See B., 1934, 47.

Evaluation of helium from radioactive minerals and rocks. V. CHLOPIN, E. HERLING, and E. JOFFÉ (Nature, 1934, 133, 28).—The amount of He evolved from different minerals, e.g., uraninite and chlopinite, at a given temp. $>$ a crit. temp. depends on the presence of H_2 and is the greater the higher is the partial pressure of H_2 . Small amounts of H_2 in a gas mixture can be detected by means of this effect. L. S. T.

New reaction for potassium. S. A. CELSI (Anal. Farm. Bioquim., 1933, 4, 55—59).—Na cobalthio-sulphate in MeOH, or, better, a mixture of a 14% solution of $Co(NO_3)_2$ in 80% aq. MeOH and 38% aq. $Na_2S_2O_3$, gives a characteristic blue cryst. ppt. with K salts in neutral solution. R. K. C.

Separation and determination of sodium and potassium. L. SZEBELLÉDY and K. SCHICK (Magyar Gyóg. Társas. Ert., 1933, 9, 40—51; Chem. Zentr., 1933, i, 1817).—In the separation and determination of Na and K as iodide the most suitable solvent is a mixture of equal vols. of anhyd. Bu^tOH and anhyd. Et_2O . The extracted NaI and the residual KI contain only traces of each other, but it is recommended to add 0.6 mg. to the K_2O found and to subtract 0.6 mg. from the Na_2O . Chlorides and sulphates are readily converted into the iodides, carbonates must be converted into chloride, whilst phosphate must be removed prior to the separation. L. S. T.

Volumetric determination of barium and of sulphates. J. C. GIBLIN (Analyst, 1933, 58, 752—753).—The $BaCl_2$ solution ($<$ 1%) is titrated into standard H_2SO_4 , and after mixing, the supernatant liquid is spotted on a filter-paper stained with Na rhodionate, the end-point being the reddish-brown colour produced with an excess of Ba. The procedure is reversed for the determination of H_2SO_4 . J. G.

Conditions for precipitation of zinc sulphide and aluminium hydroxide, and gravimetric separation of zinc from aluminium. III, IV. J. N. FREES [with J. KOLLWITZ] (Z. anal. Chem., 1933, 95, 113—142; cf. this vol., 48).—III. Pptn. of $Al(OH)_3$ occurs at p_H between 3 and 7; redissolution in excess of precipitant at $p_H >$ 9.0. By neutralisation against phenol-red (p_H 7.5) pptn. is quant. NH_4Cl and NH_4NO_3 have no effect on the pptn.; with $(NH_4)_2SO_4$ some basic Al sulphate, destroyed slowly on ignition, is formed. Wash- H_2O should contain

2% NH_4 salts and be neutralised (phenol-red). A non-hygroscopic Al_2O_3 is formed by ignition at 1200° ; from the variation of hygroscopicity with temp. of ignition, the transition point $\gamma\text{-Al}_2\text{O}_3 \rightarrow$ corundum is found to be $1010^\circ \pm 5^\circ$.

IV. For the separation of Zn and Al, the solution, containing 4% $(\text{NH}_4)_2\text{SO}_4$, is brought to p_{H} 2.8, using tropæolin OO as indicator. ZnS is pptd. by H_2S , washed with 4% $(\text{NH}_4)_2\text{SO}_4$ of p_{H} 2.8, and ignited in H_2S . Al in the filtrate is pptd. either by addition of aq. NH_3 to give p_{H} 7.5 (phenol-red), or by addition of $\text{Na}_2\text{S}_2\text{O}_3$ followed by aq. NH_3 . J. S. A.

Glycerol complexes in volumetric analysis. H. WAGNER (Z. anal. Chem., 1933, 95, 311—315).—Owing to the formation of complexes with Cu, Co, Ni, Zn, and Cd, by addition of glycerol (I) to solutions of these metals (e.g., plating-bath liquids), free acid may be directly titrated with *N*-NaOH, against Me-orange. Zn may be determined as follows. Alkali-free ZnCO_3 is pptd. by addition of Na_2CO_3 to a cold, slightly acid solution until turbidity appears, heating to boiling, and neutralising (phenolphthalein). The ppt. is dissolved in 0.1*N*-acid, 30 c.c. of (I) are added, and the excess acid is titrated back. Cd may be similarly determined, CdCO_3 being pptd. cold. J. S. A.

Determination of cadmium in presence of zinc.—See B., 1934, 22.

Determination of lead with picrolonic acid. F. HECHT, W. REICH-ROHRWIG, and H. BRANTNER (Z. anal. Chem., 1933, 95, 152—163).—0.01*N*-Picrolonic acid (I) ppts. from neutral Pb solutions at 0° a Pb salt of approx. composition $\text{Pb}(\text{C}_{10}\text{H}_7\text{O}_5\text{N}_2)_2 \cdot 1.5\text{H}_2\text{O}$, containing 27.25% Pb when dried at 130° . Excess of (I) is slowly added to the hot solution, which is cooled to 0° and the ppt. washed with the min. amount of H_2O at 0° . Pb may be accurately determined in the presence of < 5 pts. of Pt (e.g., in Pb from micro-electrolytic depositions). J. S. A.

Volumetric determination of copper and lead in babbitt metal.—See B., 1934, 64.

Potentiometric titration of copper with sodium sulphide and use of a platinum electrode. J. B. JHA (J. Indian Chem. Soc., 1933, 10, 643—647).—Accurate results are obtained when the acidity of the liquid is regulated with AcOH, a Pt wire electrode being used. F. L. U.

Electrolytic analysis of bronzes and brass.—See B., 1934, 22.

Detection of mercury. L. F. VOET (Pharm. Weekblad, 1933, 70, 1336).—The compound is reduced with SnCl_2 , the supernatant liquor poured off, and the pptd. Hg boiled repeatedly with conc. HCl until a globule is formed. S. C.

Determination of mercurous or bromide and chloride ions. L. VON ZOMBORY and L. POLLÁK (Z. anorg. Chem., 1933, 215, 255—256).—Good results are obtained in the titration of KBr or KCl by $\text{Hg}_2(\text{NO}_3)_2$ in 0.1*N* solution by using as indicators chlorophenol-red or bromocresol-green. The yellow colour of the ppt. changes to lilac at the equivalence point. F. L. U.

Sources of error in the determination of aluminium. R. RINNE (Chem.-Ztg., 1933, 57, 992).—The quantity of NH_4Cl added to 100 c.c. of solution (2.7% AlCl_3) should be < 3 g. The solubility of $\text{Al}(\text{OH})_3$ in aq. NH_3 does not introduce any considerable error. If the vol. of the $\text{Al}(\text{OH})_3$ on the filter is large, the bulk should be transferred to a beaker and the residu removed by HCl. Appreciable losses arise if a bulky ppt. is treated with HCl on the filter-paper. H. F. G.

Determination of aluminium in corrosion-resisting and plain steels.—See B., 1934, 21.

Mercurimetric determination of chromium. A. IONESCO-MATIU and S. HERSCOVICI (Bull. Soc. chim., 1933, [iv], 1032—1038).— $\text{CrO}_4^{''}$ and $\text{Cr}_2\text{O}_7^{''}$ are determined by collecting centrifugally the ppt. obtained with $\text{Hg}_2(\text{NO}_3)_2$, dissolving the ppt. in H_2SO_4 , adding KMnO_4 until the liquid is pink, and titrating the Hg^+ with NaCl after pptn. with Na nitroprusside. $\text{Cr}^{''}$ is first pptd. as $\text{Cr}(\text{OH})_3$ by aq. NH_3 and subsequently oxidised to $\text{CrO}_4^{''}$ by hot KOH and H_2O_2 . J. G. A. G.

Volumetric determination of bismuth. G. SPACU and P. SPACU (Z. anal. Chem., 1933, 55, 336—337; cf. A., 1933, 1027).—A claim for priority of prep. of salts derived from H_3BiBr_6 (cf. Mahr, *ibid.*, 924). J. S. A.

Micro-determination of gold. Application to gold-therapy. B. K. MEREJKOVSKY (Bull. Soc. Chim. biol., 1933, 15, 1336—1338).—The material is digested with $\text{H}_2\text{SO}_4 + \text{HNO}_3$; excess of H_2SO_4 is removed, and the pptd. Au dissolved in $\text{HCl} + \text{HNO}_3$. The resulting solution is diluted until the Au content is 0.02—0.002% and then treated with aq. agar followed by dimethylaminobenzylidenerhodanine reagent (A., 1928, 1108). The red colloidal suspension is compared with suitable standards. The reagent will detect 2.5×10^{-6} g. of Au per c.c. F. O. H.

Organic pseudo-compounds as reagents for active atoms in organic molecules.—See this vol., 167.

Simple, sensitive, thermostat regulator. C. E. WOODWORTH (Science, 1933, 78, 536).—Details of a thermo-regulator sensitive to 0.001° between 0° and 35° are given. L. S. T.

Temperature regulation of furnaces and thermostats. R. FONTEYNE (Natuurwetensch. Tijds., 1934, 15, 226—228).—Fouling of Hg contacts by arcing is prevented by using thermionic valves. An apparatus is described. S. C.

Calorimeter for combustion of chlorine and bromine compounds. M. M. POPOV and P. K. SCHIROKICH (Z. physikal. Chem., 1933, 167, 183—187).—Combustion is effected in a bomb containing a neutral aq. solution of As_2O_3 . By rotating the bomb rapid reaction of the solution with free halogen formed in the combustion is ensured. R. C.

Gas furnace for heating tubes to a high temperature. J. VAN DEN BERG (Chem. Weekblad, 1934, 31, 24).—Directions are given for making a small furnace to take tubes 10—20 mm. diam. from kieselhgr bricks. Heating is by a single Teclu burner with a flame spreader, and a temp. of 1000—1100° can

be obtained in a few min. The furnace is extremely economical. S. C.

Sodium glow-lamp. F. H. NEWMAN (Phil. Mag., 1933, [vii], 16, 1109—1114).—A laboratory method of electrolyzing Na from a fused NaNO_3 bath into a glow-lamp containing A is described. The Na lamp may be used as a source of D line radiation, A lines being suppressed. H. J. E.

Compensator box for polarimeters. N. DEERR and F. G. STANLEY (Intern. Sugar. J., 1933, 35, 432—433).—Access to the interior of the compensator box is obtained by making the side next to the observer a sliding element. This side carries the observation and scale-reading telescopes, in the former of which is also carried the analysing nicol. When this is slid out, the long wedge, the moving scale, and the vernier scale are exposed. The scale is read directly by transmitted light and the conventional arrangement of inclined mirrors and ground-glass plate is eliminated. J. P. O.

Symmetrically opening optical slit. J. E. SEARS (J. Sci. Instr., 1933, 10, 376—377).—The two halves of the slit are attached at right angles to thin leaf springs, by means of which they are drawn apart as the turning of a micrometer screw moves them longitudinally. C. W. G.

Improvements in the Schlieren method. H. G. TAYLOR and J. M. WALDRAM (J. Sci. Instr., 1933, 10, 378—389).—A more convenient optical system is described in detail. C. W. G.

Transportable apparatus for luminescence analysis. P. W. DANCKWORT (Chem.-Ztg., 1933, 51, 1018).—An apparatus weighing about 3 kg. is described; it is suitable for general fluorescence analysis and for fluorescence photography. H. F. G.

Fluorescence. C. C. PINES (Amer. J. Pharm., 1933, 105, 563—564).—A no. of minerals are examined under a new "argon" lamp, emitting long wavelength ultra-violet light (330—370 μ) to which glass is permeable. W. S.

Monochromator with wide field using interference in polarised light. B. LYOT (Compt. rend., 1933, 197, 1593—1595). C. A. S.

Apparatus for X-ray investigation of fine structure. W. E. SCHMID (Z. physikal. Chem., 1933, B, 23, 347—357).—By means of special X-ray tubes the time of exposure required for Debye-Scherrer diagrams can be shortened and up to four cameras can be used simultaneously with one tube. It is advantageous to build up X-ray assemblages from interchangeable elements so that any required combination may readily be obtained. R. C.

Universal camera and "self-indexing" rotating crystal camera. E. SAUTER (Z. physikal. Chem., 1933, B, 23, 370—378).—The construction and mode of operation are described. R. C.

Improvements in the 21-foot normal incidence vacuum spectrograph. G. R. HARRISON (Rev. Sci. Instr., 1933, [ii], 4, 651—655).—Additions to the instrument previously described are given (cf. A.,

1931, 1387); the range is 6000—300 Å., accurate to ± 0.005 Å. N. M. B.

Air ionisation chamber for measuring low-voltage X-ray intensities in röntgens. F. M. UBER (Rev. Sci. Instr., 1933, [ii], 4, 649—650).—A self-contained parallel plate chamber for use in dosage meters is described. N. M. B.

Ring-target X-ray generator adapted to scattering, fluorescence, and irradiation experiments. P. KIRKPATRICK and P. A. ROSS (Rev. Sci. Instr., 1933, [ii], 4, 645—648).—The essential feature is a ring-target approx. 3 in. in diam., along the horizontal axis of which a scatterer can be placed. N. M. B.

Liquids of high refractive index. B. W. ANDERSON and C. J. PAYNE (Nature, 1934, 133, 66—67).—Liquids suitable for refractometry are C_2I_4 and S in CH_2I_2 , n_D 1.81; AsPhI_3 , d^{15} 2.56, n 1.822—1.879 for 6708 to 5106 Å.; Sc_2Br_2 , n_{Li} 1.96 \pm 0.1 to 2.02. L. S. T.

Interference scheme for measuring the cell depth of a Siedentopf ultramicroscopic mounting chamber. D. L. GAMBLE and A. H. PFUND (J. Opt. Soc. Amer., 1933, 23, 416—418).—A channelled spectrum is used. C. W. G.

Focalisation of diffused X-rays by plane crystalline plates. (MLLE.) Y. CAUCHOIS (Compt. rend., 1934, 198, 76—78; cf. A., 1933, 450).—Mathematical. An alternative scheme of arriving at the same result as previously described, by means of a circular slit or knife-edge, is worked out. C. A. S.

Focalisation methods in crystal powder analysis. H. HÜLUBEI (Compt. rend., 1934, 198, 79—80).—Mathematical. Illumination of a crystal powder or of a liquid by a hollow conical beam of X-rays is discussed. C. A. S.

Dipole measurements with very small quantities of material. P. C. HENRIQUEZ (Physica, 1933, 1, 41—52).—A micro-condenser, by means of which dipole moments may be measured accurately with a few mg. of material, is described. The problem is discussed theoretically. F. L. U.

Electrolysis of sodium through Pyrex glass. E. W. PIKE (Rev. Sci. Instr., 1933, [ii], 4, 687).—A method of introducing gas-free Na into a vac. tube by electrolysis through Pyrex glass is described. N. M. B.

Dielectric constant. I. Improved voltage tuning resonance method and its application to aqueous potassium chloride solutions. II. Drude method applied to aqueous solutions of potassium chloride. J. G. MALONE, A. L. FERGUSON, and L. O. CASE (J. Chem. Physics, 1933, 1, 836—841, 842—846).—I. Divergent results for the dielectric consts. of aq. solutions of electrolytes when different types of detection are used indicate that the change in dielectric const. depends on the characteristics of the generating and receiving circuits.

II. Adaptations of the Drude method with three different types of detecting device gave concordant results for the dielectric const. of H_2O and $\text{EtOH-H}_2\text{O}$ mixtures, but divergent results for KCl and

CuSO₄ solutions, indicating dependence on the characteristics of the apparatus. N. M. B.

Simple high resistance. V. DUMERT (Nature, 1933, 132, 1005).—The characteristics of C-film and non-metal resistances (this vol., 51) are discussed. A mixture giving resistances of a few thousand to several millions of ohms can be prepared from colloidal graphite (Aquadag) and phenol-resin colloid. It is painted on a rod of insulating material and baked at 150° for 2 hr. The resistor is made variable by immersion in Hg. L. S. T.

Possibilities in connecting up Ostwald's decade rheostats for potentiometric analysis. E. ERBACHER (Chem.-Ztg., 1933, 57, 904—905). A. R. P.

Portable vacuum-tube voltmeter for measurement of glass electrode potentials with examples of p_{H} determination. F. DE EDS (Science, 1933, 78, 556—558).—The apparatus described is suitable for determining the p_{H} of biological fluids, food products, and soils. The p_{H} of arterial dog blood was const. at 7.30 for 35 min. 15 min. after administration of dinitrophenol respiration increased and the p_{H} rose to 7.34, at which val. it remained const. for 30 min. Vals. then fell to 6.94 for a sample taken 1 min. after death. L. S. T.

Laboratory apparatus for esterification. E. GUTTMANN (Chem.-Ztg., 1933, 57, 1001).—A flask is fitted with a plain vertical tube connected at the top and bottom to a condenser parallel to it. A 2-way cock at the bottom of the latter allows the apparatus to be used for refluxing and distillation as desired. C. I.

Laboratory glass filters. P. H. PRAUSNITZ (Chem.-Ztg., 1933, 57, 885—886).—Glass filters of the Büchner type with perforated and sintered porous glass filter plates, and of the ordinary funnel type with channels in the side to assist filtration, are described. A. R. P.

Gas burette. J. HUME (Chem. and Ind., 1934, 37).—A simple apparatus, giving a max. error of < 0.1 c.c. in 100 c.c., is described. E. S. H.

Vessel for acid-alkali titrations. J. JACKSON (Chem. and Ind., 1934, 36). E. S. H.

Kipp apparatus. ANON. (Chem.-Ztg., 57, 1933, 992).—The solid reactant is prevented from falling into the lowest vessel by means of a wide glass sleeve which rests on the bottom and surrounds the central tube to a point slightly above the level of the solid; the external diameter of the sleeve is only very slightly < the internal diameter of the neck between the middle and lowest vessels. H. F. G.

Large-scale laboratory extractions. P. A. ROWAAN (Chem. Weekblad, 1933, 30, 771—772).—A large vessel (I) (e.g., 10 litres) is fitted with an upright condenser and a side tube leading from a round-bottomed flask (1 litre) lying horizontally in a H₂O-bath. The neck of the flask is level with the surface of the solvent in (I), and is fitted also with a narrow-bore tube which enters the bottom of (I). Vapour passes from the flask to the condenser, the solvent falls on the material to be extracted, and the

conc. extract flows continuously through the narrow tube to the flask. The apparatus is sturdy, requires little attention, and is inexpensive. H. F. G.

Device for elutriation analysis of small quantities of material. M. VENDL (Mitt. berg-hüttenmänn. Abt. Hochschule Berg-Forstwes. Sopron, 1932, 4, 104—119; Chem. Zentr., 1933, i, 1818). L. S. T.

Simple apparatus for exact gas analysis, especially for determination of carbon dioxide and water vapour at low concentration. P. SCHUFAN (Chem. Fabr., 1933, 6, 513—515).—CO₂ is removed by absorption in conc. KOH, and H₂O by freezing at temp. < -55°. The alteration in vol. and pressure of the gas is determined by an inclined capillary manometer. The error is about $\pm 3 \times 10^{-3}$ vol.-%. E. S. H.

Apparatus for azeotropic dehydration. A. DUPIRE (Bull. Assoc. Chim. Sucr., 1933, 50, 373—374).—Laboratory apparatus for esterification, in which the H₂O formed is removed continuously by distillation with an immiscible liquid, is described with a diagram. The reaction mixture, with the immiscible liquid, is boiled in a flask with three necks, one for a thermometer, one for a stirrer with Hg seal, and one leading to a kind of Soxhlet extractor connected with a reflux condenser. The condensate from the last drops into a collecting tube in the bottom of which the H₂O remains, whilst the immiscible liquid overflows and returns to the boiling flask through the Soxhlet extractor, which may contain a dehydrating agent if necessary. This apparatus has been used for the prep. of many boric and arsenious esters (cf. A., 1932, 937) and for the dehydration of many org. and inorg. substances. J. H. L.

Laboratory aids. W. KERCKHOFF (Chem.-Ztg., 1933, 57, 866).—Simple devices made from strips of metal or metal wire are illustrated for supporting crucibles in a desiccator, a beaker in a H₂O-bath, and an extraction thimble below a reflux condenser. A. R. P.

Filtration of hygroscopic substances. G. ROEDER (Chem.-Ztg., 1934, 58, 28).—Apparatus for filtration in an atm. of dry CO₂ is described. A. G. P.

Devices for working with moisture-sensitive substances. H. GRUBITSCH and N. SKALLA (Z. anal. Chem., 1933, 95, 163—165).—Descriptions are given of a weighing bottle with spiral screw thread for opening inside a closed reaction vessel, and of a double-ended weighing tube enabling a boat to be inserted in a combustion tube without exposure. J. S. A.

Collodion membranes in low-pressure ultra-filtration. S. J. FOLLEY (Biochem. J., 1933, 27, 1775—1778).—Details are given of the prep. of collodion tubes of reproducible permeability and of a method of low-pressure ultra-filtration. H. G. R.

Mercury seal for stirrers. D. T. ROGERS (J. Amer. Chem. Soc., 1933, 55, 4901).—Stainless steel is used in place of glass. E. S. H.

More sensitive design of the Geiger-Müller counter. T. R. CUYKENDALL (Rev. Sci. Instr., 1933, [ii], 4, 676—678).—The effective surface is

increased by replacing part of the wall of the counter by Ni vanes from which recoil electrons can escape to ionise the gas in the chamber. N. M. B.

Apparatus for the growth of metal single crystals. M. F. HASLER (Rev. Sci. Instr., 1933, [ii], 4, 656—660).—A furnace is moved mechanically along a glass tube containing the growing trough. Very uniform single-cryst. rods of any orientation can be produced in any gas or in vac. for metals of low m.p. N. M. B.

Phosphoric acid as a drying agent for hydrogen chloride. F. FAIRBROTHER (J.C.S., 1933, 1539—1541).—Dry HCl has no action on P_2O_5 . In presence of a trace of H_2O , HPO_3 is formed and absorption of HCl then occurs in accordance with the reaction $3HCl + HPO_3 = POCl_3 + 2H_2O$. The H_2O thus produced forms more HPO_3 and so the absorption of HCl increases. H. S. P.

Simple pneumator pulsator. C. F. WINCHESTER (Science, 1933, 78, 607—608).—An apparatus to move a liquid in or out of a vessel, or intermittently to move a liquid in a given direction, is described. L. S. T.

Production of high pressures and temperatures. C. RAMSAUER (Physikal. Z., 1933, 34,

890—894).—Compression is effected by a projectile entering the open end of a tube containing the gas. A. J. M.

Rapid elimination of oxygen from water or aqueous solutions.—See B., 1934, 1.

Nomogram for the conversion of potentiometer readings to hydrogen-ion concentration. A. WEBSTER (Chem. and Ind., 1934, 38). E. S. H.

Lecture experiment to illustrate "topsy-turvydom" in induced reactions. K. GLEU (Z. anorg. Chem., 1933, 215, 271—272).—A solution containing H_2SO_4 , $NaVO_3$, As_2O_3 , and a trace of OsO_4 shows the yellow colour of V^V . On adding $KClO_3$, an oxidising agent, reduction of V^V to V^{IV} by the As_2O_3 is induced, and the liquid turns blue. F. L. U.

Survey of progressive science. (SIR) F. G. HOPKINS (Nature, 1933, 132, 878—880).—Presidential address to the Royal Society. L. S. T.

Negative weight of phlogiston. C. SAECHTLING (Angew. Chem., 1933, 46, 754—756).—Most supporters of the phlogiston theory in the latter half of the eighteenth century attributed the increase in wt. of a metal on losing phlogiston to a difference in d between the latter and the surrounding air. A. B. M.

Geochemistry.

Terrestrial abundance of the permanent gases. H. N. RUSSELL and D. H. MENZEL (Proc. Nat. Acad. Sci., 1933, 19, 997—1001).—Theoretical. R. S.

Existence of oxygen in the atmosphere of Mars. D. EROPKIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 100—101).— O_2 should be detectable through the O_3 absorption bands at 3200—3400 Å. H. J. E.

Electrical conductivity of the air on Mont Doré in August, 1933. G. GRENET (Compt. rend., 1933, 197, 1683—1684).—The mean conductivity of the air at 9.15 a.m., Aug. 2—21, 1933, on Mont Doré (1050 m.) was 4.26×10^{-4} , or approx. double the normal, due probably to the presence of increased emanation. The ratio λ^+/λ^- varied from 0.80 to 1.42, average 0.99. C. A. S.

Catalytic properties and the ages of the mineral waters of Vrnjacka Banja, Arandelovac, and Mladenovac. G. SCHILDER (Kroat. Aertzte-Z., 1932, 54, 243—261; Chem. Zentr., 1933, i, 1825—1826).—Catalytic effects were examined by means of the Glenard reaction (titration with 0.1N- $KMnO_4$ and determination of reaction velocity). Peroxidising effects were examined by means of acid and alkaline benzidine reactions. Fe^{++} was detected and pH measurements were made. L. S. T.

Transparency, colour, and specific conductance of the lake waters of N.E. Wisconsin. C. JUDAY and E. A. BIRGE (Trans. Wisconsin Acad. Sci., 1933, 28, 205—259).—Colour of H_2O from 500 lakes is correlated with org. C in the surface H_2O ; transparency and transmission of solar radiation

are also related. Sp. conductivity at 20° is correlated with the quantity of fixed or bound CO_2 as well as that of Ca and Mg in the surface H_2O . CH. ABS.

Transmission of ultra-violet radiation by water. C. D. HODGMAN (J. Opt. Soc. Amer., 1933, 23, 426—429).—The low transmission of fresh H_2O from lakes is due partly to the presence of dissolved salts and partly to scattering by fine particles. C. W. G.

Radioactivity of waters and natural gases. M. GESLIN and D. CHAÎNAZAROFF (Ann. Guébbard-Séverine, 1933, 9, 312—351).—Apparatus for the determination of the radioactivity of H_2O and natural gases by the boiling method and the agitation method is described, and examples of the calculation are given. The Curie electroscope is also described. A. J. M.

Petroliferous waters. D. A. CHAÎNAZAROFF (Ann. Guébbard-Séverine, 1933, 9, 293—299; cf. A., 1933, 588).—The diminution in quantity, or complete absence, of SO_4 in petroliferous waters may be ascribed to the action of anaërobic micro-organisms, which remove O from the SO_4 . The origin of petroliferous formations is related to that of salt. The factors governing the movement of waters are discussed. A. J. M.

Chemistry of sea-mud. F. KRAUSS and A. KOLLATH (Farben-Chem., 1933, 4, 415—416, 447—452).—A review. S. M.

Formation of the earth. R. PERRIN (Compt. rend., 1934, 198, 105—107).—Regarding the earth

as a metal nucleus surrounded by a slag shell with gaseous envelope, its formation might be attributed to the action of O_2 on the nucleus until further action was stopped by accumulated slag (oxides), but the amount of free O_2 remaining in the air is only such that had a layer of, e.g., Fe only 1 m. thick been oxidised in addition none would have remained. Hence it is suggested that the first materials to condense to the liquid state must have been such as would be in equilibrium with their own vapour, that being low even at a high temp., and with O_2 at very low pressure, and have been formed with evolution of much heat. Such substances are CaO , MgO , Al_2O_3 , and SiO_2 , with which last the others would have combined. These would have been deposited before condensation of the metallic nucleus, and at a temp. at which most metallic oxides would be dissociated. Relative d would then operate.

C. A. S.

Luminescence of minerals in relation to their occurrence and their generation. S. KREUTZ (Bull. Acad. Polonaise, 1933, A, 215—225).—The fluorescence excited by ultra-violet light in specimens of fluorite, apatite, topaz, and calcite varies with the colour of the mineral specimen. This phenomenon is discussed from the point of view of the age of the mineral.

J. W. S.

Activity of materials exposed to the natural electric field. H. GARRIGUE (Compt. rend., 1933, 197, 1619—1620).—The rate of disappearance of radioactivity of samples of metal, rock, and grass exposed to the air at the Pic-du-Midi (2860 m.) indicates the predominance of short-lived elements of the Ra family. A piece of Zn examined within 1 hr. of being struck by lightning was specially active.

C. A. S.

Cooperite and braggite occurring in platiniferous concentrates from the Transvaal. R. H. ADAM (J. Chem. Met. Soc. S. Africa, 1933, 34, 132—136).—Analyses are given.

C. W. G.

Reflectivities of sulphide ore-minerals. F. C. PHILLIPS (Min. Mag., 1933, 23, 458—462).—The reflectivity of simple sulphides, selenides, and tellurides shows a progressive increase with at. no. of the combining metal or of S, Se, Te. "Mol. refractivities" of a large no. of complex S-salt minerals calc. from measured reflectivities agree well with the additive "mol. refractivities" of the constituent simple sulphides. This relation gives a method of calculating the reflectivity of an ore-mineral and a check on the d .

L. J. S.

A new barium plagioclase. S. R. NOCKOLDS and F. G. ZIES (Min. Mag., 1933, 23, 448—457).—An aplitic dike rock from Broken Hill, New South Wales, showing an unusual amount of BaO (9.23 or 4.8%) contains a feldspar which gave SiO_2 44.6, Al_2O_3 33.0, CaO 14.0, BaO 5.7, Na_2O 2.0, K_2O 0.7%, corresponding with orthoclase 69.2, celsian ($BaAl_2Si_2O_8$) 13.9, albite 8.9, orthoclase 3.9, carnegieite 4.0%. It has d 2.872, n_a 1.571, n_b 1.580, n_c 1.585, optic axial angle $2V$ 78° of negative sign.

L. J. S.

Action of mineralisers. W. EITEL and W. WEYL (Chem. Erde, 1933, 8, 445—461).—A discussion

of the action of volatile constituents on the viscosity and crystallisation of magmas.

L. J. S.

Vicinal faces of topaz. S. KREUTZ (Bull. Acad. Polonaise, 1933, A, 169—172).—Goniometric measurements have been made on a no. of specimens of topaz, the results being discussed with reference to the conclusions of Schubnikov and Brunovsky (A., 1931, 788).

J. W. S.

Manganese deposit, Bombay (N.Z.). H. E. FYFE (New Zealand J. Sci. Tech., 1933, 15, 203—207).—Bands of compact amorphous psilomelane (H_4MnO_5) occur in "greywacke" areas. The formation, use, and market val. of these deposits are discussed.

A. G. P.

Occurrence of beryllium in vesuvianites. B. A. SILBERMINTZ and E. W. ROSCHKOWA (Zentr. Min. Geol., 1933, A, 249—254; Chem. Zentr., 1933, ii, 1498).—Be was determined colorimetrically with quinalizarin. Of 19 samples, 13 were free from BeO , 3 contained approx. 0.008%, and others 0.01—0.1, 0.09, and 0.18%. Nepheline syenites were free from BeO .

A. A. E.

Thorium minerals as age indicators. R. C. WELLS (J. Washington Acad. Sci., 1933, 23, 541—544).—More wt. than heretofore should be given to Th minerals as age indicators.

C. W. G.

Geology of the iron deposits of the Sierra de Smataca, Venezuela. G. ZULOAGA (Amer. Inst. Min. Met. Eng., Tech. Publ. No. 516, 1933, 36 pp.).—The Fe ores in this locality and their formation and geology are described and discussed. The ores closely resemble those found in Minas Geraes, Brazil; they have a high Fe content combined with low S, P, SiO_2 , and Mn.

A. R. P.

Barite type and its relations to the monoclinic system. W. GRAHMANN (Neues Jahrb. Min., 1933, A, Bl.-Bd., 66, 155—177; Chem. Zentr., 1933, i, 1754).

Barite deposits at Chapsordag and Taptan-Tursy in the Hakassia district. V. DOMAREV (Min. J. Moscow, 1930, 106, No. 2—3, 150).—Analyses are given.

CH. ABS.

Barite deposits in the Urals. M. GORDIENKO (Min. J. Moscow, 1931, 106, No. 12, 122—126).—Kasslinskaja Datscha barite contains 97—98% $BaSO_4$ and appreciable quantities of Au and Ag.

CH. ABS.

Bolivian thioannates. F. AHLFELD and H. MORITZ (Neues Jahrb. Min., 1933, A, Bl.-Bd., 66, 179—212; Chem. Zentr., 1933, i, 1755).—The occurrence of thioannates and germanates is discussed; kyndrite ($Pb_3Sn_4Sb_2S_{14}$), franckeite ($Pb_5Sn_3Sb_2S_{14}$), argyrodite-canfieldite, and wolfsbergite are described. Wolfsbergite contains Cu 25.65, Sb 48.83, Ge 0.91, S 24.42%.

A. A. E.

Genesis of bauxites in the Sann valley, Yugoslavia. E. DITTLER and O. KÜHN (Chem. Erde, 1933, 8, 462—495).—Andesites associated with Triassic limestones have been propylitised by post-volcanic processes and afterwards subjected to weathering, resulting in the loss of alkalis, CaO , and SiO_2 , the last combining with the limestone to form

hornstone. The remaining sesquioxides and TiO_2 were hydrated to allites. L. J. S.

Zeolites. V. Mesolite. M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1933, 23, 421—447).—Five new analyses and X-ray measurements on mesolite from various localities give a unit cell, a 56.7, b 6.56, c 18.44 Å., β 90° 0' (space-group C_2^2), containing $\text{Na}_{16}\text{Ca}_{16}\text{Al}_{48}\text{Si}_{72}\text{O}_{210}\cdot 64\text{H}_2\text{O}$. There may be replacement of Ca by 2Na and of Na by K. Crystallographic, optical, and v.-p. (isohydric) measurements were made. Base-exchange products obtained by fusion with KCNS , LiNO_3 , and AgNO_3 are identical with those obtained with natrolite (A., 1933, 141). Mesolite is an independent species, isostructural, but not isomorphous, with natrolite and scolecite. L. J. S.

Electrolyte contents of two clays. F. K. SCHLÜNZ (Chem. Erde, 1933, 8, 504—506).—The sol. constituents of two clays previously examined (A., 1933, 1030) have been determined. L. J. S.

Clay and bauxitic minerals: statistical classification. S. I. TOMKEIEFF (Min. Mag., 1933, 23, 463—482).—689 analyses taken from the literature are plotted on a triangular diagram. Al_2O_3 - SiO_2 - H_2O and frequency curves are drawn for the ratios $\text{SiO}_2:\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$, and $\text{H}_2\text{O}:\text{SiO}_2$. This method indicates the existence of only pyrophyllite ($\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$) and kaolin and its isomerides

($2\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$) as definite compounds, other clay minerals, to which many names have been applied, being regarded as mixtures of these with Al and Si hydroxides. A similar plot of 320 bauxitic minerals grading to laterite on a diagram Al_2O_3 - Fe_2O_3 - H_2O and frequency curves give clusters and peaks corresponding with diaspore ($\text{H}_2\text{O}, \text{Al}_2\text{O}_3$) and gibbsite ($3\text{H}_2\text{O}, \text{Al}_2\text{O}_3$). Bauxite ($2\text{H}_2\text{O}, \text{Al}_2\text{O}_3$) does not exist. L. J. S.

Weathering and soil formation in Chile. E. BLANCK, A. RIESER, and E. VON OLDERSHAUSEN (Chem. Erde, 1933, 8, 339—439).—Numerous chemical and mechanical analyses are given of weathered rocks and soils from different climatic zones. L. J. S.

Micro-structure of the coal of certain fossil tree barks.—See B., 1934, 49.

Character of the peat deposits of New York. B. D. WILSON and E. V. STAKER (Cornell Univ. Agric. Exp. Sta. Mem., 1933, No. 149, 20 pp.).—A no. of peat profiles are described. In most cases the deposits were high in Ca^{++} and N, the latter being largely in combination with lignocellulose complexes (I). The org. matter contains higher proportions of hemi-cellulose than of cellulose, although both are exceeded by that of (I). The character of the peats is closely related to the nature of the underlying material.

A. G. P.

Organic Chemistry.

Organic pseudo-compounds as reagents for active atoms in organic molecules. M. REBEK (Bull. Soc. Chim. Yougoslav., 1933, 4, 79—84).—The time t necessary for attainment of max. conductivity κ after mixing COMc_3 or PhNO_2 solutions of hexamethyl-*p*-rosaniline (I) and various ψ -acids varies from 0 for $\text{NH}[\text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ to 55 hr. for $\text{CH}[\text{C}_6\text{H}_3(\text{NO}_2)_2]_3$ (II); for carboxylic acids t varies from 388 min. for maleic to 2652 min. for glutaric acid. The vals. of t are independent of the P_κ of the given acid. Various org. halides react as ψ -acids with (I), the κ - t curves being similar to those obtained with carboxylic acids in the case of CPh_3Cl , and to that given with (II) in the case of picryl chloride, C_2HCl_5 , and C_3HCl_7 ; in the latter cases, the reaction is one of zero order. R. T.

Dynamics and mechanism of aliphatic substitutions.—See this vol., 151.

Pyrolysis of *n*-butane at low decomposition temperatures. C. D. HURD, C. I. PARRISH, and F. D. PILGRIM (J. Amer. Chem. Soc., 1933, 55, 5016—5019).— H_2 (trace), CH_4 , C_2H_6 , C_2H_4 , and C_3H_6 are obtained when n - C_4H_{10} is passed through a Pyrex tube at 365°, 400°, and 415°; the total decomp. is 0.46, 2.6, and 5%, respectively. Fission at a particular C-C linking does not occur (cf. Norris and Thomson, A., 1931, 1147). H. B.

Pyrolysis of hydrocarbons. Butanes. C. D. HURD and F. D. PILGRIM (J. Amer. Chem. Soc., 1933, 55, 4902—4907; cf. A., 1930, 58).—Decomp. of *n*- (I) and *iso*-butane occurs to the same extent (for a const. temp.) when tubes of widely differing size are used

provided the contact time is the same; variation in the latter alters the amount of decomp. Pyrolysis in Fe, Ni, or quartz tubes at 600° occurs in practically the same manner; monel metal exerts a pronounced catalytic action and the decomp. products are largely C and H_2 . *iso*Butene is not produced from (I) (cf. *loc. cit.*), showing that rearrangement of the C chain does not occur. H. B.

Thermal decomposition of hexane.—See this vol., 151.

Action of aluminium chloride on *n*-hexane and *n*-heptane, alone and in presence of halogen derivatives. Conversion of paraffin into cycloparaffin hydrocarbons. C. D. NENITZESCU and A. DRĂGAN (Ber., 1933, 66, [B], 1892—1900).—The action of AlCl_3 [freshly sublimed (I) or moist (II)] on *n*-hexane at 68—69° leads to very little combustible gas, a large proportion of β - or γ -methylpentane or a mixture thereof, $\text{C}_{15}\text{H}_{12}$, and dehydrogenated products among which cyclohexane (III) is identified. Compounds boiling at a higher temp. than (III) are not observed. The quantity of (III) depends on the duration of reaction. (III) and AlCl_3 in presence of AcCl give the same products and in approx. the same ratio as in its absence and also saturated fractions b.p. < 248°, including monocyclic hydrocarbons among which 1:3-dimethylcyclohexane (IV) is present and dicyclic compounds, mainly $\text{C}_{12}\text{H}_{22}$. (I) and *n*-heptane (V) yield exclusively saturated products, which are produced in addition to polymerised olefines when (II) is used. With (II) C_2H_6 and *isobutane* are evolved, also obtained with (I) after addition of

H₂O. C₁₅H₁₂, β- or γ-methylpentane, and isoheptane are formed. (IV) and large amounts of dicyclic hydrocarbons, C₁₄H₂₆, are produced. The lower layer formed when (II) is used gives, after addition of H₂O, a heptene or methylcyclohexene and, mainly, a product C₁₄H₂₄; the non-volatile fraction has the approx. composition, (C₇H₁₄)_n. In presence of EtCl, Pr^o-Cl, Pr^β-Cl, or BuCl (V) reacts very vigorously with AlCl₃, the halide being reduced to hydrocarbon so completely that a preparative method is indicated. (V) is very little converted into simpler hydrocarbons, whereas large quantities of cycloparaffins of higher b.p. and a considerable lower layer containing olefines result. H. W.

Octanes. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1933, 55, 5056).—All the structurally isomeric octanes have been synthesised; references are given. H. B.

Direct preparation of divinyl from alcohol. I. S. V. LEBEDEV (J. Gen. Chem. Russ., 1933, 3, 698—717).—The product obtained by passing EtOH vapour over an unspecified mixed catalyst consists of: H₂, 1.3—1.6, CO 0.2—0.5, CH₄ 0.4—0.6, C₂H₄ 5—8, butene 3—4, divinyl 20—25, pentene, piperilene, hexene, hexadiene, and *p*-xylene each 0.4—0.8, PhMe 0.1—0.2, Et₂O 2—5, EtOBu 0.05—0.1, BuOH 2—4, crotyl alcohol 0.5—1, amyl and hexenyl alcohol 0.5—0.8, octyl alcohol 0.3, MeCHO 2.5—5, PrCHO 0.1—0.2, crotonaldehyde 0.05, COMe₂ 0.3—0.5, and COMeEt 0.1—0.2%. The mechanism of formation of the above compounds from "nascent" C₂H₄ and MeCHO is discussed. R. T.

Syntheses in the olefine series. V. Hexenes, heptenes, and octenes. I. SCHURMAN and C. E. BOORD (J. Amer. Chem. Soc., 1933, 55, 4930—4935).—CMc₂Pr^β-OH is dehydrated (anhyd. H₂C₂O₄) to CMc₂:CMc₂, b.p. 72.9—73.2°/760 mm., m.p. -76.4°, and βγ-dimethyl-Δ^α-butene, b.p. 55.6—56°/760 mm., m.p. -123° to -120°. γγ-Dimethyl-Δ^α-butene, b.p. 41—41.2°/760 mm., γγ-dimethyl-Δ^α-pentene, b.p. 76.9°/760 mm. (dibromide, b.p. 95.3—95.6°/10 mm.), δδ-dimethyl-Δ^β-pentene, b.p. 76—76.1°/760 mm. (dibromide, b.p. 92.8—93°/14 mm.), δδ-dimethyl-Δ^β-hexene, b.p. 105.4—106°/760 mm. (dibromide, b.p. 92—93°/4 mm.), and ββ-dimethyl-Δ^γ-hexene, b.p. 100.1°/760 mm. (dibromide, b.p. 96.5—97°/8 mm.), are prepared by the Tschugaev method from CHMeBu^γ-OH (*Me xanthate*, b.p. 85—87°/6 mm.), methyltert.-amylcarbinol (*Me xanthate*, b.p. 110—112°/8 mm.), CHEtBu^γ-OH (*Me xanthate*, b.p. 92—92.5°/5 mm.), ethyltert.-amylcarbinol (*Me xanthate*, b.p. 118—120°/8 mm.), and CHPr^αBu^γ-OH (*Me xanthate*, b.p. 112—114°/8 mm.), respectively. The absence of rearrangement in the preps. is shown by reduction (H₂, PtO₂, EtOH) of the olefines to the corresponding paraffins. H. B.

Ethylenic and saturated hydrocarbons from C₈ to C₁₁. M. TUOT (Compt. rend., 1933, 197, 1434—1436; cf. A., 1933, 695).—Physical consts. for βδ-dimethyl-Δ^α-hexene (*loc. cit.*, erroneously given as heptene), b.p. 109°/737 mm.; βε-di-, b.p. 111°/739 mm., and βγε-tri-, b.p. 125°/741 mm., -methyl-Δ^β-hexene; βδ-, b.p. 131°/749 mm., and βε-dimethyl-

Δ^δ, b.p. 137°/747 mm., and βδζ-trimethyl-Δ^γ-, b.p. 142°/740 mm., -heptene; βδ-di-, b.p. 154°/752 mm., and βδη-tri-, b.p. 168°/739 mm., -methyl-Δ^δ-octene, are given. γ-Methylheptan-γ-ol, b.p. 67°/14 mm., affords γ-methyl-Δ^β-heptene, b.p. 121°/750 mm. Catalytic reduction (Adams) of these affords: βδ-, b.p. 108°/750 mm., and βε-, b.p. 107°/747 mm., -dimethyl-, and βγε-trimethyl-, b.p. 129°/738 mm., -n-hexane; γ-methyl-, b.p. 116.5°/747 mm., βδ-, b.p. 130°/749 mm., and βε-, b.p. 133°/741° mm., -dimethyl-, and βδζ-trimethyl-, b.p. 143°/746 mm., -n-heptane; βδ-di-, b.p. 152.5°/746 mm., and βδη-tri-, b.p. 167.5°/746 mm., -methyl-n-octane. J. W. B.

Mechanism of photopolymerisation of acetylene. W. KEMULA and S. MRAZEK (Z. physikal. Chem., 1933, B, 23, 358—369).—Absorption spectrum measurements during polymerisation have shown the presence of C₆H₆ vapour, C₁₀H₈ derivatives, and C₄H₄. A yellowish-white solid settles out of the gas phase, and analysis of the latter shows the presence of small amounts of C₂H₄ and C₂H₆. The first step in the polymerisation is probably 2C₂H₂ → C₄H₄, and the C₁₀H₈ ring is probably synthesised by C₆H₆ + C₄H₄ → C₁₀H₁₀. R. C.

sec.-isoAmyl chloride, γ-chloro-β-methylbutane. F. C. WHITMORE and F. JOHNSTON (J. Amer. Chem. Soc., 1933, 55, 5020—5022).—Addition of HCl to CH₂:CHPr^β at room temp. (method; Kharasch and Mayo, A., 1933, 805) gives a 90% yield of a 1:1 mixture of γ-chloro-β-methylbutane (I), b.p. 91.8—91.9°/736 mm., and tert.-amyl chloride; the latter is removed from the mixture by hydrolysis (H₂O). (I) is unaffected by heating at 100° for 24 hr.; the structure is shown by the formation of CHMePr^β-OH from its Grignard reagent and O₂. H. B.

Replacement of strongly positive hydrogen by halogen. III. Reactions of hypohalogenites. F. STRAUS and R. KÜHNEL [in part with H. WOLLSCHITT and L. SALZMANN] (Ber., 1933, 66, [B], 1834—1846; cf. A., 1930, 1158).—γ-Methyl-Δ^α-buten-γ-ol (I), b.p. 28.5—29.5°/19 mm. (*p*-nitrobenzoate, m.p. 115°), is converted by alkaline hypobromite into α-bromo-γ-methyl-βγ-oxidobutane, b.p. 50.5—51.5°/15 mm., transformed by H₂SO₄ at 55° into α-bromo-γ-methylbutane-βγ-diol, m.p. 48—49° (non-cryst. acetate), which is oxidised by HNO₃ (*d* 1.25—1.26) to α-hydroxyisobutyric acid and by Beckmann's mixture to CH₂Br-CO₂H. Reaction is largely independent of the concn. of alkali provided that non-bleaching solutions are used and the presence of BrO₃' is avoided. Use of excess of KOBr leads to the production of material rich in Br from which CBr₄ is isolated. Addition of I in KI to (I) suspended in KOH-EtOH affords α-iodo-γ-methyl-βγ-oxidobutane, b.p. 59°/13 mm., converted into α-iodo-γ-methylbutane-βγ-diol, m.p. 54—55°. (I) does not react with OCl'. Reaction is not universally applicable to tert.-allyl alcohols. Thus, γ-ethyl-Δ^α-penten-γ-ol affords α-bromo-γ-ethyl-βγ-oxidopentane, b.p. 72—73°/12.5 mm., and δ-methyl-Δ^β-penten-δ-ol, b.p. 54°/33 mm., yields CBr₄ and β-bromo-δ-methyl-γδ-oxidopentane, converted by 1% H₂SO₄ into β-bromo-δ-methylpentane-γδ-diol, m.p. 96—97°, oxidised

to $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Reaction does not take place with α -phenyl- γ -methyl- Δ^4 -buten- γ -ol. The intermediate replacement of positive H by OBr' is postulated with formation of a hypobromous ester, which becomes stabilised by isomerisation. $\text{CMe}_2\cdot\text{CHMe}$ is slowly converted by OBr' into $\beta\gamma$ -oxido- β -methylbutane, b.p. $73\text{--}74^\circ/751\text{ mm.}$, and thence into CBr_4 . $\text{CMe}_2\cdot\text{OH}$ and $\text{CMe}_2\text{Et}\cdot\text{OH}$ slowly give CBr_4 ; EtOH is attacked more rapidly than MeOH . $\text{CH}_2\text{Ph}\cdot\text{OH}$ is dehydrogenated by OBr' to PhCHO , which is then rapidly transformed into BzOH ; reactions occur much more slowly with OCl' . Cinnamaldehyde (II) with 2 OBr' yields phenylglycidic acid and brominated products, and is thence degraded to BzOH ; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ is formed only in minor amount. (II) and OCl' afford PhCHO in 70% yield accompanied by very small amounts of acidic oxidation products. $\text{CH}_2(\text{CO}_2\text{H})_2$ and OCl' give dichloromalic acid, decomp. $111\text{--}111.5^\circ$ [NH_2Ph salt, m.p. 101.5° (decomp.); dianilide, m.p. $129\text{--}130^\circ$], indifferent towards SOCl_2 . $\text{CBr}_2(\text{CO}_2\text{H})_2$, m.p. $130\text{--}131.5^\circ$, is derived similarly. H. W.

Micro-determination of methyl alcohol in presence of large quantities of homologous alcohols. M. FLANZY (Compt. rend., 1934, 198, 94—97).—Accurate micro-determination of MeOH (x mg.) in presence of EtOH (y mg.) and other homologues is effected by conversion of the primary alcohols into their iodides (Zeisel-Fanto) under distillation conditions ($43\text{--}50^\circ$) such that all MeI and some EtI are distilled into aq. AgOAc , whence, by distillation, the alcohols are regenerated. Oxidation of the distillate (50 c.c.) with cold $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ and iodometric determination of excess of CrO_3 gives the oxidation index (p =mg. O required), the wt. of AgI (P mg.) formed being determined after boiling the residue with aq. HNO_3 . Then $x=2\times 32(p/32-P/234.8)$ and $y=3\times 46(P/238.4-p/48)$. By this method 0.1% of MeOH may be determined and its presence in fermented liquors is thus proved. J. W. B.

Cryoscopic behaviour of alcohol on aqueous solution. E. BERNER (Ber., 1933, 66, [B], 1917—1921).—Mainly a reply to Pringsheim *et al.* (A., 1933, 1144). Re-examination of the behaviour of EtOH and inulin in freezing H_2O at very small concns. does not show any abnormality, and confirms the principle of additivity. The unusual behaviour of α -methylglucoside and sucrose in boiling H_2O at great dilution could not be confirmed. H. W.

Colour reaction for glycerol. K. TAUFEL and H. THALER (Z. anal. Chem., 1933, 95, 235—239; cf. B., 1932, 849).— $0.5\text{--}1\times 10^{-4}$ g. of glycerol present in a mixture may be detected by conversion into epihydrinaldehyde (I) by way of acraldehyde. (I) is then recognised by the development of a red colour with phloroglucinol. Glycol, mannitol, and various carbohydrates give a negative result. Details are given. F. L. U.

Ascaryl alcohol. F. N. SCHULZ and M. BECKER (Biochem. Z., 1933, 265, 253—259).—Ascaryl alcohol, $\text{C}_{33}\text{H}_{68}\text{O}_4$ (cf. $\text{C}_{32}\text{H}_{64}\text{O}_4$, Flury, A., 1912, ii, 464), m.p. 84° , contains two active H, does not contain

a double linking, gives a diacetate, m.p. 52° , without active H, a dibenzoate, m.p. 37° , contains glyceryl (I), and gives acraldehyde on heating, but (I) cannot be separated by hydrolysis. P. W. C.

Synthesis of *dl*-mannitol, *allodulcitol*, and *dl*-mannose. LESPIEAU and WIEMANN (Bull. Soc. chim., 1933, [iv], 53, 1107—1110).—Partly reviewed previously (A., 1932, 718; 1933, 47). 100 g. of divinyl glycol give 11 g. of mannitol and 15 g. of *allodulcitol*, new m.p. $149\text{--}150^\circ$ [dibenzylidene derivative, new m.p. $249\text{--}250^\circ$ (block)], but by more prolonged oxidation less alcohols and some *dl*-mannose. R. S. C.

Anhydrides of mannitol. P. BRIGL and H. GRÜNER (Ber., 1933, 66, [B], 1945—1949).—Mannitol $\alpha\zeta$ -dibenzoate is converted at $200^\circ/\text{vac.}$ or preferably in boiling $\text{C}_2\text{H}_2\text{Cl}_4$ into *anhydromannitol dibenzoate* (I), m.p. $137\text{--}138^\circ$, $[\alpha]_D +3.2^\circ$ in abs. EtOH , and *dianhydromannitol dibenzoate* (II), m.p. 133° , $[\alpha]_D +225.7^\circ$ in CHCl_3 . (I) is not an intermediate in the production of (II). (I) does not yield reducing substances with $\text{Pb}(\text{OAc})_4$ and does not condense with COMe_2 , CH_2O , or PhCHO . (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ gives *anhydromannitol dibenzoate di-*p*-toluenesulphonate*, m.p. 142° , $[\alpha]_D +57.9^\circ$ in CHCl_3 , identical with that described by Müller *et al.* (A., 1933, 931). (II) is unaffected by treatment with $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$ or boiling Ac_2O , but with Ac_2O containing H_2SO_4 yields a compound, m.p. 140° , containing S. Mannitol $\alpha\beta\epsilon\zeta$ -tetrabenzoate and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ give *mannitol $\alpha\beta\epsilon\zeta$ -tetrabenzoate di-*p*-toluenesulphonate*, m.p. $136\text{--}137^\circ$, $[\alpha]_D -4.8^\circ$ in CHCl_3 , converted by NaOAc and boiling Ac_2O into ill-defined products; similar treatment has no effect on mannitol hexabenzoate. H. W.

Photochemical reactions of *o*-nitrobenzylideneacetals. VIII. (1 : 2 : 5 : 6-Di-*o*-nitrobenzylidenedulcitol.) I. TANASESCU and E. MACOVSKI (Bull. Soc. chim., 1933, [iv], 53, 1097—1102; cf. A., 1933, 393).—1 : 2 : 5 : 6-Di-*o*-nitrobenzylidenedulcitol (I), m.p. $256\text{--}258^\circ$, when illuminated, gives a resin, possibly by partial isomerisation. Its Bz_2 derivative, m.p. 310° , gives 3 : 4-dibenzoyl-1 : 6-di-*o*-nitrosobenzoyldulcitol, m.p. 128° after sintering at $108\text{--}110^\circ$ [corresponding Bz_4 derivative, m.p. about 110° (decomp.)]. These and similar reactions are considered in the light of the fact that (I) has three reactive H atoms. R. S. C.

Ester enolates and keten acetals. XVI. Carbon suboxide tetraethylacetal as intermediate in the transformation of ethyl $\beta\beta$ -diethoxyacrylate into ethyl diethylmalonate. H. SCHEIBLER and H. STEIN (Ber., 1933, 66, [B], 1784—1789).—Et $\beta\beta$ -diethoxyacrylate (I) and CNaPh_3 yield the corresponding enolate; heating of the mixture with EtOBz and extraction of the product with Et_2O leads to the isolation of NaOBz in small amount, thus indicating the incidence of keten acetal fission, the expected product of which could not be isolated. (I) and NaOEt (mol. ratio 2 : 1) at 130° yield EtOH , $\text{CHEt}(\text{CO}_2\text{Et})_2$, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and $\text{CET}_2(\text{CO}_2\text{Et})_2$ (II). Carbon suboxide tetracylacetal appears to be an intermediate in the formation of (II). H. W.

Alkyl and aryl bromosulphites. P. CARRÉ and D. LIBERMANN (Compt. rend., 1933, 197, 1326—1328).—By interaction of the appropriate alkyl sulphite with SOBr_2 in Et_2O at room temp. are obtained: *Et*, b.p. 67—70°/30 mm., *Pr*^a, b.p. 90—93°/30 mm., *Pr*^β, b.p. 72—74°/30 mm., *Bu*^a, b.p. 105—107°/30 mm., *β-chloroethyl*, b.p. 118—120°/40 mm. (from *β-chloroethyl sulphite*, b.p. 146—148°/45 mm.), and *Ph*, b.p. 131—134°/40 mm., *bromosulphites*. All are less stable than the corresponding chlorosulphites (A., 1933, 696), which they otherwise resemble in properties. J. W. B.

Identification of mercaptans with 1-chloro-2:4-dinitrobenzene. II. R. W. BOST, J. O. TURNER, and M. W. CONN (J. Amer. Chem. Soc., 1933, 55, 4956—4957).—The following are prepared as described previously (A., 1932, 719): (a) 2:4-(NO_2)₂C₆H₃SR, where R is *decyl*, m.p. 85° (all m.p. are corr.), *undecyl*, m.p. 90°, *lauryl*, m.p. 89°, *allyl*, m.p. 71·5°, *o-tolyl*, m.p. 101°, *m-tolyl*, m.p. 90·5°, *p-chlorophenyl*, m.p. 123°, *p-bromophenyl*, m.p. 142°, $\alpha\text{-C}_{10}\text{H}_7$, m.p. 176°, $\beta\text{-C}_{10}\text{H}_7$, m.p. 145°, *cyclohexyl*, m.p. 148°, and *β-hydroxyethyl*, m.p. 100·5°; (b) $\alpha\beta\text{-di-2:4-dinitrophenylthiolethane}$, m.p. 248°; $\alpha\beta$ -, m.p. 226°, and $\alpha\gamma$ -, m.p. 194°, *-di-2:4-dinitrophenylthiolpropanes*; $\alpha\delta\text{-di-2:4-dinitrophenylthiolbutane}$, m.p. 176°; $\alpha\epsilon\text{-di-2:4-dinitrophenylthiolpentane}$, m.p. 170°; $\alpha\zeta\text{-di-2:4-dinitrophenylthiohexane}$, m.p. 218°; (c) 2:4-(NO_2)₂C₆H₃SO₂R, where R is *decyl*, m.p. 93°, *undecyl*, m.p. 97°, *lauryl*, m.p. 101°, *cetyl*, m.p. 105°, *o-tolyl*, m.p. 155°, *m-tolyl*, m.p. 144·5°, *p-chlorophenyl*, m.p. 170°, *p-bromophenyl*, m.p. 190°, and *cyclohexyl*, m.p. 172°. H. B.

Thermal decomposition of propyl mercaptan.—See this vol., 151.

Basis for the physiological activity of -onium compounds. XV. **Sulphonium compounds.** R. R. RENSHAW and D. S. SEARLE (J. Amer. Chem. Soc., 1933, 55, 4951—4953).—Sulphides are condensed with the appropriate halide and $\text{HgBr}_2(\text{I}_2)$ in COMe_2 or EtOH and the resulting sulphonium halide mercurihalides converted into the stable sulphonium nitrates by treatment with solid AgNO_3 in COMe_2 and subsequent removal of Hg as HgS . The following are described: *dibenzylmethylsulphonium nitrate*, m.p. 79°, and iodide mercuri-iodide, m.p. 155°; *dibenzylcarbethoxymethylsulphonium nitrate*, m.p. 120°, bromide mercuribromide, and bromide mercuri-iodide, m.p. 120°; *diphenylmethylsulphonium nitrate*, m.p. 108°, and iodide mercuri-iodide, m.p. 95°; *dimethyl-β-phenoxyethylsulphonium nitrate*, m.p. 62—65°, and bromide mercuribromide, m.p. 70—71°; *diethyl-β-phenoxyethyl-*, m.p. 78°, and *dibenzylcarbethoxymethyl-*, m.p. 127°, *-sulphonium bromide mercuribromides*; *dipropylcarbethoxymethylsulphonium bromide*, m.p. 70°. H. B.

Dynamics of elimination of tert.-butyl from sulphonium compounds.—See this vol., 152.

Mixed sulphonic anhydrides. I. Preparation of acetosulphonic anhydrides. A. BARONI (Atti R. Accad. Lincei, 1933, [vi], 17, 1081—1086).—By the action of dry NaOAc or AgOAc on the corresponding sulphonyl chlorides, anhydrides of the follow-

ing acids are obtained (b.p./20 mm.): *acetomethanesulphonic*, b.p. 100°; *acetoethanesulphonic*, b.p. 115—117°; *acetobenzenesulphonic*, b.p. 160—161°; *acetotoluenesulphonic*, b.p. 186—188°. T. H. P.

Determination of alkyl hydrogen sulphates in dilute solutions. W. KLING and F. PÜSCHEL (Textilber., 1934, 15, 21—23).—Alkyl H sulphates and inorg. sulphates are pptd. together from their slightly acid solution by benzidine hydrochloride; after filtration, the benzidine alkyl sulphate is separated from the benzidine sulphate by extraction with hot EtOH and then determined with 0·01N-KOH using bromocresol as indicator. A. J. H.

Halogenation. V. Bromination and iodination of fatty acids. P. S. VARMA and V. T. S. MENON (J. Indian Chem. Soc., 1933, 10, 591—592).— $\alpha\text{-Br-}$ and $\alpha\text{-I-}$ derivatives are obtained when AcOH (or Ac_2O), EtCO_2H , $(\text{PrCO})_2\text{O}$, $\text{Pr}^\beta\text{CO}_2\text{H}$, and lauric, palmitic, and stearic acids are heated with conc. H_2SO_4 and KBr and I , respectively; the higher acids are dissolved in CCl_4 . The yields are poor with the lower acids; those from AcOH (or Ac_2O) are improved slightly by replacing the H_2SO_4 with a mixture of fuming HNO_3 and nitrosulphonic acid (from HNO_3 and SO_2). H. B.

Determination of acetic anhydride. E. BERL and H. TÜRCK (Z. anal. Chem., 1933, 95, 143—152).— Ac_2O is determined calorimetrically by measurement of the heat of hydration of a 10-c.c. sample by 200 c.c. of 15% AcOH containing 7% of HCl as catalyst, contained in a Dewar vessel. For the analysis of acetylation mixtures of Ac_2O and H_2SO_4 , Ac_2SO_4 in a portion is converted into sulphoacetic acid by heating at 60°. The difference in the temp. rise produced by this and an untreated sample is a measure of the H_2SO_4 content. J. S. A.

Catalytic reduction of trifluoroacetic anhydride and trifluoroethyl alcohol. F. SWARTS (Compt. rend., 1933, 197, 1261—1264).—With H_2 at 20—40°/45—50 atm. and Pt-black (CF_3CO)₂O (alone or in Bu_2O solution) affords $\beta\beta\beta\text{-trifluoroethyl trifluoroacetate}$ (I), b.p. 55·0°/760 mm., m.p. —65·5° (main product), $\beta\beta\beta\text{-trifluoroethyl alcohol}$ (II), b.p. 74·05°, m.p. —43·5° (*Ac* derivative, b.p. 77·85°, with AcCl), $\text{CF}_3\text{CO}_2\text{H}$ (III), and $\alpha\alpha\alpha\text{-trifluoroethane}$ (IV), b.p. —46·8°, f.p. —107°: (III) is separated from (II) only as its azeotropic mixture, b.p. 144° [26·3% of (III)], with Bu_2O . With $\text{CrO}_3\text{-H}_2\text{SO}_4$ oxidation of (II) is slow, giving (III) but no aldehyde. With PBr_5 (II) affords $\beta\text{-bromo-}\alpha\alpha\alpha\text{-trifluoroethane}$, b.p. 26·5°, and with H_2SO_4 (followed by BaCO_3) *Ba trifluoroethyl sulphate*, + H_2O , is obtained. (I) is readily hydrolysed to (II) and (III) by cold H_2O . With Cl_2 in sunlight (IV) gives $\beta\beta\beta\text{-trichloro-}\alpha\alpha\alpha\text{-trifluoroethane}$, b.p. 46°, f.p. 13°. J. W. B.

Odour and constitution of some esters of heptonic and δ -methylhexoic acids. B. ROTHSTEIN (Bull. Soc. chim., 1933, [iv], 53, 1106—1107).—The following *n-heptoates* are described: *CH₂Ph*, b.p. 157°/14·5 mm., *CH₂Ph·CH₂*, b.p. 167°/14·5 mm., *phenylpropyl*, b.p. 180°/15 mm., *hydratropyl*, b.p. 172°/15 mm., *geranyl*, b.p. 171°/15 mm., and *terpynyl*, b.p. 170°/15 mm. The corresponding $\delta\text{-methylheptoates}$

have b.p. 160°/18 mm., 167°/17 mm., 180°/18 mm., 172°/18 mm., 172°/17 mm., and 170°/18 mm., respectively. The odours of the esters are similar to, but more fatty and feebler than, those of the alcohols.

R. S. C.

Reactions of castor oil with citric acid and phthalic anhydride. R. ODA (J. Soc. Chem. Ind. Japan, 1933, 36, 623—625B).—Castor oil and citric acid (I) at 150—170° or *o*-C₆H₄(CO)₂O at 190—245° in CO₂ gives multimol. products. Reaction with (I), but not with CH₂Cl·CO₂H, proceeds better at 20—40 mm.

R. S. C.

Phenylmethylhydrazones of glyoxylic acid and its methyl ester. M. BUSCH and W. RENNER (Ber., 1933, 66, [B], 1770—1771).—The compounds described by Meyer (A., 1904, i, 970) as the phenylmethylhydrazone and *p*-nitrophenylhydrazone of Me glyoxylate are derivatives of glyoxylic acid.

H. W.

Reactions and reagents for the identification of organic compounds. II. E. EEGRIWE (Z. anal. Chem. 1933, 95, 323—327; cf. A., 1932, 931).—Colour and fluorescence reactions for the detection of glyceric, lactic, pyruvic, and tartaric acids are given, and the behaviour of certain other OH- and keto-acids is recorded.

J. S. A.

Alkylation of enolates. II. F. ADICKES (Ber., 1933, 66, [B], 1984).—The observations of Wanag (this vol., 77) confirm the author's view (A., 1933, 697) that *C*-alkylation does not necessarily occur through the *O*-ether.

H. W.

Polymerisation and ring formation. XIX. Many-membered cyclic anhydrides. XX. Many-membered cyclic esters. XXI. Physical properties of macrocyclic esters and anhydrides. Synthetic musks. XXII. Stereochemistry and mechanism in the formation and stability of large rings. J. W. HILL and W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, 55, 5023—5031, 5031—5039, 5039—5043, 5043—5052).—XIX. When (CH₂)_n(CO₂H)₂ (*n*=4—12 and 16) are heated with Ac₂O, α -anhydrides (I) are obtained. These are linear polymerides (*M*=3000—5000) of the type $\text{—O—CO—[CH}_2\text{]}_n\text{—CO—O—CO—[CH}_2\text{]}_n\text{—CO—O—CO—[CH}_2\text{]}_n\text{—CO—}$; with NH₂Ph, they give the anilide, anilic acid, and original acid in the ratio 1:2:1. (I) heated in a mol. still (cf. A., 1932, 601) give volatile β -anhydrides (II) and the more complex ω -anhydrides (III). (II) are cyclic mono- or di-meric anhydrides which when kept, or heated above the m.p., pass into γ -anhydrides (probably large rings) which resemble (I). The monomeric (II) are usually liquids or low-melting solids which polymerise very readily; with NH₂Ph, the anilic acid is the sole product. The dimeric (II) polymerise instantly above their m.p.; with NH₂Ph, they give the same products (in the same ratio) as (I). (III) are tough, opaque solids which can be drawn into pliable, highly-oriented fibres; they are depolymerised by heating in a mol. still to (II). The following derivatives are described: *pimelic α -anhydride*, m.p. 53—55°, and *mono-*, m.p. 108—109°, and *di-*, m.p. 155—156°, *-anilides*; *suberic α -anhydride*, m.p. 65—66°, *β -anhydride* (dimeric), m.p. 55—57°, and *mono-*, m.p. 128—129°, and *di-*, m.p. 186—187°,

-anilides; *azelaic α -anhydride*, m.p. 53—53.5°, and *mono-*, m.p. 107—108°, and *di-*, m.p. 186—187°, *-anilides*; *nonamethylene- α -dicarboxylic α -anhydride*, m.p. 69—70°, and *mono-*, m.p. 112.5—113°, and *di-*, m.p. 160—161°, *-anilides*; *decamethylene- α -dicarboxylic α -anhydride*, m.p. 86—87°, *β -anhydride* (dimeric), m.p. 76—78°, and *mono-*, m.p. 123°, and *di-*, m.p. 170—171°, *-anilides*; *undecamethylene- α -dicarboxylic α -anhydride*, m.p. 76—78°, and *mono-*, m.p. 118.5—119.5°, and *di-*, m.p. 160—161°, *-anilides*; *dodecamethylene- α -dicarboxylic α -anhydride*, m.p. 89—91°, and *mono-*, m.p. 124—125°, and *di-*, m.p. 169.5—170°, *-anilides*; *hexadecamethylene- α -dicarboxylic α -anhydride*, m.p. 94—95°, and *mono-*, m.p. 128—129°, and *di-*, m.p. 162—163°, *-anilides*.

XX. (cf. A., 1930, 319). Polymeric polymethylene carbonates are prepared from (CH₂)_n(OH)₂ (*n*=5, 7—9, 11—14, and 18), Bu₂CO₃, and a little Na at 170—220°; the crude esters are then depolymerised to the monomeric and/or dimeric esters by heating in a vac. Other polymeric esters are similarly depolymerised. The following are described: (a) monomeric esters: *octa-*, b.p. 74—76°/0.5 mm., m.p. 21.5—23°, *nona-*, b.p. 63—64°/0.1 mm., m.p. 34—35°, *deca-* (I), b.p. 92—93°/1 mm., m.p. 10—11°, *undeca-*, b.p. 104.5°/7 mm., m.p. 40—41°, *dodeca-*, b.p. 118—119°/3 mm., m.p. 11—12°, *trideca-*, b.p. 149—150°/4.5 mm., m.p. 23—24.5°, *tetradeca-*, b.p. 144—146°/2 mm., m.p. 21—22°, and *octadeca-*, b.p. 165—169°/1 mm., m.p. 36—37°, *-methylene carbonates*; *tetraethylene carbonate*, b.p. 128—130°/1 mm., m.p. 42—44°; *deca-*, b.p. 125—126°/0.2 mm., and *undeca-*, b.p. 120—123°/0.5 mm., m.p. 23—24.5°, *-methylene oxalates*; *decamethylene malonate*, b.p. 117—118°/0.5 mm.; *ethylene sebacate*, m.p. 40—41°, and *nonamethylene- α -dicarboxylate*, m.p. 35°; (b) dimeric esters: *penta-*, m.p. 117—118°, *hexa-*, m.p. 128—129°, *hepta-*, m.p. 97—98°, *octa-*, m.p. 116—117°, *nona-*, m.p. 95—95.5°, *deca-*, m.p. 105—106°, *undeca-*, m.p. 97—97.5°, and *dodeca-*, m.p. 93—95°, *-methylene carbonates*; *decamethylene succinate*, m.p. 108—109°; *ethylene sebacate*, m.p. 80—81°, *nonamethylene- α -dicarboxylate*, m.p. 143°, *decamethylene- α -dicarboxylate*, m.p. 95—96°, *undecamethylene- α -dicarboxylate*, m.p. 145—146°, and *dodecamethylene- α -dicarboxylate*, m.p. 102—103°; *trimethylene sebacate*, m.p. 108—110°; *self ester*, m.p. 83—84°, of ξ -hydroxypentadecic acid. Δ^1 -*Decen- α -ol*, b.p. 85—86°/2 mm. (*phenylcarbamate*, m.p. 49—50°), has been obtained as a by-product during the prep. of (I). Macrocyclic (*i.e.*, rings of > 7 atoms) esters do not polymerise spontaneously; they polymerise when heated at 200° in presence of a little K₂CO₃.

XXI. The odours of the above monomeric cyclic anhydrides and esters (I) resemble those of ketones and lactones of the same ring size; those containing 14—19 atoms in the ring thus possess musk-like odours. The mol. refractions of (I) show negative exaltation. The m.p. of the monomeric polymethylene carbonates alternate.

XXII. Th hexadecamethylene- α - π -dicarboxylate heated in *s*-dixylylthane at 325° for 2 hr. gives a *polyketone*, probably CO₂H·[(CH₂)₁₆·CO]₇·OH, m.p. 126—128° (*Na* salt), which passes at 300—305° in a mol. still into *cycloheptadecanone*. The synthesis of large

ring ketones is considered to involve the intermediate formation of a linear polyketone which then decomposes; the changes are similar to those found for esters and anhydrides (above). The analogies and differences in the three series can be explained by the nature of the reactions involved and the steric effects of peripheral atoms. Rings of > 5 atoms are not regarded as entirely strainless; the probable nature of the strain in large rings is discussed.

H. B.

Hydrogenolysis of succinates and glutarates. B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1933, 55, 4939—4946).—Reduction (H_2 at 300 atm.; Cu-Cr oxide; 250°) of Et succinate gives $(\cdot CH_2 \cdot CH_2 \cdot OH)_2$ (74%); the yield is lowered by reducing the pressure of H_2 or the ratio catalyst: ester and butyrolactone (I); Et γ -hydroxybutyrate, $PrCO_2H$, and (probably) tetrahydrofuran (II) can be isolated also. $(\cdot CH_2 \cdot CO)_2O$ gives (I) (31%), (II) (?), $PrCO_2H$, and $(\cdot CH_2 \cdot CO_2H)_2$; Et α -methylsuccinate affords β -methylbutane- $\alpha\delta$ -diol (72%) and isoamyl alcohol (at 200—300 atm.; at 150 atm., the diol and α -methylbutyrolactone result); Et α -isopropylsuccinate yields β -isopropylbutane- $\alpha\delta$ -diol, b.p. 119—122°/3 mm., $\gamma\delta$ -dimethylamyl alcohol, b.p. 159—162°, isohexyl alcohol (main product using 100 atm. of H_2), and a mixture, b.p. 123—137°, of alcohols; Et α -acetyl- α -butylsuccinate, b.p. 136—138°/4 mm., furnishes β -*n*-butylbutane- $\alpha\delta$ -diol, b.p. 135—137°/3 mm.; Et α -acetyl- α -benzylsuccinate gives γ -benzylbutyl alcohol, b.p. 103—107°/3 mm., and β -benzylbutane- $\alpha\delta$ -diol, b.p. 162—165°/3 mm.; Et $\alpha\gamma$ -dicarbethoxyglutarate affords pentane- $\alpha\alpha$ -diol; Et $\alpha\gamma$ -dicarbethoxy- β -methylglutarate yields γ -methylpentane- $\alpha\alpha$ -diol, b.p. 134—137°/6 mm.; Et $\alpha\gamma$ -dicarbethoxy- β -phenylglutarate furnishes γ -phenylpentane- $\alpha\alpha$ -diol, b.p. 174—176°/5 mm., γ -phenylpropyl alcohol, and a little γ -phenyl- $\beta\delta$ -dimethylpentane- $\alpha\alpha$ -diol, m.p. 115—116°; Et $\alpha\gamma$ -dicarbethoxy- β -propylglutarate gives γ -propylpentane- $\alpha\alpha$ -diol, b.p. 134—136°/10 mm., *n*-hexyl alcohol, and lower alcohols; Et $\alpha\gamma$ -diacetyl- β -phenylglutarate affords γ -phenyl- $\beta\delta$ -diethylpentane- $\alpha\alpha$ -diol, b.p. 174—179°/2—3 mm. (diacetate); Et dodecamethylene- $\alpha\mu$ -dicarboxylate yields tetradecane- $\alpha\alpha$ -diol; Et α -keto- β -methylsuccinate (in EtOH at 200°) gives Et α -hydroxy- β -methylsuccinate, b.p. 109—113°/5 mm., which is reduced further to γ -methylbutane- $\alpha\beta$ -diol, β -methylbutane- $\alpha\delta$ -diol, and lower alcohols; Et α -acetyl- α -ethyladipate affords β -ethylpentane- $\alpha\alpha$ -diol and alcohols, b.p. 45—90°/4 mm.; Et $\alpha\gamma$ -diacetyl- β -phenylglutarate yields Et $\alpha\alpha$ -dihydroxy- δ -phenylheptane- $\gamma\epsilon$ -dicarboxylate, m.p. 162—163°; Et α -phenylsuccinate furnishes γ -phenylbutyl alcohol and β -phenylbutane- $\alpha\delta$ -diol, b.p. 162—165°/7 mm.; Et α -acetylsuccinate gives a lactone, $C_6H_{10}O_2$, b.p. 85—87°/5 mm., glycols, and alcohols; Et α -phenylglutarate affords γ -phenylpentane- $\alpha\alpha$ -diol, b.p. 190—192°/14 mm.; Et α -acetylglutarate yields an inseparable mixture of pentane- $\alpha\alpha$ -diol and its β -Et derivative. The majority of the above reductions are carried out at 250° under 200—300 atm. of H_2 , using 1 pt. of catalyst to 10 pts. of ester. H_2O and acids diminish the activity of the catalyst. The

effects of various groups on the position of C·C (and C·O) fission are discussed briefly.

H. B.

Derivatives of methoxymalonic acid. J. PRYDE and R. T. WILLIAMS (J.C.S., 1933, 1627—1628).— $OMe \cdot CH_2 \cdot CO_2Me$, $Me_2C_2O_4$, and Na yield *Me* α -keto- β -methoxysuccinate, b.p. 110—120°/1 mm., which on distillation gives *Me* methoxymalonate, b.p. 215°/745.5 mm. [*methoxy-malondiamide*, m.p. 203—204° (slight decomp.), and *-malonomethylamide*, m.p. 115°].

F. R. S.

Preparation of *l*-tartaric acid by oxidation of *d*-gulonolactone. J. K. DALE and W. F. RICE, jun. (J. Amer. Chem. Soc., 1933, 55, 4984—4985).—Oxidation of *d*-gulonolactone with conc. HNO_3 containing a little Na metavanadate gives *l*-tartaric (13.6% yield), *l*-saccharic, and oxalic acids; details are given for their isolation.

H. B.

Preparation of glycuronic acid from borneol-glycuronic acid. K. T. SWARTZ and C. O. MILLER (J. Biol. Chem., 1933, 103, 651—655).—Hydrolysis of borneolglycuronic acid by Quick's method (A., 1927, 990) is incomplete, but is almost quant. (69% yield of glycuronic acid) if borneol is removed by steam-distillation during hydrolysis with 0.2*N*- H_2SO_4 ; *bornyl borneolglycuronate*, m.p. 96—97°, is obtained as a by-product in either method.

J. W. B.

Preparation of pure thiolacetic acid. F. SCHÜTZ (Angew. Chem., 1933, 46, 780—781).—Use of freshly prepared, pure NaHS gives a 99% yield of $SH \cdot CH_2 \cdot CO_2H$.

R. S. C.

Condensation of sulphamide, dimethylsulphamide, and aniline-*p*-sulphonamide with formaldehyde. F. C. WOOD and A. E. BATTYE (J.S.C.I., 1933, 52, 346—349T).— $SO(NH_2)_2$ (best prepared by Ephraim and Gurewitsch's method, A., 1910, ii, 198) condenses readily with CH_2O (with production of acidity necessitating the presence of a buffer) to form a resin (I) from which clear, hard, light-stable films, sol. in boiling H_2O , may be obtained. Boiling with H_2O converts (I), with production of acidity, into an amorphous substance, which appears to be a derivative of $SO_2[N(CH_2 \cdot OH)_2]_2$. $NH_2 \cdot SO_2 \cdot NMe_2$ condenses with CH_2O (a few drops of HCl in the cold) to give a H_2O -insol., cryst. substance, darkens 175° , m.p. 185° (decomp.), probably $R \cdot N \langle \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} \rangle O$ or $R \cdot N \langle \begin{smallmatrix} CH_2 \cdot O \cdot CH_2 \\ CH_2 \cdot O \cdot CH_2 \end{smallmatrix} \rangle NR$ ($R = SO_2 \cdot NMe_2$), whereas *p*- $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ gives a resin, analytical data for which correspond with a mixture of $CH_2 \cdot N \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ and $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot OH$.

J. W. B.

Highly-polymerized compounds. LXXXIV. Constitution of polyoxymethylenes. H. STAUDINGER and W. KERN (Ber., 1933, 66, [B], 1863—1866).—A reply to Walker (A., 1933, 937).

H. W.

Glutaconaldehyde; acetals, oxime, and its ring closure to pyridine 1-oxide. P. BAUMGARTEN, R. MERLÄNDER, and J. OLSHAUSEN (Ber., 1933, 66, [B], 1802—1809).—Treatment of the Na compound (I) of *enol*-glutaconaldehyde in anhyd. MeOH with HCl-MeOH at room temp. and of the product with aq. $CaCl_2$ leads to *glutacondialdehyde di-*

methylacetal (II) ($\delta\delta$ -dimethoxy- Δ^{β} -butenal), b.p. 99—103°/16 mm., which could not be acylated, is moderately stable towards dil. acid, adds 2 Br, and is hydrolysed by aq. NaOH to (I); the *p*-nitrophenylhydrazone (III) has m.p. 160—161°. Treatment of (I) with HCl-MeOH and of the product with conc. aq. K_2CO_3 affords $\alpha\alpha\delta$ -trimethoxy- $\Delta^{\alpha\gamma}$ -pentadiene (δ -methoxy- $\Delta^{\alpha\gamma}$ -butadien- α -al dimethylacetal), b.p. 108—112°/18 mm., which rapidly decolorises Br in CCl_4 , gives (III) with *p*-nitrophenylhydrazine, and is hydrolysed by 0.1*N*-HCl at room temp. to (II) and *glutacondialdehyde didimethylacetal* ($\alpha\alpha\epsilon\epsilon$ -tetramethoxy- Δ^{β} -pentene), b.p. 115—118°/18 mm., convertible into (III) and hydrolysed by 0.1*N*-HCl to (II); it absorbs cold Br slowly. (I) is transformed by NH_2OH and NH_2OH, HCl in MeOH into *glutacondialdehydedioxime* (IV), m.p. 88°, with a little pyridine 1-oxide (IV) (picrate, m.p. 179°); (V) is formed from (IV) by treatment with boiling EtOH-HCl or directly from (I) by means of HCl and NH_2OH, HCl in MeOH. (V) is also produced from *glutacondialdehydeaminoxime* in boiling $PhNO_2$. δ -Acetoxy-, m.p. 75.5°; and δ -benzoyloxy- (VI), m.p. 118—119°, - $\Delta^{\alpha\gamma}$ -butadienal have now been obtained colourless. (VI) affords a phenylhydrazone, *o*-nitrophenylhydrazone, m.p. 183—184°, and an *azine*, m.p. 187°.

H. W.

Determination of mol. wt. of carbohydrates.

M. ULMANN and K. HESS (Ber., 1933, 66, [B], 1975—1977).—Irregularities in the behaviour of sucrose (I) in boiling H_2O (cf. Pringsheim *et al.*, A., 1933, 1144), do not occur if (I) has not been dried at too high a temp. and if it is not introduced while H_2O is boiling briskly. Desiccation over $P_2O_5/vac.$ at room temp. or by means of boiling $CHCl_3$ is adequate. (I) if dried by boiling xylene softens, but does not suffer chemical change. In boiling H_2O it causes no elevation of the b.p., but after cooling to room temp. and again heating, a normal elevation is observed. Pringsheim's objection to the use of isothermal distillation for determining the mol. wt. of Schardinger's α -dextrin is groundless.

H. W.

d-Xyloketose. O. T. SCHMIDT and R. TREIBER (Ber., 1933, 66, [B], 1765—1769).—*d*-Xylose (I) is boiled with anhyd. C_5H_5N and the resultant mixture is crystallised from 96% EtOH, whereby the bulk of unchanged (I) is removed. Treatment of the residue with *p*- $C_6H_4Br \cdot NH \cdot NH_2$ affords *d*-xyloketose-*p*-bromophenylhydrazone, m.p. 128—129°, $[\alpha]_D^{20} + 23.7^\circ \pm 0.3^\circ$ to $-31.2^\circ \pm 0.3^\circ$ in C_5H_5N in 7 days, transformed by $PhCHO$ into *d*-xyloketose (II), $[\alpha]_D^{20} - 33.2^\circ \pm 0.4^\circ$ (whence *d*-xylosephenylosazone). (II) appears to be the enantiomorphous form of the ketopentose of Levene *et al.* (A., 1914, i, 1027). It is strongly reducing and is affected by KOI (Willstätter-Schudel). It does not give a violet-red colour with 18% HCl and phloroglucinol.

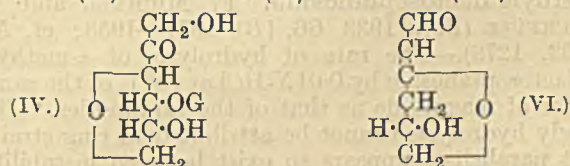
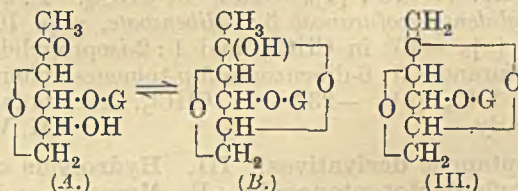
H. W.

Mechanism of carbohydrate oxidation. XVI. Action of aqueous solutions of potassium hydroxide on *l*-rhamnose. G. F. NADEAU, M. R. NEWLIN, and W. L. EVANS (J. Amer. Chem. Soc., 1933, 55, 4957—4963).—The action of aq. KOH on *l*-rhamnose is studied by the method previously described (cf. A.,

1930, 1410) for other sugars at 25°, 50°, and 75°. The amount of lactic acid produced increases with rise in the concn. of KOH (and is max. at about 2*N* at 50° and 75°); more is formed at 50° than at 75° and the yields are intermediate between those from arabinose (*loc. cit.*) and glucose, mannose, and fructose (cf. A., 1928, 1222). The effects of temp. and concn. of KOH on the amount of AcCHO produced are also studied; max. amounts are formed at 50° using approx. 0.5*N*-KOH.

H. B.

Unsaturated reduction products of sugars. XIX. *iso*Glucal, *isolactal*, and *protoglucal*. M. BERGMANN, L. ZERVAS, and J. ENGLER (Annalen, 1933, 508, 25—38).—*iso*Lactal (I), m.p. 218° (corr., decomp., darkens at 193°), $[\alpha]_D^{20} + 88.9^\circ$ in H_2O (modified prep. given; cf. A., 1924, i, 265) [*phenylbenzylhydrazone*, m.p. 145—147° (corr.)], is a 4-galactosido-*isog*lucal, since it is hydrolysed by kefir extract to galactose and *isog*lucal. The presence of the $\cdot CH_2 \cdot CO$ group is indicated by the amount of NaOI used in oxidation and the non-formation of a lactolide with $CH(OEt)_3$. Acetylation ($Ac_2O \cdot C_5H_5N$) of (I) gives a *penta*-acetate, m.p. 166—167° (corr.) [and not a hexa-acetate as stated previously (*loc. cit.*)], hydrolysed (boiling H_2O) to a *tetra*-acetate (II), m.p. 138—139° (corr.), $[\alpha]_D^{20} + 72.6^\circ$ in $C_2H_2Cl_4$. (II) and PCl_5 in $CHCl_3$ at -15° afford *isolactal* chlorohydrin tetraacetate, which with Ag_2CO_3 and EtOH gives an ethyl-lactolide tetra-acetate, m.p. 160° (softens at 140°), and with C_5H_5N at 100° yields the *tetra*-acetate, m.p. 184—185° (sinters at 182°), $[\alpha]_D^{20} + 141.3^\circ$ in $C_2H_2Cl_4$, of *anhydroisolactal* (III), m.p. 243—244° (corr.). The structures (A) \rightleftharpoons (B) ($G = C_6H_{11}O_5$) are assigned to (I). (III) in H_2O and BzO_2H in EtOAc give galactosidoanhydrofructose (IV) [*osazone*, m.p. 184—186° (corr.)], which is not oxidised by alkaline NaOI. *iso*-



Glucal (V) (*loc. cit.*) is formulated as (A, with $G = H$).

Protoglucal (VI), b.p. 104—106°/0.4 mm., $[\alpha]_D^{20} + 35^\circ$ (corr.), is formed (in small amount) with (V) when ψ -glucal diacetate is hydrolysed [$Ba(OH)_2$]. (VI) is unsaturated (Br; $KMnO_4$), reduces Fehling's solution in the cold, does not give an osazone, consumes 2 I and 1 mol. of BzO_2H , is oxidised (O_3) to $(CHO)_2$, and absorbs 4 H on reduction (H_2 , Pd-black, AcOH) to give a non-reducing product.

H. B.

Carbohydrates. XVIII. Benzoates of glucofuranose. P. BRIGL and H. GRÜNER (Ber., 1933, 66, [B], 1977—1983; cf. A., 1933, 810).—The tribenzoate (I) (*loc. cit.*) is converted by further treatment with

BzCl and C_5H_5N in $CHCl_3$ into glucofuranose penta-benzoate, m.p. 143—144°, $[\alpha]_D -55.1^\circ$ in $CHCl_3$, and hence is a glucofuranose. The absence of Bz from position 1 follows from the prep. (unpublished) of a *hydrazone*. The occurrence of a 2 : 3 : 6-tribenzoate is very improbable, since thfs would probably give a pyranose derivative on energetic treatment with $Ac_2O-ZnCl_2$ or $AcOH-HBr$. The diacetate tribenzoate obtained from (I) after successive treatment with these reagents and replacement of Br by Ac is syrupy, and not identical with α -, m.p. 162—163°, $[\alpha]_D +140.6^\circ$ in $CHCl_3$, or β -, m.p. 202°, $[\alpha]_D +111.9^\circ$ in $CHCl_3$, *-glucopyranose* 1 : 4-diacetate 2 : 3 : 6-tribenzoate. Hence (I) is *glucofuranose* 2 : 5 : 6-tribenzoate. Treatment of isopropylidene-glucose 3-acetate 5 : 6-dibenzoate with $AcOH-H_2O$ -conc. HCl at 50° leads to *glucofuranose* 5 : 6-dibenzoate (II), m.p. 145—146° after softening at 143°, $[\alpha]_D -19.9^\circ$ (equilibrium val.) in EtOH, transformed by BzCl and C_5H_5N in $CHCl_3$ into α -glucofuranose pentabenzoate, m.p. 119—120°, $[\alpha]_D +60.3^\circ$ in $CHCl_3$. With Ac_2O and C_5H_5N followed by $ZnCl_2$ and Ac_2O (II) gives β -*glucofuranose* 1 : 2 : 3-triacetate 5 : 6-dibenzoate, m.p. 97—98°, $[\alpha]_D -41.6^\circ$ in $CHCl_3$, also obtained from isopropylidene-glucose 3-acetate 5 : 6-dibenzoate. $COMe_2$ containing 1% of HCl transforms (II) into 1 : 2-isopropylidene-glucofuranose 5 : 6-dibenzoate, m.p. 118°, $[\alpha]_D +41.4^\circ$ in $CHCl_3$, formed as by-product during the prep. of glucose dibenzoate according to Fischer and Noth and differing from Ohle's product (A., 1924, i, 497). Syrupy 1 : 2-isopropylidene-glucofuranose 3-benzoate (III), $[\alpha]_D -26.5^\circ$ in EtOH, is obtained by partial hydrolysis of the diisopropylidene derivative, into which it is smoothly re-converted by $COMe_2$ and $CuSO_4$. (III), Ac_2O , and C_5H_5N afford 1 : 2-isopropylidene-glucofuranose 5 : 6-diacetate 3-benzoate, m.p. 77—78°, $[\alpha]_D -26.7^\circ$ in $CHCl_3$. 1 : 2-isopropylidene-glucofuranose 3 : 6-dibenzoate, m.p. 108—109°, $[\alpha]_D -46^\circ$ in $CHCl_3$, and 1 : 2-isopropylidene-glucofuranose 3 : 6-dibenzoate 5-*p*-toluenesulphonate, m.p. 143°, $[\alpha]_D -23.8^\circ$ in $CHCl_3$, are obtained similarly. H. W.

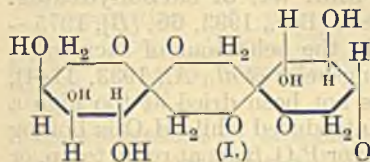
Septanose derivatives. III. Hydrolysis of α -methylgalactoseptanoside. F. MICHEEL and F. SUCKFÜLL (Ber., 1933, 66, [B], 1957—1958; cf. A., 1933, 1278).—The rate of hydrolysis of α -methylgalactoseptanoside by 0.01*N*-HCl at 95° is of the same order of magnitude as that of the furanosides. The ready hydrolysis cannot be attributed to ring strain, but parallelism appears to exist between instability of the free sugar and ready hydrolysis of its glucosides. Further purification of galactoseptanose penta-acetates leads to the data, m.p. 128.5°, $[\alpha]_D -10.8^\circ$, and m.p. 112°, $[\alpha]_D -103^\circ$, for the α - and β -compounds, respectively. H. W.

Oxidation of fructose by hypiodite. K. BAILEY and R. H. HOPKINS (Biochem. J., 1933, 27, 1965—1974).—The rate of oxidation of fructose (I) by NaOI or $Ba(OI)_2$ (cf. A., 1918, ii, 337) increases with rise of temp., whilst the extent over a range of 1—35° is min. at 15°. Presence of excess of alkali at 17—37° (but not at 1°) enolises (I) and permits a far more extensive oxidation (II). By progressive addition of small amounts of alkali, (II) is increased 4—5 times,

the (II) being independent of the concn. of (I). The products of (II) are *d*-erythronic and oxalic acids. The (II) of (I) in presence of limited amounts of alkali is possibly due to the keto- or the labile (2 : 5) form of (I). F. O. H.

Specific rotation and stability of (2 : 5)-fructose from the hydrolysis of sucrose by fructosaccharase. K. BAILEY and R. H. HOPKINS (Biochem. J., 1933, 27, 1957—1964).—Investigations of the progressive changes in $[\alpha]$ during the hydrolysis of sucrose by fructoinvertase (A., 1914, i, 339) indicate that at pH 4.6—6.1 fructofuranose (I) has $[\alpha]^{17}$ +15° to 17° in H_2O . The change of (I) into equilibrated fructose is unimol., the velocity coeff. $k_{fr}^{min.}$ being 0.3. A scheme for the mechanism of the hydrolysis of sucrose is advanced. F. O. H.

Fructose anhydrides. XIII. Synthesis of a *n*-difructose anhydride from fructose. H. H. SCHLUBACH and C. BEHRE (Annalen, 1933, 508, 16—24).—Anhyd. fructose is treated with dry liquid HCl at 14° (sealed tube), the product extracted with EtOH, and the insol. *difructose anhydride* (I), decomp. 250—270° (brown at 150°), $[\alpha]_D^{19} -43.9^\circ$ in H_2O (*hexaacetate*, m.p. 171—173°, $[\alpha]_D^{20} -59.1^\circ$ in $CHCl_3$), crystallised from H_2O . (I) is probably identical with the anhydride described by Pictet and Chavan (A., 1926, 1126). (I) does not reduce Fehling's solution and is hydrolysed only slowly by $N-H_2SO_4$ at 60°. Methylation



(Me_2SO_4 and 35% NaOH followed by MeI and Ag_2O) gives a Me_6 derivative, m.p. 143—145°, $[\alpha]_D^{20} -46.5^\circ$ in $CHCl_3$, hydrolysed (1.5*N*- H_2SO_4 at 80°) to 3 : 4 : 5-trimethylfructose, b.p. 117°/0.4 mm., $[\alpha]_D^{20} -73.5^\circ$ in H_2O (*osazone*). H. B.

Micro-determination of lactose. J. M. CLAVERA and F. M. MARTIN (Bull. Soc. chim., 1933, [iv], 53, 1103).—Priority is claimed (cf. B., 1930, 1129; A., 1933, 732). R. S. C.

Sugars containing sulphur and their derivatives. XVIII. β -Diglucosyl sulfoxysulphide. W. SCHNEIDER and A. BANSÁ (Ber., 1933, 66, [B], 1973—1975; cf. A., 1931, 939).—The compound, m.p. 169°, $[\alpha]_D^{20} -41.91^\circ$ in $C_2H_2Cl_4$, obtained by the action of KNO_2 and AcOH on *d*-glucosido-*S*-thiuronium bromide tetra-acetate (*loc. cit.*), from β -glucothiose tetra-acetate, $NaNO_2$, and AcOH, or from β -diglucosyl disulphide octa-acetate (I), AcOH, and H_2O_2 is identified as β -*diglucosyl sulfoxysulphide octa-acetate*, $C_6H_7O_5Ac_4 \cdot SO \cdot S \cdot C_6H_7O_5Ac_4$. Hydrolysis (Zemplén) and subsequent treatment with $Ac_2O-C_5H_5N$ affords (I). H. W.

Synthesis of glycosides. X. Synthesis of primeverin. E. T. JONES and A. ROBERTSON (J.C.S., 1933, 1618—1620).—The *O*-tetra-acetyl- β -glucoside of Me 4-methoxysalicylate, m.p. 138—139°, $[\alpha]_{561}^{20} -66.0^\circ$, is obtained from Me 4-methoxysalicylate, Ag_2O , and *O*-tetra-acetyl- α -glucosidyl bromide, and with $MeOH-NH_3$ forms the β -glucoside (+0.5 H_2O), m.p. 124—126°, $[\alpha]_{561}^{21} -82.36^\circ$. The

glucoside and $\text{C}_6\text{H}_5\text{N}$ give the 6-*O*-triphenylmethyl- β -glucoside, m.p. 120° , $[\alpha]_{5461}^{21} -36.72^\circ$, the triacetate, m.p. $168-169^\circ$, $[\alpha]_{5461}^{21} -103.41^\circ$, of which with $\text{HBr}\cdot\text{AcOH}$ yields the 2:3:4-*O*-triacetyl- β -glucoside, m.p. 136° , $[\alpha]_{5461}^{21} -40.82^\circ$. Condensation of (I) with *O*-triacetyl- α -xyloside bromide gives a product, deacetylated ($\text{MeOH}\cdot\text{NH}_3$) to primeverin (the β -primeveroside of Me 4-methoxysalicylate; hexa-acetate, m.p. 125°), identical with the natural product. All rotations are measured in COMe_2 .

F. R. S.

Glucosides. VII. Glucoside of *Sanguisorba officinalis*. S. ABE and M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 44-48).—Extraction of the root with MeOH affords sanguisorbin, $\text{C}_{45}\text{H}_{82}\text{O}_{18}$ (?), m.p. 233° [lit., $272.5-274.5^\circ$ (decomp.)], hydrolysed by warm 5% $\text{MeOH}\cdot\text{HCl}$ to sanguisorbigenin (I), m.p. $266-269^\circ$ [*Ac* derivative, m.p. $313-316^\circ$ [lit., $272-275^\circ$ (decomp.)], hydrolysed by $\text{MeOH}\cdot\text{KOH}$ to (I)]. (I) with CH_2N_2 in Et_2O affords the *Me* ester (II), m.p. $201-203^\circ$ [*Ac* derivative, m.p. $236-238^\circ$, hydrolysed by $\text{MeOH}\cdot\text{KOH}$ to (II)]. (I) at 280° during 20 min. loses CO_2 to give decarboxysanguisorbigenin, $\text{C}_{27}\text{H}_{41}\text{O}$, m.p. $197-199^\circ$ [*Ac* derivative + $1\text{H}_2\text{O}$, m.p. $180-181^\circ$].

J. L. D.

Reaction of starch with very dilute aqueous sodium hydroxide. M. SAMEC (Bull. Soc. Chim. Yougoslav., 1933, 4, 71-78).—The η_{inh} curve obtained on titration of amylopectin (I) with 0.01*N*- NaOH is of the same type as that obtained with H_3PO_4 . The viscosity varies irregularly with the η_{inh} , indicating that the action of alkali depends on neutralisation of H_3PO_4 combined with (I), and also on a modification in the structure of (I).

R. T.

Influence of a quaternary ammonium group on the hydrogen atoms of an adjacent methylene group. A. O. JACKSON and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 5000-5002).—Trimethylcarbethoxymethylammonium chloride (I), m.p. $166-167^\circ$ (lit. $143-144^\circ$), and bromide (II) are not ethylated by EtBr and $\text{EtOH}\cdot\text{NaOEt}$; (I) gives (II) and a small amount of a compound, m.p. $294-295^\circ$, also obtained from (II). The methobromide, m.p. $199-200^\circ$, of $\text{NMe}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ is prepared from bromocycanoacetamide, m.p. $176-177^\circ$, and NMe_3 ; it is converted by $\text{EtOH}\cdot\text{NaOEt}$ and EtBr into trimethylcarbamylmethylammonium bromide, m.p. $203-204^\circ$ (also prepared from $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NH}_2$ and NMe_3).

H. B.

Argentometric evaluation of hexamethylenetetramine. J. VON MIKÓ (Pharm. Zentr., 1933, 74, 642-643).—A 2% solution (5 c.c.) is shaken with 0.1*N*- AgNO_3 (45 c.c.) and rapidly filtered from the pptd. $2\text{C}_6\text{H}_{12}\text{N}_4\cdot 3\text{AgNO}_3$. The first 15 c.c. of filtrate are rejected and the next 25 c.c., after the addition of 5*N*- HNO_3 (10 c.c.), are titrated with 0.1*N*- KCNS .

E. H. S.

Preparation and quaternary ammonium decomposition of formocholine.—See this vol., 152.

Colorimetric determination of glucosamine and chondrosamine. L. A. ELSON and W. T. J. MORGAN (Biochem. J., 1933, 27, 1824-1828).—Glucosamine and chondrosamine are determined by

addition of a solution of CH_2Ac_2 in Na_2CO_3 , heating for 15 min. at 100° , cooling, and adding EtOH and Ehrlich's reagent. After 30 min. the colour is compared with a standard. The max. error was 5% within the range of 0.75-3.0 mg. The optimal concn. of HCl is 5%. The presence of glucose, galactose, fructose, arabinose, histidine, and tryptophan was without significant influence on the determination.

H. D.

Synthesis of peptide-like substances from amino-sugars and amino-acids. III. Acetylated glucopeptides. A. BERTHO and J. MAIER (Z. physiol. Chem., 1933, 222, 139-147; cf. A., 1932, 837, 1118).—Glucosamine tetra-acetate in CHCl_3 , when treated with $\text{C}_5\text{H}_5\text{N}$ and azidoacetyl chloride, gives (*N*-azidoacetyl)glucosamine tetra-acetate (I), m.p. 131° , $[\alpha]_{\text{D}}^{20} +6.1^\circ$ in CHCl_3 , which with PtO_2 and H_2 affords (*N*-glycyl)glucosamine tetra-acetate (II), m.p. $161-162^\circ$ (decomp.) [or a product, $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$, m.p. 188° (decomp.)]. With NH_3 in MeOH , (II) gives a non-cryst. product. The corresponding cryst. products obtained with alanylglucosamine tetra-acetate were dehydroalanyl-*N*-glucosamine anhydride, m.p. $254-258^\circ$, and alanyl-*N*-anhydroglucosamine anhydride, m.p. 198° . By the same method as (I) were prepared: *N*-(α -bromopropionylglycyl)glucosamine tetra-acetate (III), m.p. 162° , and *N*-(α -bromoisohexoylglycyl)glucosamine tetra-acetate (IV), m.p. $174-175^\circ$, *N*-(α -bromoisohexoylalanyl)glucosamine tetra-acetate, m.p. $169-170^\circ$, *N*-(α -azidopropionylalanyl)glucosamine tetra-acetate (V), m.p. 139° (decomp.). With PtO_2 and H_2 , (V) affords *N*-(dialanyl)glucosamine tetra-acetate, m.p. 212° (decomp.). With NH_3 in MeOH , (III) and (IV) give non-cryst. *N*-alanyl-glycyl- and -leucylglycyl-glucosamine, decomp. 132° , respectively. With $\text{CHMeBr}\cdot\text{COCl}$ and NaOH , chondrosamine hydrochloride gave *N*- α -bromopropionylchondrosamine, m.p. 181.5° (decomp.), $[\alpha]_{\text{D}}^{20} +68^\circ$ in H_2O falling to 49.5° , which did not afford a glucopeptide anhydride with NH_3 . J. H. B.

Complex compounds formed by certain amino-acids in presence of mercuric chloride and alkali. H. B. VICKERY and W. G. GORDON (J. Biol. Chem., 1933, 103, 543-547).—The best conditions (mols. of HgCl_2 , alkali, η_{inh} , and vol. of added EtOH , respectively) for pptn. of the following NH_2 -acids, as insol. HgCl_2 complexes, are: glycine, 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 0, or 1.5, $\text{Na}(\text{Li})\text{OH}$, 9.8, 2; alanine, 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 1; phenylalanine, 1.5, $\text{Ba}(\text{OH})_2$, 8.5, 0; leucine (I), 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 1.5; lysine (II), 2, $\text{Ba}(\text{OH})_2$, 9.3, 0; and glutamic acid, 2, $\text{Ba}(\text{OH})_2$, 9.8, 0. Except for (I) (70%), all pptns. are quant. Except that from (II) ($\text{Hg}:\text{N}:\text{Cl}=4:4:3$ atoms), all pptns. contain $\text{Hg}:\text{N}=3:2$ atoms, in addition to Cl and alkali. Attempts to employ these complexes in the separation of NH_2 -acids were unsuccessful.

J. W. B.

Gas-volumetric determination of amino-nitrogen according to Van Slyke in the case of glycine and peptides containing glycine. O. GERNGROSS and W. DESEKE (Ber., 1933, 66, [B], 1813-1814).—The gas evolved in the determination of glycine and glycylglycine contains $>$ the calc. amount of N_2 for which a correction cannot be introduced.

CO and N₂O are present to the respective extents of 0.4% and 0.6%.
H. W.

Serinephosphoric acid obtained on hydrolysis of vitellinic acid. II. P. A. LEVENE and A. SCHOR-MÜLLER (J. Biol. Chem., 1933, 103, 537—542).—An improved method of isolation of Ba *d*-serinephosphate (I) (A., 1932, 1269) from the hydrolysis products of vitellinic acid (II) involves purification through the brucine salts, two fractions (a), m.p. 89°, decomp. 105° (composition approx. that of the dibrucine salt), and (b), m.p. 120°, decomp. 130° (mixture), being obtained. Under milder conditions of hydrolysis (II) gives a phosphoric ester of serine, and serine is isolated by hydrolysis of (I). In vitellin the serinephosphoric acid is not linked to a dicarboxylic NH₂-acid.
J. W. B.

Aminosulphonic acids. II. Synthesis of taurine derivatives. B. JOSEPHSON (Biochem. Z., 1933, 265, 448—455).—The following have been prepared by a modification of James' method (J.C.S., 1885, 47, 367): methyl-, m.p. 244°, dimethyl-, m.p. 270° (cf. *ibid.*, 371), *n*-propyl-, m.p. 330°, *n*-heptyl-, m.p. 244°, phenyl-, m.p. 269°, and benzyl-, m.p. 196°, -taurine; β -*p*-carboxyanilinoethanesulphonic acid, m.p. 286°. Their properties differ largely from those of taurocholic acid.
P. W. C.

Organic reactions with boron fluoride. VI. Reaction of acetamide with alcohols and phenol. F. J. SOWA and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, 55, 5052—5053).—NH₂Ac, BF₃ (1 mol.) heated with ROH (1 mol.) gives NH₃, BF₃ and ROAc. Me, Et, Pr ^{β} , Bu ^{α} , Bu ^{γ} , and Ph acetates are thus prepared in yields of 71, 69, 32, 50, 38, and 50%, respectively.
H. B.

Metallic salts of carboxylic acids. E. C. FRANKLIN (J. Amer. Chem. Soc., 1933, 55, 4915—4917).—Salts, R·CO·NHK, where R is H, Et, Pr ^{β} , Bu, amyl, pentadecyl, and Ph, are prepared from R·CO·NH₂ and KNH₂ in liquid NH₃; when heated to 250—300°, they decompose to RH+KNCO and RCN+KOH. The salts HCO·NHNa and CHK(CO·NHK)₂ are also described.
H. B.

λ -Hydroxystearhydrazide and derivatives. J. VOŘÍSEK (Coll. Czech. Chem. Comm., 1933, 5, 466—468).— λ -Hydroxystearhydrazide, m.p. 115.5—116.5° [hydrochloride, m.p. 162—163°; N·Ac, m.p. 144—145° (warm Ac₂O and EtOH), and ON·Ac₂ derivative (Ac₂O at b.p.)], is formed from the acid and N₂H₄·H₂O at 100°, and with I in EtOH gives *s*-*di*- λ -hydroxystearylhydrazine, m.p. 153—154°.
H. A. P.

Preparation of magnesium crotyl bromide. Effect of solvents on the yield of magnesium crotyl and allyl bromides. W. G. YOUNG, A. N. PRATER, and S. WINSTEIN (J. Amer. Chem. Soc., 1933, 55, 4908—4911).—Mg crotyl bromide (I) is obtained in good yield by slow addition of a solution of crotyl bromide (II) to a rapidly stirred mixture of Mg and Et₂O or Bu₂O in N₂. (II) reacts with (I) more readily than does allyl bromide with Mg allyl bromide (III); use of Bu₂O favours these reactions. Slower stirring diminishes the yield of (I) and (III). Much larger ratios of solvent and Mg to bromide

must be used with Bu₂O than with Et₂O to obtain equiv. yields of MgRBr.
H. B.

Hydroxypropyldiarsinic acid. K. A. KIRKHOFF (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 73—74).—OH·CH(CH₂Cl)₂ (129 g.) is agitated during 4 hr. with As₂O₃ (200 g.) in H₂O (600 c.c.) and NaOH (240 g.). After 4 days the diluted mixture is boiled and Ca hydroxypropyldiarsinate pptd. with boiling CaCl₂ solution. The acid, decomp. 170—180°, is liberated with boiling dil. H₂SO₄. Reduction with Na₂S₂O₄ and NaOH affords a substance, probably

$$\text{OH}\cdot\text{CH}\left\langle\begin{array}{l} \text{CH}_2\cdot\text{As} \\ \text{CH}_2\cdot\text{As} \end{array}\right.$$
 CH. ABS.

Aliphatic germanium derivatives. III. Germanium ethyl trihalides. E. A. FLOOD (J. Amer. Chem. Soc., 1933, 55, 4935—4938).—GeI₂ and EtI at 110° for 3 days in absence of air give GeEtI₃ (I), b.p. 281°/755 mm., m.p. -2.5° to -1.5°, which decomposes at > 350° to GeI₄ and gaseous products. (I) and Ag₂O in H₂O afford ethylgermanic oxide (II), (EtGeO)₂O, decomp. > 300°, which with the appropriate HHal gives GeEtF₃, b.p. 112°/750 mm., m.p. -16.5 to -15.5°, GeEtCl₃, b.p. 144°/762 mm., and GeEtBr₃, b.p. 200°/763 mm. (I) is ammonolysed in liquid NH₃ to GeEtN, which is hydrolysed (H₂O) to (II).
H. B.

Preparation of germanium diethyl derivatives. L. HORVITZ and E. A. FLOOD (J. Amer. Chem. Soc., 1933, 55, 5055; cf. A., 1932, 606).—GeEtI₃ and an excess of 40 : 60 Pb-Bi alloy at 150° in absence of air give a product, probably (GeEtI)₂, which with EtI at 125° affords GeEt₂I₂, b.p. 252°/759 mm., m.p. -2° to -1°. GeEt₂Cl₂ has b.p. 175°/758 mm., m.p. -39° to -37°.
H. B.

Cracking of naphthene hydrocarbons. I. M. K. DIAKOVA and A. D. PETROV (J. Gen. Chem. Russ., 1933, 3, 679—684).—The stability of decahydronaphthalene and dicyclohexyl at 500—550° is > that of methylisopropyldicyclononane, of amylcyclohexane (I), and of the fractions of Grosny petroleum (II), b.p. 185—248°. A comparison of the *d* and *n* of the products of cracking indicates that (II) consists preponderatingly of naphthenes of structure similar to that of (I).
R. T.

Application of the electronic theory to the chemistry of organic compounds. I. Properties of isomeric nitro-compounds from the viewpoint of electronic theory. A. M. BERKENHEIM and M. I. GOSTEV (J. Gen. Chem. Russ., 1933, 3, 385—410).—An experimental verification by standard methods of org. chemistry of the "electrodynamic" theory of intramol. changes of NO₂-compounds giving rise to different types of N compounds. These changes are possibly of the oxidation-reduction type, involving transformation of N^V into N^{III}, and of ·NO₂ into ·O·N·O. The electronic structure of aromatic compounds is examined, and the position, nature, and firmness of the attachment of NO₂ to the nucleus, as well as the possibility of rearrangements, are demonstrated. With "abnormal" compounds, both electrostatic and electrodynamic rearrangements are possible: in the former case more stable compounds result owing to the migration

of the group in the nucleus, all the charge signs remaining unaltered, whilst in the latter case, new compounds (complex, aromatic nitrous esters) are formed. In the course of such dynamic rearrangements, secondary products appear owing to further transformations of the aromatic nitrites into OH compounds. The aromatic nitrite can be independently prepared and identified by the action of NOCl on the metallic phenoxides. With $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, NOCl gives a nitrite, m.p. 126—131°, and also Me *p*-nitrosalicylate, m.p. 114—115°. Alkalis remove the Me and cause a rearrangement, giving a mixture of *o*- and *p*-nitrosalicylic acids. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and NOCl give a nitrite isomeric with $o\text{-C}_6\text{H}_4(\text{NO}_2)_2$. Nitration of BzOH gives $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, identical with that obtained by oxidation of PhMe, in accordance with the electronic rearrangement theory; during nitration of BzOH, secondary products, corresponding with those formed when the isomeric nitrite is synthesised, are obtained. The fourth nitrobenzoic acid, m.p. 124—126° (cf. A., 1880, 251), which gave an intense coloration with FeCl₃, is identical with the aromatic nitrite. M. Z.

1-Chloro-3 : 4-dinitrobenzene series. A. MANGINI and C. DELIDDO (Gazzetta, 1933, 63, 612—629).—The structure of 1-chloro-3 : 4-dinitrobenzene (I), m.p. 38·8°, best made from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{KNO}_3\text{-H}_2\text{SO}_4$, is proved through the following derivatives. 4-Chloro-*o*-phenylenediamine hydrochloride, decomp. 260—270°, yields, with benzil, 6-chloro-2 : 3-diphenyl-1 : 4-quinoxaline, m.p. 119—121°, whence 6-chlorobenzotriazole, new m.p. 160° (*Ac* derivative, m.p. 90°; *Ag* salt). 3-Chloro-6-nitroaniline (II) (*Ac* derivative, m.p. 121°) gives 4-chloro-2-acetamidylaniline hydrochloride, decomp. 200°, and 4-chloro-2-acetamidophenol. 5-Chloro-2-nitroanisole gives 4-chloroguaiacol. 5-Chloro-2-nitrophenetole gives the 2-NH₂- (*hydrochloride*, decomp. 250—260°) and 2-NHAc-, m.p. 98°, compounds. When (I) is treated with CH₂Ph·OH, 5-chloro-2-nitrophenyl benzyl ether is formed, reduced to the 2-NH₂-compound [*hydrochloride*, m.p. 210—218° (decomp.)], whence 5-chloro-2-nitrophenol. With piperidine, (I) forms 1-chloro-4-nitro-3-piperidylbenzene [*hydrochloride*, m.p. 147—151° (decomp.)]. With N₂H₄, (I) gives 5-chloro-2-nitrophenylhydrazine, red form, m.p. 160°, yellow form, m.p. 120° (*Ac* derivative, m.p. 186—187°), which is also obtained from (II), and which with KOH-EtOH yields 6-chloro-3-hydroxybenzimidazole, m.p. 183°, decomp. 188—189°. With NHPPh·NH₂ (I) forms α -phenyl- β -(5-chloro-2-nitrophenyl)hydrazine, m.p. 140—141°. Benzaldehyde-5-chloro-2-nitrophenylhydrazone, m.p. 174°, and acetone- and benzophenone-4[5 ?]-chloro-2-nitrophenylhydrazones, m.p. 131—132° and 138—139°, respectively, are described.

E. W. W.

Supposed di-ortho-isomerism in benzene. A. CONTARDI and A. DANSI (Rend. R. Ist. lombardo Sci. Lett., 1933, [ii], 66, 203—206; Chem. Zentr., 1933, ii, 1512).—Hodgson's results (A., 1927, 47) are challenged. Substitution of Cl or Br by NH₂ is best attained by heating in a closed tube with EtOH-NH₃ for several hr. at 100°. 3-Chloro-1-bromo-4 : 6-dinitrobenzene from 3-chloro-4 : 6-dinitroaniline is

crystallographically identical with the 1-chloro-3-bromo- from the 3-bromo-1-amino-compound.

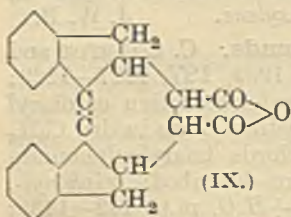
A. A. E.

Chloro-derivatives of *p*-xylene. H. WAHL (Compt. rend., 1933, 197, 1330—1332).—3-Nitro-*p*-xylylidine (Noelting *et al.*, A., 1902, i, 313; prep. modified) is converted by the Sandmeyer reaction into 2-chloro-3-nitro-*p*-xylene, b.p. 135°/15 mm., m.p. 56°, reduced by Fe-HCl to 3-chloro-*p*-xylylidine, b.p. 126—127°/15 mm., m.p. 41° (*Ac*, m.p. 179°, and *Bz*, m.p. 144°, derivatives; *picrate*, m.p. 120°), not identical with the chloro-*p*-xylylidine (I), b.p. 132—133°/15 mm., previously obtained (A., 1933, 815) by reduction of the corresponding NO₂-derivative [(II), *loc. cit.*]. (I) is therefore 6-chloro-*p*-xylylidine, and (II) is 6-chloro-2-nitro-*p*-xylene. J. W. B.

Arylsulphonium compounds. C. COURTOT and T. Y. TUNG (Compt. rend., 1933, 197, 1227—1229; cf. A., 1932, 506).—Prolonged interaction of diaryl sulphoxides and aromatic hydrocarbons in dry C₆H₆ containing AlCl₃ at 40° affords triarylsulphonium chlorides. The following are described: *triphenyl*-, m.p. 230—277° (decomp.) [+H₂O, m.p. 142—143°; +HgCl₂, m.p. 214—215° (decomp.)]; *o*-, an oil, and *m*-xylyldiphenyl-, m.p. 179° (+H₂O, m.p. 123—124°); *phenyldi-p-tolyl*-, m.p. 193—194° (+H₂O, m.p. 125—127°; +3H₂O, m.p. 62—63°); *tri-p-tolyl*-(+H₂O, m.p. 138—140°; +4H₂O, m.p. 51—52°); *di-p-tolyl-o-xylyl*-, m.p. 118—120° (+2H₂O, m.p. 56—57°); *di-p-tolyl-p-xylyl*-, oil (+HgCl₂, m.p. 86—87°); *tolyl-2 : 4 : 2' : 4'-tetramethyl*diphenyl-, m.p. 94—97°; *tri-o-xylyl*-, m.p. 102—105° (+3H₂O, m.p. 60—61°); *diphenyl-p-tolyl*-, m.p. 232—234°; *phenyl-p-tolyl-o-xylyl*-, m.p. 74—76° (+3H₂O, m.p. 59—60°), and *phenyl-p-tolyl-m-xylyl-sulphonium chloride*, m.p. 73—74°. J. L. D.

Replacement of strongly positive hydrogen by halogen. IV. Reaction of 1 : 1 : 3-trihalogenoindenes. F. STRAUS, R. KÜHNEL, and R. HAENSEL (Ber., 1933, 66, [B], 1847—1862; cf. this vol., 168).—Treatment of 1 : 1 : 3-tribromoindene (I) with boiling COMe₂-H₂O affords 3-bromoindone, m.p. 57·5—58°, in 83% yield, converted by Br and Cl₂ in AcOH into 2 : 3-dibromo-, m.p. 123°, and 2-chloro-3-bromo-, m.p. 98°, -indone, respectively. Similarly, 1 : 1 : 3-trichloroindene (II) yields 3-chloroindone, m.p. 57—57·5°, and thence 2 : 3-dichloro-, m.p. 89°, and 3-chloro-2-bromo-, m.p. 111—112°, -indone. Treatment of (I) or (II) with boiling MeOH or MeOH-H₂O gives non-homogeneous products. When heated with NaI in boiling COMe₂ or, less advantageously, with mol. Ag in C₆H₆, (I) gives 3 : 3'-dibromo-1 : 1'-diindenylenene (III), not molten below 400° after darkening at 300° [*tetrabromide*, m.p. 179° (decomp.) after darkening at 145°], converted by Zn wool and AcOH in COMe₂ into 3 : 3'-diindenylenene (IV), m.p. 130·5—131·5°. (II) and NaI in COMe₂ yield 3 : 3'-dichloro-1 : 1'-diindenylenene (V), m.p. 231·5—232·5° (decomp.) after darkening at 185°, converted by Cl₂ in CCl₄ into the *tetrachloride* (VI), m.p. 209—211° (decomp.) after darkening at 155°, with small amounts of a *substance* C₁₂H₈Cl₄, decomp. 160—162°. (VI), Zn wool, and AcOH in MeOH give 3 : 3'-diindenylenene, m.p. 232·5° (decomp.), in 85% yield with only traces of (IV).

1 : 1' : 3 : 3'-Tetrachloro-1 : 1'-di-indenyl (VII), m.p. 172.2—173.2°, is an intermediate in the production of (V) and remains dissolved in the COMe_2 ; it is converted by Zn wool and AcOH in COMe_2 into an isomeric 3 : 3'-dichloro-1 : 1'-di-indenylene (VIII), m.p. 165.5—166.5°. Trichloroindene is unchanged by Hg in C_6H_6 , but with mol. Ag it yields a small proportion of (VII) and (VIII); with Zn turnings and AcOH in COMe_2 or Et_2O it affords (V) and some indene. Treatment of (III) with Zn dust in boiling EtOH or with Zn dust and AcOH in $\text{C}_5\text{H}_5\text{N}$ gives (IV), stable in light petroleum towards O_2 in the dark but yielding a peroxide when exposed to light, which is oxidised by KMnO_4 to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and benzil-4 : 2'-dicarboxylic acid, m.p. 253° (decomp.) (Ag salt; Me ester, m.p. 187.3°). Condensation of (IV) with maleic anhydride affords the substance (IX), decomp. about 310° (block), accompanied by a colourless (?) stereoisomeric anhydride, m.p. 254—256°, and a yellow material, $\text{C}_{22}\text{H}_{16}\text{O}_3$, m.p. 258.5—261°, probably formed by displacement of H. (IX) is hydrogenated (Pd) to 1 : 1'-dihydrindenyl, b.p. 194—195°/14 mm. (IV) and 2 Br in CS_2 afford two dibromides, m.p. 135—136° (decomp.) after darkening, and m.p. 106—106.5° (decomp.), respectively, the former being re-converted into (IV) by Zn dust and EtOH. In individual cases (IV) and 4 Br in CS_2 gave a tetrabromide, m.p. > 250° after darkening at 150°, but usually a third dibromide, m.p. 184—186° (decomp.). Condensation of (IV) with PhCHO affords $\alpha\delta$ -diphenyl- $\beta\delta\epsilon\zeta$ -diphenyleneoctatetraene (X) ($\text{CHPh}\cdot\text{C}\langle\text{CH}\cdot\text{C}\rangle\text{C}_6\text{H}_4$), m.p. 217.5°; analogously, $\alpha\mu$ -diphenyl- $\delta\zeta\eta$ -diphenylene-dodecahexaene, m.p. 251°, and $\alpha\delta$ -di-*p*-methoxyphenyl- $\beta\delta\epsilon\zeta$ -diphenyleneoctatetraene, m.p. 214°, are obtained. (IV), $\text{Et}_2\text{C}_2\text{O}_4$, and NaOEt yield the ester



$\left[\text{C}_6\text{H}_4 \langle \text{C} : \text{C}(\text{OH}) : \text{CO}_2\text{Et} \rangle \right]_2$, m.p. 195—197° (decomp.).

1 : 1'-Di-indenyl is rapidly isomerised to (IV) by NaOMe in EtOH and is transformed by NaOEt and PhCHO in EtOH into (X).

H. W.

Hydrogenation of naphthalene. A. MAILLARD (Compt. rend., 1933, 197, 1422—1424).—Catalytic reduction of gaseous C_{10}H_8 (I) with Pt-H_2 < 760 mm. occurs between 20° and 180°. Above 180° C is deposited and CH_4 produced, the proportion of the latter increasing as the H_2 pressure diminishes. At 20° the $\text{C}_{10}\text{H}_{12}$ (II) is reduced more rapidly than (I), the sole reaction being $(\text{I}) + 5\text{H}_2 \rightarrow \text{C}_{10}\text{H}_{18}$ (III), but at > 60° (I) is reduced more rapidly than (II). Thus at 85° the hydrogenation curves for (II) and for (I) in equilibrium with 2H_2 are identical, no (III) being produced until all (I) has disappeared: hence at > 60° two successive reactions $(\text{I}) + 2\text{H}_2 \rightarrow (\text{II})$; $(\text{II}) + 3\text{H}_2 \rightarrow (\text{III})$, occur.

J. W. B.

Sulphonation reaction. I, II. I. S. JOFFE (J. Gen. Chem. Russ., 1933, 3, 437—447, 505—512).—Review of the lit. leads to the conclusion that the equations hitherto suggested as representing the

mechanism of sulphonation are somewhat incomplete. The reaction should be represented by the general expression $dx/dt = f(x)(A-x)(S-x) - \phi(x)(H+x)x$, where x is the concn. of the sulphonic acid formed, A that of the compound to be sulphonated, S the H_2SO_4 and H H_2O , whilst $f(x)$ and $\phi(x)$ are hitherto undetermined functions of x . In the sulphonation of C_{10}H_8 , the val. of K as obtained from the above equation falls progressively, indicating the influence of further factors. The following general conclusions are reached, however. Guyot's hypothesis that the limiting factor in sulphonation is the concn. of H_2SO_4 is incorrect. Sulphonation is a reversible reaction, which appears to cease when the two opposing rates are equal. The concn. of the H_2SO_4 is thus dependent on the quantities of the reacting substances present, and therefore has no const. limiting val. Sulphonation with fuming acid depends on the free SO_3 and is according to an equation of the second order. In general, the two opposing reactions are of the second order, becoming of pseudo-first order with large excess of one or other of the reagents. In the formation of 1- and 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ a no. of reactions of varying rates take place simultaneously: sulphonation of C_{10}H_8 to the 1-acid (II) to the 2-acid (III), hydrolysis of (II) and (III). Since (III) is considerably more stable than (II), a const. ratio between them can be reached only under special conditions and after a long period. Since this condition of equilibrium was not attained and since the rates of the various reactions depend on the actual concns. of all the reacting substances, the const., K , calc. in the earlier experiments was found to fall progressively. To give a complete and accurate picture of the sulphonation mechanism, a more detailed series of expressions representing the various interdependent reactions must be developed.

M. Z.

Kinetics of sulphonation and monosulphonation of naphthalene. I. S. JOFFE (Anilinokras. Prom., 1933, 3, 296—304).—The 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ content of the product of sulphonation of C_{10}H_8 at 100° falls from 83% after 8 hr. to 33% after 240 hr. A consideration of the velocity coeff. of the reaction of 1- and 2-sulphonation and of hydrolysis of the products indicates that at equilibrium the product should contain 22.6% of 1- and 77.4% of 2-sulphonic acid.

R. T.

Halogenation. VII. Iodination and bromination of naphthalene and β -naphthol. P. S. VARMA, D. N. MOZUMDAR, and K. K. RAJAH (J. Indian Chem. Soc., 1933, 10, 595—598; see this vol., 187).—1- $\text{C}_{10}\text{H}_7\cdot\text{I}$ is best prepared by addition of a 1 : 1 mixture (A) of fuming HNO_3 and nitrosulphonic acid to C_{10}H_8 and I in boiling AcOH. A good yield of $\text{C}_{10}\text{H}_7\cdot\text{Br}$ is similarly obtained from C_{10}H_8 and Br in CCl_4 ; some $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ is also formed. Experiments using substances (e.g., HNO_3 , CrO_3) other than (A) are described. β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ is best iodinated (I in KI) in aq. NH_3 ; bromination is best effected in AcOH at 10° in presence of conc. H_2SO_4 or oleum.

H. B.

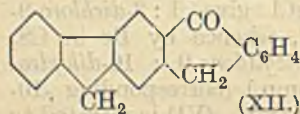
Amyrin. III. Constitution of sapotalin and the hydrocarbon $\text{C}_{14}\text{H}_{16}$. O. BRUNNER, H. HOFER, R. STEIN, and (in part) F. GROF (Monatsh., 1933, 63, 79—98; cf. A., 1932, 1253).—Confirmation that

sapotalin (I) is 1 : 2 : 7-C₁₀H₈Me₃ is obtained by oxidation with CrO₃-AcOH at >5° to the *quinone*, m.p. 113°, oxidised by KMnO₄ in H₂O-COMe₂ at 0° to 3 : 4-*dimethylphthalic anhydride*, m.p. 126° (*acid*, m.p. 149—150°; *methylimide*, m.p. 98—99°), identical with a specimen synthesised by dehydrogenation of the Δ⁴-tetrahydro-compound (Farmer *et al.*, A., 1932, 141) by Br at 200° and subsequent reduction with Na-Hg. Ruzicka's synthesis (A., 1932, 277) of (I) from γ-*p*-tolyl-α-methylbutyric acid (II) is confirmed. Similarly Ruzicka's identification of the hydrocarbon C₁₄H₁₆ as 1 : 2 : 5 : 6-C₁₀H₄Me₄ (III) (A., 1933, 495) is confirmed by failure to convert it to a quinone, production of mellophanic acid by KMnO₄ oxidation, and the following synthesis. 2 : 3-Dimethylbenzotrile is hydrolysed by conc. aq. KOH-NaOH at 200° to the *acid*, m.p. 145—146° (*amide*, m.p. 155—156°), the *chloride*, b.p. 128°/22 mm., of which is converted by Pd-BaSO₄ in xylene into 2 : 3-dimethylbenzaldehyde (*oxime*, m.p. 80—82°; *semicarbazone*, m.p. 222°), condensed with COMe₂ (10% NaOH) to 2 : 3-dimethylbenzylideneacetone, b.p. 166°/16 mm., m.p. 37° (*oxime*, m.p. 160—162°; *semicarbazone*, m.p. 215°, both in vac.), reduced by H₂ and Pd-BaSO₄ to β-(2 : 3-dimethylphenyl)ethyl *Me ketone*, b.p. 139°/10 mm. (*semicarbazone*, m.p. 204° in vac.), reduced (Na in EtOH) to the *carbinol*, b.p. 156°/20 mm., which is converted by way of the *bromide*, b.p. 151—152°, and nitrile into the *acid*, which is cyclised by conc. H₂SO₄ at 100° to 1-keto-2 : 5 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. This with MgMeI and subsequent dehydrogenation with Se affords (III). Similar dehydrogenation (Br) of 4 : 5-dimethyl-Δ⁴-tetrahydrophthalic anhydride (Diels *et al.*, A., 1929, 819) (*acid*, m.p. 189—190°; *imide*, m.p. 126.5—127.5°) affords a ready method of synthesising 4 : 5-dimethylphthalic anhydride (*acid*, m.p. 196°; *methylimide*, m.p. 150—151°; *ethylimide*, m.p. 89°). J. W. B.

Anthracene derivatives. X. E. DE B. BARNETT, N. F. GOODWAY, and J. W. WATSON (Ber., 1930, 66, [B], 1876—1891).—Condensation of *o*-C₆H₄(CO)₂O with *m*-C₆H₄Cl₂ yields 2 : 4-dichlorobenzoylbenzoic acid (I) and (?) 3 : 3-*di*-2' : 4'-*dichlorophenylphthalide*, m.p. 176°, which, after hydrolysis, could not be reduced by Zn dust and alkali. (I) is reduced by Zn dust, NH₃, and CuSO₄ to *o*-2 : 4-dichlorobenzylbenzoic acid, m.p. 128°, converted by conc. H₂SO₄ at room temp. into 2 : 4-dichloroanthrone (II), m.p. 161°. (II) is transformed by Ac₂O-C₅H₅N into 2 : 4-dichloroanthranil acetate (III), m.p. 170°, and by Br in CS₂ into 2 : 4-dichloro-10-bromoanthrone (IV), m.p. 157°, whence 2 : 4-dichloro-10-anilino-. m.p. 187°, and 2 : 4-dichloro-10-piperidino-, m.p. 154°, -anthrone. (IV), AlCl₃, and C₆H₆ at room temp. yield 2 : 4-dichloro-10-phenylanthrone, m.p. 164°, converted by successive treatment with CH₂Ph-MgCl and HCl-AcOH into 2 : 4-dichloro-10-phenyl-9-benzylanthracene, m.p. 175°. 2 : 4-Dichloro-9-benzylanthracene, m.p. 163°, prepared similarly from (II), is transformed by Br in CS₂ at room temp. into 2 : 4-dichloro-9-*α*-bromobenzylanthracene, m.p. 138° (slight decomp.), whence the corresponding *α*-piperidino-compound, m.p. 168°. (III) and HNO₃ (*d* 1-42) in AcOH at 65° afford 2 : 4-dichloro-10-nitroanthrone, m.p. 137° (decomp.), readily decomposed by Ac₂O in cold C₅H₅N. 1 : 3-Dichloro-

anthrone (V), m.p. 194°, obtained by reduction of 1 : 3-dichloroanthraquinone with Al powder and conc. H₂SO₄ [1 : 3-dichloroanthranil acetate (VI), m.p. 200°] yields 1 : 3-dichloro-10-bromoanthrone, m.p. about 180° (decomp.), whence 1 : 3-dichloro-10-anilinoanthrone, m.p. 180°, and, by action of piperidine in CHCl₃, 1 : 3 : 1' : 3'-tetrachloro-10-bromo-10 : 10'-dianthronyl, decomp. (indef.) 220—230°. (V), CH₂PhCl, and aq. KOH give 1 : 3-dichloro-10-dibenzylanthrone, m.p. 232°. (V) and CH₂Ph-MgCl give 1 : 3-dichloro-9-benzylanthracene, m.p. 127°, whence by Br in CS₂ 1 : 3-dichloro-10-bromo-9-benzylidene-9 : 10-dihydroanthracene, m.p. 197° (decomp.) (corresponding -10-piperidino-compound, m.p. 148°). (VI) is nitrated to 1 : 3-dichloro-10-nitroanthrone, m.p. 158° (decomp.), rapidly transformed by Ac₂O in C₅H₅N at room temp. into 1 : 3-dichloro-10-nitroanthranil acetate, m.p. 207°. 4 : 5-Dichlorophthalic anhydride (VII), *o*-C₆H₄Cl₂, and AlCl₃ yield 3 : 4 : 4' : 5'-tetrachlorobenzophenone-2'-carboxylic acid, m.p. 183° (*Na salt*), converted by conc. H₂SO₄ at 100° into 2 : 3 : 6 : 7- (VIII), m.p. 348°, and 1 : 2 : 6 : 7-, m.p. 242°, -tetrachloroanthraquinone. (VIII) is reduced by Al powder and conc. H₂SO₄ at 30—40° to 2 : 3 : 6 : 7-tetrachloroanthrone, m.p. 300° (decomp.). Protracted boiling of (VIII) with SnCl₂ and conc. HCl appears to yield a little of the anthraquinol. Reduction and subsequent dehydration of the phthaloyl acid proceeds very slowly, appearing to give small amounts of a trichloroanthrone, m.p. 235°. (VII), *o*-xylene, and AlCl₃ in C₂H₂Cl₄ give 4' : 5-dichloro-3 : 4-dimethylbenzophenone-2'-carboxylic acid, m.p. 184°, transformed by conc. H₂SO₄ at 100° into 6 : 7-dichloro-2 : 3-dimethylanthraquinone, m.p. 305°, which is reduced (Al powder, conc. H₂SO₄) to 6 : 7-dichloro-2 : 3-dimethylanthrone (IX), m.p. 295° (6 : 7-dichloro-2 : 3-dimethylanthranil acetate, m.p. 226°), converted by activated Zn dust and boiling aq. KOH into 6-chloro-2 : 3-dimethylanthracene, m.p. 299°. Bromination of (IX) suspended in CS₂ leads to 6 : 7-dichloro-10-bromo-2 : 3-dimethylanthrone, decomp. 175°, apparently converted by piperidine in CHCl₃ into a dianthraquinone. (IX), CH₂PhCl, and KOH in boiling CH₂Ph-OH-H₂O afford 6 : 7-dichloro-10-benzyl-2 : 3-dimethylanthranil CH₂Ph ether, m.p. 188°, converted by maleic anhydride in boiling xylene into 6 : 7-dichloro-10 : 10-dibenzyl-2 : 3-dimethylanthrone, m.p. 252°. 6 : 7-Dichloro-9-benzyl-2 : 3-dimethylanthracene, m.p. 233°, obtained from (IX) and CH₂Ph-MgCl, is brominated to 6 : 7-dichloro-10-bromo-9-benzyl-2 : 3-dimethylanthracene, m.p. 220°. 2 : 3 : 6 : 7-Tetramethylanthracene, m.p. 299° (cf. Morgan *et al.*, A., 1931, 1282), readily prepared from CH₂Cl₂, *o*-C₆H₄Me₂, and AlCl₃ [9 : 10-Br₂-derivative, m.p. 290° (decomp.)], is oxidised to the anthraquinone (X), which, contrary to Morgan, is readily reduced if very finely divided. Treatment of (X) with Al powder-conc. H₂SO₄ readily yields 2 : 3 : 6 : 7-tetramethylanthrone (XI), m.p. 271° (2 : 3 : 6 : 7-tetramethylanthranil acetate, m.p. 241°). (X), CH₂PhCl, and KOH in boiling CH₂Ph-OH-H₂O yield 10 : 10-dibenzyl-2 : 3 : 6 : 7-tetramethylanthrone, m.p. 244°. 9-Benzyl-2 : 3 : 6 : 7-tetramethylanthracene, m.p. 235°, prepared from (XI) and CH₂Ph-MgCl, affords 10-bromo-9-benzyl-2 : 3 : 6 : 7-tetramethylanthracene, m.p. 227°. (VII), C₆H₆, and AlCl₃ in C₂H₂Cl₄ give 4 : 5-

dichlorobenzophenone-2-carboxylic acid, m.p. 208°, converted by conc. H_2SO_4 into 2:3-dichloroanthraquinone, m.p. 265°. 2:3-Dichloro-9-benzylanthracene, m.p. 164°, and its 10-Br-derivative, m.p. 169°, are described. 2:3-Dichloroanthracene is quantitatively obtained from the anthrone by activated Zn dust and 10% KOH. *o*-2-Fluoroylbenzoic acid, m.p. 229°, obtained in > 80% yield from *o*- $C_6H_4(CO)_2O$, fluorene, and $AlCl_3$ in $C_2H_2Cl_4$, is reduced by Zn dust to 2'-



fluorylphenylmethane-2-carboxylic acid, m.p. 199°, which is transformed by $ZnCl_2$ at 180—190° into lin-

indenoanthrone (XII), m.p. 207° (corresponding anthranlyl acetate, m.p. 203°, and Br-derivative, decomp. about 190°). (XII) is oxidised by CrO_3 in dil. AcOH to lin-phthaloylfluorene, m.p. 269° after becoming red, and further in presence of H_2SO_4 to lin-phthaloylfluorenone, m.p. 367°. Reduction of (XII) with activated Zn dust and boiling 10% NaOH leads to lin-naphthafluorene, m.p. 317° [*di*-bromonaphthafluorene, m.p. 245° (decomp.)]. 3:6-Dichlorophthalic anhydride, fluorene, and $AlCl_3$ in $C_2H_2Cl_4$ give dichloro-*o*-2-fluoroylbenzoic acid, m.p. 172°, reduced by Zn dust, KOH, and NH_3 to a compound, (?) $C_{21}H_{15}O_2Cl$, m.p. 218°. β -Fluoroylpropionic acid (cf. Koelsch, A., 1933, 1284) from fluorene, succinic anhydride, and $AlCl_3$ in $C_2H_2Cl_4$ or $PhNO_2$ (yield 80%), is reduced in tetrahydronaphthalene (XIII) (Clemmensen) to γ -fluorylbutyric acid, m.p. 153°, transformed smoothly by $ZnCl_2$ at 180—210° into ketotetrahydro-*lin*-benzofluorene, reduced (Clemmensen) in xylene or (XIII) to tetrahydro-*lin*-benzofluorene, which is dehydrogenated by Se at 280—290° to *lin*-benzofluorene, m.p. 208°. H. W.

Sulphonation of phenanthrene. Preparation of the monosulphonic acids. I. S. JOFFE (J. Gen. Chem. Russ., 1933, 3, 448—452).—An effective method of preparing phenanthrenesulphonic acids on a technical scale free from disulphonic acids is developed. Large yields of the monosulphonic acids are obtained by shortening the reaction period and avoiding even local excess of H_2SO_4 by adding the acid to molten phenanthrene. Reduction of the quantity on dilution of the acid increases the yield, but lengthens the reaction period. The 9-isomeride can be obtained at higher temp., but rapidly passes into the others by intramol. rearrangement. The 2-isomeride increases in amount with prolongation of the reaction period. A concise scheme of separation of the isomerides from the reaction mixture is given.

M. Z.

Polycyclic aromatic hydrocarbons. XII. Orientation of derivatives of 1:2-benzanthracene, with notes on the preparation of some new homologues, and on the isolation of 3:4:5:6-dibenzphenanthrene. J. W. COOK (J.C.S., 1933, 1592—1597).—Oxidation of benzantraquinone derivatives and subsequent esterification affords: *Me*₂ anthraquinone-1:2-dicarboxylate, m.p. 208°; *Me*₂ anthraquinone-1:2:3-, m.p. 184—185°, -1:2:5-, m.p. 212—213°, -1:2:6-, m.p. 233.5—234.5°, and -1:2:7-, m.p. 204—204.5°, -tricarboxylate; *Me*₄ anthraquinone-1:2:6:7-, m.p. 193—194°, and

1:2:7:8-, m.p. 237—239°, -tetracarboxylate. 1-Benzoyl-2:3-dimethylnaphthalene when heated affords 4-methyl-1:2-benzanthracene, m.p. 124.5—125.5° (picrate, m.p. 149—150°). 5-Keto-5:6:7:8-tetrahydro-1:2-benzanthracene and $MgMeI$ give 5-methyl-1:2-benzanthracene, m.p. 157.5—158.5° (picrate, m.p. 163—163.5°), oxidised ($Na_2Cr_2O_7$) to -benzantraquinone, m.p. 173.5—174.5°. α - $C_{10}H_7\cdot COCl$, 2:3- $C_{10}H_6Me_2$, and $AlCl_3$ give 1- α -naphthoyl-2:3-dimethylnaphthalene, m.p. 191° (1- β -, m.p. 129—130°), which on heating forms 4-methyl-1:2:5:6-dibenzanthracene, m.p. 184—185° (dipicrate, m.p. 200—201°). Oxidation of 1- α -naphthoyl-2:6-dimethylnaphthalene with H_2SeO_3 yields 1- α -naphthoyl-6-methyl-2-naphthaldehyde, m.p. 185—186°. 9:10-Dihydro-1:2:5:6-dibenzanthracene, m.p. 196—198°, obtained by hydrogenation of the dibenzanthracene, is oxidised to 1:2:5:6-dibenz-9:10-, and some -3:4-anthraquinone, m.p. 326—327° (decomp.) (azine, m.p. > 300°), also formed from the oxidation of 1:2:5:6-dibenzanthracene. Separation of the mixture of acids resulting from the Pschorr reaction with di- α -*o*-aminobenzylidene-*p*-phenylenediacetic acid (Weitzenböck and Klingler, A., 1918, i, 494) gives a product oxidised to 3:4:5:6-dibenzphenanthra-1:2:7:8-diquinone, m.p. > 360° (diazine, m.p. > 360°) (decarboxylated to 3:4:5:6-dibenzphenanthrene, m.p. 177—178°), and 1:2:5:6-dibenzanthraquinone-4:8-dicarboxylic acid, m.p. > 360°.

F. R. S.

Isomerisation of the hydrocarbons $C_{42}H_{30}$, isomeric with 1:3:1':3'-tetraphenyl-1:1'-dihydorubene. A. WILLEMART (Compt. rend., 1933, 197, 1429—1432).—Fusion of the hydrocarbon $C_{42}H_{30}$ (I), m.p. 179° (A., 1927, 355), converts it into a colourless isomeride, + solvent, m.p. 250°, solvent-free, m.p. 317—318°, and a yellow isomeride, m.p. 249°, identical with the yellow substance (*loc. cit.*, m.p. 245°) formed with (I), and with the yellow "satellite" of rubrene (A., 1930, 594). J. W. B.

Rubenes: a colourless hydrocarbon with violet fluorescence derived from diphenylditolylrubene. L. ENDERLIN (Compt. rend., 1933, 197, 1332—1334).—By shaking the monoxide (A., 1932, 216) of the above rubene with 90% H_2SO_4 in C_6H_6 , or boiling it [or the corresponding (OH)₂-compound] with AcOH, is obtained a colourless hydrocarbon $C_{44}H_{30}$, m.p. 375° (block), which is the di-*p*-tolyl analogue of the hydrocarbon $C_{42}H_{26}$ previously obtained (*loc. cit.*). A trace of a yellow substance was sometimes obtained in the reaction. J. W. B.

Halogenation of the condensation products of *N*-alkyl-*o*-toluidines with chloral hydrate and nitration of the resulting compounds. A. H. ADVANI (J. Indian Chem. Soc., 1933, 10, 621—624).—5- $\beta\beta\beta$ -Trichloro- α -hydroxyethyl-*N*-methyl-*o*-toluidine (I) is brominated (under various conditions) to the 3-Br-derivative (II), m.p. 150°, the ON- Ac_2 derivative, m.p. 130°, of which is oxidised (aq. $KMnO_4$) to 3-bromo-4-*N*-acetmethylamido-5-methylphenylglyoxylic acid, m.p. 201°. (I) and Cl_2 in C_6H_6 give the 3-Cl-derivative (III), m.p. 132—133° (Ac_2 derivative, m.p. 112°). 5- $\beta\beta\beta$ -Trichloro- α -hydroxyethyl-*N*-ethyl-*o*-toluidine similarly affords 3-Br-, m.p. 115° (Ac_2

derivative, m.p. 150—152°), and 3-*Cl*-, m.p. 116—117° (*Ac*₂ derivative, m.p. 155—156°), -derivatives. (II) and (III) are converted by conc. HNO₃ into 6-*bromo*-, m.p. 230° (decomp.) (*Ac* derivative, m.p. 107°), and 6-*chloro*-, decomp. 230° (*Ac* derivative, m.p. 113°), -2-*methyl-4-βββ-trichloro-α-hydroxyethylphenyl-N-methylnitroamine*, respectively; 6-*bromo*-, m.p. 198° (decomp.) (*Ac* derivative, m.p. 127°), and 6-*chloro*-, m.p. 181° (*Ac* derivative, m.p. 132°), -2-*methyl-4-βββ-trichloro-α-hydroxyethylphenyl-N-ethyl-nitroamine* are similarly prepared. 6-*Nitro-2-methyl-4-αβββ-tetrachloroethylphenyl-N-methylnitroamine*, m.p. 199°, is obtained from the 4-βββ-trichloro-α-hydroxyethyl derivative (A., 1933, 497) and SOCl₂. H. B.

Chloro-derivatives of *p*-xylene. H. WAHL (Compt. rend., 1934, 198, 100—102).—6-*Nitro-p*-xylydine (Sonn, A., 1916, i, 391) is converted by the Sandmeyer reaction into 2-chloro-6-nitro-*p*-xylene (I), reduced (Fe-HCl) to 6-chloro-*p*-xylydine, identical with the amine, m.p. 40°, obtained (this vol., 177) by reduction of the NO₂-compound [identical with (I)] isolated from the nitration products (II) of chloro-*p*-xylene. Fractional distillation of the amines obtained by reduction of (II), or fractional crystallisation of their hydrochlorides, effects isolation of 3-chloro-*p*-xylydine (*loc. cit.*). The proportions of 5-, 6-, and 3-NO₂-derivatives in (II) are, approx., 60, 15, and 10%, respectively. J. W. B.

Introduction of the thiocyano-group into aromatic compounds by means of chloroamines. II. M. V. LICHOSCHERSTOV and A. A. PETROV (J. Gen. Chem. Russ., 1933, 3, 759—764).—*o*-C₆H₄Me·NH₂ (I) reacts with NH₄CNS and NHAcCl (II) in AcOH to yield the 5-SCN-derivative of (I) [*N*-*Ac*, m.p. 140.5°; 3-*Cl*-, m.p. 82—83.5°; 3-*Br*-derivative, m.p. 98—99.5° (*Ac* derivative, m.p. 150°)]. Under analogous conditions, *m*-C₆H₄Me·NH₂ yields the 6-SCN-derivative (*N*-*Ac*, m.p. 189°; 4-*Cl*-, m.p. 95—97°; 2-*bromo-4-chloro*-, m.p. 105°; 2 : 4-*Cl*₂-, m.p. 105—106°; 4-*Br*-, m.p. 78°; 2 : 4-*Br*₂-, m.p. 103.5°; 4-*bromo-2-chloro*-, m.p. 98°; 4-*I*-derivative, m.p. 86—87°), using 1 equiv. of (II) or of dichloro-carbamide, whilst using 2 equivs. the product is the 4 : 6-(SCN)₂-derivative, m.p. 142—143° [2-*Br*-derivative, sinters at 162°, m.p. 241° (decomp.)], which on prolonged heating in aq. HCl solution undergoes conversion into 6-*thiocyano-2-amino-5-methylbenzthiazole*, m.p. 210°. The 3-SCN-, m.p. 56°, and 3 : 5-(SCN)₂-derivatives of *p*-C₆H₄Me·NH₂, obtained as above, undergo spontaneous conversion into the corresponding benzthiazole derivatives. R. T.

Diazotisation of aromatic nitro-amines and prevention of diaryl formation in Sandmeyer reaction. H. H. HODGSON and J. WALKER (J.C.S., 1933, 1620—1621).—Diazotisation of weak bases such as 2- and 4-nitro- and 2 : 4-dinitro- α -naphthylamines is rapid and complete when a solution of the amine in abs. AcOH is added to NaNO₂ in conc. H₂SO₄. Addition of the resulting solution to cold CuCl-HCl, CuBr-HBr, or saturated aq. KI gives the corresponding halogeno-compound in > 80% yield, no diaryl formation being observed. 4 : 4'-

Dichloro-3 : 3'-dinitrodiphenyl may thus be prepared (80% of theory; cf. J.C.S., 1913, 103, 2074). Prior dilution of the diazo-solution with H₂O or ice results in tar formation or a different course of reaction [*e.g.*, 4-nitronaphthalene-1-diazo-2-oxide from 1 : 2 : 4-NH₂·C₁₀H₅(NO₂)₂]. Addition of EtOH to the diazo-solution and gradual heating to 80° eliminates the diazo-group. 1-*Bromo*-, m.p. 160°, and 1-*iodo-2 : 4-dinitronaphthalene*, m.p. 183°, are described.

H. A. P.

Action of nitrous acid and nitrosyl chloride on β -phenylpropylamine. Method of separating primary, secondary, and *tert.*-phenyl chlorides and phenylcarbinols. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, 103, 373—382).—Contrary to earlier results (A., 1930, 1287), 1- α -phenyl-*n*-propyl alcohol (I), [α]_D²⁰ -1.75°, is obtained from *d*- α -phenylpropionic acid, either by reduction of its Et ester, or by the action of HNO₂ on the amine derived from it. In mixtures of primary (II), *sec.* (III), and *tert.* (IV) phenylated carbinols, and of their respective chlorides (V), (VI), and (VII), (II) and (III) give esters with *o*-C₆H₄(CO)₂O and are thus separated from (IV) which gives unsaturated hydrocarbons, and only (III) and (IV) give their chlorides with aq. HCl. With AgOAc only (VI) gives the *Ac* derivatives of (III), (VII) again yielding unsaturated hydrocarbons, and thus (V) is separated, then (VI) and (VII) are determined by conversion, by way of the acetates, into (III) and (IV), and (III) is separated as its H phthalate. By these methods it is shown that 1- β -phenyl-*n*-propylamine, b.p. 85°/12 mm., [α]_D²⁵ -3.49° (H₂-PtO₂ reduction of nitrile), with HNO₂ affords 66% of β -phenyl-*n*-propyl alcohol and 34% of CPhMe₂·OH, but with NOCl in Et₂O at -50° it gives 90% of 1- α -chloro- β -phenylpropane, b.p. 71°/2 mm., [M]_D²⁵ -1.2°, 8% of CMe₂PhCl, and 2% of secondary chlorides. Prolonged keeping of CHMePh·CH₂Cl at room temp. causes 16% conversion into secondary and/or *tert.* chlorides. All vals. of [α] are for the homogeneous substance. J. W. B.

Optical activity of a diphenyl derivative, dissymmetry of which is caused by space effect of only one group. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1933, 1588—1592; cf. A., 1933, 388).—2-Nitro-*NN'*-dicarbethoxybenzidine (A., 1928, 283) is converted by Br in AcOH into the 3-*bromo-2'-nitro*-derivative, m.p. 145—147°, hydrolysed by aq. H₂SO₄ to 3-*bromo-2'-nitrobenzidine*, m.p. 155—156° (*corr.*), which is readily deaminated to 3-*bromo-2'-nitrodiphenyl* (I), m.p. 69—70°, b.p. 195°/11 mm., by heating the bisdiazoborofluoride (II) with abs. EtOH and conc. H₂SO₄. Reduction of (I) with SnCl₂-HCl gives the -2'-NH₂-compound, m.p. 69—70° (*corr.*), the *N*-Me₂ derivative of which, m.p. 47—48°, b.p. 176—178°/9 mm. (*platinichloride*), forms quaternary salts only with difficulty; the *methiodide* is formed by heating at 175° for 8 hr. with a large excess of MeI. Attempts at optical resolution of this failed. The corresponding *As* compound was therefore prepared. 3'-*Bromodiphenyl-2-arsinic acid*, m.p. 189—190° (*corr.*), is obtained from (II) and Na₂AsO₃ in presence of CuSO₄. It is reduced by SO₂, HCl, and I to the dichloroarsine, which is treated with MgMeI in C₆H₆;

the resulting product with MeI in EtOH gives 3-bromo-diphenyl-2-trimethylarsonium iodide, m.p. 183—184° (corr.). By crystallisation of the d- α -bromocamphor- π -sulphonate of this a d-isomeride, m.p. 184—185°, [α]_D²⁰ +46.8°, was isolated; the d-camphorsulphonate, m.p. 219—220°, has [α]_D²⁰ +19.6° to 21.8°. Mesityldimethylarsine, b.p. 138—139°/20 mm. (from Mg mesityl bromide and AsMe₂I), gives a methiodide, m.p. 219—220°, and an ethiodide, m.p. 174—175° (corr.) (cf. dimethylmesidine, A., 1872, 1021). H. A. P.

Ammonolytic reactions. E. C. FRANKLIN (J. Amer. Chem. Soc., 1933, 55, 4912—4915).—CN·NR₂ (I) (R=Et, Prⁿ, Bu ^{β}) (1 mol.) and KNH₂ (II) (2 mols.) in liquid NH₃ at 35° give NHR₂, NH₃, and CN·NK₂. NN'N''-Triphenylguanidine and NH₄Cl in liquid NH₃ at 200° afford guanidine (III) and NH₂Ph. (I) (1 mol.) and (II) (1 mol.) in cold liquid NH₃ give NR₂·C(NH)·NHK; the K salts where R₂ is Me₂, Et₂, Pr ^{β} , Bu ^{β} , and diisomyl and the Na salts where R₂ is Et₂ and Bu ^{β} , are described. Ammonolytic decomp. of NH₂·CO·NHMe affords CO(NH₂)₂ (IV), NH₂Me, and (III) [formed from (IV)], whilst CO(NHPh)₂ gives (III), (IV), and NH₂Ph. NH₂Ac or NH₄OAc heated with NH₄Cl in liquid NH₃ affords acetamidine (V); diphenylacetamidine similarly gives (V) and NH₂Ph; diphenylbenzamidine yields benzamidine and NH₂Ph; NPhAc furnishes (V) and NH₂Ph. CPhCl₃ and liquid NH₃ at room temp. give PhCN; at 100°, uni- and ter-mol. PhCN result.

H. B.

Triarylaminoethylenes. VI. Coloured by-products formed during the synthesis of triarylaminoethylenes. R. SHIBATA and T. NISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 625—630B; cf. A., 1933, 1286).—The by-product (I), m.p. 141°, obtained in the synthesis of tri-*p*-tolylaminoethylene (II) is C₆H₄Me·N:C(NH·C₆H₄Me)·CH:N·C₆H₄Me, since it yields (II) with Na-Hg and EtOH or when hydrogenated (Pd-black) in Et₂O, and is formed from (II) by PbO₂ and CaCl₂ in boiling C₆H₆, by KMnO₄ in hot COMe₂, by O₂ in hot PhMe-20% NaOH emulsion, by heating in high-boiling solvents, e.g., decahydronaphthalene, or by heating above the m.p. (which gives also a small amount of a substance, m.p. 207°). (II) with ZnCl₂ at 180° gives a substance, m.p. 100—101°, and with S at 140—150° gives tri-*p*-tolylaminothioethylene, m.p. 137°, and a trace of dithio-ox-*p*-toluidide, m.p. 201°. NH₂Ph and C₂HCl₃ give a red and a yellow compound, m.p. 115—117°. β -C₁₀H₇-NH₂ gives tri- β -naphthylaminoethylene, m.p. 200°.

R. S. C.

Preparation of *p*-azoxyanisole. B. M. BOGOSLOVSKI (Anilinokras. Prom., 1933, 3, 304—307).—96% yields of *p*-azoxyanisole, m.p. 117°, are obtained by heating *p*-nitroanisole with Na and MeOH at 65—67° during 6 hr.

R. T.

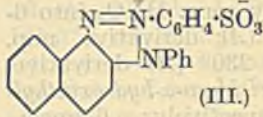
Sensitivity to light of aryl- β -naphthylamine-azo-dyes. F. KRÖLLPFEIFFER, C. MÜHLHAUSEN, and G. WOLF (Annalen, 1933, 508, 39—51).—Exposure of a dil. (1 : 10,000) aq. solution of 1-*p*-sulphobenzene-azo-*N*-phenyl- β -naphthylamine (I) to sunlight gives *ang*-naphthphenazine (II) and (mainly) the betaine (III), m.p. about 360° (decomp.), of 3-phenyl-2-*p*-

sulphophenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolium hydroxide.

Aq. solutions of (III) show strong green fluorescence; treatment with alkaline reducing agents regenerates (I). (III) is also prepared by oxidation (amyl nitrite or K₂Cr₂O₇ in AcOH) of (I). Exposure of 1-benzeneazo-*N*-phenyl- β -naphthylamine (IV) (on cotton; immersed in H₂O) gives (after concn. of the extract and treatment with picric acid) 2 : 3-diphenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolium picrate, m.p. 244—245°; (II) is not produced. The *N*-Bz derivative of (IV) is much more stable to light; it is oxidised (H₂O₂, AcOH) to the *N*-Bz derivative, m.p. 173—174° (decomp.), of 1-benzeneazoxy-*N*-phenyl- β -naphthylamine, m.p. 132—133°, which is converted by AcOH-HCl at 150° into 2 : 3-diphenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolium chloride. 2 : 3-Diphenyl- (V), decomp. 305°, 3-phenyl-2-*p*-chlorophenyl-, decomp. 278—279°, 3-phenyl-2-*p*-nitrophenyl-, m.p. 215° (decomp.), 2-phenyl-3-*p*-tolyl-, decomp. 270°, and 2-phenyl-3-chlorophenyl-, decomp. 237—238°, - $\alpha\beta$ -naphth-1 : 2 : 3-triazolium nitrates are prepared by oxidation (amyl nitrite, AcOH) of the requisite 1-aryloxy-*N*-aryl- β -naphthylamines and subsequent treatment with a little conc. HNO₃. Successive treatment of wool or cotton with these salts and alkaline Na₂S₂O₄ gives the azo-dye on the fibre; e.g., (IV) is thus prepared from (V). Diphenyl-4 : 4'-bis-(1-azo-*N*-phenyl- β -naphthylamine) (VI), m.p. 281—282° (from tetrazotised benzidine and β -C₁₀H₇-NPh), is oxidised (as above) to 2 : 2'-(4 : 4'-diphenyl)bis-(3-phenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolium nitrate) [corresponding picrate, m.p. 320—321° (decomp.)]. 2 : 2'-(3 : 3'-Dichloro-4 : 4'-diphenyl)-bis-(3-phenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolium nitrate), decomp. 250—260° (corresponding picrate, m.p. 305—306°), is similarly prepared. (VI) (on cotton) is bleached rapidly by sunlight in air or O₂; in N₂, bleaching is very slow. Azo-dyes from *N*-alkyl- β -naphthylamines are not so readily convertible into triazolium salts and are much more stable to light. Bleaching of, e.g., (IV) probably involves initial oxidation of >NH.

H. B.

Action of halogens on nitrophenylazobenzoyl-acetones. F. D. CHATTAWAY and D. R. ASHWORTH (J.C.S., 1933, 1624—1627).—Action of Cl₂ in CHCl₃ on *p*-nitrobenzeneazobenzoylacetone (I), m.p. 143°, replaces the COMe group with formation of ω -chlorophenylglyoxal-*p*-nitrophenylhydrazone, m.p. 243°; in AcOH in presence or absence of NaOAc nuclear substitution also occurs giving ω -chlorophenylglyoxal-2-chloro-4-nitrophenylhydrazone, m.p. 183°. Similarly, from *o*-nitrobenzeneazobenzoylacetone (II), m.p. 145°, ω -chlorophenylglyoxal-*o*-nitro-, m.p. 151°, and 4-chloro-2-nitro-phenylhydrazone, m.p. 157°, are formed. ω -Bromophenylglyoxal-*p*-nitrophenylhydrazone, m.p. 247° (decomp.), is formed from (I) and Br in AcOH in presence of NaOAc only; in CHCl₃ or boiling AcOH substitution of the CH₃ group occurs with formation of δ -bromo- (III), m.p. 172° (decomp.), and $\delta\delta$ -di-bromo- $\alpha\beta$ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone (IV), m.p. 190° (decomp.). Action of KOAc in boiling EtOH on (III) and (IV), respectively, gives



(III.)

4-hydroxy- (V), m.p. 211.5°, and 5-bromo-4-hydroxy-3-benzoyl-1-p-nitrophenylpyrazole, m.p. 167°. Cl_2 in CHCl_3 converts (V) into 5:5-dichloro-3-benzoyl-1-p-nitrophenyl-4-pyrazolone, m.p. 145°, which with aq. HI gives 5-chloro-4-hydroxy-3-benzoyl-1-p-nitrophenylpyrazole, m.p. 177°, and with boiling EtOH gives Et $\alpha\beta\gamma$ -triketo- γ -phenyl-n-butylate- β -p-nitrophenylhydrazone (VI), m.p. 135° [free acid, m.p. 154° (cold dil. NaOH)]. (VI) is also formed from diazotised $\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and Et sodiobenzoylpyruvate. The following are similarly prepared from (II): δ -bromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -o-nitrophenylhydrazone, m.p. 155° (decomp.); 4-hydroxy-3-benzoyl-1-o-nitrophenylpyrazole, m.p. 121° (5-Cl-derivative, m.p. 120°); 5:5-dichloro-3-benzoyl-1-o-nitrophenyl-4-pyrazolone, m.p. 166°; Et, m.p. 108°, and Me $\alpha\beta\gamma$ -triketo- γ -phenyl-n-butylate- β -o-nitrophenylhydrazone, m.p. 119°. Many of the above are dimorphous, but the stable form only is described.

H. A. P.

Manufacture of azo dyes.—See B., 1934, 89.

Azo-derivatives of methyleneindoline.—See this vol., 195.

Replacement of diazo- by acetoxy-group. H. L. HALLER and P. S. SCHAFFER (J. Amer. Chem. Soc., 1933, 55, 4954—4955).—*m*-Chlorobenzene-diazonium borofluoride heated with AcOH gives about 50% of *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OAc}$. *p*-Acetamidobenzene-diazonium borofluoride and Ac_2O similarly give about 52% of diacetyl-*p*-aminophenol; AcOH can be used, but the product is less pure.

H. B.

Preparation of trihydroxyarylsulphonium derivatives of *o*- and *p*-substituted phenols and arylsulphonium bases. D. LIBERMANN (Compt. rend., 1933, 197, 1425—1427).—Thermal decomp. of aryl chlorosulphites (A., 1933, 48; reacting as $\text{HO}\cdot\text{Ar}\cdot\text{SOCl}$) in a suitable solvent affords tri(hydroxy-aryl)sulphonium chlorides (I) isolated as the Bz_4 derivative of the corresponding hydroxides, PhOH yielding tribenzoyloxyphenylsulphonium benzoate $+\text{H}_2\text{O}$. Similar derivatives are obtained from *p*-cresol, m.p. 53°, *p*-chlorophenol, m.p. 57—58°, and guaiacol, m.p. 51°. Treatment of conc. solutions of (I) in EtOH at 95° with NaCN affords tri-(*p*-hydroxyphenyl)-, m.p. 235°, and tri(hydroxytolyl)- (from *o*-cresol), m.p. 264°, -sulphonium hydroxides. The aryl derivatives of orthosulphurous acid obtained by Richter (A., 1919, i, 73) are also sulphonium bases.

J. W. B.

Germicidal action of 2-chloro-4-*n*-alkylphenols. F. F. BLICKE and R. P. G. STOCKHAUS (J. Amer. Pharm. Assoc., 1933, 22, 1090—1092).—The phenol coeffs. of homologous 2-chloro-4-*n*-alkylphenols (cf. Klarmann *et al.*, A., 1933, 817) increase progressively from Me to C_7H_{15} . The m.p. of their α -naphthoates are, respectively: 108—110°, 70—72°, 71—73°, 44—46°, 63—65°, 43—45°, 45—47°. The following are also mentioned: *p*-tolyl α -naphthoate, m.p. 61—63°, and diphenyl-*p*-carboxylate, m.p. 122—124°; *m*-chloro-*p*-tolyl *p*-nitrobenzoate, m.p. 88—90°, diphenyl-*p*-carboxylate, m.p. 111—113°, and benzoate, m.p. 67—68°; 2-chloro-4-ethylphenyl benzoate, m.p. 44—46°; 2-chloro-4-*n*-hexoyl-, m.p. 79—81°, 4-*n*-

hexoyl-, m.p. 61—62°, and 2:6-dichloro-4-*n*-hexylphenol, b.p. 308—310°/745 mm. W. S.

Derivatives of *o*-aminophenol. L. GALATIS (Ber., 1933, 66, [B], 1774—1779).—Treatment of *o*-benzylideneaminophenol (I) with Ac_2O in presence or absence of NaOAc at 110—120° affords the *O*-Ac derivative and *N*-acetyl-2-phenylbenzoxazoline (II),

$\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \cdot \text{Ac} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CHPh}$, m.p. 98.5°, in 50% yield. The intermediate production of *o*-hydroxyacetbenzylamidophenol is established by the formation of PhCHO, *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, and 2-methylbenzoxazole when the product obtained from the cold reactants is treated with dil. HCl; addition of AcOH to $\cdot\text{N}\cdot\text{C}<$ does not occur in absence of Ac_2O . (II) is converted by conc. HCl into the hydrochloride of a compound, m.p. 245—255°. (I) is very readily hydrolysed by acid, whereas the corresponding *p*-derivative is stable.

H. W.

Organic compounds of sulphur. XXIV. "Free" radicals with univalent sulphur. A. SCHÖNBERG, E. RUPP, and W. GÜMLICH (Ber., 1933, 66, [B], 1932—1945; cf. A., 1933, 291, 487).—Solutions of di- α -thionaphthoyl disulphide (I) in $\text{C}_2\text{H}_4\text{Br}_2$ at 97°, PhOMe at 100°, C_{10}H_8 at 100°, phenanthrene at 110°, xylene, and Ph_2O do not obey Beer's law. Similar observations are made with Ph_2S_2 (II) in C_{10}H_8 , PhOMe, and $\text{C}_2\text{H}_4\text{Br}_2$ at 100°, whereas diphenylene disulphide (III) behaves normally. The behaviour is explained by the hypothesis of radical dissociation of (I) and (II) and the normal behaviour of (III) is expected, since dissociation, if occurring, does not lead to an increase of the no. of mols. in the dissolved phase. Solutions of (I) and (III) are markedly thermochromic. The following chemical evidence in favour of radical dissociation is adduced. (II) and CPh_3 afford $\text{SPh}\cdot\text{CPh}_3$. Solutions of the Na derivative (IV) of $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$ are almost instantaneously decolorised by (I) and (II). (I) reacts instantaneously with CH_2N_2 , but the nature of the amorphous product could not be established. (II) and CPh_2N_2 yield $\text{CPh}_2(\text{SPh})_2$. (I) in boiling COMe_2 or $\text{COMe}_2\text{-CHCl}_3$ readily dissolves Ag or Zn with formation of Ag ($+0.5\text{C}_5\text{H}_5\text{N}$) and Zn ($+0.5\text{C}_5\text{H}_5\text{N}$) α -dithionaphthoate. Solutions of (I) and (II) are stable towards atm. O_2 . Determination of mol. wt. does not give evidence of radical dissociation in any case, but experiments have not been made in media of high b.p. on account of the danger of thermal decomp. Solutions of (I) in C_{10}H_8 at 100° are not electrolytes. Solutions of Ph_2Se_2 are strongly thermochromic and with (IV) produce $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$ and NaSePh .

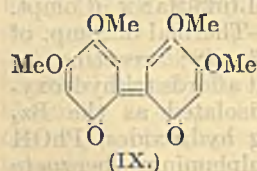
H. W.

Constitution of resorcinol and acetylacetone viewed from the Raman effect. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 16—21; cf. A., 1933, 764).—A reply to criticism (*ibid.*, 1144). Further work confirms the existence of the diketone-form of *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ in equilibrium with the phenolic form in MeOH solution. Repetition of the work on CH_2Ac_2 revealed lines previously overlooked, but the main conclusions are unaltered thereby. The data for $(\cdot\text{CH}_2\text{Ac})_2$ are further discussed. D. R. D.

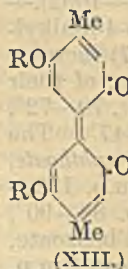
Formation of complex oxidation and condensation products of phenols. Origin and nature of humic acid. I. Reactivity of simple monocyclic quinones. II. Coupling of simple phenols and quinones to diphenyl derivatives. III. Rearrangements of oxidation-reduction type in the diquinone group. IV. Termolecular polymerisation products of *p*-benzoquinone, toluquinone, and α -naphthaquinone. H. G. H. ERDTMAN (Proc. Roy. Soc., 1933, A, 143, 177—191, 191—222, 223—228, 228—241).—I. The reactivity of various methoxyquinones towards $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ (I) and oxidative coupling is in qual. agreement with the predictions of electronic theory. Methoxybenzoquinone [prep. by oxidation of methoxyquinol (Ac_2 derivative, m.p. 95—96°) with $\text{PbO}_2-\text{MgSO}_4$ in hot dry C_6H_6 described] with Ac_2O containing 2 wt.-% H_2SO_4 affords 2:4:5-triacetoxyanisole, m.p. 142°, hydrolysed ($\text{H}_2\text{SO}_4-\text{MeOH}$ in H_2) and methylated to 1:2:4:5-tetramethoxybenzene, oxidised by HNO_3 to 2:5-dimethoxybenzoquinone, which, like the 2:6-compound, is unattacked by (I). 2:3-Dimethoxybenzoquinone similarly affords 1:2:3-triacetoxy-3:4-dimethoxybenzene, m.p. 96—97°, *m*- and *p*-xyloquinones giving 2:4:5-triacetoxy-*m*-, m.p. 103—104° (lit., m.p. 99°), and 2:3:5-triacetoxy-*p*-xylene, respectively. 5-Methoxytoluquinone (II) gives 2:3:5-triacetoxy-4-methoxytoluene, m.p. 91—92°, hydrolysed and methylated to 2:3:4:5-tetramethoxytoluene, m.p. 51—52°, identical with a specimen similarly prepared from the Ac_4 derivative of Thiele and Winter (A., 1900, i, 504), the phenol obtained by these authors being, therefore, 2:3:4:5-tetrahydroxytoluene. With $\text{AcCl}-\text{AcOH}$ (II) similarly affords 3-chloro-2:5-diacetoxy-4-methoxytoluene, m.p. 126°. Thymoquinone with (I) gives a mixture of 2:3:6-, m.p. 87—88° (38%), and 2:3:5-, m.p. 136—137° (57%), -triacetoxy-1-methyl-4-isopropylbenzene, separated by fractional crystallisation from EtOH , and synthesised by the action of $\text{Ac}_2\text{O}-\text{AcOH}$ and Zn on 3- and 6-hydroxythymoquinone, respectively; 3:5:3':5'-tetramethyldibenzoquinone (Auwers *et al.*, A., 1905, i, 219) similarly gives 2:4:4'-triacetoxy-3:5:3':5'-tetramethyldiphenyl, m.p. 141—142°. With Br in AcOH creosol gives its 6-*Br*-derivative, b.p. 270—275° (slight decomp.), m.p. 82—83° (Br entering *p* to OMe), converted by Me_2SO_4 into 6-bromohomoveratrole.

II. All bishydroxyquinols in the lit. obtained by oxidative coupling of hydroxyquinols are derivatives of 2:4:5:2':4':5'-hexahydroxydiphenyl. The dipyrrogallol obtained by Harries (A., 1902, i, 771) by autoxidation of pyrogallol (III) in aq. $\text{Ba}(\text{OH})_2$ is 2:3:4:2':3':4'-hexahydroxydiphenyl (IV), darkens 280°, m.p. 310—320° (decomp.) (Ac_6 derivative, m.p. 163—164°), the Me_6 ether, m.p. 123° (Br_2 -compound, m.p. 110—111°), of which is identical with a specimen synthesised by heating 4-iodopyrogallol Me_3 ether (Graebe and Suter, A., 1905, i, 703) with Cu powder. With NaOH in place of $\text{Ba}(\text{OH})_2$ the sole product is the humic acid which also accompanies (IV), and no (IV) is obtained by anodic oxidation of (III) in $\text{N}-\text{H}_2\text{SO}_4$, but such oxidation of the Me_3 ether of (III) gives 2:6-dimethoxybenzoquinone and tarry products. Partial oxidation of methoxybenzoquinone (from vanillin and $\text{H}_2\text{O}_2-\text{NaOH}$) with FeCl_3-HCl at

30—40°, or the action of $\text{H}_2\text{SO}_4-\text{AcOH}$ affords a coupled product (V), probably 4:4'-dimethoxydiquinhydrone, sinters 210°, decomp. 230°, also obtained (with methoxyquinol) by thermal decomp. of methoxyquinhydrone, m.p. 97° (rapid heating) (prepared from its components), at 95—100°. When oxidised with dil. CrO_3 (V) gives 4:4'-dimethoxydiquinone (VI), decomp. 212—214°, converted by prolonged action of (I) into 2(?):3:6:2'(?):3':6'-hexa-acetoxy-4:4'-dimethoxydiphenyl, m.p. 200°, which when demethylated and acetylated gives only a trace of an unidentified *Ac* derivative, m.p. 264—266°. Passage of HCl into a $\text{CHCl}_3-\text{AcOH}$ suspension of (VI) gives a chlorophenol (probably 6:6'-dichloro-2:4:2':4'-tetrahydroxy-4:4'-dimethoxydiphenyl), dissociating into its components on heating and giving an Ac_2 derivative, m.p. 232°, with cold 1% H_2SO_4 in Ac_2O . With hot Ac_2O the main product is (VI) together with an (?) anhydride, m.p. 253°. Reduction of (VI) with SO_2 in H_2O suspension at 100° gives (V), but with HI and $\text{NHPh}-\text{NH}_2$, 4:4'-dimethoxydiquinol, m.p. 210° (decomp.) [oxidised to a humic acid in alkaline solution, and by HNO_3 to (VI)], the Ac_4 derivative, m.p. 186—187°, of which is hydrolysed and methylated to 2:4:5:2':4':5'-hexamethoxydiphenyl (VII), m.p. 177—179°, identical with the products obtained by Fabinyi and Szeki (A., 1910, i, 837) and Schuler (A., 1907, i, 700), whereas HBr followed by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ gives the corresponding (OAc)₆-derivative (Barth and Schreder, A., 1885, 520) and 2:3:6:7-tetra-acetoxydiphenylene oxide, m.p. 262° (Brezina, A., 1901, i, 700). With ICl, or $\text{I}+\text{HgO}$, the Me_3 ether (VIII) of hydroxyquinol gives (VII) as its labile additive compound with I, but anodic oxidation of (VIII) in acid solution, or CrO_3 followed

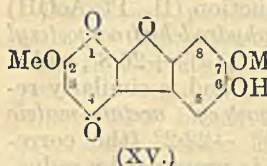


by Zn dust, gives (VII), and a small yield of the indigoid quinone (IX) (bluish-violet), m.p. 185—187°, converted by conc. HNO_3 into (VI). With 3% H_2O_2 and NaOH followed by acetylation dehydrodivanillin (Elbs and Lerch, A., 1916, i, 315) gives the Ac_4 derivative (X), m.p. 176—178° (6:6'- Br_2 -derivative, m.p. 207—208°), of 3:3'-dimethoxydiquinol which cannot be isolated owing to its rapid polymerisation to a humic acid, but hydrolysis and methylation gives 2:3:5:2':3':5'-hexamethoxydiphenyl, m.p. 119—120° [6:6'- Br_2 - (XI), m.p. 271—272°, and 6:6'-(NO_2)₂-, m.p. 300—301°, -derivatives]. Cold conc. HNO_3 converts (XI) into 6:6'-dibromo-3:3'-dimethoxydibenzoquinone, sinters 236°, m.p. 240—242° (decomp.). The Me_2 ether (XII) of toluquinol (improved prep.) with HNO_3 (*d* 1.42)- AcOH gives its 5- NO_2 -derivative, m.p. 117—118°, and with $\text{I}-\text{HgO}$ at 85—95° affords its 5-*I*-derivative, m.p. 85°. The ditoluquinone (XIII, R=Me) of Nietzki and Bernard (A., 1898, i, 529) with Zn- Ac_2O gives tetra-acetoxyditolyl (XIV) converted into 2:5:2':5'-tetramethoxydi-*p*-tolyl, m.p. 135—136°, identical with a specimen obtained from 4-iodotoluquinol Me_2 ether and Cu powder at 210°, thus proving the above struc-



ture for (XIII). Spica's "toluquinone polymeride" (A., 1882, 196) also gives (XIV) by reductive acetylation. Reduction (SO_2 in boiling EtOH) of Nietzki's quinone and subsequent ethylation (EtI-NaOEt) affords 5 : 5'-dimethoxy-2 : 2'-diethoxydi-p-tolyl, m.p. 116—118°, not identical with 2 : 2'-dimethoxy-5 : 5'-diethoxydi-p-tolyl, m.p. 94—96°, similarly obtained by reduction and methylation of the diquinone obtained by Noeltling and Werner (A., 1891, 209) from toluquinol Et₂ ether. Noeltling's diquinone is therefore (XIII, R=Et). With (I) ditoluquinone gives 2(?) : 3 : 6 : 2'(?) : 3' : 6'-hexa-acetoxydi-p-tolyl, m.p. 202—203°, and with HCl affords a chlorophenol analogous to that obtained from (VI). Reduction of nitroquinol (CH_2Ph)₂ ether affords the corresponding NH_2 -compound, m.p. 100—102° (Ac, m.p. 86—87°, and p-nitrobenzylidene, m.p. 105°, derivatives). With the appropriate aldehyde 2-iodo-4-nitroaniline affords its p-, m.p. 194—196°, and m-, m.p. 177—178°, -nitrobenzylidene derivatives.

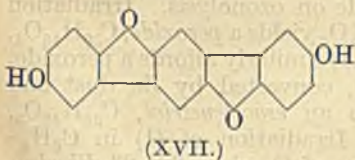
III. When heated at 250—280° in 1-C₁₀H₇Br (VI) affords 6-hydroxy-2 : 7-dimethoxydiphenylene oxide-



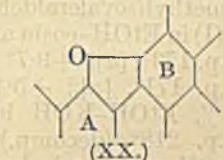
(XV.)

1 : 4-quinone (XV), sinters 242°, m.p. 250° (Ac derivative, m.p. 252—254°), reduced by Zn-AcOH to 1 : 4 : 6-trihydroxy-2 : 7-dimethoxydiphenylene oxide, decomp. 210° (tri-p-nitrobenzoyl derivative, m.p. > 300°), the Ac₃ derivative, m.p. 232—233°, of which with 2% H₂SO₄-MeOH, followed by methylation, affords 1 : 2 : 4 : 6 : 7-pentamethoxydiphenylene oxide, m.p. 109—110°. Ditoluquinone undergoes a similar rearrangement to give 6-hydroxy-2 : 7-dimethoxydiphenylene oxide-1 : 4-quinone, m.p. 218—220°, converted by reductive acetylation into 1 : 4 : 6-triacetoxy-2 : 7-dimethoxydiphenylene oxide, m.p. 168—171°, and a trace of the Ac₄ derivative of 4 : 4'-dimethoxydiquinol.

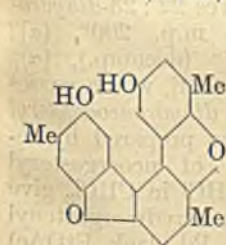
(IV). With cold conc. H₂SO₄-AcOH p-benzoquinone (XVI) affords quinol (about 50%) and a dark-coloured ppt. which, after reductive acetylation, gives dihydroxytriphenylene dioxide C₁₈H₁₀O₄ (XVII), m.p. 336—340°, isolated and purified as its Ac₂ derivative, m.p. 236—237°, together with amorphous products. With



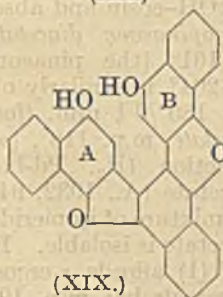
(XVII.)



(XX.)



(XVIII.)



(XIX.)

Me₂SO₄-NaOH in H₂ (XVII) affords a Me₂ ether, m.p. 210—211° (Br₂-derivative, decomp. about 300°).

Analysis of the products of reductive acetylation or methylation of the quinone humic acids obtained by polymerisation of (XVI) in NaOH indicates a lower C content than is present in the amorphous products of acid polymerisation. Similar acid polymerisation of toluquinone affords a dihydroxytriphenylene dioxide C₂₁H₁₆O₄, +2H₂O and anhyd. (XVIII), m.p. >300° (rapid heating) [Ac₂ derivative, m.p. 285—286°; Me₂ ether, m.p. 233—234° (Br-, m.p. 274—275°, and NO₂-, m.p. 305°, -derivatives)], identical with the substance given the composition (C₇H₅O)_x by Brunner (A., 1889, 996). Polymerisation of α-naphthaquinone occurs more slowly, but with AcOH-H₂SO₄ at 40—50° is isolated the Ac₂ derivative C₃₄H₂₀O₆, m.p. 340—343° (sol. in quinoline), of a bisanhydrotrinaaphthaquinol, probably (XIX), and the trioxide C₃₀H₁₂O₆ (XX), sublimes at 300—330°/high vac., charring > 400° (insol.). The above structures are assigned on the basis of the previous results. J. W. B.

Alkyl-substituted aromatic hydroxy-compounds.—See B., 1934, 54.

1-Cyano-Δ¹-cyclohexene. R. VAN COILLIE (Bull. Soc. chim. Belg., 1933, 42, 419—426).—1-Hydroxy-1-cyanocyclohexane, b.p. 119.5°/10 mm., 132°/20 mm., m.p. 26° (lit. 29°), and SOCl₂ first in the cold and then at 100° (bath) give 2-chloro-1-cyanocyclohexane (I), b.p. 121—121.4°/12 mm., m.p. 22.4—23°, a stereoisomeride (II), b.p. 109—110°/12 mm., m.p. -8° to -6°, and a product (A), b.p. 75—76°/12 mm., which consists mainly of (III) (below) and could not be freed from Cl by repeated distillation. PCl₅ gives similar products. (A) absorbs dry HCl to yield (I). (I) and C₅H₅N at 100° afford 1-cyano-Δ¹-cyclohexene (III), b.p. 73.9—74.2°/11.5 mm., also formed (together with a little of the corresponding amide) from (I) or (II) and 5% NaOH at 100° (bath). Contrary to Cocker *et al.* (A., 1931, 1037), (I) is unaffected by boiling H₂O. H. B.

β-2-Naphthylethyl alcohol and 2-vinylnaphthalene. (MLLE.) D. SONTAG (Compt. rend., 1933, 197, 1130—1132).—β-2-Naphthylethyl alcohol, m.p. 67.5—68° [prepared from 2-C₁₀H₇-MgBr and (CH₂)₂O, in small amount from 2-C₁₀H₇-CH₂-MgBr and CH₂O, and by reduction (Bouveault) of 2-C₁₀H₇-CH₂-CO₂Et], heated with KOH gives 2-vinylnaphthalene, b.p. 135—137°/18 mm., m.p. 66° (dibromide, m.p. 84.5—85°). Dehydration of α-2-naphthylethyl alcohol [by reduction (Na-Hg) of 2-C₁₀H₇Ac] with NaHSO₄ gives a small amount of a liquid product. H. B.

Displacement in the allyl group. J. MEISENHEIMER and G. BEUTTER (Annalen, 1933, 508, 58—80).—The amounts of α-phenylallyl acetate (I) formed when cinnamyl chloride (II) is treated with various metal acetates (1.5 equivs.) in AcOH (containing about 3.5% H₂O) at 100° (bath) are: Li, about 9%; Na, 20%; K, 22%; Mg, 0; Ca, about 6%; Ba, 21%; Pb, 30%; the amount of "abnormal substitution" increases with increased at. wt. of the metal. The change (I) → cinnamyl acetate (III) occurs more rapidly in AcOH alone at 100° (bath) than in presence of metal acetates; retardation is most marked with the most electropositive metals. Addition of H₂O to the AcOH causes acceleration either in absence or presence of acetates. The "abnormal substitution"

with (II) and KOAc in AcOH is diminished by addition of H_2O ; normal substitution [formation of (III)] is favoured. Increase in the concn. of KOAc (or LiOAc) favours "abnormal substitution" and suppresses the change (I) \rightarrow (III). (II) also reacts with AcOH alone forming about 16% of the theoretical amount of HCl: $CHPh:CH:CH_2Cl + AcOH \rightarrow CHPh:CH:CH_2OAc$ (or $OAc:CHPh:CH:CH_2$) + HCl. The reaction between (II) and KOAc in AcOH and Ac_2O is studied kinetically; reaction occurs about ten times as fast in AcOH, but in Ac_2O (III) is the sole product. The reaction in AcOH is considered to involve direct participation of the solvent and to be termol. H. B.

Law of periodicity. IX. Constitution of triarylmethyl compounds. L. PETRENKO-KRITSCHENKO (Ber., 1933, 66, [B], 1771—1774; cf. A., 1933, 1048).—A reply to Hantzsch *et al.* (*ibid.*, 1158). H. W.

Rates of thermal decomposition of triphenylmethyl alkyl ethers.—See this vol., 151.

Preparation of higher ethers.—See B., 1934, 54.

Production of α -*p*-aminophenyl- β -methylamino-*n*-propyl alcohol.—See B., 1934, 54.

Catalytic oxidations. IV. Photochemical oxidation of some ethylenic double linkings. V. Oxidation of ergosterol.—See this vol., 155.

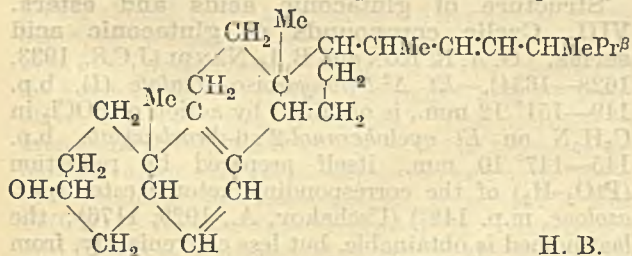
Ergosteryl acetate-maleic anhydride and its hydro-derivatives. H. H. INHOFFEN (Annalen, 1933, 508, 81—88).—Ergosteryl acetate (I) and maleic anhydride (II) in xylene at 135° give the adduct *ergosteryl acetate-maleic anhydride* (III), m.p. 216° , $[\alpha]_D^{20} -19^\circ$ (all rotations are in $CHCl_3$) (*dibromide*, m.p. $252-253^\circ$), which differs from that obtained by Windaus and Lüttringhaus (A., 1931, 840) from ergosterol-maleic acid and Ac_2O . (III) is hydrolysed (EtOH—conc. H_2SO_4) to *ergosterol-maleic anhydride*, m.p. 202° (5—10% yield), re-acetylated (Ac_2O) to (III). Hydrolysis (10% MeOH—KOH) of (III) gives ergosterol-maleic acid, m.p. $198-199^\circ$ (decomp.) [Me_2 ester (IV), m.p. 163° , the *acetate*, m.p. 164° , of which is also obtained from (III), Me_2SO_4 , and alkali with subsequent acetylation]. (III) distils practically unchanged at $240^\circ/0.0002$ mm.: at 220° /about 15 mm., almost quant. fission into (I) and (II) occurs. Reduction (H_2 , Pd-black, $COMe_2$) of (III) gives 22:23-*dihydroergosteryl acetate-maleic anhydride* (V), m.p. $202-203^\circ$ (sinters at $172-174^\circ$), $[\alpha]_D^{20} -9.1^\circ$, which does not absorb Br and affords no α -methylisovaleraldehyde on ozonolysis. Similar reduction of (IV) and subsequent acetylation gives 22:23-*dihydroergosteryl acetate-Me maleate*, m.p. $116-117^\circ$, also obtained by successive hydrolysis, esterification, and acetylation of (V). Reduction (H_2 , Pt, AcOH) of (III) yields *tetrahydroergosteryl acetate-maleic anhydride*, m.p. $187-187.5^\circ$, $[\alpha]_D^{20} -25.4^\circ$, which does not undergo thermal fission; hydrolysis (EtOH—KOH) gives tetrahydroergosterol-maleic acid, m.p. $218-220^\circ$ (decomp.) (Me_2 ester *acetate*, m.p. 138° , $[\alpha]_D^{20} -69.8^\circ$). Structures for (III) are suggested. H. B.

Adducts from maleic anhydride and dehydroergosterol and their hydrogenation products. H. HONIGMANN (Annalen, 1933, 508, 89—104).—The

adduct dehydroergosteryl acetate-maleic anhydride (I) [*dibromide*, m.p. 245° (decomp.)], prepared by Murke's method (Diss., Göttingen, 1931; cf. A., 1931, 840), is usually obtained with m.p. $220-240^\circ$ (decomp.) (according to rate of heating); in two cases, the m.p. was 205° (as found by Murke). (I) distils at $210-220^\circ/0.0004$ mm., but at $240^\circ/0.1$ mm. the components are regenerated. Hydrolysis (10% MeOH—KOH) of (I) gives dehydroergosterol-maleic acid, m.p. $170-175^\circ$ (decomp.), $[\alpha]_D^{20} +67.5^\circ$ (all rotations are in $CHCl_3$) (Me_2 ester *acetate*, m.p. 180°). (I) is reduced (H_2 , Pd-black, $COMe_2$) to *dihydrodehydroergosteryl acetate-maleic anhydride* (II), m.p. 216° , $[\alpha]_D^{20} +81.6^\circ$, which when distilled at about 15 mm. affords 22:23-*dihydrodehydroergosteryl acetate* (III), m.p. 128° , $[\alpha]_D^{20} +219.9^\circ$, the absorption curve of which resembles that of dehydroergosteryl acetate. *Dihydrodehydroergosterol-maleic acid* (+ $0.5H_2O$) [Me_2 ester *acetate*, m.p. 163° (sinters about 155°)] has m.p. 180° (decomp.). Reduction (Na, EtOH) of (III) gives a *tetrahydrodehydroergosterol* (+ H_2O), m.p. 132° , $[\alpha]_D^{20} -12.5^\circ$ (*acetate*, m.p. 141° , $[\alpha]_D^{20} -9.7^\circ$), which contains two double linkings (BzO_2H). Reduction (H_2 , Pt, AcOH) of (I) or (II) yields *tetrahydrodehydroergosteryl acetate-maleic anhydride*, m.p. 197° , $[\alpha]_D^{20} +26.8^\circ$, which does not undergo thermal fission and is similarly reduced to *hexahydrodehydroergosteryl acetate-maleic anhydride* (IV), m.p. 187° , $[\alpha]_D^{20} -22.2^\circ$ [the corresponding Me_2 ester, m.p. 138° , is prepared by reduction (H_2 , Pt-black, AcOH) of *tetrahydrodehydroergosteryl acetate-Me maleate*, m.p. 135°]. *Tetrahydrodehydroergosterol-maleic acid* has m.p. 180° (decomp.), $[\alpha]_D^{20} +63^\circ$. (IV) is identical with tetrahydroergosteryl acetate-maleic anhydride (preceding abstract). Structures are suggested for the above adducts. H. B.

22:23-Dihydroergosterol. A. WINDAUS and R. LANGER (Annalen, 1933, 508, 105—114).—22:23-*Dihydroergosteryl acetate* (I), m.p. $157-158^\circ$, $[\alpha]_D^{20} -74.8^\circ$ (all rotations are in $CHCl_3$), is obtained when its adduct with maleic anhydride (Inhoffen, see above), is heated at 220° /about 15 mm. and then distilled in a high vac. Hydrolysis (EtOH—KOH in N_2) affords 22:23-dihydroergosterol (II), m.p. $152-153^\circ$, $[\alpha]_D^{20} -109^\circ$, which does not give α -methylisovaleraldehyde on ozonolysis. Irradiation of (I) in EtOH—eosin and O_2 yields a *peroxide*, $C_{30}H_{48}O_4$, m.p. 173° , $[\alpha]_D^{20} +9.7^\circ$ [(II) similarly affords a peroxide, m.p. 171° , $[\alpha]_D^{20} +5.4^\circ$], converted by Zn dust and 10% EtOH—KOH into an *ergostenetriol*, $C_{28}H_{48}O_3$, m.p. 218° (decomp.). Irradiation of (I) in C_6H_6 —EtOH—eosin and absence of O_2 gives 22:23-*dihydroergopinacone diacetate*, $C_{60}H_{94}O_4$, m.p. 200° , $[\alpha]_D^{20} -161^\circ$ [the pinacone, m.p. 197° (decomp.), $[\alpha]_D^{20} -204^\circ$, is similarly obtained from (II)], which passes at $180^\circ/0.1$ mm. (for 1 hr.) into *dihydroergosteryl acetate*, m.p. 118° , $[\alpha]_D^{20} -3.1^\circ$, also prepared by reduction (H_2 , Pd-black, $COMe_2$) of neoergosteryl acetate (A., 1932, 944). (I) and HCl in $CHCl_3$ give a mixture of isomerides from which dehydroergosteryl acetate is isolable. Reduction (H_2 , Pd-black, EtOAc) of (I) affords α -ergostenyl acetate (the 3:5-*dinitrobenzoate* has m.p. $196-197^\circ$), whilst reduction (Na, PrOH) of (II) yields γ -ergostenol, m.p. $145-146^\circ$, $[\alpha]_D^{20} \pm 0^\circ$ [*acetate*, m.p. 157° , $[\alpha]_D^{20} -5.3^\circ$; *benzoate*

(III), m.p. 179°; 3:5-dinitrobenzoate, m.p. 209—210°]. (III) is isomerised by HCl-CHCl₃ to a mixture containing β -ergostenyl benzoate (Heilbron and Wilkinson, A., 1932, 845). When γ -ergostenol is shaken with H₂ and Pt- or Pd-black, α -ergostenol is produced. Ultra-violet irradiation of (I) gives product possessing antirachitic properties. The following constitution is now preferred for ergosterol.



Constitution of cholesterol and ergosterol. A. WINDAUS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 92—102; Chem. Zentr., 1933, ii, 1366—1367).—A discussion. A. A. E.

Oxidation product of α -ergostenol. T. ACHTERMANN (Z. physiol. Chem., 1933, 222, 70—72).—Oxidation of ergostenone with CrO₃ in 90% AcOH gave the unsaturated ketone, C₂₈H₄₄O₂, m.p. 183°, [α]_D²⁰ +105.9° in CHCl₃, which on catalytic reduction gave α -ergostenol. No product C₂₁H₃₂O₂ (?) was isolated (cf. Heilbron *et al.*, A., 1932, 845).

J. H. B.
Cerevisterol: composition, properties, and relation to other sterols. E. M. HONEYWELL and C. E. BILLS (J. Biol. Chem., 1933, 103, 515—519).—New analytical data for cerevisterol (I) and its Ac₂ derivative confirm the composition C₂₈H₄₆O₃ (two double linkings). Two O are present as OH, and the third is not present in a CHO, CO, OR, CO₂H, or lactone group, or in the ring structure, and is tentatively located to a *tert.*-alcohol group, failure to acetylate it being ascribed to steric hindrance. (I) does not form an insol. digitonide, but, like ergosterol, gives a positive reaction with CCl₃·CH(OH)₂ and CCl₃·CO₂H (Rosenheim). J. W. B.

Halogenation. VI. Bromination and iodination of benzonitrile. P. S. VARMA and N. B. SENGUPTA (J. Indian Chem. Soc., 1933, 10, 593—594).—Careful addition (not mixing) of PhCN to conc. H₂SO₄ followed by KBr gives *p*-C₆H₄Br·CN, a little *o*-C₆H₄Br·CN, BzOH, and NH₂Bz; *o*- and *p*-C₆H₄I·CN, BzOH, and NH₂Bz are similarly obtained using KI. H. B.

Addition of alkali alkoxides to acid esters. VIII. Sodium alkoxides and esters at higher temperatures. F. ADICKES, S. VON MULLENHEIM, and W. SIMSON (Ber., 1933, 66, [B], 1904—1909).—Prolongation of the action of EtOBz and NaOEt at 100° in absence of H₂O does not lead to a marked increase of the NaOBz produced, thus rendering improbable Scheibler's explanation that the effect is due to the change, ester+alkoxide=salt+C₂H₄+alcohol. The interaction of MeOBz (I), PrOBz, CH₂Ph·OBz (II), PhOBz, *o*-C₆H₄(CO₂Et)₂, *o*-C₆H₄(CO₂CH₂Ph)₂ (III), CO(OEt)₂, and CO(O·CH₂Ph)₂ (IV) with the corresponding Na

alkoxide has been investigated at about 180°. With (I), (II), (III), and (IV) production of ethers is observed, but subsidiary changes occur leading to production of H₂O, and hence of hydrolysis of the esters, since the yield of ethers attains only 50—83% of that expected from the amount of acid produced and 50—100% of the missing ether appears as alcohol. Repetition of Scheibler's experiments with EtOBz and NaOEt shows that CO is evolved in addition to C₂H₄ (ratio 20 : 1), and that there is no equivalence between NaOBz and C₂H₄; COPhMe and CH₂Bz₂ are obtained, the latter derived from the former, EtOBz, and NaOEt. In the case of *o*-C₆H₄(CO₂Et)₂, CH₂O is produced, which is partly condensed to methylenbisindandione. PrOBz reacts in the same manner as EtOBz, whereas CO(OEt)₂ does not react at atm. pressure. PhOBz does not react sufficiently rapidly at 250—270°. Ether is not formed and partial resinification affords the H₂O necessary for hydrolysis of the ester. *p*-Hydroxybenzophenone is formed to the extent of 8%. H. W.

Syntheses with acids of the type CHR·CH·CH₂·CO₂H and mixed organomagnesium derivatives. D. IVANOV and G. PCHÉNTCHNY (Compt. rend., 1933, 197, 1230—1231; cf. A., 1931, 483).—Interaction of CHPh·CH·CH₂·CO₂H (I) with MgPr^FCl or I-C₁₀H₇·MgBr followed by CO₂ affords *styrylmalonic acid*, m.p. 133° (decomp.). (I) with *m*- and *p*-C₆H₄Me·MgBr, and MgPhBr affords respectively *β -hydroxy- ϵ -phenyl- β -m.*, m.p. 138—139°, and *-p-tolyl.*, m.p. 165°, and *β - ϵ -diphenyl- α -styryl- Δ^{δ} -hexenoic acid*, m.p. 142—143°. Similarly, interaction of Δ^{δ} -hexenoic acid (II) with MgPr^FCl and CO₂ affords *Δ^{α} -butenylmalonic acid*, m.p. about 100°. MgPhBr and *p*-C₆H₄Me·MgBr with (II) afford, respectively, *β -hydroxy- β -phenyl.*, m.p. 145°, and *- β -p-tolyl- α -(Δ^{α} -butenyl)- Δ^{δ} -octenoic acid*, m.p. 124.5°. (I) and (II) afford no Na derivatives with NaOEt.

J. L. D.
Fixation of SbO₂H by aromatic monohydroxy-monobasic acids. DUQUÉNOIS (Compt. rend., 1933, 197, 1335—1336; cf. A., 1933, 1142).—Only α -OH-aromatic acids react with Sb₂O₃, max. fixation occurring with an equimol. mixture of the acid and its neutral salt, and max. reaction velocity with *tert.*-OH (OH·CPh₂·CO₂H). The following are described: *K antimonylmandelate* (cf. A., 1933, 948); *Na*, m.p. 257°, and *K*, m.p. 231°, *antimonyl- β -phenyl-lactate* Sb(OH)[O·CH(CH₂Ph)·CO₂H][O·CH(CH₂Ph)·CO₂K], and *Na*+H₂O and anhyd., m.p. 235° (decomp.), *K*+2H₂O, and NH₄, giving anhydride at 135°, decomp. 140°, *antimonylbenzilate*, of type Sb(OH)(O·CPh₂·CO₂H)(O·CPh₂·CO₂M). J. W. B.

Components of the Kawa root. XIV. Ethyl cinnamoylacetate. W. BORSCHÉ and M. LEWINSOHN [with, in part, R. SCHIFFNER] (Ber., 1933, 66, [B], 1792—1801; cf. A., 1933, 829).—Treatment of Et cinnamoylacetate (I) with 75% AcOH at 100° leads to *Et cinnamoylacetate* (II), m.p. 46° (*Cu* compound, m.p. 185—187°; 2:4-dinitrophenyl-hydrazone, m.p. 170—171°), CHPh·CH·CO₂Me, and CHPh·CH·CO₂H. (II) and NHPh·NH₂ in AcOH at 100° yield 3-styryl-1-phenylpyrazol-5-one, m.p. 148—149°. Distillation of (II) under 15 mm. gives

3-cinnamoyl-6-styryl-2:4-pyrone, m.p. 162° after softening at 158°. Treatment of (I) with $m\text{-C}_6\text{H}_4(\text{OH})_2$ or of its Na derivative (III) with $\text{COPh}\cdot\text{CH}_2\text{Br}$ leads to ill-defined products, whereas with chloro-2:4-dinitrobenzene and $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$, respectively, (III) gives *Et* α -2:4-dinitrophenylcinnamoylacetate, m.p. 120—121° (hydrolysed by H_2O at 130° to 2:4-dinitrobenzyl styryl ketone, m.p. 152—153°), and *Et* dicinnamoylacetate, m.p. 129° (hydrolysed at 120—130° to dicinnamoylmethane, m.p. 142°). Hydrogenation ($\text{Pd}\text{-EtOH}$) of (I) affords *Et* β -keto- δ -phenylvalerate (IV), b.p. 170—171°/13 mm. (*Cu* compound; 2:4-dinitrophenylhydrazone, m.p. 78°), and 3- β -phenylpropionyl-6-styryl-2:4-pyrone, m.p. 95°, transformed by fuming HCl at 120° into 2:6-di- β -phenylethyl-4-pyrone, m.p. 140°. (IV) is transformed by $m\text{-C}_6\text{H}_4(\text{OH})_2$ and conc. H_2SO_4 into 7-hydroxy-4- β -phenylethylcoumarin, m.p. 175—176°, and by Na in Et_2O followed by $\text{COPh}\cdot\text{CH}_2\text{Br}$ into non-cryst. *Et* α -diketo- α -diphenyl- n -hexane- γ -carboxylate, which yields *Et* iminoketo- α -diphenylhexane- γ -carboxylate, m.p. 147°, with $\text{NH}_3\text{-MeOH}$ at room temp. and *Et* 2- β -phenylethyl-1:5-diphenylpyrrole-3-carboxylate, m.p. 139—140°, with $\text{NH}_2\text{Ph-AcOH}$ at 100°. (IV), NaNH_2 , and $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ give *Et* β -keto- α -cinnamoyl- δ -phenylvalerate, m.p. 57° (*Cu* compound, m.p. 204—205°), whence γ -diketo- α -diphenyl- Δ^6 -heptene, m.p. 84—85° (*Cu* derivative, m.p. about 200°). Hydrogenation (colloidal $\text{Pd}\text{-EtOH}$) of (I) leads to *Et* β -keto- α -acetyl- δ -phenylvalerate (V), b.p. 130°/0.6 mm. (*Cu* compound, m.p. 136°), converted by 2:4-dinitrophenylhydrazine into *Et* 1:2':4'-dinitrophenyl-3- β -phenylethyl-5-methylpyrazole-4-carboxylate, m.p. 144—145°, and a small amount of 4-acetyl-1:2':4'-dinitrophenyl-3- β -phenylethylpyrazol-5-one, m.p. 178°. Hydrolysis of (V) gives γ -diketo- α -phenyl- n -hexane, b.p. 153—155°/14 mm. [converted by $m\text{-C}_6\text{H}_4(\text{OH})_2$ and HCl in AcOH into the benzopyrylium chloride, $\text{C}_{18}\text{H}_{17}\text{O}_2\text{Cl}$, isolated as the compound $\text{C}_{18}\text{H}_{17}\text{O}_2\text{Cl}\cdot\text{FeCl}_3$, m.p. 154°], better obtained by hydrogenation of $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$.

3:4-Methylenedioxy inamic acid (VI) and SOCl_2 in C_6H_6 yield 3:4-methylenedioxy-cinnamoyl chloride, m.p. 143° (corresponding amide, m.p. 183°), converted by *Et* sodioacetate in Et_2O into *Et* methylenedioxy-cinnamoylacetate (VII), m.p. 104° (*Cu* derivative, m.p. 208°), a little regenerated (VI), and a substance $\text{C}_{15}\text{H}_{16}\text{O}_4$, m.p. 132°. (VII) and 2:4-dinitrophenylhydrazine in MeOH give a pyrazole $\text{C}_{22}\text{H}_{18}\text{O}_8\text{N}_4$, m.p. 212°, and methylenedioxy-cinnamoyl-acetonedinitrophenylhydrazone, m.p. 200°. Boiling 75% AcOH transforms (VII) almost exclusively into (VI), whereas saturation with NH_3 of a solution of (VII) in $N\text{-NaOH}$ leads to *Et* 3:4-methylenedioxy-cinnamoylacetate, m.p. 58—60° (*Cu* derivative, m.p. 222°; 2:4-dinitrophenylhydrazone, m.p. 204°). The non-cryst. *Et* β -keto- α -acetyl- δ -3:4-methylenedioxyphenylvalerate (*Cu* compound, m.p. 173°) is transformed by 2:4-dinitrophenylhydrazine into a pyrazole $\text{C}_{22}\text{H}_{20}\text{O}_8\text{N}_4$, m.p. 175°, and γ -diketo- α -3:4-methylenedioxyphenylhexane-2':4'-dinitrophenylhydrazone, m.p. 116°. α -Phenylcinnamic acid is converted through the chloride into non-cryst. *Et* α -phenylcinnamoylacetate (VIII) (*Cu* derivative, m.p. 125°, or, on an isolated occasion, m.p. 185°),

hydrolysed by H_2O at 130° to γ -diketo- α -diphenyl- Δ^6 -hexene, m.p. 81°. Treatment of (VIII) with 75% AcOH at 100° gives *Et* α -phenylcinnamoylacetate, m.p. 91° (*Cu* derivative, m.p. 213°), hydrolysed to γ -keto- α -diphenyl- Δ^6 -butene, m.p. 56°. H. W.

Substitution products of aminobenzoyl- o -benzoic acid.—See B., 1934, 54.

Structure of glutaconic acids and esters. VIII. Cyclic compounds of glutaconic acid series. G. A. R. KON and B. L. NANDI (J.C.S., 1933, 1628—1634).—*Et* Δ^2 -tetrahydroisophthalate (I), b.p. 149—151°/12 mm., is obtained by action of SOCl_2 in $\text{C}_5\text{H}_5\text{N}$ on *Et* cyclohexanol-2:6-dicarboxylate, b.p. 145—147°/10 mm., itself prepared by reduction ($\text{PtO}_2\text{-H}_2$) of the corresponding ketonic ester (pyrazolone, m.p. 148°) (Uschakov, A., 1929, 1176); the last-named is obtainable, but less conveniently, from cyclohexanone and $\text{Et}_2\text{C}_2\text{O}_4$ in presence of NaOEt . The corresponding free acid, m.p. 197—198°, is also produced by condensing *Et* tetrahydrobenzoate with $\text{Et}_2\text{C}_2\text{O}_4$ (NaOEt), hydrolysing the resulting *Et* 3-carbethoxy- Δ^2 -cyclohexenylglyoxylate, m.p. 105°, with alkali [*H* ester, m.p. 178°; free acid, m.p. 224° (decali)], and finally oxidising the alkaline solution with H_2O_2 . It is unaffected by prolonged contact with 25% KOH at 100°, but rapidly isomerised to the Δ^3 -acid by HCl at 180—190°. The ester (I) on ozonisation gives glutaric acid and on ethylation gives *Et* 1-ethyl- Δ^2 -cyclohexene-1:3-dicarboxylate, b.p. 149—150°/9 mm. (free acid, m.p. 162°). Me_2 (cf. J.C.S., 1894, 67, 950) and *Et*₂ (II), b.p. 136—139°/23 mm., Δ^1 -cyclobutene-1:2-dicarboxylates are unaffected by the corresponding Na alkoxides and on ozonisation give the corresponding $\alpha\alpha'$ -diketo adipates. *Et*₂ 1:2-dibromocyclobutane-1:2-dicarboxylate, b.p. 150—158°/14 mm., gives (II) with Zn and EtOH , but not with KI in EtOH or COMe_2 . Attempts at prep. of the Δ^2 - and Δ^3 -acids corresponding with (II) failed. The Na derivative of [$\text{CH}(\text{CO}_2\text{Et})_2$]₂ with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in C_6H_6 gives (?) *Et*₄ cyclobutan-3-one-1:1:2:2-tetracarboxylate (phenylhydrazone, m.p. 128°) and the liquid fraction of the crude product with $\text{H}_2\text{-PtO}_2$ gives (?) 3-hydroxycyclobutane-1:1:2:2-tetracarboxylic acid, m.p. 191°, in poor yield. *Et*₂ Δ^1 -cyclopentene-1:2-dicarboxylate gives *Et*₂ $\alpha\alpha'$ -diketopimelate on ozonisation and is not isomerised, giving only the *Et H* ester, b.p. 135—140°/13 mm., by NaOEt ; the free acid is unaffected by 25% KOH at 100° or hot conc. HCl . Δ^2 -Tetrahydrophthalic acid (*Et*₂ ester, b.p. 155°/12 mm.) is conveniently prepared by dehydrating the cyanohydrin, b.p. 147—150°/10 mm., of *Et* cyclohexanone-2-carboxylate with SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ and hydrolysing the resulting *Et* 1-cyanocyclohexene-2-carboxylate, b.p. 135—137°/10 mm., with aq. alcoholic KOH . *Et*₂ Δ^1 -tetrahydrophthalate, b.p. 160°/14 mm. (from the Ag salt of the acid), like the Δ^2 ester does not react with Cl_2 or Br , and is unaffected by distillation/1 atm. Hot NaOEt-EtOH causes addition of EtOH . The anhydride of the Δ^1 -acid is hydrolysed by alkali to the Δ^2 -acid (approx. 75% at equilibrium). The latter is unaffected by 25% KOH at 100°. H. A. P.

3-Chlorophthalic acid. J. C. SMITH (J.C.S., 1933, 1643—1644).—3-Chlorophthalic acid (modified prep. from 3-nitrophthalic anhydride and PCl_5) has

m.p. 202° (decomp.) (lit. 184—186°) [anhydride, m.p. 126° (lit. 122°)].
R. S. C.

Formation of rings attached to *m*-position of benzene nucleus. S. G. P. PLANT (J.C.S., 1933, 1586—1588).—Stereochemical considerations demand that a ring joining the *m*-positions of the C₆H₆ nucleus should be at least 10-membered, and that a *p*-ring should be 14-membered. Attempts at cyclisation of *δ*-5-amino-2-methoxybenzoylvaleric acid (I), m.p. 118° [Ac derivative (+H₂O), m.p. 112° (decomp.)], its hydrochloride, m.p. 168° (decomp.), and Bz derivative, m.p. 146°, however, failed. (I) is prepared by nitration (HNO₃, *d* 1.5, at -5° to 0°) of *δ*-*o*-methoxybenzoylvaleric acid (prep. improved) and reduction of the resulting 5-NO₂ compound, m.p. 112°, with Fe(OH)₂. Its structure is proved by converting it into the 5-Cl-compound, m.p. 94°, by the Sandmeyer reaction, and synthesis of this by methylation (Me₂SO₄-KOH) of *δ*-5-chloro-2-hydroxybenzoylvaleric acid (II), m.p. 136°. (II) is obtained among other products by hydrolysis of 6-chloro-2:3-dihydroxypentachromone, m.p. 129—130°, b.p. 233—235°/23 mm., prepared by condensation of *p*-C₆H₄Cl·OH with Et cyclopentanone-2-carboxylate in presence of P₂O₅ (cf. A., 1933, 511).

H. A. P.

Pyrolysis of hydrogenated diphenic acids. Blanc's rule. F. VOCKE (Annalen, 1933, 508, 1—11).—Reduction (H₂ at 200—250 atm., Ni, and methylcyclohexane at 230—240°) of Me diphenate [and subsequent hydrolysis (20% MeOH-KOH)] gives two hexahydrodiphenic acids, m.p. 242° (I) and 220° (II), and two perhydrodiphenic acids, m.p. 245° (III) and 213° (IV); the former are separable from the latter through their Ba salts. Further reduction of (I) or (II) affords (III) and (IV) in each case. (I) heated at 300° in N₂ passes into (II), which at > 300° is converted into hexahydrofluorenone (V) [semicarbazone, m.p. 220° (darkening and decomp.)]. (II) and boiling Ac₂O give an anhydride, m.p. 120°, which when distilled at atm. pressure passes largely into (V). (III) heated at 300—325° gives a small amount of a ketone [semicarbazone, m.p. 215° (darkening and decomp.)], also formed [together with an anhydride (VI), C₁₄H₂₀O₃, m.p. 115°, re-solidifying with m.p. 265°] when the anhydride (VII), m.p. 265° [from (III) and Ac₂O], is heated at 300—310°. (VI) passes into (VII) when heated above its m.p.; both are hydrolysed (alkali) to (III). (IV) and its anhydride, m.p. 86°, are practically unaffected under similar conditions. The above results are in accordance with Blanc's rule.

Reduction (H₂, Pt-black, AcOH) of diphenic acid is slow and gives a mixture of stereoisomeric acids from which a dodecahydrodiphenic acid, decomp. 273° (Me ester, m.p. 57°), is isolated. Distillation of this with Ac₂O affords dodecahydrofluorenone, m.p. 37° [semicarbazone, m.p. 209—210° (decomp.)]; oxime, m.p. 172°].
H. B.

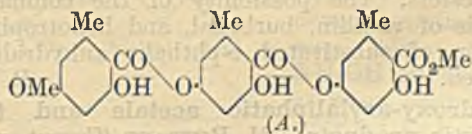
Condensation of benzylpyruvic acid with phenylacetonitrile. P. CORDIER (Compt. rend., 1933, 197, 1427—1429).—In KOH-EtOH, CH₂Ph·CN (I) condenses with CHPh·CH(OH)·CO·NH₂ (which affords CH₂Ph·CH₂·CO·CO₂H *in situ*) to give *α*-hydroxy-*γ*-phenyl-*α*-cyanobenzyl-*n*-butyric acid, m.p. 192° (decomp.), decomposed by boiling alkalis to give

(I), but converted by cold alkali or HCl into *β*-phenyl-*α*-(*β*-phenylethyl)malamic acid, NH₂·CO·CHPh·C(OH)(CH₂·CH₂Ph)·CO₂H, m.p. 198—200° (decomp.), hydrolysed by HCl-AcOH to an anhydride [CH₂Ph·CH₂·C<<CPh-CO<<CO-O (II) or the isomeric with an exocyclic double linking], m.p. 74°, of the corresponding maleic acid. Warm KOH-C₅H₁₁·OH converts (I) into a mixture of this ethylenic acid, m.p. 180° (insol. in C₆H₆) and an anhydride, m.p. 80° (sol.), isomeric with (II).
J. W. B.

Constituents of *Filix Mas*. II. **Synthesis of filicic acid.** A. ROBERTSON and (the late) W. F. SANDROCK (J.C.S., 1933, 1617—1618).—Et H dimethylmalonate, b.p. 135—136°/19 mm., and PCl₅ give dimethylmalonyl chloride Et ester, b.p. 74—78°/19 mm. (anilide, m.p. 47—48°), which with Et sodioacetone-dicarboxylate affords Et *β*-methylhexane-*γ*-*δ*-dione-*βδ*-tricarboxylate, b.p. 175—180°/5 mm., converted by NaOEt into Et 1:1-dimethylecyclohexane-2:4:6-trione-3:5-dicarboxylate, m.p. 147—148°. Hydrolysis and decarboxylation of this ester yields filicic acid, identical with the natural product (cf. Boehm, A., 1902, i, 37; 1904, i, 405).
F. R. S.

Bile acids. XLI. M. SCHENCK (Z. physiol. Chem., 1933, 222, 131—138; cf. A., 1933, 1161).—The gel C₂₄H₃₃O₉N (A., 1932, 1132) prepared by the action of HNO₃ on bilianic acid dioxime or NO-compound is the 7-NO₂-compound (I), cryst. from hot 40% AcOH, darkens 220°, m.p. 256—258° (decomp.). With 10% NaOH, (I) gives bilianic acid, and with HNO₃, bilodanic acid. Reduction with Zn dust and AcOH affords the 7-monoxime.
J. H. B.

Lichen substances. XXXII. **Tenuiorin, a methyl gyrophorate monomethyl ether.** Y. ASAHINA and M. YANAGITA. XXXIII. **Enzymic fission of lichen depsides and related compounds.** Y. ASAHINA and T. HIGUTI (Ber., 1933, 66, [B], 1910—1912, 1959—1964).—XXXII. The thalli of *Lobaria pulmonaria*, Hoffm., *f. tenuior Hue*, are extracted successively with hot COMe₂ and EtOH, the extract from the latter affording *d*-mannitol in 1.6% yield. Tenuiorin (I), m.p. 178—180°, and decomp. 238° after re-solidification, obtained from the COMe₂ extract in 0.5% yield, is neutral, contains 2 OMe, and is scarcely coloured by FeCl₃ or CaOCl₂ in EtOH. It is transformed by CH₂N₂ in COMe₂ into Me gyrophorate Me₃ ether, m.p. 195°, and is hydrolysed by KOH-MeOH to evernic acid, its Me ester, and Me orsellinate. Partial methylation of gyphoric acid yields (I), which is therefore A.



XXXIII. Most lichen depsides are hydrolysed by tannase from *Aspergillus niger* or the enzyme from *A. oryzae*, technical takadiastase (I) being very suitable. The alkali salts of the depsides in H₂O are treated with (I) at 37° and *p*_H 7.0—8.5. Incidence of hydrolysis is marked by the appearance of turbidity due to the phenolcarboxylic acid (II) and liberated

depside (III). The original p_H is restored, and more (I) is added, and the operation is continued until further change is not observed. Acidification of the solution yields a mixture of (II) and unchanged (III), which are usually readily separated from one another. Difficulties in the separation of individual phenol-carboxylic acids from one another are obviated by use of the Me ester of (III). Ready fission is observed of lecanoric, gyrophoric, evermic, olivetoric, sekikaic, divaricatic, squamatic, and salicylsalicylic acid, atranorin, and the tannin from Chinese oak galls. Diffractaic, benzoysalicylic, and 4-4'-hydroxybenzoxybenzoic acids and Me gallate and salicylate are more resistant. Depsides containing a free OH in *o*- or *m*-position to the CO of the depside linking appear, therefore, to be more readily hydrolysed. H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. II. Polynitrobenzaldehydes. G. LOCK (Ber., 1933, 66, [B], 1759—1765; cf. A., 1933, 1295).—Treatment of 2:4-dihydroxybenzaldehyde with molten KOH affords only traces of HCO_2H and a nearly molar proportion of H_2 . Reaction therefore does not consist in elimination of $\cdot\text{CHO}$, but in hydroxylation and dehydrogenation to K 2:4-dihydroxybenzoate, which, under these conditions, affords K_2CO_3 and $m\text{-C}_6\text{H}_4(\text{OH})_2$. In consequence of decomp., the amount of CO_2 invariably exceeds that expected. Similar behaviour is shown by 2-, 3-, and 4-hydroxy-, 3:4-dihydroxy-, and 2:4:6-trihydroxybenzaldehyde and by 2-hydroxynaphthaldehyde. 2:4-Dinitrophenol and HCO_2H are obtained when 2:6-dinitro-3-methoxy- or 4:6-dinitro-3-methoxy- (I) benzaldehyde is treated with 5% NaOH at 100° ; (I) is best prepared by methylation of 4-nitro-3-hydroxybenzaldehyde and nitration of the Me ether. Similarly, 2:6-dinitroisovanillin affords HCO_2H and 3:5-dinitroguaiacol. 4:6-Dinitro- yields HCO_2H , whereas 4:6-dibromo-3-hydroxybenzaldehyde suffers the Cannizzaro change. 2:4-Dinitrobenzaldehyde gives nearly the calc. amount of HCO_2H without apparently yielding $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$. The conversion of 2:4:6-trinitrobenzaldehyde into $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ by NH_2Ph , EtOH-NH_3 , or aq. NaOH is accompanied by evolution of HCO_2H . The presence of 2 NO_2 in *o*- and *p*-position has the same effect on $\cdot\text{CHO}$ as 2 Cl in positions 2 and 6. H. W.

Synthesis of valuable aromatic aldehydes from new sources. A. L. RUSCHTSCHINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1933, 118—123).—The CHO group can be introduced into carbohydrates, phenols, and their ethers by condensation with mesoxalic esters. The possibility of the commercial synthesis of vanillin, burbonal, and heliotropin by reduction of substituted *o*-phthalic anhydrides is envisaged. R. T.

β -Hydroxy-arylaliphatic acetals and their hydrolytic products. M. ROTBART (Compt. rend., 1933, 197, 1225—1227).—Interaction of bromodiethylacetal with Na arylalkoxides (cf. A., 1933, 1037) affords β -arylalkoxy-diethylacetals. The following are described: benzyloxy- (cf. A., 1932, 384); anisyl-oxy-, b.p. $181^\circ/16$ mm.; β -phenylethoxy-, and β -phenylpropoxy-diethylacetal, b.p. $130\text{--}132^\circ/5$ mm., which are hydrolysed by dil. (up to 7%) H_2SO_4 to

the corresponding aldehydes, b.p. $109\text{--}111^\circ/11$ mm. (semicarbazone, m.p. 119°), b.p. $157\text{--}160^\circ/15$ mm. (semicarbazone, m.p. $160\text{--}160.5^\circ$), b.p. $120\text{--}122^\circ/15$ mm. (semicarbazone, m.p. 88.5°), b.p. $134\text{--}136^\circ/16$ mm. (semicarbazone, m.p. $89\text{--}89.5^\circ$). α -Phenylethoxy-diethylacetal, b.p. $138\text{--}140^\circ/15$ mm., is hydrolysed by 1% H_2SO_4 to give $\text{CHPhMe}\cdot\text{OH}$, but no aldehyde. Similarly, phenyldimethyl-, b.p. $138\text{--}140^\circ/15$ mm., and benzyldimethyl-methoxy-diethylacetal, b.p. $115\text{--}118^\circ/2$ mm., are hydrolysed to alcohols rather than to aldehydes. Et α -phenylethyl and α -anisylmethyl ether are hydrolysed under the same conditions as the above, indicating that the behaviour of the acetals is not exceptional. J. L. D.

Replacement of groups by hydrogen in substituted methanes. $\omega\omega\omega$ -Tribromoacetophenones. C. H. FISHER (J. Amer. Chem. Soc., 1933, 55, 5003—5008).— $\omega\omega\omega$:3:5-Pentabromo-2:4:6-trimethylacetophenone (I) and its 1:1 compound with $\omega\omega$:3:5-tetrabromo-2:4:6-trimethylacetophenone (II) are converted by KI in COMe_2 into the ω :3:5- Br_3 -derivative, m.p. $126\text{--}127^\circ$, which is prepared from 3:5-dibromoacetomesitylene and Br (1 mol.) in AcOH . (I) is converted into (II) by MgEtBr , $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, PhOH , or COPhMe ; COMe_2 and cold 10% KOH have no action. Alkali-sol. products are formed from (I) and hot aq. KOH ; a pure compound could not be isolated. 4-Chloro- $\omega\omega$ -dibromoacetophenone and aq. 10% KOH give *p*-chloromandelic acid; $\omega\omega$ -dibromo-2:4:6-trimethylacetophenone reacts much more slowly to give an unidentified substance. H. B.

Molecular rearrangement of $\alpha\beta$ -unsaturated ethers. W. M. LAUER and M. A. SPIELMAN (J. Amer. Chem. Soc., 1933, 55, 4923—4930).—The following are prepared by the methods previously described (A., 1931, 710): β -bromo- α -phenylethyl Me, b.p. $117\text{--}118^\circ/15$ mm., P_r^a , b.p. $146\text{--}148^\circ/27$ mm., Bu^a , b.p. $165\text{--}166^\circ/32$ mm., and isoamyl, b.p. $140\text{--}143^\circ/12$ mm., ethers; β -bromo- α -*p*-chlorophenylethyl Me ether, b.p. $154\text{--}156^\circ/26$ mm.; α -*n*-butoxystyrene (I), b.p. $134.5\text{--}135.5^\circ/26$ mm.; *p*-chloro- α -methoxystyrene (II), b.p. $118\text{--}121^\circ/23$ mm., which with semicarbazide acetate in aq. EtOH gives *p*-chloroacetophenonesemicarbazone, m.p. $202\text{--}204^\circ$. α -Methoxystyrene (III) heated at about 300° for 2 hr. gives COPhEt (main product), $\alpha\beta$ -dibenzoylpropane (IV) (dioxime, m.p. $166\text{--}167^\circ$), and CH_4 . (IV) is dehydrated (conc. HCl) to 2:5-diphenyl-3-methylfuran, m.p. $57\text{--}58^\circ$, and is synthesised from $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ and $\text{COPh}\cdot\text{CHMeBr}$ (with subsequent hydrolysis). (IV) is probably formed [from (III)] thus: $\text{CH}_2\cdot\text{CPh}\cdot\text{OMe} + \text{COPhEt} \rightarrow \text{CHMeBz}\cdot\text{CH}_2\text{Bz} + \text{CH}_4$. In agreement with this view, (III) or α -ethoxystyrene (V) heated with an excess of COPhMe gives $(\cdot\text{CH}_2\text{Bz})_2$, whilst (V) and COPhEt similarly afford (IV). (V) heated at 300° for 1 hr. affords COPhPr^a , $\alpha\beta$ -dibenzoylbutane, b.p. $234\text{--}245^\circ/20$ mm., C_2H_6 , and a little C_6H_4 ; α -*n*-propoxystyrene similarly yields COPhBu^a , C_2H_6 , and C_3H_6 ; (I) furnishes *Ph n*-amyl ketone; (II) gives *p*-chloropropiophenone (semicarbazone, m.p. $175\text{--}176^\circ$) and some $\alpha\beta$ -*di-p*-chlorobenzoylpropane, m.p. $116.5\text{--}117^\circ$; α -isoamyloxystyrene affords *Ph isohexyl ketone*, b.p. $145\text{--}148^\circ/18$ mm. (semicarbazone, m.p. $144\text{--}145^\circ$),

COPhMe, (CH_2Bz)₂, isopentane, and isopentene. The formation of the above olefines indicates that the change $\text{CH}_2\text{:CPh}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{R} \rightarrow \text{COPhMe} + \text{CH}_2\text{:CHR}$ occurs to some extent. When (I) and (II) are heated together at 265°, a mixture of products (from which COPhEt is isolable as its semicarbazone) results; an intermol. exchange of radicals must occur. A reaction mechanism [similar to that formulated by van Alphen (A., 1928, 57) for the rearrangement of phenol ethers] is advanced. Rearrangement of $\text{CHMe:CPh}\cdot\text{OMe}$, $\text{CHEt:CEt}\cdot\text{OMe}$, and $\text{OEt}\cdot\text{CMe:CH}\cdot\text{CO}_2\text{Et}$ could not be effected. H. B.

Oxidation products of benzophenoneoxime. W. H. HUNTER and W. S. DYER (J. Amer. Chem. Soc., 1933, 55, 5053—5055; cf. von Auwers and Wunderling, A., 1933, 505).—Oxidation [alkaline $\text{K}_3\text{Fe}(\text{CN})_6$] of $\text{CPh}_2\text{:N}\cdot\text{OH}$ (I) in EtOH gives COPh_2 (II), a compound (III), $\text{C}_{26}\text{H}_{20}\text{ON}_2$, m.p. 156—157°, and a substance (IV), $(\text{C}_{13}\text{H}_{10}\text{ON})_4$, m.p. 193° (decomp.). Hydrolysis (conc. HCl) and attempted reduction of (III) affords (II). (IV) is reduced to (I)+(II), is decomposed slowly by COMe_2 to (I)+(II), and is converted by PCl_5 into (II) and NHBzPh . Oxidation of the Na salt of (I) in absence or presence of C_6H_6 gives (II) and tarry material. With Ag_2O in C_6H_6 , (I) gives (II) and a little (IV); in Et_2O , (II) and (III) (?) result. H. B.

Dipole moments of chlorobenzophenone oximes.—See this vol., 131.

Oxidation-reduction reaction of desyl chloride, and the supposed tolane oxide. G. RICHARD (Compt. rend., 1933, 197, 1432—1434).—Contrary to Madelung and Oberwenger (A., 1932, 62), the action of dry, powdered KOH on $\text{COPh}\cdot\text{CHClPh}$ yields BzOH , $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ (I) (as salts), $\text{COPh}\cdot\text{CH}_2\text{Ph}$ (II) (unattacked by HCl at 120°), and benzil, the supposed tolane oxide (*loc. cit.*) probably being impure (II). $\text{CPh}_2\text{:CO}$ is probably the intermediate from which (I) is obtained, and in one case an orange substance, transformed into tetraphenylcyclobutane-1:3-dione by heating, was isolated. J. W. B.

Condensation of *m*-iodoacetophenone with nitrobenzaldehydes. W. KRASZEWSKI and S. KOTOWICZÓWNA (Rocz. Chem., 1933, 13, 601—606).—*m*-Iodophenyl o-, m.p. 123° (*Br*-derivative, m.p. 145°; phenylhydrazone, m.p. 50°), *m*-, m.p. 147° (*Br*-derivative, m.p. 164°; phenylhydrazone, m.p. 54°), and *p*-nitrostyryl ketone (I), m.p. 164° (*Br*-derivative, m.p. 148°; phenylhydrazone, m.p. 92°), are produced when *m*-iodoacetophenone and the appropriate $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ interact in EtOH in presence of NaOH; in the case of *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, *m*-iodophenyl β -hydroxy- β -*o*-nitrophenylethyl ketone (II), m.p. 82° (*Bz* derivative, m.p. 127°), is also formed at 16°, but not at 0°. The *m*-, m.p. 92° (*Bz* derivative, m.p. 158°), and *p*- NO_2 -isomerides of (II), m.p. 108° (*Bz* derivative, m.p. 168°), are prepared analogously to (I) in aq. EtOH in presence of NaOH and K_2CO_3 , respectively. (II) is decomposed by aq. NaOH to yield indigotin and *m*- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. R. T.

Action of the Grignard reagent on benzanthrone. Case of 1:6-addition. M. NAKANISHI (Proc. Imp. Acad. Tokyo, 1933, 9, 394—397).—Benz-

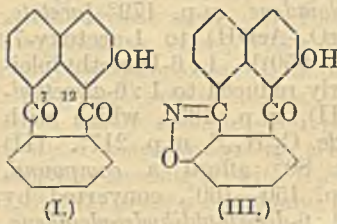
anthrone and an excess of MgPhBr in Et_2O give *Bz*-3-phenylbenzanthrone (I), m.p. 186°, the structure of which is proved by its yellowish-brown colour, reddish-brown halochromy in conc. H_2SO_4 , oxidation by $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ to anthraquinone-1-carboxylic acid, formation of a *Br*-derivative which with NaOEt gives a blue isoviolanthrone, and synthesis of 1-phenylbenzanthrone, m.p. 182° (oxidised to 1-benzoylanthraquinone; the *Br*-derivative does not give an isoviolanthrone), from anthrone and $\text{CH}_2\text{Bz}\cdot\text{CH}_2\text{Cl}$. Benzylideneanthrone and MgPhBr give analogously anthra-fuchsone. MgBu^nI gives probably *Bz*-3-*n*-butylbenzanthrone, m.p. 96°. (I) and KMnO_4 give a colourless substance, $\text{C}_{22}\text{H}_{16}$, m.p. 242°. R. S. C.

Preparation of phenylacetylcarbinol and its ethers. (MLLE.) M. DARMON (Compt. rend., 1933, 197, 1328—1329).—With $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ in Et_2O at 40°, $\text{OH}\cdot\text{CH}_2\cdot\text{CN}$ (I) gives a 15% yield of $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, similar treatment of the Me and Et ethers of (I) affording, respectively, benzyl methoxymethyl, b.p. 139—140°/27 mm. (semicarbazone, m.p. 127—128°), and ethoxymethyl, b.p. 116—118°/1 mm. (semicarbazone, m.p. 100°), ketone; the corresponding benzyloxymethyl compound, b.p. 235°/40 mm. (semicarbazone, m.p. 105°), is similarly obtained from $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (by the action of NH_3 on the mixed esters from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ on $\text{CH}_2\text{Ph}\cdot\text{ONa}$). J. W. B.

Beryllium benzoylacetate. R. W. BAILEY, F. M. BREWER, and H. M. POWELL (J.C.S., 1933, 1546—1547).—Beryllium benzoylacetate, $\text{Be}(\text{C}_{10}\text{H}_9\text{O}_2)_2$, m.p. 210°, is prepared by interaction of $\text{CH}_2\text{Bz}\cdot\text{COMe}$ with basic Be carbonate in boiling EtOH. Crystallographic data are given.

H. A. P.

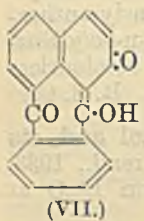
Reaction of phthaloylnaphthol with hydroxylamine and diazomethane. L. F. FIESER (J. Amer. Chem. Soc., 1933, 55, 4963—4976).—1:8-Phthaloyl- β -naphthol (=1-hydroxy-7:12-pleiadenedione) (I) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in hot EtOH-NaOH (small amount) give the 7-oxime (II), m.p. 243° (diacetate, m.p. 237°), which passes at 300—320°/vac. into the dehydro-derivative, probably (III), m.p. 260° (acetate, m.p. 208°). (II) is converted by 82% H_2SO_4 at 200° into an isomeric substance, m.p. 251°. Similar oximation of (I) using more alkali gives (II) and (mainly) the 12-oxime (IV), m.p. 262° (with loss of H_2O) (diacetate, m.p. 174°), which is readily dehydrated (conc. acids; Ac_2O ; aq. NaOH) to the (1:12-)anhydro-derivative, m.p. 227°. The anhydro-derivative of 1:6-dihydroxy-7:12-pleiadenedioneoxime has m.p. 292°. (I) and NH_2OH in aq. NaOH at room temp. give an additive 1:1 compound (V), decomp. about 135°, which regenerates its components when treated with AcOH, and with cold $\text{Ac}_2\text{O}\text{-C}_5\text{H}_5\text{N}$ affords a little of the acetate of (I) and (mainly) a diacetate, m.p. 163°, of (IV). (V) heated with $\text{C}_5\text{H}_5\text{N}$ gives (II) and (IV). The production of (V) is considered to involve both CO groups of (I), viz., $\text{OH}\cdot\text{C}_7\cdot\text{O}\cdot\text{C}_{12}\cdot\text{NH}\cdot\text{OH}$. Similar



(I) and (II) are shown in the diagram above.

additive compounds are obtained from 1:2- and 1:6-dihydroxy-, 1-hydroxy-2:6-dimethyl-, and 1-hydroxy-4:5-benz-7:12-pleiadenediones. An additive compound is also obtained from (I) and N_2H_4 ; it is acetylated ($Ac_2O-C_5H_5N$) to a *hydrazone diacetate* (?), m.p. 199—200°. (V) and $Et_2O-MeOH-CH_2N_2$ give (I) and its Me ether (VI). (VI) is not obtained from (I) and CH_2N_2 (see below); its formation from (V) suggests that (V) undergoes decomp. to an unstable modification [which must be formulated as

the 1-OH derivative, *i.e.*, (I)] of the phthaloylnaphthol; the stable form may be (VII). (I) does not react with CH_2N_2 in Et_2O ; in $C_2H_2Cl_4$, a *compound* (VIII), $C_{20}H_{14}O_3$ (alternative structures suggested), m.p. 208°, is formed by addition of two CH_2 groups. (VIII) contains OMe and CO groups and one active (enolic) H, and is reduced (Zn dust, AcOH) to a *dihydro-derivative*, m.p. 245° (acetate, m.p. 184°).



H. B.

Derivatives of pleiadene. L. F. FIESER (J. Amer. Chem. Soc., 1933, 55, 4977—4984).—3:7-Dimethyl- β -naphthol (1 pt.), $o-C_6H_4(CO)_2O$ (I) (10 pts.), and $AlCl_3$ (2 pts.) at 200° give 1-hydroxy-2:6-dimethyl-7:12-pleiadenedione, m.p. 209° (acetate, m.p. 205°); 2:3- $C_{10}H_6(OH)_2$ and 2-phenanthrol similarly afford 1:2-dihydroxy-, m.p. 233°, and 1-hydroxy-4:5-benz-, m.p. 240° (acetate, m.p. 227°), -7:12-pleiadenedione, respectively. 3:7-Dimethyl- β -naphthyl Me ether, m.p. 82°, (I), and $AlCl_3$ in $C_2H_2Cl_4$ give small amounts of *o*-6-methoxy-3:7-dimethyl-1(or 2)-naphthoylbenzoic acid, m.p. 212° [converted by 82% H_2SO_4 at 100° (bath) into 3'-methoxy-4:2'-dimethyl-1:2-benzanthraquinone, m.p. 235°], and *o*-2-methoxy-3:7-dimethyl-1-naphthoylbenzoic acid (?), m.p. 223°. 3:7-Dimethyl- α -naphthyl Me ether, m.p. 58°, and (I) similarly give a little *o*-4-methoxy-2:6-dimethyl-1-naphthoylbenzoic acid, m.p. 261°, reduced (Zn dust, aq. NaOH) to the -1-naphthylmethylbenzoic acid, m.p. 236°, which is cyclised (82% H_2SO_4 at 100°) to 4-methoxy-2:6-dimethyl-12-pleiadone, m.p. 241°. This is demethylated ($AlCl_3$ in C_6H_6) to the 4-OH-derivative, m.p. 286°. 2:7- $C_{10}H_6(OMe)_2$ and (I) afford *o*-2:7-dimethoxy-1-naphthoylbenzoic acid, m.p. 201° (Me ester, m.p. 114°); the -1-naphthylmethylbenzoic acid, m.p. 161°, is cyclised to the Me₂ ether, m.p. 201°, of 1:6-dihydroxy-12-pleiadone, m.p. 233° (diacetate, m.p. 220°). Reduction (H_2 , Cu chromite, EtOH) of 1:8-phthaloyl- β -naphthol gives 1-hydroxy-7:12-dihydropleiadene, m.p. 179° [acetate, m.p. 136°, oxidised (CrO_3-AcOH) to 1-acetoxy-7-pleiadone (cf. A., 1933, 950)]. 1:6-Dimethylpleiadone (*loc. cit.*) is similarly reduced to 1:6-dimethyl-7:12-dihydropleiadene (II), m.p. 133°, which with S at 260° gives a *sulphide*, $C_{20}H_{16}S$, m.p. 217°. (II) and Br in AcOH at 80° afford a *compound*, $C_{20}H_{17}Br$, AcOH, decomp. 150—160°, converted by cold C_5H_5N into a *bromo-1:6-dimethyldihydropleiadene*, m.p. 179°.

H. B.

Reaction of *o*-phenylenedi(phenylglyoxal) and the retrograde benzoic acid change. Preparation of 1:4-dihydroxy-2:3-diphenylnaphthalene. R. WEISS and K. BLOCH (Monatsh., 1933, 63,

39—51).—An improved prep. of dibenzylidene-phthalan (I), $o-C_6H_4(CO-CBr_2Ph)_2$ (II), decomp. 114°, and $o-C_6H_4(COBz)_2$ (III) (A., 1932, 396) is given. With Cl_2 in AcOH (I) affords *s*-dichlorodi(dichlorobenzyl)phthalan (IV), m.p. 242—248°, similar treatment with I in AcOH giving 2-phenyl-3-benzylindone. With Zn in hot AcOH both (II) and (IV) give 1:4-dihydroxy-2:3-diphenylnaphthalene (V), softens 220°, m.p. 236—243°, oxidised in AcOH by air or $Na_2Cr_2O_7$ to 2:3-diphenyl-1:4-naphthaquinone (VI). With Zn and $Ac_2O-H_2SO_4$ (III) affords the Ac_2 derivative, m.p. 200—202°, of (V), which is obtained by hydrolysis with dil. HCl at 150°. Distillation of (V) with excess of Zn dust gives a little 2:3-diphenyl- α -naphthol (VII), the main product being a mol. *compound* $C_{34}H_{30}O_3$, m.p. 133—136°, of (VI) and (VII), also obtained by heating these together in AcOH, and resolved into its components by hot KOH-EtOH. The substance, m.p. 193° (decomp.), obtained by the action of amyl nitrite on $o-CH_2Ph \cdot CO \cdot C_6H_4 \cdot CH_2Bz$ in presence of NaOEt, previously designated 4-hydroxy-3-phenyl-1-benzylisoquinoline (A., 1925, i, 937), is actually 4-nitroso-2:3-diphenyl- α -naphthol. When heated with KOH in EtOH (III) affords diphenylphthalancarboxylic acid, $C_6H_4 \left\langle \begin{array}{l} CPh(CO_2H) \\ CPh \end{array} \right\rangle O$ (VIII), m.p. 200—202° (decomp.) (Me ester, m.p. 197°, by CH_2N_2), converted by heating with Ac_2O into diphenylindone [also obtained by distilling (VIII) at 265—275°/18 mm.] and *o*-benzoylbenzoic acid (IX), m.p. 176° (decomp.), probably $C_6H_4 \left\langle \begin{array}{l} CPh(OH) \cdot CO \\ CPh(OH) \cdot O \end{array} \right\rangle$, since it does not react with CH_2N_2 , and forms a salt only with KOH-EtOH. Reduction of either (VIII) or (IX) with red P and HI in AcOH affords *s*-diphenylhomophthalide, m.p. 166°.

J. W. B.

Synthesis of brazilinic acid. J. N. RAY, S. S. SILOOJA, and P. R. WADHA (J. Indian Chem. Soc., 1933, 10, 617—620).—Et *m*-methoxyphenoxypropionate, veratroyl chloride (I), and $AlCl_3$ in cold $PhNO_2$ give 2-hydroxy-4:4':5'-trimethoxy- (II), m.p. 141°, and a little 4-hydroxy-2:4':5'-trimethoxy- (III), m.p. 175°, -benzophenone; the structures are assigned from the colours with $FeCl_3$. (II) and (III) are also obtained in approx. equal amounts from (I), *m*-OMe- C_6H_4-OH , and $AlCl_3$ in $PhNO_2$. (II) and HNO_3 (*d* 1.42) in AcOH-conc. H_2SO_4 at 48—52° give the 2'- NO_2 -derivative, m.p. 211° (oxidised to nitroveratric acid), which is converted through the 2'- NH_2 - (hydrochloride, m.p. 240°) and 2'-CN- (IV), m.p. 152—154°, -derivatives into 2-hydroxy-4:4':5'-trimethoxybenzophenone-2'-carboxylic acid, m.p. 203°. Condensation of this with $CH_2Cl \cdot CO_2H$ gives brazilinic acid, also obtained from (IV) and $CH_2Cl \cdot CO_2H$ with subsequent hydrolysis.

H. B.

Lipins of tubercle bacilli. XXXVII. Synthesis of phthicol, the pigment of the human tubercle bacillus. R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, 103, 405—412).—2-Methyl-1:4-naphthaquinone (*oxime*, m.p. 166—168°) heated with Zn- Ac_2O -AcOH-NaOAc gives the Ac_2 derivative of 1:4-dihydroxy-2-methylnaphthalene, converted by NaOEt-EtOH into 3-hydroxy-2-

methyl-1:4-naphthaquinone, m.p. 173—174° (isolated in 12% yield by acidification and steam-distillation), identical with phthiocol (A., 1933, 1083), and oxidised by H_2O_2 -0.1N-NaOH to $o-C_6H_4(CO_2H)_2$. J. W. B.

Methyl ether and bromine derivatives of α -elemolic and α -elemonic acids. H. LIEB and M. MLADENOVIC [with A. REZEK and M. SOBOTKA] (Bull. Soc. Chim. Yougoslav., 1933, 4, 85—99).— α -Elemolic acid (I) or its Ac derivative on heating during 5—6 hr. with 4% H_2SO_4 in MeOH yields the *Me ether* (II) of (I), m.p. 242° (*Ac derivative*, m.p. 224°); the reaction consists in addition of MeOH to the ethylenic linking of (I), as is shown by the non-addition of Br or HBr to (II). The *Me ether* of α -elemolic acid (III), m.p. 280—281° (*oxime*, m.p. 243°), is prepared analogously to (II) from (III), or by oxidising (II) with CrO_3 in AcOH. The Br_2 -derivative (IV), m.p. 235°, of (III) is prepared directly from Br and (III), or by oxidising the Br_2 -derivative of (I), and the *Br-derivative* (V), m.p. 273°, of (III) by oxidising the *Br-derivative* (VI) of (I), or from (IV) and KOMe. The presence of OH in (VI) is demonstrated by preparing its *Ac derivative*, m.p. 260°. (VI) and (V) with Pd- H_2 yield, respectively, dihydro-derivatives of (I) and (III). R. T.

Sapic acid, a constituent of American pine resin. F. VOCKE (Annalen, 1933, 508, 11—15).—When the fresh resin is kept in absence of air, crystals of *sapic acid* (I), $C_{20}H_{30}O_2$, m.p. 143°, $[\alpha]_D^{25} -123^\circ$ (all rotations are in 96% EtOH for Hg green), separate. (I) is reduced (H_2 , PtO_2 , EtOH) to a *dihydro-derivative*, m.p. 195°, $[\alpha]_D^{25} +28.7^\circ$, and thence to a non-homogeneous *tetrahydro-derivative*, m.p. 173° (not sharp), $[\alpha]_D^{25} +28.3^\circ$ [probably identical with the product similarly prepared from abietic acid (II)]. (I) rearranges to (II) when boiled with AcOH. Irradiation of (I) gives a non-cryst. product, $[\alpha]_D^{25} +35^\circ$. (I) may be identical with the similar acid isolated from European pine resin (Ruzicka and Schinz, A., 1923, i, 818). A reply is made to Ruzicka (A., 1933, 279, 820). H. B.

Plant heart-poisons. I. Constitution of uzarin. R. TSCHESCHE. II. Dehydrogenation of uzarigenin with selenium. R. TSCHESCHE and H. KNICK (Z. physiol. Chem., 1933, 222, 50—57, 58—62).—I. Catalytic hydrogenation of the acetate of α -dianhydrouzarigenin, m.p. 263—265°, $[\alpha]_D^{25} -29.5^\circ$ (cf. lit.), gave as acetates α_1 - (I), m.p. 217°, $[\alpha]_D^{25} +11.4^\circ$ (*acetate*, m.p. 248°, $[\alpha]_D^{25} +3.9^\circ$), and α_2 - (II), m.p. 230°, $[\alpha]_D^{25} +20.2^\circ$ (*acetate*, m.p. 205°, $[\alpha]_D^{25} +20.2^\circ$), *hexahydrodianhydrouzarigenins*, $C_{22}H_{36}O_3$. Oxidation of (I) and (II) with CrO_3 in AcOH afforded the α_1 - (III), m.p. 248—249°, $[\alpha]_D^{25} +39.3^\circ$ (*oxime*, decomp. 275—278°), and α_2 - (IV), m.p. 216—217°, $[\alpha]_D^{25} +42.5^\circ$ (*oxime*, m.p. 251—253°), *ketones*, $C_{23}H_{36}O_3$. Clemmensen reduction of (III) and (IV) gave the *lactones*, $C_{23}H_{36}O_2$, α_1 -, m.p. 178°, $[\alpha]_D^{25} +11.3^\circ$, α_2 - (V), m.p. 180°, $[\alpha]_D^{25} +24.3^\circ$, which are oxidised by CrO_3 to the *dicarboxylic acids*, $C_{23}H_{34}O_6$, α_1 -, m.p. 270°, $[\alpha]_D^{25} +37.6^\circ$ (*Me₂ ester*, m.p. 134—135°, $[\alpha]_D^{25} +18.7^\circ$), α_2 - (VI), m.p. 245—246°, $[\alpha]_D^{25} +38.5^\circ$ (*Me₂ ester*, m.p. 146—147°, $[\alpha]_D^{25} +25.0^\circ$). When heated with Ac_2O , (VI) gives a *pyroketone*, $C_{22}H_{32}O_3$, m.p. 215°, $[\alpha]_D^{25} +150.9^\circ$ (*oxime*, decomp. 248—250°), indicating that

the secondary OH group of uzarigenin (VII) occurs in a 6-C ring. (V) is probably identical with octahydro-trianhydroperiplogenin, showing that (VII) has the same C skeleton as the other heart-poisons. From the crude dianhydrouzarigenin (VIII), there was isolated a β -*isomeride*, m.p. 236—237°, $[\alpha]_D^{25} +4.95^\circ$ (*acetate*, m.p. 167—168°, $[\alpha]_D^{25} +4.9^\circ$). All rotations are in $CHCl_3$.

II. Se dehydrogenation of (VIII) gives a mixture of hydrocarbons from which Diels' hydrocarbon, $C_{16}H_{16}$, obtained from cholesterol, was isolated, indicating for (VII) the same skeleton as in the sterols and bile acids.

J. H. B.

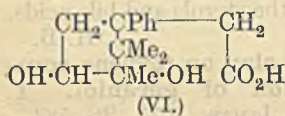
Action of Japanese acid clay on terpene compounds. IV. Isomerisation of geraniol. T. KUWATA (J. Soc. Chem. Ind. Japan, 1933, 36, 583—585B; cf. A., 1933, 830).—In $COMe_2$ at 60° α -terpineol, other terpenes, and polymerised products (I) are formed. In MeOH less (I) and much terpineol *Me ether* are formed. R. S. C.

Acid-catalysed enolisation of menthone.—See this vol., 153.

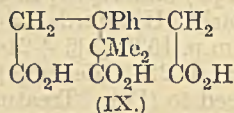
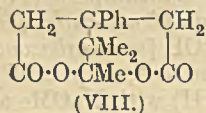
***d-epi*Camphor.** Y. ASAHINA and M. ISHIDATE [with T. JOYAMA] (Ber., 1933, 66, [B], 1913—1917).—Passage of CO_2 at 0° through a mixture of KCN in H_2O and *d-5-ketocamphor* in Et_2O leads exclusively to addition of HCN at 5-CO with production of a mixture of hydroxy-nitriles, hydrolysed by fuming H_2SO_4 (30% SO_3) to α - (I), m.p. 248—249°, $[\alpha]_D^{25} -1.24^\circ$ in EtOH, and β - (II), m.p. 190—191°, $[\alpha]_D^{25} +44.79^\circ$ in EtOH, *-5-hydroxycamphor-5-carboxylamide*. (I) is hydrolysed by 10% HCl at 100° to *α -5-hydroxycamphor-5-carboxylic acid*, m.p. 151—152°, b.p. about 250°/20 mm., $[\alpha]_D^{25} -6.48^\circ$ in EtOH [*semicarbazone* (III), m.p. 267° (decomp.); *quinine salt*, m.p. 178°], oxidised by $Na_2Cr_2O_7$ and H_2SO_4 in H_2O to 5-ketocamphor (IV). Similarly, (II) affords *β -5-hydroxycamphor-5-carboxylic acid*, m.p. 153°, $[\alpha]_D^{25} +21.58^\circ$ in EtOH [*semicarbazone*, (V), m.p. 225° (decomp.); *quinine salt*, m.p. 219°], oxidised to (IV). Treatment of (III) with NaOMe at 180° leads to *α -5-hydroxycamphane-5-carboxylic acid* (VI), m.p. 151°, $[\alpha]_D^{25} -59.2^\circ$ in EtOH, whereas the corresponding β -*compound* (VII) has m.p. 130°, $[\alpha]_D^{25} -39.8^\circ$ in EtOH. Oxidation of (VI) or (VII) with CrO_3 and a little H_2SO_4 at 100° affords *d-epicamphor*, m.p. 183—184°, $[\alpha]_D^{25} +50.0^\circ$ in EtOH [*semicarbazone*, m.p. 236° (decomp.)], transformed by Br in $CHCl_3$ at 100° into *bromo-d-epicamphor*, m.p. 133—134°, $[\alpha]_D^{25} -86.9^\circ$ in EtOH. H. W.

Degradation of 4-phenylcamphor to phenylisocamphoronic acid. M. BREDT-SAVELSBERG and J. BUCHKREMER (Ber., 1933, 66, [B], 1921—1932).—Phenylcamphoroxime (I), m.p. 143°, is transformed by boiling Ac_2O into its *acetate*, b.p. 150—160°/0.35 mm., which partly resinifies and partly yields AcOH and *phenyl- α -campholenonitrile* (II), m.p. 80°, better obtained by heating (I) with H_2SO_4 (*d* 1.18). With 50% H_2SO_4 (I) gives a compound containing S and N and (?) *phenyl- β -campholenolactone*, b.p. 143—145°/0.3 mm., m.p. 52—53°. The best method for the prep. of (II) consists in treating (I) with $PhSO_2Cl$ in C_5H_5N , whereby *phenyl- α -campholenolactam*, m.p. 203—204°, unchanged by boiling 50% H_2SO_4 , scarcely attacked by molten KOH, and transformed by 30% KOH-MeOH at 180° in small amount into *phenyl- α -camphol-*

enic acid (III), results. Hydrolysis of (II) by KOH-H₂O-EtOH at 150° leads to *phenyl-α-campholenamide*, m.p. 126—127° after softening, and (III), m.p. 123—124° [Ag salt and thence by EtI the Et ester, b.p. 125—126°/0.2 mm.; Me ester (IV), b.p. 122.3—123°/0.4 mm., from (III) and CH₂N₂]. (III) is obtained in poor yield by the action of molten KOH on *phenylcamphor-ω-sulphonic acid*, m.p. 239—240° (decomp.) after darkening at 200°, obtained from phenylcamphor (V), Ac₂O, and conc. H₂SO₄. (III) is very



stable towards HNO₃ but smoothly oxidised by KMnO₄ to *dihydroxy-phenyldihydro-α-campholenic acid* (VI), m.p. 252—253° [Ag and Na (+2H₂O) salts]. (VI) is unchanged by Pb(OAc)₄, molten KOH, HNO₃ (*d* 1.3), or CrO₃-H₂O. CrO₃ in AcOH converts it into a *keto-lactone* (VII) C₁₆H₁₈O₃, m.p. 177—178° [*semicarbazone*, m.p. 200° (decomp.)], also obtained by treatment of (VI) with Pb(OAc)₄ and subsequently with CrO₃, whereas dihydroxydihydro-α-campholenic acid and its esters give *isoketocamphoric* and *isocamphoronic* acid when treated similarly. (VII) is converted by KOH-MeOH into the monobasic acid C₁₆H₁₈O₄, m.p. 205—206°, which does not react with NH₂OH or NH₂CO-NH-NH₂ and is transformed by Br-KOH into the dibasic acid C₁₆H₁₈O₆, m.p. 240—241° (decomp.). (VII) is accompanied by a (?) *phenylterphenylic acid* C₁₄H₁₆O₄, m.p. 185°. Ozonisation of (III) leads to BzOH as sole recognisable product, whereas similar treatment of (IV) yields *phenylisoketocamphorodilactone* (VIII), m.p. 207—208° (the corresponding acid being stable as its salts), and a honey-like mass from which two *oximino-acids*, m.p. 290° (decomp.) and



m.p. 133—134°, are isolated. Oxidation of (VIII) by Br and KOH affords *phenylisocamphoronic acid* (IX), m.p. 184° [K₃ salt (+H₂O)], thereby locating Ph at 4 in the phenylcamphor.

Reasons are advanced for considering that the Nametkin transformation depends primarily on the camphane bridged ring. H. W.

Hydrogenation of the furan nucleus using osmium catalyst. N. D. ZELINSKI and N. I. SCHUIKIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 60—65).—When the vapour of 2-methylfuran mixed with H₂ is passed over an Os-asbestos catalyst at 80—82° the tetrahydro-derivative is obtained. Using Pt catalyst the product consists chiefly of acyclic alcohols. R. T.

Attempted synthesis of primetin. S. SUGAWA (J.C.S., 1933, 1621—1624).—5 : 6-Dimethoxyanthranilic acid affords 6-bromo-2 : 3-dimethoxybenzoic acid, an oil (*anilide*, m.p. 135—137°), which with NaOAc and Cu(OAc)₂ gives only veratric acid (I). 6-Iodo-2 : 3-dimethoxybenzoic acid (II), m.p. 137—138° (similarly prepared), with CH₂Ph·ONa and Cu in CH₂Ph·OH at 130—150° gives 6-benzoyloxy-2 : 3-di-

methoxybenzoic acid, m.p. 128—129°, the chloride, m.p. 75—76°, of which with ZnMeI yields 6-benzoyloxy-2 : 3-dimethoxyacetophenone, m.p. 90—91°. This with AcOH-HCl at 100° affords (?) 5-hydroxy-8-methoxyflavone, m.p. 129—130° (Ac derivative, m.p. 146—147°), demethylated by HI-Ac₂O to (?) 5 : 8-dihydroxyflavone, m.p. 179—180°, not identical with primetin. Hydrogenation (Pd-CaCO₃) of (II) in EtOH-KOH gives (I). The Et ester, an oil, of (II) (prepared by way of the chloride) with Cu at 250° gives Et, 3 : 4 : 3' : 4'-tetramethoxydiphenate, m.p. 124—125°, which resisted hydrolysis. R. S. C.

Synthesis of tricrin. K. C. GULATI and K. VENKATARAMAN (J.C.S., 1933, 1644).—Identity of 5 : 7 : 4'-trihydroxy-3' : 5'-dimethoxyflavone and tricrin is confirmed. R. S. C.

2 : 3-Dichlorodioxan. W. BAKER and A. SHANNON (J.C.S., 1933, 1598).—A pure form, m.p. 30°, b.p. 97—98°/20 mm. (isolated by distillation), of 2 : 3-dichlorodioxan (I) gives with (·CH₂·OH)₂ a mixture of ethylenedioxydioxans (eutectic, m.p. 86°, contains 77% of the form, m.p. 111°), inversion occurring during the reaction. Cl₂ and boiling 1 : 3-dioxacyclopentane give an inseparable mixture of the 2- and some 4-Cl-derivatives. Attempts to prepare 2 : 3-dicyanodioxan from (I) failed. R. C. S.

Rotenone, the active constituent of *Derris* root. XI. Rotenone resin. Determination of rotenone and deguelin in rotenone resin. S. TAKEI, S. MIYAJIMA, and M. ONO (Ber., 1933, 66, [B], 1826—1833; cf. A., 1933, 512; Clark, A., 1931, 357, 1065, 1208; 1932, 950).—Agitation of rotenone resin (I) in Et₂O with 2% NaOH followed by dil. H₂SO₄ leads to l-deguelin, m.p. 163°, [α]_D²⁰ -23.22° in C₆H₆. Treatment of the crude mixture of rotenone (II) and deguelin with H₂ in EtOH-KOH (Pd-BaSO₄) and removal of the portion sol. in alkali affords readily dl-deguelin (III), m.p. 166° (oxime, m.p. 220°; isooxime, m.p. 149°). Hydrogenation (Pd-BaSO₄ in EtOAc) of (III) gives dihydrodeguelin, m.p. 170°, identical with Clark's β-dihydrorotenone; in KOH-EtOH, (III) does not absorb H₂ (Pd-BaSO₄), thereby differing from (II). (III) is transformed into deguelinol I, m.p. 197°, and deguelinol II, m.p. 251°, identical with tephrosin and isotephrosin of Clark. The deguenols are transformed by H₂SO₄-EtOH into dehydrodeguelin, m.p. 227°, which with boiling KOH-EtOH affords *deguelic acid* C₂₃H₂₄O₈, m.p. 177°. Hydrolysis of (III) gives β-tubaic acid, m.p. 161°, in poor yield, hydrogenated to dihydro-β-tubaic acid, m.p. 170°, identical with the product obtained from β-dihydrorotenone. Towards *Cobitis fossilis* (III) is approx. one half as toxic as (II) in 0.02—0.002% solution; at lower concns. its toxicity diminishes more rapidly. At high concn. (I) has about the same toxicity as (II), but loses its effect more rapidly with increasing dilution. The non-cryst. components of (I) are not more toxic than colophony. (II) and (III) are determined in (I) by treating its solution in EtOH-NaOH with O₂ and weighing the dehydro-mixture (IV) thus produced. (IV) is hydrogenated (Pd-BaSO₄ in EtOH-NaOH) and the dehydrodeguelin and isodihydrodehydrorotenone so formed are weighed. H. W.

Complex compounds of bivalent silver of new type. G. A. BARBIERI (Atti R. Accad. Lincei, 1933, [vi], 17, 1078—1081).—Red *Ag dipicolinate*, $\text{Ag}(\text{C}_5\text{H}_4\text{N}\cdot\text{CO}_2)_2$, obtained from the normal salt by treatment with persulphate or by electrolytic oxidation, is highly stable and forms mixed crystals with the analogous Cu compound (cf. Ley and Ficken, A., 1917, i, 706). T. H. P.

Complex iron compounds of 2-pyridylhydrazine. B. EMMERT and O. SCHNEIDER (Ber., 1933, 66, [B], 1875—1876).—Gradual addition of Et_2O to 2-pyridylhydrazine and FeCl_2 in MeOH in absence of O_2 ppts. the salt $\left[\left(\begin{array}{c} \text{C}_5\text{H}_4\text{N} \\ \text{NH}\cdot\text{NH}_2 \end{array} \right)_3 \text{Fe} \right] \text{Cl}_2$, oxidised by air in presence of HCl to the compound, $\text{C}_{15}\text{H}_{21}\text{N}_9\text{Cl}_2\text{Fe}$. H. W.

Poly-membered ring systems. II. Improved syntheses of hexamethyleneimine. K. ZIEGLER and P. ORTH (Ber., 1933, 66, [B], 1867—1871; cf. A., 1933, 951).—Equiv. quantities of $\alpha\zeta$ -dibromohexane (I) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ (II) are dissolved in hot BuOH and treated gradually with 0.5 atom of Na in BuOH. After removal of excess of (I) and (II), *p*-toluenesulphon- ζ -bromohexylamide (III) is obtained in 65—70% yield. Slow addition of equiv. solutions of (III) and Na in BuOH to boiling BuOH gives *p*-toluenesulphonylhexamethyleneimine (IV), b.p. $164^\circ/0.3$ mm., m.p. 75° , in 70% yield. A 74% yield is obtained when the solutions are slowly run into $\text{CH}_2\text{Ph}\cdot\text{OH}$ at 170° so that the BuOH distils continuously. Hydrolysis of (IV) is effected conveniently by 48% HBr. H. W.

Azo-derivatives of methyleneindoline. (SIGNA.) E. GIUGI (Gazzetta, 1933, 63, 701—708; cf. A., 1924, i, 420, 1002).—*COMePr*^o *o*-tolylhydrazone, b.p. $176^\circ/33$ mm., when treated with ZnCl_2 in EtOH forms 2 : 3 : 3 : 7-tetramethylindolenine (I), b.p. $135^\circ/22$ mm., of which the 1-methiodide (II) (new m.p. 245° ; cf. A., 1905, i, 718) gives with $\text{NHPh}\cdot\text{NH}_2$ a substance $\text{C}_{19}\text{H}_{22}\text{N}_3\text{I}$, m.p. 232° (decomp.). The last is decomposed by picric acid to the *picrate*, m.p. 208° , of 1 : 3 : 3 : 7-tetramethyl-2-benzeneazomethyleneindoline, m.p. 146° , also obtained by action of PhN_2Cl on 1 : 3 : 3 : 7-tetramethyl-2-methyleneindoline. Similarly *COMePr*^o *m*-tolylhydrazone, b.p. $190^\circ/50$ mm., yields 2 : 3 : 3 : 6-tetramethylindolenine, m.p. 61 — 62° , b.p. $140^\circ/27$ mm., which forms a *picrate*, m.p. 169° , a *Bz* derivative, m.p. 186° , and a *methiodide*, m.p. 230° , whence the compound $\text{C}_{19}\text{H}_{22}\text{N}_3\text{I}$, m.p. 250° , and the *picrate*, m.p. 200° , of 1 : 3 : 3 : 6-tetramethyl-2-benzeneazomethyleneindoline (hydrochloride, m.p. 240°), also obtained by action of PhN_2Cl on 1 : 3 : 3 : 6-tetramethyl-2-methyleneindoline. 1 : 3 : 3-Triethyl-2-methyleneindoline and PhN_2Cl form 1 : 3 : 3-triethyl-2-benzeneazomethyleneindoline (*picrate*, m.p. 168°). E. W. W.

Quinoline synthesis. G. A. KIRKHOFF and M. FEDOTOV (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1930, 40—41; cf. Russ. Pat. 29,173).— NH_2Ph (1 mol.), 94% glycerol (2 mols.), H_2SO_4 (d 1.84, 1.44 mols.), and PhNO_2 (0.55 mol.), with $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (34 g.) + infusorial earth (10 g.) as catalyst, are heated to 136° , PhNO_2 and H_2O evaporating being condensed and the former returned to the reaction vessel. The

mixture is then kept at 150 — 154° for 4—5 hr. The cold product is diluted with ice and H_2O and nitrite is added until N oxides are liberated. After steam-distillation the residue is made alkaline and the quinoline distilled with steam. The yield is 85% on NH_2Ph and 42—43% on glycerol. CH. ABS.

Cytisine group. I. Attempted synthesis of Ewins' structure for cytisine. S. CHAKRAVARTI and A. VENKATASUBBAN (J. Annamalai Univ., 1933, 2, 227—237).—Unsuccessful attempts to synthesise a compound having Ewins' cytisine formula (J.C.S., 1913, 103, 97) are described. Attempted oxidation of $\omega\omega'$ -dibromomesitylene to the dialdehyde with different reagents and by conversion into the $(\text{NHPh})_2$ -compound and oxidation with KMnO_4 failed. Nitration of *m*-tolualdehyde and subsequent condensation with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ (+ $\text{C}_5\text{H}_{11}\text{N}$) gives a mixture of 2- (I) and 6-nitro-3-methylcinnamic acid (II), m.p. 224° ; 6-nitro-*m*-tolualdehyde-*p*-tolil has m.p. 89° . *m*-Methylcinnamic acid with HNO_3 (d 1.48) at $<0^\circ$ gives the 4- NO_2 -compound, m.p. 251° (*Me* ester, m.p. 124°), (I), and (II). The *mono-p*-tolil, m.p. 161° , of 1 : 4 : 3 : 5- $\text{C}_6\text{H}_2\text{Me}(\text{OH})(\text{CHO})_2$ with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ gives 2-hydroxy-3-aldehyde-5-methylcinnamic acid, m.p. 212° (*Me* ester, m.p. 129°). Attempts at cyclisation of 1-nitroso-6 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline between the 1 : 8-groups failed. Diazotised 8-amino-6-methylquinoline with KCN - CuCN gives only a small amount of substance, m.p. 90° . 6-Methylquinoline-8-carboxylic acid, m.p. 169° , obtained from 4-amino-*m*-toluonitrile by the Skraup reaction, is reduced by Sn - HCl to the H_4 -compound, m.p. 190 — 191° , the 1-*NO*-derivative, m.p. 138° (decomp.), of which loses the *NO* group when reduced with Zn dust and AcOH . Na - Hg and NH_4 sulphide also failed to give the expected hydrazine or its cyclisation product. H. A. P.

Acridones. V. 3-Nitrophenylanthranil. I. TANASESCU and E. RAMONTIANU (Bull. Soc. chim., 1933, [iv], 53, 918—923; cf. A., 1933, 956).—3-Nitrophenylanthranil (I), m.p. 174 — 175° (0.5 HgCl_2 compound, m.p. 190° after decomp. from 185°), is isolated from the reaction product of 2 : 4-dinitrobenzaldehyde (II), C_6H_6 , and H_2SO_4 . It is reduced by SnCl_2 to the 3- NH_2 -compound (III), m.p. 135 — 136° (HgCl_2 compound, m.p. 192° ; *Bz* derivative, m.p. 260° after decomp.), also obtained similarly from (II). (I), (II), or (III) with Zn dust and CaCl_2 gives 2 : 4-diaminobenzophenone, m.p. 132° (*Bz* derivative, m.p. 201°). R. S. C.

Isolation of amino-acids as carbamido-acids and hydantoins. I. Derivatives of monoaminomonocarboxylic acids. W. J. BOYD (Biochem. J., 1933, 27, 1838—1848).—The properties of the carbamido-acids (I) and hydantoins (II) corresponding with the NH_2 -acids present in protein hydrolysates were investigated with a view to the isolation and determination of NH_2 -acids. Many vals. of m.p. (lit.) are corr. Separation of (I) by EtOH at p_{H} 4 and conversion into (II) permits the removal of the derivatives of leucine, isoleucine, valine, phenylalanine, alanine, proline, and hydroxyproline by Et_2O or CHCl_3 , whilst that of tyrosine is obtained from the residue insol. in Et_2O . Separation of (II) by solvents

appears to be possible. New compounds described are: α -*carbamido-sec.-butylacetic acid*, m.p. 205°; *sec.-butylhydantoin*, m.p. 145—150° (*hydrate*, m.p. 95°).

F. O. H.

Tautomerism of pyrazoles. K. VON AUWERS (*Annalen*, 1933, 508, 51—58).—The following compounds are shown (from their sp. exaltations) to be entirely or largely homogeneous: 3-phenyl- and 3-phenyl-5-methyl-pyrazoles; Me 3-phenyl- and 3-phenyl-1-methyl-pyrazole-5-carboxylates; Me 5-phenyl-1-ethylpyrazole-3-carboxylate; the constitutions are assigned from the spectrochemical data. The 3- and 5-positions in pyrazole can no longer be regarded as equiv.

H. B.

2-Benzoylglyoxaline. A. SONN and P. GREIF (*Ber.*, 1933, 66, [B], 1900—1903).—*d*-Tartaric acid is converted by fuming HNO_3 and conc. H_2SO_4 into dinitrotartaric acid, which is dissolved in Et_2O and treated successively with $\text{CH}_2\text{Ph}\cdot\text{CHO}$ and $\text{EtOH}\cdot\text{NH}_3$, thus leading to 2-benzoylglyoxaline-4:5-dicarboxylic acid (I), decomp. 248° (NH_4 salt). Decarboxylation of (I) in anthracene at 300° gives 2-benzoylglyoxaline, m.p. 125—126° (*picrate*, m.p. 172°), oxidised by CrO_3 in AcOH to 2-benzoylglyoxaline (III), m.p. 161—162°, not identical with the product of Oddo *et al.* (*A.*, 1927, 1098). (II) is transformed by Br in CHCl_3 into 4:5-dibromo-2-benzoylglyoxaline, m.p. 218—220°, and its *perbromide*, m.p. 117—120°. Hydrogenation ($\text{Pd}\text{-AcOH}$) of (II) affords 2- α -hydroxybenzoylglyoxaline, m.p. 199—201°.

H. W.

Bis- β -halogenoethylamines. III. N-Phenylpiperazine. V. PRELOG and G. J. DRÍZA (*Coll. Czech. Chem. Comm.*, 1933, 5, 497—502).—Interaction of NH_2Ph with $\beta\beta'$ -dichlorodiethylamine hydrochloride or $\beta\beta'$ -dibromodiethylamine hydrobromide in MeOH gives *N*-phenylpiperazine (I), b.p. 162—164°/22 mm. [*hydrochloride*, m.p. 247° (decomp.); *hydrobromide*, m.p. 250—252°; *Ac*, m.p. 96° (*hydrochloride*, m.p. 213—214°), *Bz*, m.p. 96—97° (*hydrochloride*, m.p. 244°), and *p*-toluenesulphonyl derivative, m.p. 199—200°; *p*-nitrobenzeneazo- (brownish-red), decomp. about 250°, and *p*-sulphobenzeneazo-derivative (*Na* salt, decomp. about 210°)], and a little $\beta\beta'$ -dianilindodiethylamine, b.p. 268—276°/22 mm. (*hydrochloride*, m.p. 237°). (I) has marked physiological action.

H. A. P.

Spontaneous resolution of a racemic compound (histidine monohydrochloride). R. DUSCHINSKY (*Chem. and Ind.*, 1934, 10; cf. *A.*, 1928, 653).—A hot solution of 660 g. of *dl*- (I) and 340 g. of *l*-histidine hydrochloride (II) when rapidly cooled to 20° affords pure (II); the mother-liquor with $\text{EtOH}\cdot\text{Et}_2\text{O}$ at 0° gives pure (I). Concn. of the second filtrate and rapid cooling gives the *d*-isomeride (46 g.), $[\alpha]_D^{25} +38^\circ$ to $+39.5^\circ$.

J. L. D.

Complex dipyridyl and phenanthroline salts of bivalent metals.—See this vol., 159.

Oxidation of uric acid in presence of glycine. FRÉREJACQUE (*Compt. rend.*, 1933, 197, 1337—1339).—Oxidation of uric acid with O_2 in alkaline solution in presence of MnO_2 and glycine (I) (cf. *A.*, 1932, 67) affords the *K* salt, $+\text{H}_2\text{O}$

$\text{CO} \left\langle \begin{array}{c} \text{NH}\cdot\text{CH} \\ \text{NH}\cdot\text{C}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K})\cdot\text{NH} \end{array} \right\rangle \text{CO}$ (II), of *isoallantoylglycine* (III) [double *Cu*, $\text{CuR}_2\cdot 2\text{CuSO}_4\cdot 11\text{H}_2\text{O}$; $\text{CuR}_2\cdot\text{CuCl}_2\cdot 3\text{H}_2\text{O}$; and *Ag*, $\text{AgR}\cdot\text{AgNO}_3$, salts ($\text{R}=\text{C}_6\text{H}_8\text{O}_4\text{N}_5$)]. With dil. AcOH (II) gives an equimol. double salt, $+\text{H}_2\text{O}$, of (II) and (III), hydrolysed by mineral acids completely to (I) and allantoin. Using $\text{NH}_2\cdot\text{CHMc}\cdot\text{CO}_2\text{H}$ in place of (I) gives the *K* salt $+\text{3H}_2\text{O}$, of *isoallantoylalanine*.

J. W. B.

Reductions with zinc dust in pyridine. III. Reversible hydrogenation and dehydrogenation of chlorophylls. R. KUHN and A. WINTERSTEIN (*Ber.*, 1933, 66, [B], 1741—1745; cf. *A.*, 1932, 1138).—Chlorophyll *a* or *b* or methylchlorophyllide is rapidly reduced by Zn dust in presence of $\text{C}_5\text{H}_5\text{N}$ and AcOH , giving brown solutions which become green with red fluorescence on exposure to air. Chromatographic treatment of the solution in light petroleum with sucrose removes decomp. products; the regenerated dyes are identical with the initial materials. Similar treatment of phæophorbide *a* or phæophytin *a*+*b* gives leuco-compounds converted by air into complex Zn compounds. Hæmin is not decolorised. The bearing of the observations on photosynthesis is discussed.

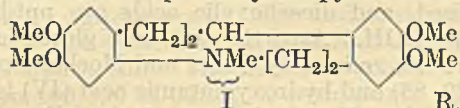
H. W.

Effect of ultra-violet rays on nicotine. V. A. GANT (*J. Pharm. Exp. Ther.*, 1933, 49, 408—427).—Irradiation of 0.1% nicotine (I) destroys its basicity in 105 min. and causes slight acidity in 150 min. At the neutral point the solution has a slight vasopressor activity. The product contains nicotinic acid (II), NH_2Me (III), and unchanged (I). After 12 hr.' exposure a 0.1% solution becomes neutral again, corresponding with the destruction of (II), malonic acid (IV), and (III); traces of NO_3' , NO_2' , and NH_3 are found. (II) on irradiation gives similar end products; 70% of a (IV) solution is destroyed and 73% of a (III) solution giving NO_3' , NO_2' , and NH_3 as end-products. H_2O_2 produces the same series of changes.

H. D.

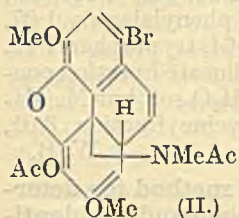
Synthesis of *dl*-homolaudanosoline and its dehydrogenation. S. SUGASAWA and H. YOSHIKAWA (*J.C.S.*, 1933, 1583—1585).—Homoveratrylamine and β -veratrylpropionyl chloride in Et_2O -aq. NaOH at 0° give β -3:4-dimethoxyphenylpropiono- β -3':4'-dimethoxyphenylethylamide, m.p. 99—100°, which with POCl_3 in PhMe at 120—130° yields 6:7-dimethoxy-1- β -3':4'-dimethoxyphenylethyl-3:4-dihydroisoquinoline (I), m.p. 96—97° (lit. 94°; *hydrochloride*). Diveratrylideneacetone (modified prep.; 85% yield), m.p. 84°, is quantitatively hydrogenated (PtO_2) to di- β -3:4-dimethoxyphenylethyl ketone, m.p. 84°, the oxime, m.p. 138—139°, of which with POCl_3 in PhMe at 120—130° gives (I). (I) with MeI in hot MeOH gives *dl*-homolaudanosine methiodide, decomp. 132.5—133.5° (*perchlorate*, decomp. 183—185°); the corresponding methochloride affords, when hydrogenated, the *tert.* base, which with $\text{HI}\text{-Ac}_2\text{O}$ at 150° gives *dl*-homolaudanosoline (II) [*perchlorate*, m.p. 183—185° (decomp.)]. The *hydriodide*, amorphous, hygroscopic, of (II) with chloranil in hot AcOH yields 2:3:11:12-tetrahydroxy-8-methyl-6:7:15:16-tetrahydro-5:18:9:14-dibenzpyridocolinium iodide, decomp. 252—253°, methylated (Me_2SO_4) in H_2 to

2 : 3 : 11 : 12 - tetramethoxy - 6 : 7 : 15 : 16 - tetrahydro - 5 : 18 : 9 : 14 - dibenzpyridocoline methiodide, decomp. 237—238°; the corresponding crude methochloride, decomp. 204—205°, at 220—230° gives a substance, m.p. 153.5—154.5°, probably the pyridocoline base



R. S. C.

Sinomenine. XXXVII. Acetolysis of 1-bromosinomenine. K. GOTO, K. IIDA, and H. SHISHIDO (Bull. Chem. Soc. Japan, 1933, 8, 366—370).—1-Bromosinomenine (I) is converted by Ac_2O and NaOAc at the b.p. into 1-bromodiacetylsinomenine, m.p. 135° (sinters 125°), to which formula (II) is assigned, and which on



(II.)

further treatment (e.g., hydrolysis, reduction) is converted into amorphous products. De-*N*-methyl - 1 - bromosinomenine, however, on acetolysis gives 90% of theory of 1-bromodiacetylsinomenol (III) (1-bromo-4 : 6 - diacetoxy - 3 : 7 - dimethoxy - phenanthrene), m.p. 187°, converted by catalytic reduction into diacetylsinomenol, m.p. 151°. (III) is also obtained similarly but in poor yields from 1-bromosinomenine methiodide (IV), and the hydrochloride, methiodide, and de-*N*-methyl derivative of 1-bromosinomenine. De-iodination of (IV) by AgOAc in AcOH and acetolysis of the product gives 1-bromo-4 : 6 : 7 (?) - triacetoxy - 3 - methoxyphenanthrene, m.p. 216°, which is also formed by acetolysis of 1-bromosinomenine ketone, and on catalytic reduction gives 4 : 6 : 7 (?) - triacetoxy - 3 - methoxyphenanthrene, m.p. 168°. H. A. P.

Asymmetric quaternary arsonium compounds and attempted fission into their optically active components. G. KAMAI (Ber., 1933, 66, [B], 1779—1783).— AsMeEtI is converted by MgPhBr into phenylmethylarsine, b.p. 89—90.5°/12 mm., which with CH_2PhI affords phenylbenzylmethyl ethylarsonium iodide (I), m.p. 140°. Ethyl-*n*-propylphenylarsine (II), b.p. 245°/760 mm. (compound $\text{C}_{11}\text{H}_{17}\text{AsCuBr}$, m.p. 134°), and CH_2PhCl at 140° yield phenylbenzylethyl-*n*-propylarsonium chloride (III), m.p. 156°. (II) does not give cryst. derivatives with $\text{COMe}\cdot\text{CH}_2\text{Cl}$ or $\text{COPh}\cdot\text{CH}_2\text{Br}$. *p*-Tolylethyl-*n*-propylarsine, b.p. 127—128°/10 mm. (compound $\text{C}_{12}\text{H}_{19}\text{AsCuBr}$, m.p. 117—118°), and CH_2PhI at room temp. yield *p*-tolylbenzylethyl-*n*-propylarsonium iodide (IV), m.p. 119—120°. α -Naphthylethyl-*n*-propylarsine, b.p. 181°/10 mm. (additive compounds with Br and CuBr), affords α -naphthylbenzylethyl-*n*-propylarsonium iodide (V), m.p. 154—155°, and α -naphthylphenacyl-ethyl-*n*-propylarsonium bromide (VI), m.p. 136—137°. (I), (III), (V), and (VI) give non-cryst. products with Ag *d*- α - and *d*- π - (VII) bromocamphorsulphonates. (IV) and (VII) give a salt which can be separated into fractions of differing $[\text{M}]_D$; treatment of the first fraction, m.p. 137°, with aq. KI leads to *d*-*p*-tolylbenzylethyl-*n*-propylarsonium iodide, m.p. 120°, $[\alpha]_D^{20} + 9.86^\circ$ in COMe_2 , which rapidly becomes inactive. H. W.

Asymmetric arsenic atom. Attempts to prepare optically active arsenicals. J. D. A. JOHNSON (J.C.S., 1933, 1634—1637).—2-Methyl-10-*n*-propyl-5 : 10-dihydrophenarsazine and CH_2PhBr or CH_2BzBr (I) at 100° give 10-benzyl-, m.p. 206—207° [*d*-camphor- β -sulphonate, m.p. 262° (decomp.), $[\alpha]_D^{20} + 21^\circ$, irresolvable], and 10-phenacyl-2-methyl-10-*n*-propyl-5 : 10-dihydrophenarsazonium bromide, respectively. $\text{CH}_2\text{Ph}\cdot\text{MgBr}$ and 10-chloro-2-methyl-5 : 10-dihydrophenarsazine give $(\text{CH}_2\text{Ph})_2$ and 10-benzyl-2-methyl-5 : 10-dihydrophenarsazine, m.p. 132.5°, which with (I) gives 10-phenacyl-10-benzyl-2-methyl-5 : 10-dihydrophenarsazonium bromide, m.p. 203° (*d*-camphor- β -sulphonate, m.p. 187—188°, $[\alpha]_D^{20} + 17.5^\circ$ in EtOH , irresolvable). The corresponding iodide, m.p. 179°, with Ag_2O in hot H_2O gives (?) 10-benzyl-2-methyl-5 : 10-dihydrophenarsazonium dihydroxide (II), m.p. indefinite. 10 : 10'-Bis-5 : 10-dihydrophenarsazinyll (III) and EtBr at 100° give (?) 10 : 10-diethyl-5 : 10-dihydrophenarsazonium bromide, m.p. 129—132° (decomp.), also obtained similarly from 10-ethyl-5 : 10-dihydrophenarsazine. 10-Chloro-5-acetyl-5 : 10-dihydrophenarsazine and H_3PO_2 in hot $\text{EtOH}\cdot\text{COMe}_2$ afford 10 : 10'-bis-5-acetyl-5 : 10-dihydrophenarsazinyll, unchanged by EtBr . (III) and $(\text{CH}_2)_3\text{Br}_2$ give a substance, m.p. 166° (decomp.). R. S. C.

Additive products of *p*-phenoxyphenyldialkylphosphines and carbon disulphide. W. C. DAVIES and C. J. O. R. MORRIS (Bull. Soc. chim., 1933, [iv], 53, 980—986).—*p*-Phenoxyphenyldichlorophosphine and the appropriate Grignard reagent give the *p*-phenoxyphenyldialkylphosphines, $p\text{-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{PR}_2$, which with CS_2 give additive compounds (A) (1 mol. of each), in which $\text{R} = \text{Me}$, m.p. 87.5°, *Et*, cryst. (with MeI gives the phosphine methiodide, m.p. 163°), and *Pr*^a, m.p. 57°. (A) are partly dissociated in solution and are considered to contain a co-ordinate C·P linking. *p*-Chlorophenyldi-*n*-propylphosphine and CS_2 give a red colour, but no ppt. R. S. C.

Preparation of selenophen. Attempts to prepare tellurophen. F. A. McMAHON, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1933, 1644).—Selenophen (CHPh_3 derivative, m.p. 57°, decomposes into its components when heated) is best obtained from C_2H_2 , Se, and roasted bauxite at 400°; it is formed in traces from P_2Se_3 and Na succinate (cf. A., 1910, i, 187). Tellurophen, probable b.p. 136°, could not be obtained pure; mixtures containing it are formed from C_2H_2 , roasted bauxite, and Te, or better Al_2Te_3 , at 400°. R. S. C.

Antimonial analogues of the acridine series. Dihydrostibacridines. G. T. MORGAN and G. R. DAVIES (Proc. Roy. Soc., 1933, A, 143, 38—47).—2-Aminodiphenylmethane is converted by the Bart-Schmidt process into diphenylmethane-2-stibinic acid (I), reduced by SO_2 in presence of HCl and a trace of KI to diphenylmethane-2-dichlorostibine (II), m.p. 129—130°, converted by $\text{NaI}\cdot\text{COMe}_2$ into the corresponding I_2 -compound, m.p. 95°, and by aq. $\text{NH}_3\cdot\text{COMe}_2$ (or EtOH) at 0° into the stibine oxide (III), m.p. 82—83°, which with HBr (*d* 1-3) affords the Br_2 -compound, m.p. 121°. Ring-closure of (I) with warm AcOH —

H_2SO_4 gives *stibacridinic acid* $\text{CH}_2\langle\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix}\rangle\text{SbO}_2\text{H}$, converted by HCl at 0° into *stibacridine trichloride*, reduced by SO_2 to 10-chloro-9:10-dihydrostibacridine, m.p. 105° , whence the corresponding 10-Br-, m.p. 112° , and 10-I- (IV), m.p. $160\text{--}162^\circ$, -derivatives, and 10:10'-bis-9:10-dihydrostibacridine oxide, softens 211° , sinters 215° , are obtained. With MgMeI (IV) gives 10-methyl-9:10-dihydrostibacridine, softens 98° , m.p. 101° (dichloride, m.p. $177\text{--}178^\circ$; Br_2 - and I_2 -compounds unstable), the corresponding 10-Ph derivative (using MgPhBr) being isolated only as its dichloride, m.p. $221\text{--}223^\circ$. With excess of warm aq. NH_3 in COMe_2 (II) gives tetrakis(diphenylmethane-2-stibine oxide) $[(\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4)_2\text{Sb}]_2\text{O}$, m.p. 117° , from which by similar methods are obtained bis(diphenylmethane)-2-chloro- (V), m.p. $87\cdot5^\circ$, -2-bromo-, m.p. $86\cdot5^\circ$, and -2-iodo-, m.p. $73\text{--}75^\circ$, -stibine. With Cl_2 in CH_2Cl_2 (V) gives a trichloride (VI), m.p. 129° , converted by warm dil. aq. NH_3 into bisdiphenylmethane-2-stibinic acid, m.p. 248° , also obtained by oxidation of (III) with H_2O_2 . Heated at $150\text{--}180^\circ/18\text{--}20$ mm. (VI) gives 10:2'-diphenylmethane-9:10-dihydrostibacridine dichloride, m.p. $220\text{--}224^\circ$ (decomp.), purified through the corresponding oxide, softens at $158\text{--}160^\circ$. J. W. B.

Thermolysis of neutral, aqueous solutions of polypeptides with increasing chain-length in relationship to the thermolysis of proteins. O. GERNGROSS and W. DESEKE (Ber., 1933, 66, [B], 1810—1813).—The progress of the hydrolysis of alanyl-glycyl- and -diglycyl-glycine, of leucyl-di- and -tetra-glycylglycine in neutral aq. solution at 100° is followed by determination of NH_2 (Van Slyke). The rate in the case of the initial members of an analogously constituted series increases with increasing chain-length, but rapidly tends to a const. val. There is no evidence that polypeptides with increasing chain-length become more resistant towards hydrolysis in H_2O at 100° . Immediately after dissolution it is considered that gelatin exists in more or less intact micelles; the peptide linking is protected for a time from hydrolysis, since the partial valencies are saturated with the corresponding groups of vicinal mols. in the micelle. The peptide chain does not suffer more rapid hydrolysis until it is severed completely from the micelle. H. W.

Formalin titration of proteins. D. W. STEUART (Analyst, 1933, 58, 754—755).—Vals. of total N (c.c.) / formol titration (0.1N-NaOH) are: ordinary milk 23 (calc.), gelatin 40, casein 22, albumin 33, peptone 16 and 17, pepsin 11, and pancreatin 5 (cf. B., 1933, 1080). As these vals. decrease, buffer action (for growth of lactic bacteria) increases, and the action of pepsin on casein produces a better buffered peptone than Witte's peptone. J. G.

Basic amino-acids of casein. H. B. VICKERY and A. WHITE (J. Biol. Chem., 1933, 103, 413—415).—Determination of the basic NH_2 -acids from casein by the Ag. pptn. method (A., 1928, 511) gives histidine 1.83, arginine 3.85, and lysine 6.25%. J. W. B.

Fractionation of the amino-acids of livetin. T. H. JUKES (J. Biol. Chem., 1933, 103, 425—437).—

A method for fractionating NH_2 -acids (protein hydrolysis) is described. Humin, NH_3 , and basic NH_2 -acids are first removed and determined by Vickery's methods (cf. *inter alia*, A., 1928, 511; 1932, 1148), and from the combined mother-liquors tyrosine (I) is crystallised, and dicarboxylic acids are pptd. with $\text{Ba}(\text{OH})_2\text{-EtOH}$. Aspartic (II) and glutamic (III) acids are determined by Jones and Moeller's method (A., 1929, 85) and hydroxyglutamic acid (IV) is pptd. as its Ag salt. Monoamino-monocarboxylic acids are then converted into Cu salts and fractionated (Brazier, A., 1930, 1458, modified). Application of this method to hen's yolk livetin (containing 15.5% N; hydrolysed with 20% HCl) affords 87% recovery of total N, 56% of which is allocated thus: NH_3 8.3, histidine 1.62, arginine 11.6, lysine 6.15, (III) 4.18, (II) 2.04, (IV) (?) trace, (I) 1.80, leucine 7.29, phenylalanine 1.07, alanine 6.3, proline 1.71, cystine 2.64, tryptophan 1.11, and glucosamine 0.4%. The unallocated portion consists of Cu salts, H_2O -insol. 10.1, H_2O -sol. but MeOH-insol. 19.7, MeOH-sol. 17.7; glycine fraction 3.01, valine + isoleucine fraction 7.18%. J. W. B.

Elementary microanalytical method for determination of halogens and nitrogen and for identification of organic substances. V. STANEK and T. NEMES (Z. anal. Chem., 1933, 95, 244—260).—The method previously described (A., 1932, 529) has been elaborated so as to give accurate quant. results for C, H, N, and halogens. 3—10 mg. of substance are used. In trials with eight pure substances the max. error on any element was $< 0.4\%$. F. L. U.

Micro-determination of sulphur in organic compounds. Modification of ter Meulen's method. H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 611—615).—Ter Meulen's method (A., 1922, ii, 311; 1930, 357) is adapted for use with about 2—10 mg. of substance. H. B.

Determination of the impurities in ethyl ether produced by autoxidation. L. SZÄHLENDER (Magyar Gyóg. Társ. Ert., 1932, 8, 425—435; Chem. Zentr., 1933, i, 1820).—To 100 c.c. of 20% H_2SO_4 and 5 c.c. of starch solution are added 5 g. of coarse-grained KHCO_3 , 0.5 g. of KI, and 1 g. of KHCO_3 , and shortly before the end of the evolution of CO_2 , 5 c.c. of the Et_2O . The mixture is well shaken and after 10 min. the liberated I titrated with 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$. Degree of oxidation (II) = no. of c.c. of 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$ required for 10 c.c. of Et_2O , oxidation no. = (II) \times 1.27 = mg. of I. Samples of Et_2O for narcosis gave vals. of 0.0, 0.0, 0.36, and 1.57 for (II), whilst other samples gave vals. > 100 . L. S. T.

Differentiation between and determination of formaldehyde and acetaldehyde in mixtures of the two. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1933, [iv], 53, 909—918).— CH_2O , MeCHO , and (if the total aldehyde content is known) mixtures of the two are determined by the time taken for formation of a ppt. with dimethyldihydroresorcinol under defined conditions. R. S. C.

Aminometry. D. VORLÄNDER [with J. FISCHER and F. WILDNER] (Ber., 1933, 66, [B], 1789—1792).—The term "aminometry" is applied to the volumetric determination of amines with acids with as complete

as possible exclusion of aq. and alcoholic solvents and of all conditions under which amines become bases. A solution of HCl in CHCl_3 is employed which is standardised (daily) by titration with $\text{N}(\text{CH}_2\text{Ph})_3$ in presence of dimethylaminoazobenzene (I) as indicator or by agitation with H_2O and titration of the emulsion with 0.05N-Ba(OH) $_2$ or NaOH in presence of phenolphthalein. The indicator solution, 0.05 g. of (I) in 100 c.c. of CHCl_3 , is permanent. Titration is effected directly or with volatile amines by dissolution in excess of acid and back titration with $\text{N}(\text{CH}_2\text{Ph})_3$. $\text{C}_5\text{H}_5\text{N}$ does not give a satisfactory endpoint. With *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ the mean errors are -4.4%, -4.0%, and -2.5%, respectively. Errors < 1% are observed with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$, *as-m*-xylylidine, ψ -cumidine, and α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$. Dibasic alkaloids react accurately with 2 HCl when the titration is slowly performed. The method is inapplicable to technical aromatic amines on account of their colour. HBr offers no advantage over HCl, whilst $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ do not give sharp colour changes if (I) is used. H. W.

Analysis of mixtures of amines. A NELUBINA (Anilinokras. Prom., 1933, 3, 355).—Good results for determination of NH_2Ph in its mixtures with NHPhMe and NPhMe_2 are obtained by using a modification of Linke's method (A., 1932, 1149). R. T.

Determination of *o*-toluidine. S UENO and H. SEKIGUCHI (J. Soc. Chem. Ind. Japan, 1933, 36, 613—615B).—This is effected by the m.p. of the dehydrated hydrochloride (216°), figures for the depression by the *m*- and *p*-isomerides being given. Similar figures are given for the hydrobromide, m.p. 198.7°.

R. S. C.

Azo-compounds in volumetric analysis. E. ROZOVITSEVA (Anilinokras. Prom., 1933, 3, 308).—Better results are obtained in titration of β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ by standard PhN_2Cl by adding gelatin or gum arabic, which prevents flocculation of the dye formed.

R. T.

Gasometric determination of cysteine and cystine. W. C. HESS (J. Biol. Chem., 1933, 103, 449—453).—Addition of glucose to mixtures of NH_2 -acids free from cysteine (I) gives positive results for (I) by the Baernstein gasometric method (II) (A., 1931, 108) [10 mg. glucose=1.64 mg. of (I)], but not by the Sullivan, Okuda, or Folin-Marenzi methods. ($\cdot\text{CHO}$) $_2$ and AcCHO give negative results, but AcCO_2H [10 mg.=1.0 mg. of (I)] gives a positive reaction, and the presence of carbohydrates in protein matter may thus explain the discrepancies observed between (II) and other methods for determination of (I). J. W. B.

Reactions of terpenes with antimony trichloride. V. E. LEVINE and E. RICHMAN (Biochem. J., 1933, 27, 2051—2054).—The reaction has been studied both with and without the addition of Ac_2O . Reactivity is greatest in presence of CHO, OH, CO, and general unsaturation. The camphane group is the least and the olefine group the most reactive.

H. G. R.

Shear's aniline-hydrochloric acid reaction for vitamin-D. I. Furan and derivatives. V. E. LEVINE and C. L. SEAMAN. II. Terpenes. V. E.

LEVINE and E. J. SHAUGHNESSY (Biochem. J., 1933, 27, 2047—2048, 2048—2050).—I. The colour reactions given by Shear's reagent (cf. A., 1927, 282) for furan and derivatives are tabulated.

II. Terpenes do not, generally, react in the cold, and Sexton's conclusion (A., 1928, 1161) that the coloration is due to the CO group was not confirmed. The reaction is given by the fat-sol. vitamins, carotene, and irradiated ergosterol. H. G. R.

Micro-determination of histidine; method for the separation of histidine and tyrosine. K. LANG (Z. physiol. Chem., 1933, 222, 3—5).—The separation of histidine (I) and tyrosine depends on the pptn. of (I) with Hg mixture (Hinsberg and Laszlo, A., 1930, 494). (I) is determined by step-photometer after dissolving the ppt. in 5% aq. NaCN, adding aq. Na_2CO_3 and the diazo-reagent of Kocessler and Hanke (A., 1920, ii, 67). J. H. B.

Determination of nicotine by the silicotungstate method. L. BENVENNY (Mitt. Lebensm. Hyg., 1933, 22, 217—220; Chem. Zentr., 1933, ii, 1402).—100 c.c. of the solution (approx. 1% nicotine) and 10 c.c. of 50% KOH are distilled in steam, the distillate (375 c.c.) being collected in 25 c.c. of 10% HCl. 12 c.c. of 10% silicotungstic acid solution are added to the receiver, stirred, left for 24 hr., filtered (Gooch crucible), dried for 2 hr. at 120°, and weighed ($\times 0.1012$ =nicotine). $\text{C}_5\text{H}_5\text{N}$, if present, is removed before addition of KOH by distillation in presence of 40 c.c. of glacial AcOH. A. A. E.

Determination and separation of alkaloids from *Peganum harmala*. N. I. BUNTZELMAN (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 71—72).—The ground seeds are left over-night in contact with 15% AcOH; the extract is filtered through cotton and then through paper moistened with 15% AcOH. Filtrate corresponding with 0.8 g. of seeds is mixed with 20 c.c. of 30% KOH and extracted six times with Et_2O . The residue from Et_2O is dissolved in 5 c.c. of 0.1N- H_2SO_4 and 15—20 c.c. H_2O , the excess of acid being titrated with 0.1N-NaOH (Merck); 1 c.c. of 0.1N- H_2SO_4 =0.0213 g. of alkaloids. Harmine is separated from harmaline by mixing 20 c.c. of a solution of the base (< 0.1%) in 2% AcOH with 0.5 c.c. of 30% NaOH, neutralising (phenolphthalein) with N-NaOH, acidifying with AcOH, neutralising with 0.1N-NaOH, and adding 0.4 c.c. in excess. After 5—10 min. on a H_2O -bath the crystals which appear are collected on a dry, hot filter; the harmine is dissolved in hot 2% AcOH and reprecipd. with 0.1 c.c. excess of 0.1N-NaOH. The combined filtrates are treated with 25 c.c. of 30% NaOH and extracted four times with Et_2O ; on titration, 1 c.c. of 0.1N- H_2SO_4 =0.0214 g. of harmaline. The harmine on the filter is dissolved in hot 2% AcOH and determined in the usual manner; 1 c.c. of 0.1N- H_2SO_4 =0.0212 g.

CH. ABS.

Analysis of emetine hydrochloride. B. A. KLYACHKINA and F. D. ZILBERG (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 103—109).—Pharmacopœical methods for the separation of Na cephalinate are inaccurate. Et_2O extraction of emetine (I) from aq. NH_3 solutions is incomplete, whilst cephaline (II) is extracted unless the NaOH concn. is high. 1.5

times the calc. quantity of NH_3 should be used. CHCl_3 extracts psychotrine as well as (II). For the separation of (I) from (II) the alkaline mixture is treated with aq. NH_3 after acidifying, followed by repeated Et_2O extraction; the residue after evapor-

ation of the Et_2O consists of (II). To the neutralised aq. solution of (I) hydrochloride and (II) NaOH is added to approx. 50% and the alkaline liquid is shaken 2—3 times with Et_2O , (I) being left on evaporation of the Et_2O .
CH. ABS.

Biochemistry.

Respiratory exchange of the adult white mouse. Effect of external temperature. L. CHEVILLARD (Compt. rend. Soc. Biol., 1933, 113, 181—184).—The smaller is the mouse the greater is the effect of low environmental temp. (I) in increasing the energy exchange. The ratio (II) loss of H_2O by evaporation : O_2 consumption is the same at any fixed temp. for mice of various wt. As (I) is lowered (II) becomes smaller. At temp. below thermic neutrality, (II) in mice is > in larger animals. NUTR. ABS. (m)

Continuous gas analysis. Determination of basal metabolic rate. H. W. BANSI (Deut. med. Woch., 1933, 59, 729—730).—The expired air (I) is measured and its composition determined by comparing its density with that of atm. air (II). The comparison is made in an apparatus which gives a differential measurement of the kinetic energies of (II) and (I) moving at equal velocity in opposite directions. A complete determination requires 6 min. and an accuracy of $\pm 0.02\%$ CO_2 and $\pm 0.07\%$ O_2 is claimed. NUTR. ABS. (m)

Clinical model of the Haden-Hausser hæmoglobinometer. R. L. HADEN (J. Lab. Clin. Med., 1933, 18, 1062—1065). CH. ABS.

Normal hæmoglobin level during the first year of life. H. M. M. MACKAY (Arch. Dis. Child., 1933, 8, 221—225).—Revised figures are given for a proposed standard normal hæmoglobin curve for the first year of life. The average hæmoglobin vals. of breast-fed infants (I) and of those (II) bottle-fed from the second month are compared. (II) show a progressive fall from 80 in the first to second month to 69.1 at 12—13 months; the lowest val. for (I) is 72.8 at 10—11 months. NUTR. ABS. (m)

Hæmoglobin content of chicken blood. A. D. HOLMES, M. G. PIGOTT, and P. A. CAMPBELL (J. Biol. Chem., 1933, 103, 657—664).—The hæmoglobin (I) content of young cocks fed on a high-grade diet increased from 9.6 to 10.1 g. per 100 c.c. of blood in 63 days and that of pullets from 9.3 to 9.7. Restriction of the dietary H_2O failed to influence the (I) vals. H. D.

Refraction of the hæmoglobins of different animals. S. SCHÖNBERGER (Biochem. Z., 1933, 267, 57—63).—The average n of solutions of horse, dog, and ox hæmoglobin (I), expressed as multiples (10^5) of the const. used by Stoddard and Adair (A., 1924, ii, 76), are, respectively, 194, 203, and 209. For solutions of oxyhæmoglobin (II) the val. is the same in H_2O , dil. aq. NaHCO_3 , and dil. aq. NH_3 . Horse (I) gives reproducible results only after $\times 3$ crystallisations. CO -(I) shows the same val. as (II). W. McC.

Absorption of light by neutral solutions of oxy- and carbon monoxide-hæmoglobin. V. SEBESTA

and A. HERZOG (Biochem. Z., 1933, 267, 157—166; cf. A., 1933, 622, 1180).—The curve of light absorption of neutral solutions of cryst. oxyhæmoglobin (I), exhibits max. at 575.2 and 541.3 $m\mu$ and that of solutions of cryst. natural or synthetic CO -hæmoglobin (II) exhibits max. at 566 and 537 $m\mu$. The curve of (II) exhibits a min. at 551 and that of (I) a false min. at 557.5 $m\mu$. Horse (II) does not differ in the respect concerned from ox (II). One crystallisation of (II) suffices to give correct results, which are confirmed by determination of other optical constns. W. McC.

Physiological degradation of blood-pigment. R. NOTHHAAS (Z. klin. Med., 1933, 124, 490—496; Chem. Zentr., 1933, ii, 1386).—Hæmoglobin is very sensitive to the action of H_2O_2 when catalase has been removed from the blood. Bingold's observation that blood treated with Na silicate and heated requires less H_2O_2 for decolorisation than normally is presumably due to removal of catalase. A. A. E.

Prosthetic group of blood-pigments. H. FISCHER and K. ZEILE (Z. physiol. Chem., 1933, 222, 151—154).—The hæmin prep. of Herzog (A., 1933, 1180) was impure owing to drying at 100° and retention of NH_3 ; hence his conclusions are not justified. J. H. B.

Carbon content of prosthetic group of blood-pigment. Methyl and ethyl esters of hæmoprostheticin. A. HERZOG (Biochem. Z., 1933, 267, 48—56).—The composition of the mono- and dimethyl and -ethyl esters of hæmoprostheticin (I) prepared by Küster's method (A., 1913, i, 110, 1005) and of the substance $\text{C}_{34}\text{H}_{33}\text{N}_4\text{O}_4\text{Fe}$ shows that (I) has 33 C. If removal of globin (II) is incomplete substances similar to (I), but containing C atoms from (II) in addition, are obtained. W. McC.

"Normal" carbon monoxide content of the blood. A. O. GETTLER and M. R. MATTICE (J. Amer. Med. Assoc., 1933, 100, 92—97).—Average vals. for city (min. exposure) and rural residents were 0.27 and 0.24 vol.-%, respectively. Street-cleaners gave 0.69 and taxicab drivers 1.47—4.33 vol.-%. Tobacco-smoking increases blood-CO. CH. ABS.

Significance of copper and iron in blood restoration. C. A. ELVEHJEM (Amer. J. Pub. Health, 1933, 23, 1285—1289).—A discussion.

Hæmoglobin production. IV. Evaluation of therapeutic agents in anæmia due to milk diets, based on study of blood and bone marrow of rats from birth to maturity. T. FITZ-HUGH, jun., G. M. ROBSON, and D. L. DRABKIN (J. Biol. Chem., 1933, 103, 617—628).—The blood hæmoglobin (I), erythrocytes (II), reticulocytes (III), and the degree of hyperplasia (IV) of the marrow in the long bones of

rats were used as criteria of the anæmia produced on a milk diet. At weaning the rats studied were anæmic. On the milk diet (I) fell more rapidly and reached a relatively lower level than (II). (III) increased from 17 to 35% of (II) in 20 days; at 70 days the count was 15%, and at 130 days 40%. A small increase in marrow-(IV) was observed. Fe alone fed to anæmic rats produced a small increase in (I) and a greater increase in (II); the (III)-crisis reached its peak after 20 days, but never subsided to normal levels corresponding with a continued (IV) of the marrow. With Fe-Cu therapy recovery of (I) and (II) was almost complete; the peak of the (III)-crisis occurred on the eleventh day, followed by a normal subsidence of (III) and a return to the normal cellular state of the marrow. Fe + Na glutamate gave generally more complete returns to normal states, the (III)-crisis reaching its peak in 3—8 days. H. D.

Blood grouping by means of preserved muscle. W. C. BOYD and L. G. BOYD (*Science*, 1933, 78, 578).—Dried human muscle and even muscle preserved at necropsy and several years old contains agglutinogens and can be used to determine the blood groups of individuals. L. S. T.

Influence of fasting on the concentration of blood-lipins in the rat. B. SURE, M. C. KIK, and A. E. CHURCH (*J. Biol. Chem.*, 1933, 103, 417—424).—There is a decrease in the fatty acids and lecithin, but no change in the cholesterol. H. G. R.

Micro-determination of fatty acid in blood. M. E. SMITH and M. C. KIK (*J. Biol. Chem.*, 1933, 103, 391—398).—The methods of Bloor, Pelkan, and Allen and of Stoddard and Drury (*A.*, 1930, 103) have been combined and modified for use with 0.5 ml. of blood. H. G. R.

Micro-determination of oxalic acid in blood. S. IZUMI (*Japan. J. Med. Sci.*, 1933, 2, 195—204).—Blood or serum (4.0 c.c.) is deproteinised with $\text{CCl}_3\cdot\text{CO}_2\text{H}$, brought to p_{H} 2.5—3.0, and $\text{H}_2\text{C}_2\text{O}_4$ pptd. by 0.25% aq. CeCl_3 . The ppt. (I) is washed, dissolved in 5 c.c. of $N\text{-H}_2\text{SO}_4$, and titrated at 70—80° with 0.01N- KMnO_4 . Alternatively (I) is dissolved in 1 c.c. of $N\text{-H}_2\text{SO}_4$, and 1 c.c. of 30% aq. K_2CO_3 and H_2O_2 are added, giving a brown solution for colorimetric determination. F. O. H.

Distribution of sugar and rate of glycolysis in blood of some mammals. M. SOMOGYI (*J. Biol. Chem.*, 1933, 103, 665—670).—There is no correlation between the rates of glycolysis (I) and the distribution ratios of sugar in the serum and erythrocytes of various mammals. (I) conform to the Engelhardt-Liubimova (*A.*, 1931, 108) series of phosphate cleavage. H. D.

Diurnal variations in blood-sugar level of lactating cow. W. M. ALLCROFT (*Biochem. J.*, 1933, 27, 1820—1823).—A rhythmic variation in the blood-sugar of lactating cows, absent in dry cows, is observed. H. D.

Comparison of sugar-tolerance curves obtained on venous and capillary blood. J. W. CAVETT and S. R. SELJESKOG (*J. Lab. Clin. Med.*, 1933, 18, 1103—1107).—Vals. for finger-tip blood are slightly > those for venous blood only during hyperglycæmia. CH. ABS.

Determination of blood-sugar. C. BIRT (*J. Roy. Army Med. Corps*, 1933, 61, 401—411).—A simple technique for the Hagedorn-Jensen method is described. R. K. C.

Diazo-reaction, especially of blood. I, II. Serum and urine. III. Red blood-corpuscles. G. NAKAYAMA (*Japan. J. Med. Sci.*, 1933, 2, 215—227, 229—235, 237—244).—I. Human and animal blood gives Leimdörfer's modification of the diazo-reaction (I) (*A.*, 1924, i, 1126), which is due to the erythrocytes and not to the plasma. Pathological urine frequently yields a marked (I), whilst the corresponding blood response is normal or even negative. The blood-(I) is not influenced by fever or starvation, but acute inflammation causes a decrease. No relation exists between (I) and the blood content of bilirubin, urobilin, or residual N. The reactant of (I) is stable to acids, readily destroyed by alkalis, extracted by dil. AcOH or $\text{CCl}_3\cdot\text{CO}_2\text{H}$, and pptd. by phosphotungstic acid. Extracts of adrenal glands, spleen, and liver frequently give a positive (I).

II. In uræmic blood (II) a urochromogen present is probably the cause of the characteristic response of (II) to (I) (cf. *A.*, 1925, i, 726). Indican is also frequently present in (II), whilst a further substance (probably histidine) takes part in the response of (II) and of the urine of consumptives to (I).

III. The intensity of (I) of the corpuscles of various animals is approx. proportional to the content of residual N and, more particularly, to that of ergothioneine. Substances such as tryptophan, glyoxaline derivatives, and cyclic compounds may be involved. F. O. H.

Colloid-osmotic (oncotic) pressure. XXIX. Serum-albumin and -globulin. E. KYLIN (*Arch. exp. Path. Pharm.*, 1933, 173, 549—552).—The colloid-osmotic pressures (*A.*, 1932, 540) of 1% aq. serum-albumin and -globulin (horse, man) are 55—75 and 17—30 mm. of H_2O , respectively. F. O. H.

Determination of bases of serum and whole blood. P. M. HALD (*J. Biol. Chem.*, 1933, 103, 471—494).—Serum is ashed in a muffle furnace with H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$; the SO_4'' formed is pptd. with benzidine in the Fe-free filtrate, and determined by titration with NaOH or gravimetrically. No appreciable loss of Mg occurs after heating at 750° for 9 hr. The sparingly sol. residue from the ashing of whole blood consists of FePO_4 . In the determination of Ca, Mg, K, and Na in the dissolved ash Ca is pptd. as CaC_2O_4 , and determined with KMnO_4 ; Mg is pptd. as MgNH_4PO_4 , and determined colorimetrically by the Benedict-Theis method (*A.*, 1924, ii, 700). The P is then removed by $\text{Fe}_2(\text{SO}_4)_3$ and aq. NH_3 . The supernatant fluid is ashed and the SO_4'' of one portion of the solution of the ash pptd. with benzidine and in the other the Na and K platinichlorides are pptd. The Na salt is dissolved in 80% EtOH and determined by the Barber-Kolthoff method (*A.*, 1928, 859) and the K salt is determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$. In several cases the total acid of normal human serum exceeded the total base. H. D.

Serum-calcium in normal boys. M. MOLITCH, S. WEINSTEIN, and R. F. COUSINS (*Amer. J. Med.*



Sci., 1933, 186, 378—382).—From 8 to 20 years the serum-Ca ranged from 7.6 to 12.5 mg. per 100 c.c., irrespective of age, nationality, or race. CH. ABS.

Calcium content of ultrafiltrates of plasma and the influence of changes in hydrogen- and hydrogen carbonate-ion concentration on it. L. M. DILLMAN and M. B. VISSCHER (J. Biol. Chem., 1934, 103, 791—799).—The Ca in the plasma of dog's blood becomes more completely dialysable as acidity increases, when the acidity is produced by increase in CO₂ tension. At p_{H} 7.0, 59%, and at p_{H} 7.7, 45%, is dialysable. W. O. K.

Diffusibility of plasma-calcium following parathormone administration. Comparison of the calcium, phosphate, and protein concentrations of serum and oedema fluids. D. R. GILLIGAN, M. C. VOLK, and M. D. ALTSCHULE (J. Biol. Chem., 1934, 103, 745—756).—In many pathological conditions, administration of parathormone produces a rise in the Ca and a fall in the inorg. P concn. of oedema and ascitic fluid closely parallel to that occurring in the serum. The change in P precedes that in Ca. The Ca and P concns. of the cerebrospinal fluid (I) remains approx. const. and thus (I) is not a simple dialysate of serum. W. O. K.

Relation of filterable to non-filterable calcium in chicken blood. J. T. CORRELL and J. S. HUGHES (J. Biol. Chem., 1933, 103, 511—514).—Whilst the serum-Ca (I) of laying hens is 25.1 as against 12.0 and 11.7 mg. per 100 c.c. for non-laying hens and cocks, respectively, their ultrafilterable Ca is the same (approx. 6.4 mg. per 100 c.c.), so that the ratio of filterable to total (I) decreases as (I) rises. H. D.

State of calcium and phosphate of the blood. D. M. GREENBERG, W. E. COHN, and E. V. TUFTS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1005—1007).—The loss of Ca during ultrafiltration (I) reported by Smith and Sternberger (A., 1932, 635) is negligible except when the serum-Ca is considerably > normal. There is then adsorption of PO₄^{'''} also, so that it becomes partly non-diffusible. Possibly a colloidal compound of Ca, PO₄^{'''}, and (possibly) CO₃^{'''} is formed. Adsorption of ions does not occur, since there is no loss of Mg during (I). NUTR. ABS. (m)

Forms of calcium and inorganic phosphorus in human and animal sera. III. Comparison of physiological and experimental hypercalcaemia. H. R. BENJAMIN and A. F. HESS (J. Biol. Chem., 1933, 103, 629—641).—By methods previously described (A., 1933, 521) the serum-Ca is resolved into four components. In hypercalcaemia (I) in laying hens the two filterable fractions remain const., whilst each of the non-filterable fractions (II) rises, together with the serum-proteins. There is no correlation between the serum-cholesterol and the adsorbable (II) fraction. In (I) produced by parathyroid extracts and vitamin-D in dogs, the 4 Ca fractions tend to maintain their normal proportions, except for a small increase in (II); the total P is raised, its filterability is diminished, and up to 2.5 mg. per 100 c.c. of the adsorbable P becomes non-filterable. H. D.

Normal range of calcium and inorganic phosphorus in the serum of healthy non-preg-

nant women. J. W. MULL and A. H. BILL (J. Lab. Clin. Med., 1933, 18, 1034—1041).—Serum-Ca in women is normally 10—11.5 mg. per 100 c.c., and is unaffected by age or diet if the Ca intake is adequate. Serum-inorg. P is 3.2—4.4 mg. at < 30 years and 2.6—4.2 mg. at > 30 years. There is no seasonal variation in Ca or inorg. P. CH. ABS.

Normal serum-calcium and -magnesium of the rat; their relation to sex and age. E. WATCHORN (Biochem. J., 1933, 27, 1875—1878).—The serum-Ca (I) of females is slightly < (I) of males, and of adults (11.77 mg./100 c.c.) < (I) of young (12.16 mg./100 c.c.). The serum-Mg of young males (5.36 mg./100 c.c.) is > that of adult males and all females (4.4 mg./100 c.c.). A. L.

Magnesium in serum and milk. H. R. BENJAMIN, A. F. HESS, and J. GROSS (J. Biol. Chem., 1933, 103, 383—390).—Mg is adsorbable from sera and ultrafiltrates on BaSO₄ and may be separated into (1) a filterable, adsorbable form (I), (2) a filterable, non-adsorbable form containing Mg^{''}, (3) a non-filterable form, possibly bound to protein. In hypercalcaemia, (I) is reduced to a negligible amount. The concn. of (I) varies directly with P and inversely with Ca content, suggesting that it is adsorbed in combination with P. The presence of (I) in milk could not be demonstrated. H. G. R.

Biochemistry of copper. I. Colorimetric micro-determination. II. Determination in blood. U. SARATA (Japan. J. Med. Sci., 1933, 2, 247—260, 261—275).—I. The red colour given by Cu salts with "cryogenine" (*m*-benzamidosemicarbazide) is used for the determination of 0.0005—0.02 mg. of Cu with an accuracy of ±1.5%. The reaction is sp.

II. Blood (1 c.c.) is digested with H₂SO₄—H₂O₂, the digest is neutralised (using MgCl₂ as indicator) and re-acidified with H₂SO₄, Cu is pptd. as CuS, the ppt. is dissolved in dil. HNO₃, and Cu is determined in the filtered solution. In addition to data for the blood-Cu of various fishes, the following vals. (in mg. per 100 c.c.) were obtained: man, 0.073—0.081; ox, 0.125—0.171; horse, 0.103—0.133; rabbit, 0.070—0.104; pig, 0.062—0.098. F. O. H.

Determination of bromine in blood. E. D. YATES (Biochem. J., 1933, 27, 1763—1769).—A method for the determination of Br in amounts of 5—1000×10⁻⁶ g. accurate to within 2×10⁻⁶ g. is described. H. G. R.

Fibrinogen and a plasma-globulin producing clotting. A. SCHMITZ (Z. physiol. Chem., 1933, 222, 155—160).—Hammarsten's fibrinogen (I) differs from Mellanby's (II) in composition. (I) is not homogeneous, but cannot be fractionated by salting out with (NH₄)₂SO₄, which separates (II) into true fibrinogen (III) and a protein which produces clotting and is apparently identical with Mellanby's prothromb-ase. The flocculation max. is at p_{H} 5.3—5.6. The clotting rate of (III) is independent of its concn. J. H. B.

Hæmolysis by Australian snake venoms. I. Comparative hæmolytic power. II. Peculiarities in behaviour. C. H. KELLAWAY and F. E. WILLIAMS (Austral. J. Exp. Biol. Med., 1933, 11,

74—80, 81—94).—I. The venoms are of two types: those which hæmolyse directly without serum activation (black, copperhead), and those which have a negligible action on washed cells (death adder, tiger).

II. Hæmolysis depends on a lecithinase acting at the limiting surface of the corpuscle and is subject to the same ionic effects as cobra venom. Complement effect is insignificant. Inhibition by serum is frequent. Venoms are adsorbed on red blood-corpuscles at 0° and cause hæmolysis when warmed. Blood-lipins alone activate the process, but the natural protein-lipin complex causes inhibition.

CH. ABS.

Relationship between structure of antigen and specificity of anti-body. VIII. Changes in the specificity of cholesterol on its conversion into a complex antigen. E. BERGER (Biochem. Z., 1933, 267, 143—150; cf. A., 1933, 1066).—Anti-sera (I) obtained by coupling diazotised cholesteryl amino-benzoate (II) with pig-sera do not react with cholesterol (III) nor with (III) coupled with horse- or hen-sera. (I) have reduced or no immunological relationship with the native protein with which the product used is condensed for immunisation (IV). Structural specificity is exhibited by (I) solely towards products obtained from the interaction of (II) with the serum-protein of the complex antigen used for (IV). (I) to (III) obtained by (IV) with mixtures of (III) with serum do not react with (II) coupled with sera. The changes in serological specificity which (III) undergoes on conversion into (II) followed by coupling with protein (sera) (V) chiefly concern (III), but also affect (V).

W. McC.

Chemistry of the antigen of brain. II. Purification. H. RUDY (Biochem. Z., 1933, 267, 77—88; cf. A., 1932, 765).—The antigen (I), further purified by a method described, contains N and combined sugar, but no P, and is stable towards alkali. The purification is accompanied by increasing solubility in H₂O and acquisition of the ability to dialyse. Solutions of (I) in EtOH are acid. Crude (I), which is probably adsorbed on lipins, is sol. in lipins, scarcely sol. in H₂O, and incapable of dialysing. (I) is not a sterol or cerebroside nor is it identical with creatine.

W. McC.

Antigen nephelometer solidified with pectin. H. R. BAKER and G. L. BAKER (J. Amer. Vet. Med. Assoc., 1933, 36, 472—473).—For the agglutination test for pullorum disease antigen turbidity standards can be preserved in pectin gel.

CH. ABS.

Oxygen affinity of muscle-hæmoglobin. R. HILL (Nature, 1933, 132, 897—898).—Dissociation curves showing that muscle-hæmoglobin (I) has a higher affinity for O₂ than blood-hæmoglobin have been obtained by a spectroscopic method. The distinctive properties of (I) are due to its protein, globin. The presence of (I) in muscle cells will be advantageous in O transport. (I) can be the intermediate carrier of mol. O₂ from blood to the oxidase-cytochrome system in the cells.

L. S. T.

Chemical composition of living organisms and periodic system. A. VINOGRADOV (Compt. rend., 1933, 197, 1673—1675).—The % of each element in animal and vegetable bodies, based on analyses of some 2000 and 5000 species, respectively, is plotted

against the at. no. in two curves, for odd- and even-numbered elements, respectively, the curve for the latter being above that for the former, and both steadily declining as at. no. increases; above elements nos. 1 and 2 there is a max. at every sixth element in both curves.

C. A. S.

Determination of dry matter in the retina.

R. W. J. MÜLLER (Biochem. Z., 1933, 267, 43—44).—The retina (I) in the ox, pig, sheep, and guinea-pig contains about 12% of dry matter; in the dog and rabbit it contains about 16%. In all these animals the average thickness of (I) is 0.22—0.31 mm.

W. McC.

Brain-creatine. M. MATSUMOTO (Japan. J. Med. Sci., 1933, 2, 205—213).—Pig's brain is hydrolysed, the hydrolysate pptd. by CCl₃·CO₂H, the filtrate neutralised and treated with Al(OH)₃, and the final filtrate extracted with Et₂O. The Et₂O extract contains some creatinine (I) (which is extracted with H₂O and combined with the main aq. layer) and a substance (also present in egg-lecithin etc.) which responds to the Jaffé reaction. Results (0.08—0.09% as creatine) are < previous vals.

F. O. H.

Cetacea. XLIV. Isoelectric flocculation of porphyrins. Y. OKAHARA (Japan. J. Med. Sci., 1933, 2, 189—194).—Hæmato- and uro-porphyrin are isoelectrically flocculated in PO₄' or OAc' buffer at p_H slightly > 5; a somewhat less marked region occurs at p_H 3.9—4.2 and 2.2—2.9, respectively. The porphyrin from whale's intestine (A., 1927, 85) flocculates between p_H 5.66 and 6.64 and again at p_H 7.66; a secondary region appears at p_H 3.2—3.8. The coagulation is a function of the salts present as well as of [H⁺].

F. O. H.

Reactivity of the sulphur linking in wool. J. B. SPEAKMAN (Nature, 1933, 132, 930).—Super-contraction is associated with the breakdown of ·S·S· linkings in wool, so that when strained fibres are exposed to steam the first reaction which occurs is R·S·S·R + H₂O ⇌ R·SH + R·S·OH. The hypothesis is supported by the fact that wool heated with H₂O even at 55° in presence of Hg vapour is rapidly contaminated by HgS. The rebuilding of new linkings probably takes place according to the reaction R·S·OH + R·NH₂ = R·S·NH·R + H₂O, for when fibres are treated with saturated Ag₂SO₄ to convert ·S·S· into R·SO₃H, their power to assume a permanent set is reduced.

L. S. T.

Body-fats of the pig. III. Influence of body temperature on composition of depôt-fats. H. K. DEAN and T. P. HILDITCH (Biochem. J., 1933, 27, 1950—1956).—The back fat of a sow fed on a diet of maize meal, thirds, and whey was divided into five layers and the constituent fatty acids were determined. The acids of the three layers under the "streak" were identical, whilst the outermost layer contained less palmitic and stearic and more oleic acids.

H. D.

Iodine-containing substance of the thyroid gland. III. Ultra-filtration and dialysis of thyroid press-juice. G. LUNDE, K. WÜLFERT, and P. LALAND (Endokrinol., 1933, 13, 29—35; Chem. Zentr., 1933, ii, 1697—1698).—Most of the I-containing substance does not pass through the filter. Pptn. with

COMe₂ affords a substance (I 0.225%) which contains practically all of the I. Electrodialysis afforded ppt. (I 0.329%) containing 77% of the total I. Biological tests on the mouse were performed. A. A. E.

Iodine content of foetal, new-born, and infants' thyroid glands. Z. LELKES (Endokrinol., 1933, 13, 35—40; Chem. Zentr., 1933, ii, 1697).—I can be detected from the fourth month onwards; the I content is greatest in winter. The abs. I content increases, and the relative I content decreases, until birth occurs. Afterwards the wt. of the thyroid diminishes; hence its relative I content suddenly increases. A. A. E.

Functional significance of the structural elements of the thyroid gland. W. GRAB (Klin. Woch., 1933, 12, 1102—1103; Chem. Zentr., 1933, ii, 1538).—The colloidal fraction (60—70%) of the sheep's and cat's thyroid contains 0.065—0.074% I (on undried colloid); 50% is thyroxine-I and the remainder probably di-iodotyrosine. The epithelial tissue contains 0.0072—0.0094% I, of which 33% is thyroxine-I. 95% of the I content of medicinal dried thyroid preps. consists of colloidal I compounds. Stimulation of the thyroid gland, e.g., with thyreotropic hormone, diminishes the quantity of colloid and its I content (to 0.012%), but the ratio total: thyroxine-I is unaltered. Epithelial total I and I distribution are practically unchanged. A. A. E.

Block-staining of nervous tissue with silver. IV. **Embryos.** H. A. DAVENPORT, W. F. WINDLE, and R. H. BEECH (Stain Tech., 1934, 9, 5—10).—Fixation of embryos in a solution containing 4% CH₂O and 0.5% CCl₃·CO₂H improved the staining of neural elements by Bielschowsky's method. Ranson's C₂H₅N-Ag method was modified slightly for staining neurofibrillar elements. H. W. D.

Marchi's staining method. R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1934, 9, 11—19).—The actions of the various reagents used by Marchi for staining degenerating myelin have been studied. H. W. D.

Staining of neuroglia. F. PROESCHER (Stain Tech., 1934, 9, 33—38).—The exposure of the section, after staining with Victoria-blue (Heidelberger's method), to sunlight induces an oxidative process. Artificial ultra-violet rays, or chemical oxidising agents, produce the same effect. Victoria-blue may be replaced by Me-, Et-, or crystal-violet. H. W. D.

Cerebrospinal fluid. I. **Chemical and spectrographic detection of lead.** II. **Occurrence of lead in cerebrospinal fluid.** I. M. RABINOVITCH, A. DINGWALL, and F. H. MACKAY (J. Biol. Chem., 1934, 103, 707—723, 725—732).—I. The Behrens-Kley triple nitrite reaction ("Mikrochemische Analyse," 1915), detects Pb reliably in cerebrospinal fluid (I), the sensitivity being 10⁻⁴ mg. The results were controlled by spectrographic methods of which the sensitivity is 1 in 10⁻⁹, with 6 c.c. of fluid.

II. Pb was found in the (I) in every case definitely diagnosed as Pb poisoning, but with one exception, > traces (1:5×10⁷) were present where there had been no exposure to Pb. The production of an acidosis by administration of NH₄Cl increased the rate of

excretion of Pb in the urine as the result of mobilisation of stored Pb. Acidosis occasionally also caused small quantities of Pb to appear in the (I) where previously absent. W. O. K.

Natural pigments of raw silk of the domestic cocoon. V. **Detection of violaxanthin in the yellow cocoon.** VI. **Decolorisation of the yellow cocoon.** M. OKU (J. Agric. Chem. Soc. Japan, 1933, 9, 580—586, 587—592).—V. Violaxanthin, m.p. 185°, and a red resin were obtained from the mother-liquor after separation of lutein.

VI. Decolorisation in air is due to the oxidation of xanthophyll. CH. ABS.

Influence of chlorides and phosphates of saliva on its amyolytic activity. W. L. ADAMS and V. C. MYERS (J. Dental Res., 1933, 13, 311—322).—The amyolytic index of human saliva is 25—50; it is unusually const. in a normal person and is closely related to salivary Cl and total P. It may decrease by 50% in severe "colds." CH. ABS.

Sugar content of semen. K. YAMADA (Japan. J. Med. Sci., 1933, 2, 245).—Human semen contains sugar (probably fructose), three samples yielding 62.5, 83, and 140 mg. per 100 c.c., respectively. The prostatic fluid is free from reducing substances. F. O. H.

Gastric-juice colloids and their determination by the gold number. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 92—95).—The Zsigmondy Au no. of normal gastric juice (I) (induced by histamine) varies between 0.8 and 2.0 mg., the no. being approx. proportional to the acidity (II). This is true for (I) of subnormal (II) due to disease. The correlation of the colloidal secretion of the gastric mucous membrane and (II) is discussed. F. O. H.

Gastric secretion during pharmacological tests. C. DIENST (Klin. Woch., 1933, 12, 741—744).—Changes in the acidity of gastric juice (I) are explained on the assumption that they depend on the ratio of a const. acid (II) and a const. alkaline (III) secretion. (II) is determined as total Cl', (III) is indicated by the N content of (I). Histamine stimulates (II), pilocarpine (III). When these are given together the Cl' and the N content of (I) increase and more (I) can be recovered than after each alone. Ingestion of HCl produces an increase in the N content, whilst NaHCO₃ produces an increase of Cl' in (I). NUTR. ABS. (m)

Osmotic relations between blood and body-fluids. IV. **Pancreatic juice, bile, and lymph.** A. GILMAN and G. R. COWGILL (Amer. J. Physiol., 1933, 104, 466—469).—The blood, hepatic bile, lymph (from the thoracic duct), and pancreatic juice collected simultaneously from dogs under amytal anaesthesia are approx. isotonic (Hill's method) and remain so even following extreme variations in the osmotic pressure of the blood brought about by injecting NaCl or H₂O. NUTR. ABS. (m)

Relation between sugar content, chlorine content, and serum refraction of milk. T. SUNDBERG (Svensk Kem. Tidskr., 1933, 45, 253—275; cf. B., 1932, 45).—Tables are given for calculating the "osmotic factor" of milk from its lactose (I) and Cl

content. Gravimetric and polarimetric methods of determining (I) are compared. The (I) and Cl contents and "osmotic factors" are given for 100 samples of milk, and compared with the n of the serum. The n and Cl content can be used as a preliminary test for dilution with H_2O . R. P. B.

Composition of the "isotonic diluent" in samples of milk low in solids-not-fat. W. L. DAVIES (J. Dairy Res., 1933, 4, 273—278).—In milks having low solids-not-fat contents, the caseinogen-N bears a lower proportion to the total N than in normal milks (76%). Such milk may be represented as containing two fractions: (a) true milk, (b) an "isotonic diluent" (I). From analytical data obtained, the proportion and distribution of N in the diluent are calc. The composition of (I) resembles that of a modified blood-serum or lymph-serum or a caseinogen- and lactose-free lacteal secretion. The Cl content conforms more nearly to that of a lymph-serum. A. G. P.

Cow's milk poor in non-fatty solids. G. L. PESKETT and S. J. FOLLEY (J. Dairy Res., 1933, 4, 279—284).—The presence of blood serum-albumin (I) in normal milks is demonstrated. In many cases milks poor in solids-not-fat (II) have an increased proportion of (I). Deficiency of (II) in milks may be due to dilution of normal secretion by a fluid resembling oedema fluid (cf. preceding abstract). A. G. P.

Phospholipins in milk. I. Distribution among some milk products. G. E. HOLM, P. A. WRIGHT, and E. F. DEYSHER. II. Phospholipins in skim milks and their effect on the accuracy of the various fat tests. P. A. WRIGHT and G. E. HOLM. III. Phospholipins in buttermilk and their effect on the accuracy of various fat tests. P. A. WRIGHT, E. F. DEYSHER, and G. E. HOLM (J. Dairy Sci., 1933, 16, 445—454, 455—459, 460—466).—I. Up to 45% of the total phospholipin (I) content of creams passed into the butter. The amounts concerned were sufficient to be of significant val. in fat determinations. Acidity is probably not an important factor influencing the distribution of (I) in milk products.

II. The (I) of skim milk averaged 0.13%. The Röse-Gottlieb method (II) removes \approx 20% of the natural (I). In samples containing 0.10% of fat the error due to extraction of (I) is approx. 15%. The Babcock method and its various modifications remove negligible amounts of (I), but give low vals. for skim milks (cf. Thurston and Peterson, B., 1928, 942).

III. The (I) content of sweet cream buttermilks averaged 0.27%. Only insignificant amounts of this are removed by the various Babcock methods. Results of (II) were 6—17% high owing to the inclusion of (I) in the extract. A. G. P.

Blood-lipins and milk-fat production. J. MARCQ and A. DEVUYST (Bull. Inst. Agron. Gembloux, 1933, 2, 101—126).—The coeff. of correlation between the total lipins and the lecithin of the blood (0.684 ± 0.062) is the only significant factor to serve as an index of productive capacity (measured in terms of butter-fat), although the coeffs. of correlation between mean total blood-lipins and milk-fat production per

lactation (0.1904 ± 0.161) and mean blood-lecithin and total butter-fat production (0.144 ± 0.195) are slightly positive. NUTR. ABS. (m)

Effect of organotherapy on the production of fat in the milk of cows. G. MONNOT (Compt. rend., 1934, 198, 119—120).—Daily oral administration of a mixture of bovine serum and organotherapeutic products to cows during their lactation period causes a 25—40% increase (especially after the first month) in the milk-fat and increase in body-wt. of the animal, without otherwise affecting the quality of the milk. J. W. B.

Nutritive value of proteins for milk production. I. Comparison of proteins of beans, linseed, and meat meal. S. MORRIS and N. C. WRIGHT (J. Dairy Res., 1933, 4, 177—196).—Replacement of bean meal (I) by equiv. proportions of meat meal (II) or linseed meal (III) in a ration of minimal protein content resulted after 4—18 days in a reduced milk yield. In the intervening period body-N was utilised in maintaining milk production. Wastage of N (urinary N) with the (I) ration was low, with (II) high, and with (III) intermediate. A. G. P.

Loss of minerals through the skin of infants. W. W. SWANSON and L. V. IOB (Amer. J. Dis. Children, 1933, 45, 1036—1039).—The skin secretions of infants aged 2—28 weeks contain: Cl 0.22—1.48, Na 0.17—0.94, K 0.24—1.86, Ca 0.07—0.23, and P 0.01—0.26 g. for six-day periods. Loss of K through the skin reaches 38% of the calc. retention. NUTR. ABS. (m)

Constituents of the sweat, urine, and blood; gastric acidity and other manifestations resulting from sweating. X. Basic metals. G. A. TALBERT, C. HAUGEN, R. CARPENTER, and J. E. BRYANT (Amer. J. Physiol., 1933, 104, 441—442).—100 c.c. of sweat contain: K 40—50 (occasionally 28.3—145.4); Ca 0—11.8 (average 5); Mg 0—4.5 mg. NUTR. ABS. (m)

Urinary acidity. II. S. MORGULIS (J. Biol. Chem., 1934, 103, 757—761).—Analysis of the P of urine by the $CaSO_4$ method of Kugelmass (A., 1924, ii, 275) gives results agreeing with those calc. from the p_{H_2} , provided the latter is < 6.0 , whilst when H_2PO_4' and HPO_4'' are added to urine, analytical results are satisfactory. The hypothesis of Berg that phosphates, especially H_2PO_4' , undergo substantial changes in urine and other body-fluids thus receives no support. W. O. K.

[Determination of urinary ammonia.] **Action of ammonia on phenols.** B. HARROW, I. M. CHAMBLIN, and H. WAGREICH (Science, 1933, 78, 514).—Orr's work on the colorimetric determination of NH_3 in urine by PhOH and NaOCl (A., 1925, i, 184) has been confirmed. The method gives results in good agreement with those obtained by Folin's aeration method. L. S. T.

Colorimetric determination of urinary cholesterol. I. A. MIRSKY (J. Lab. Clin. Med., 1933, 18, 1068—1071).—Cholesterol (I) is pptd. with protein by H_2WO_4 and extracted with EtOH—Et₂O (3:1). Total (I) is determined colorimetrically in one portion, and free and combined (I) in another, free (I) being fixed as the digitonide. CH. ABS.

Determination of bilirubin in urine. K. FELLING and K. MENKES (Wien. klin. Woch., 1933, 46, 133—134; Chem. Zentr., 1933, i, 1819).—A modification of Franke's method (A., 1932, 1158). 5 c.c. of non-icteric urine are coloured a definite blue by 1—2 drops of 2% methylene-blue (I). Icteric urine becomes green and is coloured blue only by the addition of further amounts of (I). The use of a comparison fluid, prepared from alcoholic (I) and $K_2Cr_2O_7$, is recommended. L. S. T.

Preparation of homogentisic acid from urine. G. MEDES (Proc. Soc. Exp. Biol. Med., 1933, 30, 751).—5—6 g. $Pb(OAc)_2$ are added to each 100 c.c. of boiling urine, which is then filtered and the p_H of the hot filtrate adjusted to about 5.6 with aq. NH_3 . On cooling, Pb homogentisate separates. Recrystallisation from hot H_2O is conducted similarly. The Pb salt is decomposed with H_2S ; the solution is conc. under reduced H_2 pressure and saturated with SO_2 . The acid rapidly separates on cooling.

CH. ABS.

Dietary acidosis in dairy cattle. A. E. PERKINS and C. F. MONROE (J. Dairy Sci., 1933, 16, 413—426).—The feeding to cattle of lactic acid or AcOH in amounts > those likely to be eaten in silage (1.5—1.75 lb. daily) produced no urinary symptoms of acidosis (I), but marked acidosis followed the ingestion of 2—3 oz. daily of HCl, H_2SO_4 , or H_3PO_4 . Silage fed alone produced no (I), and prevented or delayed acidic effects when fed in conjunction with rations producing these. All leguminous diet had a definitely alkaline action on urine. Timothy hay resembled silage in this respect. Exclusive grain rations reduced the HCO_3^- and increased the NH_3 of the urine. The protein of the grain had no influence on the acidic symptoms thus produced. Alkaline mineral supplements did not correct (I) satisfactorily. A. G. P.

CH. ABS.

Blood-sugar in allergic persons. J. H. BLACK (Texas State J. Med., 1933, 29, 257—260).—Blood-sugar and -P are frequently low in allergy.

CH. ABS.

Digestion of protein in gastric anacidity. D. C. HINES (Amer. Med. J. Sci., 1933, 185, 684—695).—In patients with gastric anacidity without response to histamine and without cancer or anæmia there is no increase in faecal N either on high-N (I) or low-N diet. On (I) positive N balance is present. When ground beef is given, increase in the urea-N of the urine occurs in the normal time.

NUTR. ABS. (m)

Composition of the globin of normal and anæmic persons. K. LANG (Arch. exp. Path. Pharm., 1933, 174, 63—68).—Whilst the contents of the main constituent NH_2 -acids [tyrosine (I), tryptophan, cystine, arginine, and histidine (II)] of human globin (A., 1930, 948) differ in normal individuals [the most const. being (I), 2.75—3.38%, and (II), 7.58—8.33%], variations occur in anæmia (III) which are characteristic of (III) and also to some extent of the type of (III).

F. O. H.

Blood regeneration in dogs as influenced by liver and iron preparations. A. E. MEYER (J. Lab. Clin. Med., 1933, 18, 1127—1135).—Colloidal Fe is an important factor in regeneration of hæmoglobin

(I) in experimental hæmorrhagic anæmia in dogs. Purified liver extract stimulates erythropoiesis, but does not affect the formation of (I). CH. ABS.

Blood of normal human subjects during foetal liver feeding. O. S. WALTERS and P. H. WOODWARD (Amer. J. Physiol., 1933, 104, 364—370).—The statistically significant variations in hæmoglobin vals. and erythrocyte counts (I) found in normal subjects remain unchanged in individuals who consume the equiv. of 300 g. of fresh foetal calf liver (II) daily for a period of 10 days. (II) has a high Cu content. Discontinuance of liver feeding is followed, after about 12 days, by a fall of (I) below control val. A similar tendency is noted after feeding stomach and ox-liver extract.

NUTR. ABS. (m)

Blood formation. I. Arsenic in relation to blood formation. Testing therapeutic agents in anæmia. WICHELS and I. HÖFER (Klin. Woch., 1933, 12, 591—593).—Reticulocytes (I) increase considerably within a few days in healthy subjects (II) receiving daily 0.0075—0.015 g. of As. The increase is accompanied by toxic symptoms. The increase of (I) in (II) is suggested as a suitable test for antianæmic agents.

NUTR. ABS. (m)

Lack of copper as a cause of disease in animals and plants. B. SJOLLEMA (Biochem. Z., 1933, 267, 151—156).—In farm animals (I) lack of Cu in the diet and in crops (wheat, rye, oats) or such lack in the soil leads to disease which is cured by administration of, or manuring with, $CuSO_4$, respectively. The action of the Cu in (I) is probably direct, although the blood of the diseased (I) is often low in hæmoglobin.

W. McC.

Presence, in the urine of cancerous subjects, of a principle having an action on the adrenal cortex. M. ARON (Compt. rend., 1933, 197, 1702—1704).—Although injection of large vols. of normal urine is without effect, injection of urine from a cancer subject into rabbits causes a large excretion of lipins of the adrenal cortex. The active substance is contained in the material pptd. from the urine by $COMe_2$.

J. W. B.

Therapeutic application of amino-acids in spontaneous cancer in mice. F. VLES and A. DE COULON (Compt. rend., 1933, 197, 1779—1781).—By suitable treatment with NH_2 -acids and endocrine gland preps. a disappearance of spontaneous tumours was obtained in two strains of mice in 40% of the cases.

P. G. M.

Blood chemistry of hens bearing Rous sarcoma No. 1. H. M. DYER and J. H. ROE (Amer. J. Cancer, 1933, 18, 888—898).—Intramuscular inoculation produces mild hyperglycæmia, lowered glucose tolerance, increase in glycolytic activity, and slight decrease in CO_2 -combining power, fatty acid, and carotene of the blood. Numerous other constituents are unchanged.

CH. ABS.

Effect of enzymes on the pathogenicity of Rous and Fujinami tumour viruses. A. PIRIE (Biochem. J., 1933, 27, 1894—1898).—The enzyme, present in preps. of dried pancreas (I), responsible for the inactivating effect on the agents of Rous and Fujinami tumours is unstable at 0° in glycerol solutions. It is adsorbed by $Al(OH)_3$ B at p_H 4.0 together

with lipase, but is not lipase. The protease and carboxypeptidase present in (I) are inert. A. L.

Calcium metabolism and malignant tumours. M. TABANELLI (Riv. Patol. sper., 1933, 10, 234—252).—With malignant tumours at an early stage of development, Ca vals. (blood, urine, faeces) remain normal, but when the cancer (I) is well advanced, there is a considerable fall (II) in the blood-Ca, and a corresponding fall in the urinary Ca. (II) also occurs in diseases other than (I), and is due, not to the tumour itself, but to the general lowering of health occurring in the later stages of the disease. NUTR. ABS. (m)

X-Ray therapy. I. Insulin and adrenaline. F. EICHHOLTZ, H. G. ZWERG, and L. KLUGE (Arch. exp. Path. Pharm., 1933, 174, 210—216).—The growth-inhibiting action of X-rays on rats' sarcoma is increased by previous subcutaneous injection of insulin, whilst that of adrenaline reverses the action to a growth-promoting one. The phenomena are probably related to changes induced by the hormones in the lactic acid content of the tumours. F. O. H.

Immunological reactions in dental caries. G. G. MACPHEE (J. Dental Res., 1933, 13, 273—274). CH. ABS.

Metabolic studies of children with dental caries. J. D. BOYD, C. L. DRAIN, and G. STEARNS (J. Biol. Chem., 1933, 103, 327—337).—Incidence of dental caries (I) is not dependent on serum-Ca and -P, the acid-base relationship, dietary deficiency of P, or the inorg. constituents of the saliva. A definite relation exists between the retention of Ca and P, the metabolic efficiency of the body as a whole, and the resistance to (I). (I) depends primarily on factors operating from within the tooth. H. G. R.

Cholesterosis of the gall-bladder in Indians. A. C. GHOSE (Indian J. Med. Res., 1933, 20, 939—949).—Cholesterosis (I) of the gall-bladder (II) occurs in (II) diseases. Lipins are present in the various coats of (II). There is a definite rise in the blood- and bile cholesterol content. NUTR. ABS. (m)

Hydrogen-ion concentration of nasal secretion in children with acute coryza. M. C. HILL and A. R. HARNES (J. Lab. Clin. Med., 1933, 18, 1029—1032).—In the early stages the p_H is 7.69 ± 0.039 ; the normal val. is 7.02 ± 0.021 . CH. ABS.

Kidney-function during diabetes insipidus. Action of pituitary extract and of adrenaline. [Glomerular] filtration. P. IVERSEN, E. JACOBSEN, and J. BING (Arch. exp. Path. Pharm., 1933, 174, 69—76).—Injection of pituitary extract into a patient with diabetes insipidus and one kidney removed produced a diminution of the glomerular filtration (I) and an increase in the ratio of urine- to blood-creatinine due to a sp. action on the tubules affecting the re-absorption of H_2O . The excretions of PO_4 -P and Cl were partly proportional to (I), whilst that of PO_4 appeared to have a threshold val. The (I), which was not influenced by adrenaline, amounted to 111.5 litres for the one kidney in 24 hr. F. O. H.

Metabolism of galactose in diabetes mellitus. W. G. KARR and T. V. LETONOFF (Amer. J. Med. Sci., 1933, 185, 596—597).—Galactose disappears very

quickly from the blood of diabetics, probably owing to ready formation of glycogen. Insulin does not aid the removal of galactose from the blood-stream.

CH. ABS.

Sorbitol (sionon) for diabetics. W. W. PAYNE, R. D. LAWRENCE, and R. A. McCANCE (Lancet, 1933, 225, 1257—1258).—*d*-Sorbitol (I) can be used as a sweetening agent for diabetics (II), since it does not enter directly into carbohydrate metabolism. Administration of (I) to (II) produces only a slight rise in blood-sugar. Less $COMe_2$ is excreted in urine when (I) is given. (I) has no effect in relieving insulin hypoglycaemia, and fails to increase the glycogen in the liver of starved rats. L. S. T.

Utilisation of sorbitol. A. ROCHE and A. RAYBAUD (Compt. rend. Soc. Biol., 1933, 113, 320—322).—Sorbitol does not act as a source of glycogen in the young guinea-pig. In normal and diabetic man and in the insulinised rabbit it is not metabolised; in the phloridzinised animal it apparently produces hexose. NUTR. ABS. (m)

Influence of vitamin-B on carbohydrate metabolism. M. LABBÉ, F. NEPVEUX, and J. D. GRIGNOIRE (Bull. Acad. Méd., 1933, [iii], 109, 689—702; Chem. Zentr., 1933, ii, 1391).—In diabetes, administration of vitamin-B diminishes glycosuria and glycaemia, raises the carbohydrate tolerance, improves the general condition, and increases the body-wt. The improvement appears slowly, and combination at first with insulin is recommended. A. A. E.

Methylglyoxal in the urine and cerebrospinal fluid of infants with toxic dyspepsias and of dogs and rats in experimental vitamin-B₁ deficiency. I. A. GEIGER and A. ROSENBERG (Klin. Woch., 1933, 12, 1258—1260).—Laboratory animals require more vitamin-B₁ (I) when kept at high temp. than when kept cool. The pathological findings in dogs suffering from (I)-deficiency resemble those in infants (II) suffering from certain types of acute dyspepsia (III). AcCHO occurs regularly in the urine of dogs and rats in (I)-deficiency and is also found in the urine and cerebrospinal fluid of (II) with toxic (III). Such (II) often respond dramatically to the giving of (I) and the AcCHO rapidly disappears from the urine. NUTR. ABS. (m)

Acid-base equilibrium of the blood in epilepsy. F. L. McLAUGHLIN and R. H. HURST (Quart. J. Med., 1933, [ii], 2, 419—429).—Between fits variations in alkaline reserve (I) and lactic acid (II) are normal, but the p_H tends to be slightly high. (I) falls during and after a fit owing to accumulation of (II). CH. ABS.

Experimental production of simple goitre. A. W. SPENCE, F. H. A. WALKER, and E. F. SCOWEN (Biochem. J., 1933, 27, 1992—1997).—Thyroid hyperplasia (I) is produced in rabbits by feeding cabbage when the diet is free from antigoitrogenic substances, e.g., hay or oats. Small doses of MeCN also produce (I), the mechanism being different from that of the diminished resistance to MeCN poisoning on administration of thyroxine. F. O. H.

Iodine metabolism in disease of the thyroid gland. L. SCHEFFER (Klin. Woch., 1933, 12, 1285—

1286; Chem. Zentr., 1933, ii, 1697).—Much I may be excreted through the skin and the intestines as well as in the urine. In exophthalmic goitre there is no equilibrium between I ingested (I) and I excreted (II); (II) > (I). In some cases the I excreted through the skin (III) = 10 × that excreted through the kidneys (IV). In hyperthyrosis and simple goitre (III) and (IV) diminish, whilst faecal I is high; (II) < (I).

A. A. E.

Cretinism and hypothyroidism in childhood. I. P. BRONSTEIN (J. Amer. Med. Assoc., 1933, 100, 1661—1663).—In hypothyroid children the blood-cholesterol (I) is markedly > in healthy children. The improvement wrought by thyroid extract is reflected by a fall in (I). NUTR. ABS. (m)

Lipins of spleen and liver in various types of lipinosis. H. SOBOTKA, D. GLICK, M. REINER, and L. TUCHMAN (Biochem. J., 1933, 27, 2031—2034).—In Gaucher's disease a shift from the phosphatide fraction (I) to neutral fat (II) together with the presence of considerable amounts of kersin was observed. Niemann-Pick's disease was characterised by increase in (I) with almost complete absence of (II). These changes in lipin distribution are explained by a deficiency of liver-esterase. H. G. R.

Fluorescent substance in human urine. P. NIEDERHOFF and G. HOLLAND (Klin. Woch., 1933, 12, 1184; Chem. Zentr., 1933, ii, 1700).—A substance exhibiting strong sky-blue fluorescence is usually present in malaria, obstructive conditions, and high fever. A. A. E.

Lactic acid of the cerebrospinal fluid in meningitis. A. G. DE SANCTIS, J. A. KILLIAN, and T. GARCIA (Amer. J. Dis. Children, 1933, 46, 239—249).—The increased concn. varies directly with the leucocyte count and is > and independent of that of the blood. CH. ABS.

Carbohydrate metabolism and acid-base equilibrium in experimental intestinal obstruction. U. FOGLIANI (Riv. Patol. sper., 1933, 10, 261—280).—In rabbits, when the pylorus is obstructed, blood-sugar (I) falls, lactic acid (II) vals. vary, and the alkali reserve (III) rises, but when the intestine is obstructed at levels lower than the duodenum (IV), (I) rises and (II) and (III) fall. In dogs, when (IV) is obstructed, (I) and (III) rise, and (II) falls, but with obstruction at lower levels, (III) still rises and (I) and (II) fall.

NUTR. ABS. (m)

Experimental dermatitis (pellagra) in rats. M. KELLOGG and W. H. EDDY (Science, 1933, 78, 609).—Pellagra develops most uniformly in rats fed on a diet in which low or sub-min. amounts of vitamin-B₂ are coupled with high or adequate amounts of -B₁. L. S. T.

[Rapid decolorisation of iodine solutions by pellagra blood.] C. H. CAMPBELL (Amer. J. Med. Sci., 1933, 186, 266—270). CH. ABS.

Carbohydrate metabolism in pregnancy and the puerperium. B. KRIS and S. HIRSCHHORN (Wien. klin. Woch., 1933, 46, 616—617).—In pregnant women and in women early in the puerperium ad-

ministration of glucose (2 × 50 g.) causes disturbance in the functional capacity of the islets of the pancreas.

NUTR. ABS. (m)

Endocrine factors in the causation of the creatinuria of pregnancy. I. SCHIRRE and H. ZWARENSTEIN (Nature, 1934, 133, 27—28).

L. S. T.

Occurrence of the melanophore-dilating factor in the urine in certain diseases. R. COLLIN and P. L. DROUET (Bull. Acad. Méd., 1933, [iii], 109, 794—802; Chem. Zentr., 1933, ii, 1538).—Urine of menstruating women, but not normal urine, frequently gives the (frog) melanophore reaction. The reaction is frequently obtained in hyperthyroidism, and sometimes in pituitary tumour and in Cl retention.

A. A. E.

Porphyria without porphyrinuria. A. A. H. VAN DEN BERGH and W. GROTEPASS (Klin. Woch., 1933, 12, 586—589).—In a case of chronic porphyria the urine contained a normal amount of porphyrin (I) [exclusively coproporphyrin (II)]. The (I) content of the red cells was raised only slightly, but the serum was very rich in (I) (6.1 mg. per 100 c.c.). Duodenal juice contained 35 mg. of (II) and 20 mg. of protoporphyrin (III) per 100 c.c. (II) was derived from aetio-porphyrin I, not from haemoglobin. The source of the (III) in the faeces is unknown. NUTR. ABS. (m)

Occurrence of protoporphyrin in urine. I. BOAS (Klin. Woch., 1933, 12, 589—591).—In a significant no. of liver and bile-duct diseases involving porphyrinuria, besides coproporphyrin, a CHCl₃-sol. porphyrin spectroscopically identical with protoporphyrin is found in the urine. NUTR. ABS. (m)

Blood-sugar in relation to resection of the stomach. F. W. LAPP and H. DIBOLD (Klin. Woch., 1933, 12, 547—548).—Ingestion of glucose (100 g.) by patients with resected stomach causes a more rapid rise in the blood-sugar level and an earlier decline to a lower level than is normal (lowest val. 42 mg. per 100 c.c. after 2 hr.). This alteration is not due to a significant alteration in carbohydrate metabolism, but to changed conditions in gastroduodenal passage. NUTR. ABS. (m)

Mineral metabolism in renal disease. III. Regulative excretion of minerals by the kidney on acid and basic diet. H. GLATZEL (Z. ges. exp. Med., 1933, 88, 454—477).—In nephritis (I) the first and occasionally only sign of impaired renal function is reduction in the ability to concentrate all minerals (hyposthenuria). In advanced renal impairment the excretion of minerals depends almost entirely on the vol. of H₂O secreted. The renal regulation of acid-base equilibrium in (I) depends on changes in the excretion of Na, Ca, Cl, and P. In health (II) on the acid diet there is at first increase in the output of NH₄, Na, and Ca, but later a decrease in Na and further increase in NH₄ and Ca. The increase in NH₄, Na, and Ca is much less marked in (I) where K supplies a large part of the extra base required; Cl and P output in (I) is > in (II) probably due to inefficiency in dealing with HCO₃' and org. acids. On the alkaline diet the output of Cl, P, Na, and more especially K in (I) is > in (II). NUTR. ABS. (m)

Concentration test of renal function. II. Measurement of proteinuria. F. H. LASHMET and L. H. NEWBURGH (J. Amer. Med. Assoc., 1933, 100, 1328).—A suspension formed with 1 c.c. of 0.1N-NaOH and 0.16 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 125 c.c. can replace Folin and Denis' standard of turbidity. CH. ABS.

Cereals and rickets. IV. Effect of immaturity of the maize kernel on its rachitogenic properties. V. Effect of germination and autolysis on the rachitogenic properties of the maize kernel. V. M. TEMPLIN and H. STEENBOCK (Biochem. J., 1933, 27, 2055—2060, 2061—2068).—IV. Immature maize (I) gives better calcification than mature (I). Canned sweet (I) is also better than the seed. The variation in the P content was not sufficient to account for the observed differences.

V. Germination and heating to 50° did not affect the antirachitic activity of (I), whereas autolysis decreased it. H. G. R.

Calcium-phosphorus ratio in the genesis of experimental and human rickets. G. MOURIQUAND and A. LEULIER (Compt. rend., 1934, 198, 208—210).—The Ca/P ratio is approx. the same in cow's (I) and human milk. The possibility of human rickets being due to an incorrect Ca content of (I) is thus eliminated. R. S. C.

Calcification of teeth and bones on rachitic and non-rachitic diets. M. KARSHAN (J. Dental Res., 1933, 13, 301—304).—A severe rachitic diet (Ca : P = 7.27) decreased rats' tibia-ash, -Ca, and -P, but had no influence on these constituents of teeth. Addition of KH_2PO_4 and cod-liver oil did not affect vals. for teeth in 30—45 days, but in 64—80 days the teeth-Ca and -P were slightly > in rats receiving the basal diet with KH_2PO_4 . CH. ABS.

Correlation of chemical and pathological changes in teeth and bones on rachitic and non-rachitic diets. M. KARSHAN and T. ROSEBURG (J. Dental Res., 1933, 13, 305—310).—A high-Ca, low-P diet affected the ash, Ca, and P of bone, but not of teeth. Low Ca, with low or high P, affected both teeth and bone. CH. ABS.

Phosphorus metabolism in rickets. VIII. Quantitative relationship of glycerol- and hexosediphosphatase in human faeces in rickets, spasmophilia, intestinal infantilism, and febrile hypophosphatæmia. W. HEYMANN (Z. Kinderheilk., 1933, 55, 92—100).—The glycerophosphatase (I) and hexosediphosphatase (II) contents of faeces are greater in the youngest individuals, the vals. for infants, children, and adults being in the ratios 72 : 42 : 15 and 70 : 38 : 15, respectively. In uncomplicated rickets of infancy the average (I) is 59, and the average (II) 56; when tetany is present the vals. are 81 and 86; during the healing phase of rickets the vals. are 71 and 69. In cœliac disease the vals. are 15 and 16, indicating very defective enzyme production by the alimentary mucosa. In non-rachitic hypophosphatæmia associated with fever, the vals. are normal. NUTR. ABS. (m)

Scurvy in the seventeenth and eighteenth centuries. E. G. T. LIDDELL (Nature, 1934, 133, 67).—Historical. L. S. T.

Silica content of the lungs of a group of tunnel workers. C. S. SMITH and H. L. WIKOFF (Amer. J. Public Health, 1933, 23, 1250—1254).—Analyses of the lungs of 9 men who worked in the same tunnel show correlation between the severity of silicosis (I) as determined histologically and the % SiO_2 in the dried lung substance. The latter varied from 0.33 to 5.09% and is regarded as a better criterion of the intensity of (I) than is the % SiO_2 in the total ash. C. J.

Enzyme biology and enzyme diagnosis of syphilis. A. MARCHIONINI and B. OTTENSTEIN (Arch. Dermatol. Syphilis, 1933, 167, 244—278; Chem. Zentr., 1933, i, 1792).—The diastase content of skin dialysate (Ottenstein) is high in syphilis; the effect is detectable in the primary period. Neurosyphilis affords particularly high vals. Similar high vals. are found in diabetes. A. A. E.

Diastase content of cerebrospinal fluid in syphilis. A. MARCHIONINI and B. OTTENSTEIN (Klin. Woch., 1932, 11, 1424—1426; Chem. Zentr., 1933, i, 1792).—Vals. are : normal, 11—40 (sometimes > 80); syphilitic, < 10 (often 0) mg. per 100 c.c. The various forms of syphilis are related to the frequency with which this disappearance of diastase is observed. The effect is independent of the result of the Wassermann blood-reaction. A. A. E.

Calcium of whole blood, serum, and plasma in human diseases, including tetany. F. K. HERBERT (Biochem. J., 1933, 27, 1975—1977).—With various diseases, including three cases of tetany of non-parathyroid origin, Ca was absent from the red blood-corpuseles. Comparison of plasma from citrated blood with serum from defibrinated blood did not indicate the passage of abnormal amounts of Ca into the fibrin coagulum (cf. A., 1925, i, 857; 1930, 1319). F. O. H.

Mechanism of chemotherapeutic action. XI. "Immunising effect" in treatment of experimental trypanosomiasis with neoarsphenamine. L. REINER and C. S. LEONARD (Arch. Int. Pharm. Ther., 1933, 44, 434—445).—Blockade (with Indian ink) or splenectomy (or both) decreases the efficiency of chemotherapeutic treatment of rats infected with *T. equiperdum* (I), but influences very little, or not at all, the course of infection produced by (I) which have been treated *in vitro* with the therapeutic agent. Blockade inhibits the production of immune bodies (II), and thus interferes with the treatment of an infection with neoarsphenamine, which normally leads to the production of (II). A. W.

Action of lipins of healthy mammalian organs on evolution of experimental tuberculosis in guinea-pig and rabbit. L. NÈGRE (Ann. Inst. Pasteur, 1933, 51, 697—706).—Repeated subcutaneous injections of COM_2 -extracted fats of the lung, liver, and kidney of the guinea-pig (I), rabbit (II), or man favour the development of experimental tuberculosis (III) in (I) and in (II). The evolution of (III) in (I) is not modified by repeated injections of aq. suspensions of defatted organs of (I). Since in (III) the lipin content of the organs increases progressively, the conditions will become more and more suitable for the growth of the bacilli. A. W.

Total and diffusible serum-calcium and calcium of cerebrospinal fluid in human cases of hypo- and hyper-calcæmia. F. K. HERBERT (Biochem. J., 1933, 27, 1978—1991).—During hyper- and hypo-calcæmia (I), the cerebrospinal fluid-Ca (II) remains relatively const. The level of (II) is no criterion of that of the diffusible serum-Ca (III), (III) being $>$ (II) during hyperparathyroidism [when the normal ratio of (III) to total Ca is maintained] and $<$ (II) during some cases of uræmia. Normal vals. of (III) occur with the (I) associated with low serum-protein and normal -inorg. PO_4 , whilst with severe (I) of uræmia, (III) is subnormal and tetany [during which the relation of (III) to total Ca is variable] may occur. F. O. H.

Relation between respiration, gelatinase content, and pigmentation of skin. S. BLAZSÓ (Biochem. Z., 1933, 267, 11—17).—The respiration of non-pigmented (I) rabbit skin does not differ from that of pigmented (II). The gelatinase content of (I), determined by a capillary method described, is 50—80% $>$ that of (II). Histologically (I) differs greatly from (II). W. McC.

Effect of carbohydrates on respiration of tissues. B. KISCH (Biochem. Z., 1933, 267, 32—42; cf. A., 1932, 1281).—The alterations in the respiration of retina (I), heart, diaphragm, liver, and kidney (II) of ox, sheep, guinea-pig, rat, and rabbit caused by arabinose, xylose, rhamnose, glucose, fructose, galactose, lactose, maltose, sucrose, mannose, and glucosamine vary in the same tissue (III) with the carbohydrate (IV) used, with the same (IV) when different (III) of the same animal are used, and in the cases of (I) and (II) with the species of animal when the same (III) and (IV) are used. W. McC.

Influence of *l*- and *d*-lactate on oxygen consumption of rabbits. K. W. BUCHWALD, C. F. CORI, and R. E. FISHER (J. Biol. Chem., 1934, 103, 763—776).—Na *l*-lactate (I) administered to rabbits intravenously increases the O_2 consumption to an extent which accounts for only 25% of the lactate which disappears (70% of that administered). Of *d*-lactate (II) only 10—30% is removed, but all the removed fraction is accounted for by the increase in O_2 consumption. It appears that (I) is partly oxidised and partly converted into glycogen (III), whilst (II), although capable of oxidation, is not converted into (III). W. O. K.

Metabolism of sea urchins' eggs. I. Influence of dyes on respiration and lactic acid formation. A. W. H. VAN HERK (Arch. néerl. Physiol., 1933, 18, 578—602).—The addition of methylene-blue (I), chrysoïdine (II), or Janus-green (III) to unfertilised sea-urchins' eggs (*Sphærechinus granulatus*) greatly increases respiration; with fertilised eggs the increase is less. Before and after fertilisation, the R.Q. is the same, but whilst (I) and (II) are without effect, (III) causes an increase with the unfertilised eggs. Mature eggs leaving the ovary have a relatively high lactic acid (IV) content which decreases rapidly aerobically, remaining unchanged under anaerobic conditions. The amount of O_2 taken up is, however, much $<$ that required for the oxidation

of (IV). The presence of (I), (II), or (III) increases the formation of (IV) both anaerobically and aerobically. A. L.

Metabolism of surviving tissue, especially of the thyroid gland. B. WALTHARD (Endokrinol., 1933, 13, 5—9; Chem. Zentr., 1933, ii, 1696).—The respiration of normal thyroid tissue is high; aerobic (I) and anaerobic glycolysis and Warburg's coeff. are zero. In exophthalmic goitre respiration is increased, but (I) is 0; administration of I causes return to normal respiration and slight (I) is observed. Malignant tumours behave as regards respiration and glycolysis like those of other organs. A. A. E.

Oxidation of fatty acids in the liver. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1933, 27, 1753—1762).—Fatty acids (I) increase the respiration of guinea-pig liver, each (I) having an optimum concn., above which there is a fall in Q_{O_2} (cu. mm. of O_2 produced per hr., per mg. dry wt. of tissue) and in production of ketonic substances, which are formed only with (I) containing an even no. of C atoms. Crotonic and isocrotonic acids yield $CH_3Ac \cdot CO_2H$ (II), which is not broken down appreciably to $COMe_2$ and CO_2 in the liver. Neither glucose nor lactic acid affects Q_{O_2} or $Q_{(II)}$ for $PrCO_2H$ (III), but $EtCO_2H$ lowers $Q_{(III)}$. Glycogen and increase in PO_4''' concn. lower both Q_{O_2} and $Q_{(II)}$, and replacement of Locke solution by saline lowers the oxidation of (III). Minced liver cannot oxidise (I).

H. G. R.

Metabolism of azelaic acid. H. G. SMITH (J. Biol. Chem., 1933, 103, 531—535).—When azelaic acid was fed to dogs in quantities from 10 to 45 g. in 6-day periods, an average of 60% was recovered in the urine. H. D.

Nutritive value of fatty acid esters. W. M. COX, jun. (J. Biol. Chem., 1934, 103, 777—790).—The mixed Et esters of the fatty acids of coconut oil are utilised by rats and promote growth practically as well as the original fat, but the individual esters are relatively inefficient. When 77% of the cal. of the diet are in the form of the pure esters, death occurs with butyrate and hexoate as the result of refusal to eat them; palmitate and stearate are hydrolysed in the intestine, but the fatty acids are largely unabsorbed; deoate and laurate usually cause death within two weeks. The higher, but not the lower (up to C_{10}), fatty acids accumulate in the depôt fats. W. O. K.

Rôle of phosphoaminolipins in the metabolism of fats. II. Oral administration of iodised fats. C. ARTOM and G. PERETTI (Arch. internat. Physiol., 1933, 36, 351—370).—Iodised fat (I), after oral administration as emulsions to rabbits, is fixed by the liver during the succeeding 44 hr. Most of the lipin-I is sol., a smaller part is insol., in $COMe_2$. In the blood, (I) increases up to 20 hr. after ingestion and then decreases. A considerable portion of this (I) is insol. in $COMe_2$. At the peak of absorption, the concn. of lipin-I in the corpuscles is $>$ in the plasma, the difference being largely in I precipitable by $COMe_2$. Much of the I administered is liberated in the liver and is present as non-lipin I in the blood. The

phosphoaminolipins of liver and blood probably participate in the intermediate metabolism and transport of fatty acids. NUTR. ABS. (m)

Diet and blood-lipins. II. Effect of occasional over-feeding on the post-absorptive level. W. R. BLOOR (J. Biol. Chem., 1934, 103, 699—705).—In dogs on const. diet the level of the plasma-lipins in the post-absorptive state remains const.; single over-feeding with fat or carbohydrate but not with protein, to the extent of half the cal. intake of the ordinary diet, usually produces high plasma-phospholipins and often high fat vals., whilst the cholesterol level is not affected. The high vals. generally last \times 2—3 days. W. O. K.

Accumulation of lipins in the gall-bladder. J. BERENDES (Arch. klin. Chirurg., 1933, 175, 266—282).—Storage (I) of lipins in the wall of the gall-bladder (II) is the result of absorption. It is not due to a primary disturbance of cholesterol metabolism of the whole animal, and there is no causal relationship between it and the production of gall-stones, although a relationship between (I) and inflammatory processes cannot be excluded. (I) results from an accumulation of cholesteryl esters in (II) bile and slowing of the lymph stream from (II) also appears important. NUTR. ABS. (m)

Effect of cholesterol feeding on lipins of rat livers. R. OKEY (Proc. Soc. Exp. Biol. Med., 1933, 30, 1003—1005).—Rats fed on a standard diet containing cholesterol show a marked increase in the fatty acid (I) content of the livers and a very considerable increase of sterol as ester (II). Free sterol is not increased. Litter mates fed vitamin-B+cholesterol at the 10% fat level show 16.6% of (I) and 6.0% of (II) for livers of males and 23.2% of (I) and 6.6% of (II) for females, whilst those deprived of vitamin-B show 11.9% of (I) for males, 13.9% for females, and 4.5 and 2.5% of (II) for males and females, respectively. NUTR. ABS. (m)

Synthesis and destruction of cholesterol in the organism. R. SCHOENHEIMER and F. BREUSCH (J. Biol. Chem., 1933, 103, 439—448).—On a bread diet mice synthesised in a month as much cholesterol (I) as was initially contained in their bodies. When (I) was fed in quantity, much was destroyed. Fat and carotene had no effect on the (I)-balance, but bile acids increased the destruction of (I). H. G. R.

Nerve metabolism. VII. Rôle of lactic acid. T. H. CHANG and R. W. GERARD (Amer. J. Physiol., 1933, 104, 291—297).— $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (I) gradually depresses the respiration and abolishes the action potentials of nerve. The presence of lactate (II) antagonises and delays these effects. (I) also causes breakdown (III) of phosphocreatine (IV) [max. effect at 0.005M-(I)]. With split nerves, presence of (II) largely prevents (III). The loss of (IV) due to tetanisation of the nerve is not, however, increased by the presence of (I). It is improbable that (II) is produced and removed during conduction, but more probable that it can be oxidised as part of the resting metabolism of the nerve. NUTR. ABS. (m)

Production of lactic acid in the auricle of the rabbit heart. F. GOTTDENKER and M. WACHSTEIN

(Biochem. Z., 1933, 267, 192—201).—The average time of survival of the striæ in N_2 is 6, in Tyrode's solution (I) 17, in (I) containing glucose 37 min. Anaërobic conditions lead to increased production (II) of lactic acid (III), most of which diffuses into the nutrient medium (IV). (II) is independent of the nature of the (IV). In presence of O_2 (III) disappears after about 8 hr. W. McC.

Liver- and muscle-carbohydrate of wild and domesticated ducks. S. SUZUKI (Japan. J. Med. Sci., 1933, 2, 277—283).—During winter the carbohydrate (I) of the liver of wild ducks (II) diminishes, whilst the muscle-(I) remains unchanged. With both wild and tame (II) the pectoral muscle contains more (I) than the leg muscle. F. O. H.

Carbohydrate metabolism of dogs during continuous carbohydrate ingestion. L. FALIN (Arch. exp. Path. Pharm., 1933, 174, 12—27).—Continuous ingestion (2×50 g. daily for 19—125 days) of sucrose (I) or glucose by dogs produces with each dosage a mild hyperglycæmia (II) followed by a hypoglycæmia, the levels of both of which vary with the period of treatment. A second administration 30 sec. after the first results in less marked deviations of the blood-sugar from normal. With dogs treated for 53 days with (I), the extent of (II) is small, whilst after 83 or 120 days, the (II) resembles that occurring with normal dogs. The (II) due to adrenaline and the sensitivity to insulin are also modified. The correlation of these findings with changes in the secretion of insulin is discussed. F. O. H.

Carbohydrate metabolism. I. Effect of pre-vious diet on utilisation of glucose injected intravenously. J. A. JOHNSTON (Amer. J. Dis. Children, 1933, 46, 309—321).—The amount of glucose injected intravenously is directly related to that available in the basal oxidised mixture. CH. ABS.

Cutaneous blood-sugar curves after administration of fructose, mannose, and xylose. V. J. HARDING, T. F. NICHOLSON, and A. R. ARMSTRONG (Biochem. J., 1933, 27, 2035—2042).—Administration of fructose (I) produces an increase in blood-glucose, and small quantities of (I) can be detected in blood (II) and urine (III). Mannose, owing to slow absorption and rapid utilisation, was not found in (II), but was detected in (III) after administration. Large amounts of xylose are found in both (II) and (III) after ingestion. H. G. R.

Carbohydrate metabolism with partial exclusion of liver. F. MEYTHALER and T. NAEGELI (Klin. Woch., 1933, 12, 596—597).—Dogs with Eck's fistula receiving a diet rich in carbohydrates show increased hyperglycæmia after ingestion or injection of glucose. When only the blood of the pancreaticoduodenal vein passes through the liver, normal blood-sugar curves are obtained. NUTR. ABS. (m)

Glycogen synthesis in the small intestine. E. A. HORNE and H. E. MAGEE (J. Physiol., 1933, 78, 289—294).—There is no evidence that glycogen is synthesised in the small intestine (dog, rabbit, cat, rat) during glucose absorption. NUTR. ABS. (m)

Relation of the chemical change in frog's muscle to the degree of tension. O. RIESSER and

R. MIURA (Pflüger's Archiv, 1933, 232, 513—538; Chem. Zentr., 1933, ii, 1708).—In anaerobic excitation of frog's muscle *in vitro* the formation of lactic acid (I) is max. at moderate tension. *In situ* all tensions and performances result in the same increase in (I). The "all or nothing" rule appears to hold.

A. A. E.

Chemical changes accompanying muscular contraction and overheating. I. Analytical methods. T. CAHN, J. HOUGET, and R. JACQUOT (Ann. Physiol. Physicochim. biol., 1933, 9, 205—243; Chem. Zentr., 1933, ii, 1708).—Methods for the determination of muscle-, blood-, and liver-H₂O, total reducing substances, lactic acid, phosphate, creatine-, adenylypyro-, and hexose-phosphoric acids, total acid-sol. P, total P, total fat, fatty acids, unsaponifiable matter, lipin-P, urea, NH₃, creatine, creatinine, nuclein-P, Na, K, and Ca are discussed. A. A. E.

Regulation of nitrogen metabolism by nervous centres. C. RICHEL and J. DUBLINEAU (J. Physiol. Path. gén., 1933, 31, 64—81).—In fatal cerebral puncture in rabbits N retention in the blood-stream occurs, accompanied by increased urea excretion (I). (I) also occurs with less severe lesions. Sometimes, however, there is no disturbance of N metabolism.

NUTR. ABS. (m)

New-formed hæmoglobin and protein catabolism. Conservation of intermediates in the anæmic dog on protein-free diet. F. S. DAFT, F. S. ROBSCHER-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1933, 103, 495—510).—Normal (I) and anæmic dogs (II) were fasted for 3 days; and after a week's feeding on carbohydrate were given 400 mg. Fe. In (I) the urea and NH₃ fraction of urine decreased by 38% and in (II) by 62%. The total hæmoglobin (III) produced [112 g. in (II)] was > accounted for by the diminished N excretion. Before Fe feeding (II) excreted more N than (I); the excretion of creatine and uric acid was also high. The total N excretion of (II) fed for 3 weeks with sugar without Fe decreased by 36% and (III) formation was 36 g., whilst with sugar+Fe it decreased by 53% and (III) formation was 128 g.

H. D.

Availability of mesocystine for promotion of growth in connexion with cystine-deficient diets. H. S. LORING, R. DOREMANN, and V. DU VIGNEAUD (J. Biol. Chem., 1933, 103, 399—403).—Mesocystine (I) is capable of supporting growth in absence of *l*-cystine. This is probably due to formation of *l*-cysteine by reduction of (I). It is confirmed that *d*-cystine does not promote growth (this vol., 89).

H. G. R.

Cystine requirements of fleece growth. A. T. KING and J. E. NICHOLS (Nature, 1933, 132, 966).—A discussion.

L. S. T.

Cow's milk as a balanced food for mammals. R. JACQUOT (Compt. rend., 1933, 197, 1755—1757).—Cow's milk has a high coeff. of digestive utilisation in the calf (92%) and young pig (97%), but the lactosuria is greater in the latter (49 g. *per diem*). The coeff. of N retention in the calf is 60—70%, but in the pig only 20%; no N retention occurs in young rats, which will subsist, but not grow, on a cow's milk diet; hedgehogs die within 10 days.

P. G. M.

Nutritive value of boiled and raw milk in infant feeding. N. MORRIS and S. GRAHAM (Lancet, 1933, 225, 1314—1315).—Retention of N, Ca, and P appears to be greater when infants are fed on pasteurised as compared with raw milk.

L. S. T.

Growth and development. XXVI. Energy increment of standing over lying and the cost of getting up and lying down in growing ruminants (cattle and sheep): comparison of pulse rate, respiration rate, tidal air, and volume of pulmonary ventilation during lying and standing. W. C. HALL and S. BRODY. XXVII. Endogenous urinary nitrogen and total creatinine excretion in rats as functions of dietary protein level, time on N-free diets, age, body-weight, and basal metabolism. XXVIII. Decline of endogenous nitrogen excretion per unit weight with increasing weight in growing rats, and its relation to the decline in basal metabolism. Decline in live weight, nitrogen and energy metabolism with the advance of the period of nitrogen starvation, and of the influence of live weight and of preceding level on protein intake on these declines and on the survival periods. XXIX. Age curves of creatinine and urinary nitrogen coefficients in dairy cattle and their relations to energy metabolism. U. S. ASHWORTH and S. BRODY. XXX. Partition of digestible nitrogen intake between growth, milk secretion, and urinary excretion in growing dairy cattle. S. BRODY and A. C. RAGSDALE. XXXI. Influence of the plane of nutrition on the utilisability of feeding stuffs. Review of literature and graphic analysis of published data on the net energy and specific dynamic action problems. S. BRODY and R. C. PROCTER (Missouri Agric. Exp. Sta. Res. Bulls., 1933, No. 180, 31 pp.; No. 189, 68 pp.; No. 190, 19 pp.; No. 191, 18 pp.; No. 192, 28 pp.).—XXVII. The average creatinine-N (I) coeff. (15.1) was practically independent of age and protein intake. The limiting max. val. of the ratio total (I): total endogenous N (II) was approx. 15% and the average val. 11%. The ratio of cal. (basal metabolism) to mg. total (I) declines with increasing wt. at approx. the same rate as the ratio cal.: body-wt. The cal. per mg. of urinary (II) approaches 1.5 for young rats with high basal metabolism and 0.8 g.-cal. for heavier animals. A greater proportion of adipose tissue in rats on high-proteins diet is associated with lower (I) and (II) coeffs.

XXVIII. The total (I) coeff. of rats is const. between 20 and 600 days of age, but the total urinary (II) coeff. falls with increasing live wt. Prolonged feeding with a N-free diet (III) reduces the energy metabolism to the same level as prolonged abs. starvation. The time taken to reach the endogenous level of N excretion is a function of the level of protein intake prior to N starvation (IV). The faecal N on (III) is a nearly const. proportion of the total N excretion, increasing slightly with prolonged (IV). The ratio of faecal N to food intake increases as (IV) proceeds. The time-live wt. curve on (III) indicates the utilisation of tissues in successive stages.

XXIX. The preformed (I) coeff. of growing dairy

cattle is the same as for man and remains const. over the age 7—40 months. The ratio of basal energy metabolism to creatinine excretion declines with increasing live wt. in approx. the same manner as the ratio of basal metabolism to live wt.

XXX. Under dietary conditions examined, the % of the digestible N intake excreted in urine varied from 45 to 92% after the age of 10 months. High vals. were obtained between 12 and 20 months and low vals. during the last months of gestation and during the flush of lactation. Data showing the efficiency of diets in producing live-wt. increases are given for varying ages of cattle. A. G. P.

Acid-base equilibrium of inhabitants of the tropics. I. Acid-base ratio in the 24-hours' urine. II. Alveolar CO_2 tension, concentration of hydrogen ions, and CO_2 content of blood. G. M. STREEF and J. V. KLERKS (Arch. néerl. Physiol., 1933, 18, 415—535, 536—577; cf. A., 1932, 1277).—I. Analyses of the urine of Europeans (I), students (II), and native servants (III) are given. In comparison with the urine of (I), that of (III) has a lower p_{H} , less PO_4''' and fixed alkali, and more NH_3 .

II. [With W. RADSMAN.] Measurements of the alveolar CO_2 tension and the p_{H} of the blood of (I), (II), and (III) indicate that the acidity increases in this order. A. L.

Effect of nutritional status on the phosphorus content of protein of tissue. O. H. FULCHER (J. Lab. Clin. Med., 1933, 18, 1144—1148).—Dog's muscle- and liver-protein-P increases after prolonged fasting. Human liver-protein-P is high in malnutrition. Cretinism in pigs is not attended by such changes. CH. ABS.

Calcium precipitation and alkalisation in aerobic tissue cultures. W. C. HUEPER and M. A. RUSSELL (Amer. J. Med. Sci., 1933, 186, 383—390).—The pptn. of Ca in tissue cultures does not depend on the formation of excess of lactic acid. It has been observed in Carrel flask cultures with supernatant fluid having p_{H} 8.2—9.0. Alkalisation of the supernatant fluid and plasma medium occurs in cultures of normal and malignant cells grown under aerobic conditions, whilst acidification is observed in anaerobic conditions. CH. ABS.

Calcium and phosphorus in the chick. C. A. ELVEJHEM and B. E. KLINE (J. Biol. Chem., 1934, 103, 733—744).—The whole blood of chicks 1—2 days old contains 12 mg. CaI per 100 g. When the vitamin-D (I) supply is adequate, it increases to 13—14 mg. during the first week, then falls to 10—11 mg. at 3—6 weeks. With (I)-deficiency it falls to 9—10 mg. during the first week, rises during the second week, and then falls at four weeks. With adequate (I) the inorg. P decreases from 9 mg. during the first week to 6—7 mg. at six weeks, but with inadequate (I) it falls to 5 mg. at four weeks until death from rickets ensues. On a ration low in PO_4''' it falls to 7 mg. at one week and decreases to 5 mg. at six weeks in presence of (I), slightly lower vals. being obtained with (I)-deficiency. On the rachitogenic diet, the ash content of the bones decreases

from 30—32% at one week to 27—29% at five weeks, whilst with ample (I) the ash increases to 36% during the first week and reaches 40—42% in six weeks. A low-P diet with adequate (I) may slightly reduce the ash, but seems not to disturb calcification.

W. O. K.

Sexual differences in calcification of chicks and effect on assays. C. H. SCHROEDER (Poultry Sci., 1933, 12, 256—260).—The proximal end of the metatarsi of cockerels (I) showed 81% of the calcification in female chicks (II). The tibia-ash of (I) is 96.4% of that of (II). CH. ABS.

Magnesium in animal diets. Influence of the level of dietary magnesium on the magnesium and calcium contents of the bones, the bodies, and the blood-serum of rats. I. J. CUNNINGHAM (New Zealand J. Sci. Tech., 1933, 15, 191—193).—Diets containing subnormal proportions of Mg lowered the Mg content of the bones and the blood-serum. Introduction of Mg salts into such diets raised the vals. in some instances > normal. The increase was greater with higher amounts fed and greater with carbonate than with chloride, sulphate, or phosphate. The Mg content of bones was not greatly affected by the level of Mg feeding, but the blood-Ca fell slightly when Mg vals. were high. The calcification of bones proceeded normally with low-Mg feeding; with higher proportions the ash, CO_3''' , and SO_4''' contents of bones decreased and the H_2O content increased. A. G. P.

Action of salt-free diets. Partition of calcium in the blood. H. SCHWARZ (Arch. exp. Path. Pharm., 1933, 173, 558—570).—The total serum-Ca of rabbits fed on either NaCl-rich (I) or -poor diets (II) remains const. Deprivation of NaCl by means of (II) and administration of diuretin produce an increase in the protein-bound Ca and a decrease in the free Ca, whilst (I) produces the opposite effect. F. O. H.

Deprivation of chlorine from the organism. I—III. J. MICHELSEN (Arch. exp. Path. Pharm., 1933, 173, 737—745, 746—749, 750—758).—I. Diuresis (I) induced in rabbits produces a markedly negative Cl balance, the threshold of Cl being independent of that of H_2O . The assimilated N exceeds the excreted N with normal animals, but *vice versa* during (I), when the increased N and Cl excretions are directly related. Deprivation of Cl therefore appears to result in increased protein decomp.

II. The urica- and residual N are increased during (I) due to endogenous renal deficiency. Lack or excess of Cl in the organism produces an increased formation of protein catabolites and an impairment of the N-concn.-regulating properties of the kidney.

III. The acid-base equivalence is displaced during (I), the deprivation of Cl producing a marked acidosis due to accumulation of lactic and other org. acids. A concomitant hyperglycæmia indicates disturbances in the fat and carbohydrate metabolism parallel with those occurring in diabetes. The changes in the distribution of Cl between plasma and corpuscles are discussed. F. O. H.

Distribution and fate of ethyl alcohol in the organism of the dog. E. M. P. WIDMARK (Biochem.

Z., 1933, 267, 128—134).—A formula expressing the relationship between amount of EtOH consumed and its concn. in the blood in man (cf. Kungl. Fysiogr. Sällskapet's Handl., N.F. 41, No. 9; Mellanby, M.R.C. Spec. Rept., 1919, No. 31) can be applied also to the dog. By considering only the post-resorptive period (I) and calculating the body-vol. in which the concn. of EtOH would everywhere be the same as in the blood, results more significant than those of Mellanby are obtained. In (I) the EtOH disappears from the blood more slowly in the dog than in man. Variations amongst dogs are > those in men and dogs are less suitable than men for such experiments. W. McC.

Effect of diet on the alcohol content of the blood. E. M. P. WIDMARK (Biochem. Z., 1933, 267, 135—142; cf. this vol., 105).—The improbabilities of explanations, other than that previously given, of the fact that the EtOH content of the blood is lower when glycine or alanine is administered with the EtOH than when it is given alone, are demonstrated. W. McC.

Absorption of ethyl alcohol and alcohol habituation. G. JUNGMICHEL (Arch. exp. Path. Pharm., 1933, 173, 388—397).—The blood-EtOH (I) (A., 1922, ii, 789) is a suitable criterion of the rate of absorption (II) of orally administered EtOH. With normal fasting persons, (II) is complete 40—60 min. after ingestion, but the rate is influenced by the state of the person and by the amount and form of the EtOH. The changes in (I) with chronic alcoholism are not significantly different from the normal; with intravenous injection, however, a more rapid combustion of EtOH is indicated. F. O. H.

Inhibition of local anæsthesia due to alcohol habituation. K. BALODIS (Arch. exp. Path. Pharm., 1933, 173, 589—594).—Continuous ingestion of EtOH produces a gradual diminution in the sensitivity of the corneal reflex to local anæsthetics, probably related to the change in Ca distribution. F. O. H.

Influence of orally administered alkali and acid on cocaine anæsthesia of the cornea. E. RENTZ (Arch. exp. Path. Pharm., 1933, 173, 595—604).—Oral administration of aq. HCl or NaH₂PO₄, but not of Na₂CO₃, to guinea-pigs diminishes the corneal anæsthesia (I) due to cocaine. Acute alkalinisation or acidification by intravenous injection does not produce any marked change in (I). The above and similar phenomena are probably related to changes in the Ca distribution. F. O. H.

Quantitative applications of the modified Türk test [for narcotics]. J. C. MUNCH, H. J. PRATT, and A. M. DE PONCE (J. Amer. Pharm. Assoc., 1933, 22, 1078—1080).—Using a period of 60 sec. immersion, and a sufficient no. of frogs (*Rana pipiens*), it is possible to detect variations of $\pm 10\%$ in the concns. of local anæsthetics etc. W. S.

Poisoning by barbitone and allied drugs. (SIR) J. PURVES-STEWART and (SIR) W. H. WILLCOX (Lancet, 1934, 226, 6—7). L. S. T.

Gaseous metabolism during cardiac insufficiency. II. Barbituric acid derivatives and avertin. A. RÜHL (Arch. exp. Path. Pharm., 1933, 174, 96—110; cf. A., 1933, 1323).—With heart-lung

preps., the cardiac insufficiency (I) due to nunal, somnifen, pernocton, or avertin is accompanied by a marked diminution of O₂ consumption (II) (due to œdematous changes in the capillaries) despite the increased dilation of the heart. This lack of O₂ produces an increase in the R.Q. For a given amount of work, the (II) with (I) is < that of the normal heart. F. O. H.

Alteration of the blood-[H⁺] and mineral metabolism during narcosis. III. Influence of alkalosis and acidosis on narcosis. J. BEČKA (Arch. exp. Path. Pharm., 1933, 174, 173—181; cf. A., 1933, 977).—With the exception of morphine (which produces an alkalosis), all the narcotics (I) tested produce in rabbits an acidosis (II) which can be corrected by parenteral administration of colloidal Mg(OH)₂. Such an inhibition of (II) results in an increase (100—200%) in the efficacy of (I), whilst the post-narcotic disturbances are avoided. That veronal is an exception is probably due to the formation of a non-dissociated alkali salt. When the acidosis is emphasised by treatment with glucose, H₃PO₄, or NH₄Cl, the narcosis is deeper and frequently lethal. F. O. H.

Fate of morphine in the body. E. KEESER, H. A. OELKERS, and W. RAETZ (Arch. exp. Path. Pharm., 1933, 173, 622—632).—Subcutaneous injection of single doses of morphine (I) into guinea-pigs is followed by its appearance in the kidney (II), liver (III), and, to a smaller extent, in the muscle, blood, and brain; 24 hr. after injection it is found only in (II) and (III). With continuous injection for 3—6 weeks, (I) occurs in all tissues except muscle. After injection for 4 days, the total amount administered may be recovered from the tissues, urine, and fæces. With mice injected for long periods, approx. 90% of the (I) injected is found in the excreta. Hence (I) is not catabolised in the organism, its action being one of reversible adsorption and inhibition of enzyme action. F. O. H.

Absence of morphine from the stomach following parenteral administration. P. ELLINGER and H. SEEGER (Arch. exp. Path. Pharm., 1933, 174, 168—172).—Subcutaneous injection of morphine (I) into dogs [both normal and habituated to (I)] with gastric fistulæ produced a complete inhibition of gastric secretion within 2—3 hr., followed by a slow return to normal. In no instance was (I) detectable in the gastric juice. F. O. H.

Determination of morphine in excreta, secretions, and tissue. P. ELLINGER and H. SEEGER (Arch. exp. Path. Pharm., 1933, 174, 160—167).—The methods depending on the pptn. of morphine (I) by phosphotungstic acid (A., 1924, ii, 794; 1929, 846) have an accuracy of $\pm 3\%$ when applied to pure aq. (I). A method for the recovery (90—95%) of (I) from gastric juice, urine, fæces, and tissue is described. F. O. H.

Physiological action of *l*- and *d*-derivatives of morphine alkaloids. K. GOTO and T. TAKEBE (Proc. Imp. Acad. Tokyo, 1933, 9, 390—393).—The *d*-derivatives of sinomenine are mainly convulsive poisons and show neither the tail reaction

nor the analgesic action characteristic of the corresponding morphine *l*-derivatives (I); the action on respiration is also less. The action of (I) depends not only on constitution but also on configuration.

F. O. H.

Effect of narcotic gases on brain oxidations. M. BULOW (Biochem. J., 1933, 27, 1832—1837; cf. A., 1932, 424).—The inhibition of the O_2 uptake of brain tissue by narcotic gases (I) (C_2H_2 , C_2H_4 , $CHMe:CH_2$) is not due to their solubility in the tissue-lipins (cf. A., 1932, 1284). With tissue depleted of its substrate by washing with H_2O and in presence of glucose, lactate, or succinate, no inhibition occurs. With tissue washed with Ringer's solution, without added substrate and in presence of (I), the O_2 consumption is partly inhibited by C_2H_2 , but not by CH_4 or $CHMe:CH_2$ (cf. *loc. cit.*). This inhibition is irreversible and is due to the toxic action following prolonged exposure to C_2H_2 .

F. O. H.

Biological evaluation of a new *Digitalis* hybrid. V. AUGUSTIN (Magyar Gyóg. Táras. Ert., 1933, 9, 69—73; Chem. Zentr., 1933, i, 1811).—In *D. Ujhelyii*, a hybrid from *D. lutea* (I) and *D. lanata* (II), the morphological characters of (I) are modified by (II), but the pharmacological properties of (I) are unaltered.

L. S. T.

"Senso," a drug from the dried cutaneous secretion of the toad. I. Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1933, 9, 552—555).—Many derivatives of ψ -bufotalin (I) have a digitalis-like action on the isolated frog heart. A concn. of 1 in 10^9 of (I) is detected.

J. L. D.

Influence of sinomenine and parasinomenine on the excretion of total nitrogen, creatine, creatinine, ammonia, and urea in the urine of rabbits in comparison with the influence of quinine. Y. ARAKAWA (Folia Pharmacol. Japon., 1933, 16, No. 2, 182—193).—In large quantities (0.1—0.15 g. per kg.) all three drugs decrease the total N; urea, creatinine, and creatine are decreased in that (diminishing) order. Small quantities (0.05 g. per kg.) have no effect on the N.

CH. ABS.

Influence of sinomenine and parasinomenine on the excretion of total sulphur, neutral sulphur, total inorganic sulphur, and ethereal sulphuric acid in the urine of rabbits in comparison with the influence of quinine. Y. ARAKAWA (Folia Pharmacol. Japon., 1933, 16, No. 2, 194—206).—0.05 g. per kg. has no effect. > 0.1 g. per kg. decreases the total S; decrease in inorg. S is $>$ that in neutral S. With > 0.15 g. per kg. there is a change in the form in which S is excreted.

CH. ABS.

[Physiological] activity of maize smut (*Ustilago maidis*). S. S. BARJAKTAROVIC and S. B. BOGDANOVIĆ (Arch. exp. Path. Pharm., 1933, 173, 381—387).—Subcutaneous injection of aq. extracts of fresh (but not of old) spores produces a mild hyperglycaemia (I) in rabbits. When extracts of either fresh or old spores are injected before or just after administration of adrenaline (II), the (I) due to (II) is partly or completely inhibited and the return of the blood-sugar to normal levels occurs more rapidly.

Hence the spores contain a substance which has an ergotamine-like action on the (I) due to (II).

F. O. H.

Effect of smoking on blood-carbon monoxide. H. B. HANSON and A. B. HASTINGS (J. Amer. Med. Assoc., 1933, 100, 1481).—In a small no. of individuals the % saturation of haemoglobin was for non-smokers and smokers, respectively, 1.5 and 3—4%.

CH. ABS.

Effect of intravenous administration of lecithin and sodium chloride on blood-sugar. D. E. GREGG (Amer. J. Physiol., 1933, 104, 344—346).—In dogs, injections of 100 c.c. of hypotonic saline increase the blood-sugar (I) up to a max. of 20% above the fasting level. Other saline solutions or 3% lecithin in saline have no effect on (I).

NUTR. ABS. (m)

Dependence of the action of oxytocic substances (histamine and ergotamine) on concentration and temperature. W. LIPSCHITZ and F. KLAR (Arch. exp. Path. Pharm., 1933, 174, 223—244).—The latent period, its temp. coeff., and the time of the contraction itself of the same guinea-pig uterus prep. with histamine (I) are markedly $<$ those with the oxytocic pituitary principle (II). The temp. coeff. of the rapidity of contraction with (I), however, is approx. = that with (II). The concn.-activity curve of (I) resembles in some respects that of (II), the differences being more marked at 19—24° than at 37°. The contraction curve of ergotamine in general resembles those of (I) and (II), indicating that it induces pendulum- and not tetanus-motion of the uterus.

F. O. H.

Neosine. O. FLÖSSNER and P. VON MILLER (Z. Biol., 1933, 94, 307—311).—Neosine has a choline-like action on blood-pressure, heart, uterus, and intestine (I). The activity on (I) is 2000 times that of choline and 400 times that of γ -homocholine.

R. K. C.

Substances that decrease blood-pressure. II. Yeast-nucleic acid. M. TOKI and T. MIYOSHI (J. Agric. Chem. Soc. Japan, 1933, 9, 705—714).—Aq. (Boehringer's) yeast Na nucleate, or the hydrolytic products of nucleic acid, when administered to rats by injection or orally, decreased the blood-pressure.

CH. ABS.

Blood-sugar-reducing properties of aqueous extract of brewers' yeast. L. BINET, R. FABRE, and D. BARGETON (Compt. rend. Soc. Biol., 1933, 113, 235—236).—The blood-sugar level of the depancreatized dog is reduced by injection of the extract.

NUTR. ABS. (m)

Action of halogenated substances on lactic acid fermentation in normal and cancerous animal tissues, *in vivo* and *in vitro*. J. BRISON (Compt. rend. Soc. Biol., 1933, 112, 1391—1393).—Non-toxic doses of $CH_2Br:CO_2H$ and other halogenated acids greatly diminish the production of lactic acid in rats' tissues (particularly kidney).

NUTR. ABS. (m)

Catalytic processes in the liver. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 88—91).—The icterus in dogs or rabbits due to ligation of the bile duct or to poisoning by P or tolylenediamine produces

a decrease in the total glutathione (I) of the liver (II) which is most marked when (II) has a low content of glycogen (III). Similarly, the levels of both (I) and (III) in (II) are diminished in phloridzin diabetes. Hence the catalytic processes of (II) are dependent on the carbohydrate content. F. O. H.

Acceleration of tissue respiration by a nitrophenol. E. C. DODDS and G. D. GREVILLE (*Nature*, 1933, 132, 966).—4:6-Dinitro-*o*-cresol produces a large increase in the respiration of thin slices of surviving rat tissues when added in suitable concn. ($10^{-5}M$) to the medium supporting respiration. The respiration of kidney tissue in the presence of glucose is increased in HCO_3^- but not in PO_4^{4-} containing media. L. S. T.

Diuresis. I. Assay of antidiuretic substances. H. MARX (*Arch. exp. Path. Pharm.*, 1933, 173, 526—535).—A method of assay, based on the amount and NaCl content of urine excreted by rats suffering from excess H_2O dosage, is described. F. O. H.

Absorption of salicylic acid after oral and rectal administration. W. BLUME and F. S. NOHARA (*Arch. exp. Path. Pharm.*, 1933, 173, 413—430).—Following oral or rectal administration (rabbit), salicylic acid (I) appears in the urine within approx. 1 hr. and in the blood within 2 min. The total amount excreted varies from 50% to 80% of that administered. Traces of (I) are detectable in the blood 7—8 hr. after administration. The blood-(I) after administration of (I) into the mouth (cf. A., 1931, 1087), intestine, and rectum indicates that the rates of absorption from these sites are in the ratio of 3:6:8. F. O. H.

Action of germanin. I, II. B. VON ISSEKUTZ (*Arch. exp. Path. Pharm.*, 1933, 173, 479—498, 499—507).—I. Whilst neosalvarsan (I), trypaflavine, etc. diminish the respiration of *Trypanosoma Brucei* (II) *in vitro* and, with very dil. cultures, are lethal, germanin (Baeyer 205) (III) has no action. Also with (I) but not with (III), the serum of rabbits injected 24 hr. previously exhibits a trypanocidal action. *In vivo* (rats) injection of (III) eliminates (II) within 24 hr.; with (II) removed from such animals 9 hr. after injection, active movement is shown, but their respiration and glycolysis are depressed, their period of survival at room temp. (but not at body temp.) being, however, > that of the *in-vivo* (II). Hence (III) yields *in vivo* a substance trypanocidal only at body temp.

II. With infected rats treated with (III), (II) separated from the serum contains 0.005—0.0105% of (III), whilst the serum contains 0.024—0.042%. The O_2 consumption of (II) grown in serum-Ringer solution is not affected by (III), whilst the virulence is diminished but not totally eliminated. F. O. H.

Gastric hunger-mechanism. IV. Influence of experimental alterations in blood-sugar concentration on the gastric hunger-contractions. M. G. MULINOS (*Amer. J. Physiol.*, 1933, 104, 371—378).—In dogs with gastric fistulae spontaneous or experimental increases in blood-sugar (I) do not affect gastric motility. Insulin (II) given intravenously

decreases it temporarily and then increases it when (I) falls. This hypermotility (III) is depressed by oral or intravenous glucose. Starvation or diabetes causes (III). Adrenaline (temporarily) or atropine depresses the hyperactivity induced by food, starvation, saline injections, diabetes, and (II).

NUTR. ABS. (m)

Influence of vagotomy on stimulation-hyperglycaemia. F. HÖGLER and F. ZELL (*Arch. exp. Path. Pharm.*, 1933, 173, 674—679).—The hyperglycaemia (I) induced by adrenaline after either uni-(II) or bi-lateral vagotomy (III) is of more rapid onset and of longer duration than normal. The (I) due to pyrimidone or $MgSO_4$ is not affected by (II) or (III). Hence the influence of the vagi on insulin production appears to be over-emphasised. F. O. H.

Influence of the nervous system on the sugar excretion threshold. M. B. HANDELSMAN and K. OBERDISSE (*Arch. exp. Path. Pharm.*, 1933, 174, 81—87).—Complete denervation of the kidney in dogs has no effect on the alimentary glycosuria following injection of glucose, whilst the kidney threshold val. is unchanged. F. O. H.

Influence of vago-sympathetic stimulation on the gaseous exchange in the lungs. H. BECKER, M. HOCHREIN, and K. MATTHES (*Arch. exp. Path. Pharm.*, 1933, 173, 466—478).—In dogs, electric stimulation of the vago-sympathetic nerves increases the O_2 -saturation of the arterial blood. The mechanism of this phenomenon is discussed. F. O. H.

Absorption of essential oils by the skin. H. PAFFRATH (*Arch. exp. Path. Pharm.*, 1933, 174, 143—150).—Methods of determining essential oils (I) in expired air (II) or urine (III), based on Et_2O extraction and steam-distillation, are described. Inunction of the chest with a balsam containing (I) results in the appearance of significant amounts of (I) in (II) and, to a smaller extent, in (III). F. O. H.

Chemistry of the production of oedema of the lungs after contact with poison gases. A. KLING (*Compt. rend.*, 1933, 197, 1782—1784).—The presence of free cholesterol enables a fat to be penetrated by H_2O . Saturation (by Cl_2 or Br) and esterification (by $COCl_2$) destroy this property, and are responsible for the oedema of the lungs produced by the action of these gases. P. G. M.

Permeability of animal membranes to aluminium salts. G. KÄRBER (*Arch. exp. Path. Pharm.*, 1933, 173, 697—709).—Aq. $AlCl_3$, $K_2Al_2(SO_4)_4$, and $Al(OH)(OAc)_2$ do not significantly permeate frog's or toad's skin, whilst aq. $AlCl_3$ or $Al(NO_3)_3$ permeates cat's intestine to only a slight extent. The permeability of aq. $AlCl_3$ is not markedly influenced by saponin, whilst that of neutral aq. Na Al tartrate is not appreciably increased by bile. F. O. H.

Action of acute and chronic acid and alkali administration on the organism. E. RENTZ (*Arch. exp. Path. Pharm.*, 1933, 173, 605—613).—The various effects of the administration of acid and alkali and their correlation with changes in the distribution of Ca in the organism are discussed. F. O. H.

Influence of small amounts of arsenic on metabolism. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 77—80).—Rats receiving $1-3 \times 10^{-4}$ mg. of As daily for 14—20 days experience a decrease in body-wt. and an increase in liver- (I) and muscle-glycogen (II). No significant changes occur in the urine- or organ-N and in the liver- or muscle-fat. With toxic doses of As, (I) and (II) do not increase, whilst with acute As poisoning (I) diminishes.

F. O. H.

Catalytic action of iron. F. EICHHOLTZ and A. ORTEGA (Arch. exp. Path. Pharm., 1933, 174, 217—222).—When injection of aq. FeSO_4 or Na ferricitrate into mice is followed by that of normally harmless doses of Na pyrogalloldisulphonate, convulsions and other symptoms of toxicity appear. The degree of toxicity being parallel with the general catalytic action (I) of the administered Fe in the body, the phenomenon affords a method for the determination of (I). The normal body-Fe has no detectable (I).

F. O. H.

Pharmacology of indium. H. STEIDLE (Arch. exp. Path. Pharm., 1933, 173, 458—465).—The action of $\text{In}_2(\text{SO}_4)_3$, $\text{In}(\text{NO}_3)_3$, and InCl_3 was investigated. Rats tolerate oral administration of 2 g. of $\text{In}_2(\text{SO}_4)_3$ per kg. body-wt., but rabbits are killed by that of 1.3—2.0 g. per kg. The min. lethal dose by subcutaneous injection into rats is 0.15 g. per kg.

F. O. H.

Storage of halogens in hens' eggs and animal tissues. II. B. PURJESZ, L. BERKESY, and K. GÖNCZI (Arch. exp. Path. Pharm., 1933, 173, 553—557; cf. A., 1933, 979).—Small amounts (approx. 0.0001%) of Br normally occur in the tissues [greatest in muscle (I) and smallest in blood (II)] and eggs of hens. Intravenous injection of aq. NaBr into hens is followed by storage of Br in the liver, (I), (II), and especially in the brain, whilst the Br content of the eggs increases.

F. O. H.

Affinity between various parts of the brain and "physiological" amounts of bromine. A. BIER (Arch. exp. Path. Pharm., 1933, 173, 508—512).—Following oral administration of NaBr and Na monobromo-oleate (I) to rabbits, Br is found not only in the cerebral cortex but in the mid-brain, cerebellum, and medulla oblongata. For a definite amount of Br administered, the Br contents of the various parts of the brain are higher with (I) than with NaBr. This is probably due to the lipin-solubility of (I).

F. O. H.

Effect of fluorine on growth, calcification, and parathyroids in the chicken. H. M. HAUCK, H. STEENBOCK, J. T. LOWE, and J. G. HALPIN (Poultry Sci., 1933, 12, 242—249).—0.15% NaF in the diet produces no unfavourable effect; 1.2% is toxic. 0.6—1.2% lowered serum-Ca in young chicks. NaF has no significant effect on bone-ash, kidney-phosphatase, or size and structure of parathyroids.

CH. ABS.

Action of light on iodine in the atmosphere and in the organism.—See this vol., 155.

Physiological effect of heavy water and ice water. T. C. BARNES and E. J. LARSON (J. Amer. Chem. Soc., 1933, 55, 5059—5060; cf. A., 1933,

1329).—A filament of 31 cells of *Spirogyra nitida* in "heavy" H_2O (d 1.000061) (I) exposed to northern light at $10-14^\circ$ had 43 cells (3 dead) after 6 days; no cell division occurred in "ordinary" H_2O (II). In ice- H_2O (III) renewed twice daily, a filament of 50 cells showed 15 abnormal after 5 days; in freshly condensed H_2O , all the cells died. *Oscillatoria* spread more extensively in (I) probably owing to its p_{H} of 6.77. A solution of pancreatic amylase in (I) (which has been kept for 24 hr.) does not digest starch as readily as in (II). A 10% decrease in the amount of CO_2 evolved during fermentation with zymase [exposed to (I) for 66 hr.] is found. Oxidation of guaiaconic acid (IV) by the peroxidase-oxygenase system is increased if the solution is made in fresh (III) and allowed to warm to room temp. When a solution of (IV) and peroxidase is frozen, oxidation occurs when the ice melts.

H. B.

Intervention of thermal phenomena in the biological action of ultrasonic (vibrations). E. BIANCANI, H. BIANCANI, and A. DOGNON (Compt. rend., 1933, 197, 1693—1695).—When submitted to ultrasonic vibrations in a const.-temp. bath, fats and lipins (e.g., tap-grease, liver, brain matter) exhibit a considerable rise in temp., whereas no such increase is observed with sols and gels (agar, ovalbumin).

J. W. B.

Catalysis of hydration of carbon dioxide and dehydration of carbonic acid by an enzyme isolated from erythrocytes. W. C. STADIE and H. O'BRIEN (J. Biol. Chem., 1933, 103, 521—529).—The velocity coeffs. for the hydration, k_{CO_2} , and dehydration of CO_2 , $k_{\text{H}_2\text{CO}_3}$, are determined by mixing solutions of $\text{HPO}_4^{''}$ and CO_2 and solutions of NaHCO_3 and AcOH buffer all saturated with quinhydrone, and observing the p_{H} at different times with a calomel electrode. The enzyme is prepared by adding a 3 : 1 $\text{EtOH}-\text{CHCl}_3$ mixture and then 95% EtOH to the diluted cells, and extracting the evaporated filtrate with 50% EtOH . KCN and heating at 70° inactivate the enzyme. In a $\text{HPO}_4^{''}-\text{CO}_2$ mixture, addition of washed corpuscles or the enzyme prep. increases k_{CO_2} linearly with the concn. The effect of the enzyme on k_{HCO_3} is approx. 38% of that on k_{CO_2} , and is less the greater is the concn. of CO_2 in the substrate.

H. D.

Yeast-catalase. M. MATSUYAMA (J. Fac. Agric. Hokkaido, 1933, 32, 109—199).—Bottom- and top-yeast catalase, respectively, had optimum p_{H} 6.6, 6.3; optimum temp. for 15—20 min. reaction 15° , 22° ; optimum p_{H} for max. heat-stability 7.0, 6.8; inactivation temp. (1 hr.) 55° , 55° . Aeration in the early stages of growth increased the catalase in both.

CH. ABS.

Digestibility of raw starch. E. POZERSKI (Bull. Soc. sci. Hyg. aliment., 1933, 21, 1—29; Chem. Zentr., 1933, ii, 1368).—Heated, but not raw, starch is digested by saliva and pancreatic juice. Raw starch can be digested with the aid of large quantities of amylase. Comminution produces a digestible substance.

A. A. E.

Physiological importance of mineral elements in plants. VI. Influence of potassium chloride on rate of diastatic hydrolysis of starch. W. O. JAMES and M. CATTLE (Biochem. J., 1933, 27, 1805—

1809).—The rate of destruction of Lintner's starch by enzyme extracts from potato tubers (I), sprouts, and large shoots is increased in all cases by 5% KCl, whereas sugar formation is increased only in the case of (I). Sugar formation from dextrin is uninfluenced by KCl in all cases. The hydrolysis of starch involves two enzymes, only one being activated by KCl.

H. D.

Amylases. VI. Mechanism of activation of the ampholytic action of pancreatin by ethylamine hydrochloride. F. CAUJOLLE and S. LAFITE (Bull. Sci. pharmacol., 1933, 40, 213—219; Chem. Zentr., 1933, ii, 1691).—Salts or salt mixtures containing free Na⁺ or NH₃Et⁺ ions as well as Cl⁻ activate the amylolytic action of pancreatin.

A. A. E.

Amylosynthase. XIV, XV. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 688—692, 740—744).—XIV. Amylosynthase (I) polymerises dextrin from malt amylase, but not that obtained by heating starch. β -Glucosidomaltose is polymerised by (I) to a non-reducing substance.

XV. Lower-mol. dextrin was acetylated and then deacetylated; the product was polymerised by (I) to a substance giving a bluish-white colour with I—KI. The hydrolytic products of amylopectin, but not of amylose, was polymerised by (I). CH. ABS.

Enzymic hydrolysis of maltose- and lactose-carboxylic acids. P. PRATESI (Biochem. Z., 1933, 267, 238—242).—The acids C₁₃H₂₄O₁₃ (Ba and Na salts) are hydrolysed, the first to glucose by maltase from yeast to the extent of 40% (32% in 48 hr.), the second to galactose by *Saccharomyces fragilis* (38% in 48 hr.) and by emulsin (30%). W. McC.

Phosphatase content of the whole rat and of the vasoligated kidney. F. W. KINARD and A. CHANUTIN (J. Biol. Chem., 1933, 103, 461—470).—Phosphatase (I) in the whole rat increased from birth to a max. in 13—20 days, when it decreased to remain const. after about 60 days. Irradiated ergosterol caused an increase after 15—20 days, but had no effect on the adult rat. Ligation of the kidney caused an immediate decrease in (I), which reached zero after 16 days. H. G. R.

Kinetics of the action of kidney-phosphatase. II. E. JACOBSEN (Biochem. Z., 1933, 267, 89—101; cf. A., 1932, 882).—Between p_{H} 6.9 and 9.2 the rate (I) of hydrolysis by the phosphatase varies with the concn. of enzyme, substrate, and phosphate (II) as expressed in a formula given. (II) causes a relative (III) and an abs. (IV) inhibition, (III) being dependent on the ratio substrate:orthophosphate. As [H⁺] decreases (IV) decreases, but (III) increases. To a certain limit (I) increases with increasing substrate concn.; at p_{H} 9 the increase is great, whilst at 8.5 it is scarcely perceptible. W. McC.

Kinetics of ester hydrolysis by enzymes. V. Behaviour of esterases towards acid anhydrides such as lactic acid lactide and lactyl-lactic acid. Cause of the relative specificity of lipases. E. BAMANN, E. SCHWEIZER, and M. SCHMELLER (Z. physiol. Chem., 1933, 222, 121—130; cf. A., 1931, 392).—Lactide and (less readily) glycolide are

hydrolysed by esterase to the ester anhydride stage, whereas diphenylglycolide, benzilide, tetra- and polysalicylide are not attacked owing to lack of affinity between the enzyme and these substances. No intermediate compounds are formed with the simple ester anhydrides lactyl-lactic, acetylmandelic, acetyl- and salicylo-salicylic acids. The hydrolysis of Ph esters of aromatic acids is even slower than that of Me and Et esters. The enzyme-binding power of the ester group of a substrate is controlled by the electrochemical nature of the adjacent groups. J. H. B.

Comparison of esterases from human pancreas and liver. R. AMMON and E. TABOR (Biochem. Z., 1933, 267, 26—31).—Human pancreas-esterase (I) preferentially hydrolyses the *l*-form in *dl*-Me and *dl*-Pr^a mandelates, but its action is not affected by addition of strychnine or by the initial concn. of the substrate. (I) synthesises Bu butyrate and oleate from their constituents. Heat alters the specificity of (I). In a mixture of (I) with human liver-esterase (I) acts independently on Me mandelate. W. McC.

Directive influences in biological systems. III. Effect of proteases on lipase actions. K. G. FALK (J. Biol. Chem., 1933, 103, 363—372).—Lipase action was decreased in every case by trypsin. Papain was variable in its effect, giving decreased actions with esters other than glyceryl triacetate (I). The addition of inactive proteins greatly increased the hydrolysis of (I). H. G. R.

Are there two separate enzymes—rennin and pepsin? I. S. KLEINER (Hahnemannian Monthly, 1933, 68, 610—613).—A conc. rennin, 1 part of which coagulates 1.45×10^6 parts of skimmed milk, has no proteolytic power; it differs from cryst. pepsin in behaviour on dialysis, and response to pptn. and colour reactions. Apparently rennin is a thioprotease and pepsin a simple protein. CH. ABS.

Adsorption of pepsin on tricalcium phosphate. L. UTKIN (Biochem. Z., 1933, 267, 64—68).—The pepsin of fresh autolysed gastric mucous membrane is preferentially adsorbed by suspensions of Ca₃(PO₄)₂ at p_{H} 5.0—5.5, although the adsorption is independent of the concn. of the enzyme and separation from impurities is incomplete. W. McC.

Ultracentrifugal study of crystalline pepsin. J. ST. L. PHILPOT and I. B. ERIKSSON-QUENSEL (Nature, 1933, 132, 932—933).—The velocity method gives a sedimentation const. (I) of $3.3 \pm 0.15 \times 10^{-13}$, and the equilibrium method a mean mol. wt. of 35,500. Comparison of these vals. shows that the pepsin (II) mol. is spherical. Northrop's cryst. pepsin thus belongs to the same class of proteins as ovalbumin, Bence-Jones protein, and insulin. The homogeneity of the preps. was determined by the ultracentrifuge. Exposure of (II) to *N*-HCl for 10 min. followed by 0.1*N*-HCl+0.1*N*-NaCl had little effect on (I), indicating that a low p_{H} has no instantaneous effect on mol. wt., but causes only slow acid hydrolysis. Exposure to p_{H} 9 for 10 min. produces approx. 50% of an aggregate having a (I) of approx. 12.

L. S. T.

Heat-inactivation of crystalline pepsin; critical increment of the process. W. J. LOUGHLIN (Biochem. J., 1933, 27, 1779—1788).—Heat-inactivation (I) of pepsin is unimol. and varies with the p_H , having a min. at p_H 3—4.5. Temp. has a very marked effect, the crit. increment (II) being of the order 80,000 g.-cal. (II) varies with the p_H and is max. (96,000 g.-cal.) where (I) is min. (I) is analogous to the heat-denaturation of proteins, except in the location of the min. speed. H. G. R.

Isolation of a crystalline protein from pancreas and its conversion into a new crystalline proteolytic enzyme by trypsin. M. KUNITZ and J. H. NORTHROP (Science, 1933, 78, 558—559).—Fresh pancreas is extracted with $M/8\text{-H}_2\text{SO}_4$. The extract (I) has no measurable proteolytic activity but becomes highly active when enterokinase (IV) or relatively large amounts of trypsin (V) are added. (I) contains a protein (III), called chymo-trypsinogen, sol. in 0.4 saturated $(\text{NH}_4)_2\text{SO}_4$ (II), but insol. in 0.7 saturated (II). (III) can be crystallised from (II) at p_H 5.0. It cannot be activated by (IV), but becomes very active when a small amount of (V) is added. The crude (I) and the mother-liquor from crystals of (III) are completely activated by (IV), but not by small amounts of (V), owing to the presence of an inhibitor. (IV) forms sufficient active (V) to overcome this inhibition. The active protein formed from (III), chymo-trypsin, has been crystallised. L. S. T.

Preparation of protaminase. E. WALDSCHMIDT-LEITZ and E. KOFRANYI (Z. physiol. Chem., 1933, 222, 148—150).—Protaminase (I) (A., 1931, 984) is freed from tryptic proteinase (II) by pptn. of the peptidase-free mixture with COMe_2 in presence of ovalbumin (III). (II) is pptd. with the (III), leaving (I) in solution. The activity of (I) is not increased by added enterokinase. J. H. B.

Muscle autolysis. III. Changes in reaction, surface tension, viscosity, and refraction. I. A. SMORODINCEV, N. V. SCHIROKOV, and N. N. KRYLOVA (Biochem. Z., 1933, 267, 18—21; cf. this vol., 111).—During autolysis the p_H of muscle (I) falls, reaching a min. after 24 hr., but the n of (I) extracts (II) remains unaltered. The η of (II) reaches a min. and the γ a max. in 12—24 hr. after death. Change of temp. (4—25°) during storage slightly checks the fall of p_H and causes slight decrease in γ and increase in η ; the ratio $\eta : \gamma$ remains unchanged. The coeff. of the ratio $p_H : \gamma$ reaches a min. between the 12th and 24th hr. W. McC.

Action of arginase. E. WALDSCHMIDT-LEITZ and W. KOCHOLATY (Naturwiss., 1933, 21, 848).—Whilst arginase is partly inhibited by $\text{Fe}^{II} + \text{cysteine}$ (I) in H_2 and, to a smaller extent, by $\text{Fe}^{III} + \text{cystine}$ in air, it is accelerated by labile systems, e.g., $\text{Fe}^{III} + \text{(I)}$ in air (cf. A., 1932, 85; 1933, 315). This activation, which is optimal at p_H 5 and appears to be due to an oxidation rather than a reduction process, is also effected by Fe-alloxan or oxyhæmoglobin, but not by methæmoglobin. Oxidation-reduction systems may play a part in intracellular proteolysis. F. O. H.

Action of metals on enzymes. III. M. JACOBY (Biochem. Z., 1933, 267, 167—168; cf. A., 1933, 865).

—No irreversible oxidative destruction of urease (I) occurs when it is shaken in air with Se or Se compounds. The inactivation of (I) by metals is probably due to production of inactive complex compounds. W. McC.

Influence of preservatives on enzymic reactions. B. BLEYER, W. DIEMAR, and K. LEONHARD (Arch. Pharm., 1933, 271, 539—552).—The inhibitory influence of a no. of preservatives on the action of amylase, pepsin, trypsin, lipase, the dehydrase of muscle, and crude peroxidase varies widely. $(\text{CH}_2)_6\text{N}_4$ and H_2O_2 are generally ineffective, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $o\text{-CO}_2\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2$ most effective. Some substances are in certain cases activators. R. S. C.

Effects of radiations from a mercury-vapour arc in quartz on enzymes. H. J. FULLER (Ann. Missouri Bot. Gard., 1932, 19, 505—531).—Taka-diaxase and Difco invertase are partly inactivated. Injury of bean and tomato plants by ultra-violet rays increases the activity of amylase, invertase, peptase, and catalase. When mycelium of *Fusarium lini*, Bolley, is killed by ultra-violet rays there is no effect or a slight increase in the activity of amylase and peptase. CH. ABS.

Effects of monochromatic light on fermentation products of yeast. II. R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1933, 9, 672—679).—EtOH production was max. at 6130 Å., and of MeCHO at 4000—5500 Å. Ester production was generally high at long λ . In the first stage of the fermentation much acid was produced at long λ ; the reverse held in the last stage. CH. ABS.

Butylene glycol as a fermentation product. J. ŠTASTNÝ (Vestník českoslov. Akad. Zemed., 1932, 8, 687—692; Chem. Zentr., 1933, i, 1861).—The oxidation method with Ni dimethylglyoxime reveals only traces of $\beta\gamma$ -butylene glycol (I) in distillery mash, chiefly that of potatoes. Fellenberg's method (II) gives higher vals. which, however, do not correspond with (I). (II) is thus unsuitable and previous statements concerning the ratio between (I) and glycerol (III) are untrustworthy. The (III) content in (I) varies between limits wider than 1 : 3. L. S. T.

[Fermenting power of] yeast maceration juice. A. C. VAN WILK and F. M. MULLER (Biochem. Z., 1933, 267, 102—118).—The fermenting power (I) of bottom yeast depends on the treatment which it has undergone, being greater when kept at 1° for 24—48 hr. after pressing than when used at once. Increased duration of maceration (II) has a very favourable effect on (I) in initially poor samples. Destructive proteolysis does not occur during (II) of ordinary duration, but in very long-continued (II) the zymase is destroyed by proteolytic enzymes. Anti-proteolytic power (III) is conferred on (II) juice by boiling, and addition of boiled juice results in increased rate and extent of fermentation. Hexose diphosphate, which has no (III), increases the rate, but not the extent. W. McC.

Utilisation of pentoses by the yeast *Oospora* No. 208. E. A. PLEVAKO and N. I. ALTOVSKAYA (Schr. zentr. biochem. Forschungsinst. Nahr.-

Genusm., Moscow, 1932, 2, 212—220).—According to time and temp., 40—99% of xylose is utilised. Without aëration oxidation proceeds to CO₂; with aëration 10% each of EtOH and glycerol are formed.

CH. ABS.

Carotenoids of red yeast. E. LEDERER (Compt. rend., 1933, 197, 1694—1695).—Differential absorption from a ligroin extract of the unsaponifiable pigment of *Torula rubra* by Al₂O₃ affords β-carotene, a new carotenoid hydrocarbon *torulene*, decomp. 180° (bands at 566, 522, 491, and 461 mμ in CS₂), and a third unstable hydrocarbon, not obtained pure. A fourth acidic or lactic carotenoid (600—535 mμ in CS₂), sol. in alkaline EtOH and closely resembling astracene, is also present.

J. W. B.

Concentration of ionisable benzene derivatives by yeast-cells and the spontaneous conversion of salicylic acid. F. AXMACHER (Arch. exp. Path. Pharm., 1933, 173, 722—736).—The adsorption (I) of C₆H₆ derivatives (II) by yeast-cells is proportional to their degree of dissociation and to the [H⁺] of the medium, the acidic (II) being more readily adsorbed in acid and the basic more readily in alkaline media. The extent of (I) is not related to the partition of the substance between olive oil and H₂O. The (I) of *o*-HO-C₆H₄-CO₂H (III) is not proportional to its initial concn., being relatively lower at lower concns., whilst with dead cells (I) is considerably lowered. With (III), (I) is reversible and produces a liberation of NH₃ in the medium, probably from hydrolysis of CO-NH₂ groups of complexes of the cell-wall proteins or by ionic exchange with intracellular NH₃. Multivalent anions and cations respectively inhibit and increase (I).

F. O. H.

Products of fermentation of the *Mucor* group. II. **Products of fermentation in the presence of calcium carbonate.** T. TAKAHASHI and T. ASAI (Zentr. Bakt. Par., 1933, II, 89, 81—84).—Of five species examined four produced, from glucose, MeCHO, EtOH, AcCO₂H (one exception), succinic acid, and traces of lactic acid (one exception).

A. G. P.

Products of fermentation by *Penicillium*. G. ITO (J. Agric. Chem. Soc. Japan, 1933, 9, 552—562).—Oxalic, citric, gluconic, glycuronic, fumaric, *l*-malic, and succinic acids were found. Some varieties produce a yellow material, separable with CHCl₃ into a sol. yellowish-brown substance, m.p. 92—94°, and an insol. reddish-brown substance, m.p. 226—229°.

CH. ABS.

Biochemistry of micro-organisms. XXXV. Metabolic products of *Byssoschlamys fulva*, Olliver and Smith. H. RAISTRICK and G. SMITH (Biochem. J., 1933, 27, 1814—1819).—*B. fulva* grown on Czapek-Dox solution at 24° produces *byssoschlamic acid*, C₁₈H₂₀O₆, m.p. 163.5°, [α]_D²⁰ +127° in CHCl₃, a tetrabasic acid, toxic to mice; the main metabolic product is mannitol in amounts up to 30% of the glucose utilised.

H. D.

Fermentation products of moulds. X. *Aspergillus glaucus*. 4. Y. SUMIKI (J. Agric. Chem. Soc. Japan, 1933, 9, 714—716).—A monobasic acid, "glaucic acid," C₁₇H₂₂O₅, m.p. 237—238°, containing no OH or OMe, was found.

CH. ABS.

Reaction of *Aspergillus repens* on ammonium nitrate: production of ammonia. D. BACH and D. DESBORDES (Compt. rend., 1933, 197, 1772—1774).—In a medium of initial *p*_H 1.89 the mould liberates NH₃ at the expense of the NO₃ of NH₄NO₃, the reaction attaining a max. at about *p*_H 5.0. As the medium becomes more alkaline, NH₃ again begins to penetrate the cells.

P. G. M.

Nutritive value of the mycelium of moulds. J. T. SKINNER, W. H. PETERSON, and H. STEENBOCK (Biochem. Z., 1933, 267, 169—178).—The moulds (I) (*A. fischeri*, *A. oryzae*, *A. sydowi*, and *P. chrysogenum*) are not markedly toxic to rats, but their N contents, although assimilable, are inadequate for maintenance of life and growth. The mycelium of (I), given in amounts of < 20% of the diet, contains sufficient vitamin-B to prevent polyneuritis and maintain growth.

W. McC.

Amylopectin as a nutrient medium for moulds. H. HÄRDTL (Biochem. Z., 1933, 267, 6—10).—Amylopectin serves well as a C source (I) for the growth of *Aspergillus niger* (II), little acid being produced. The assimilation of N depends as to extent and course on (I). In the degradation of starch by (II) it is chiefly the grains which are attacked; the more resistant envelope is attacked later.

W. McC.

Effect of vitamins on the growth of fungi in pure culture. W. G. SOLHEIM, S. S. SEARS, and R. C. ROLLINS (Phytopath., 1933, 23, 929—930).—Addition of vitamins-B₁ and -B₂ to culture media increased the fructification of certain fungi and in the case of *Aspergillus niger* and *Penicillia* induced yellow pigmentation.

A. G. P.

Effect of vitamins on the reproduction and toxin formation of diphtheria bacilli. I. ANNÓK and J. BUCHGRABER (Magyar orvosi Arch., 1933, 34, 220—223; Chem. Zentr., 1933, ii, 1535).—Toxin formation is increased by vitamins, particularly by -B and least by -A. Colony size was less affected.

A. A. E.

Growth of *Clostridium botulinum* on synthetic media. W. BURROWS (J. Infect. Dis., 1933, 52, 126—137).—Cystine, leucine, and proline are essential; lysine and glycine are active in growth promotion, but not essential. Leucine and proline can be replaced by isoleucine and hydroxyproline. *C. welchii*, *C. chauvaxi*, *C. sporogenes*, *C. histolyticum*, and *C. tetani* did not grow on the medium.

CH. ABS.

Relation of gastrointestinal poison to other toxic substances produced by staphylococci. O. C. WOOLPERT and G. M. DACK (J. Infect. Dis., 1933, 52, 6—19).—A gastrointestinal poison, a hæmolysin, dermatotoxin, and killing toxin were produced when the organisms were grown on a semi-solid medium in a partial CO₂ atm.

CH. ABS.

Acidity produced in *Brucella* cultures. S. H. McNUTT and P. PURWIN (J. Infect. Dis., 1931, 48, 292—294).—Broth or peptone solution without sugar became strongly alkaline. When glucose (I), fructose (II), galactose (III), xylose (IV), or arabinose (V) was added the medium still became alkaline. When (I)—(IV) was added to nutrose solution *Brucella* pro-

duced acid; with (V) the quantity was greater. When sugar is the only source of C, growth took place in (IV) and (V). CH. ABS.

Delayed sugar utilisation by bacteria. A. G. WEDUM (Proc. Soc. Exp. Biol. Med., 1933, 30, 693—695).—Certain organisms grow in carbohydrate liquid media for several days without utilising sugar (I); sudden utilisation of (I) was accompanied by decrease in p_H . CH. ABS.

Influence of the origin of bacterial strain on the amount of nitrogen in aërobic cultures. M. LEMOIGNE and R. DESVEAUX (Compt. rend., 1933, 197, 1697—1699).—The loss of (Kjeldahl) N caused by bacteria in peptone media (A., 1926, 979) is irregular. This effect is the smaller the longer is the period during which the strain has been conserved on sugar-gelose. J. W. B.

Mechanism of respiration of pneumococci. II. M. G. SEVAG (Biochem. Z., 1933, 267, 211—237; cf. A., 1933, 1333).—At first at p_H 8 all the O_2 absorbed is converted into H_2O_2 , which then reacts with $AcCO_2H$ to give $AcOH$, H_2O , and CO_2 , and in another way. Results obtained by adding $AcCO_2H$, catalase, and KCN confirm those previously obtained, and, with other evidence, permit distinction between virulent and non-virulent types as well as between members and different strains of the same type. W. McC.

Dehydrogenases of *Bacterium coli*. I. Effect of dilution; existence of a co-enzyme of glucose dehydrogenase. J. YUDKIN (Biochem. J., 1933, 27, 1849—1858).—The product, activity \times dilution, is const. (within certain limits) for formic- (I) and succinic- (II), but not for glucose-dehydrogenase (III) of *B. coli* (cf. A., 1924, i, 913; 1925, i, 1015, 1217). (I), (II), and (III) are not affected by keeping for 1 hr. at 40°; (I) is unaffected by 5 hr. with methylene-blue (IV) or 1 hr. with PO_4^{3-} buffer (V). (II) is slowly poisoned to an extent of 40% by (IV), especially in presence of (V) or succinate, and (III) to an extent of 80% by (IV), especially in presence of (V) or glucose. The action of PhMe and of Ag⁺ indicates that the acceleration of (III) by glucose is due to the production of H donators from glucose by activation by *B. coli*. The accelerating action by heated *B. coli* on the reduction indicates the presence of a thermostable co-enzyme of (III). F. O. H.

Dehydrogenase activity of *B. coli communis* on higher aliphatic acids. F. P. MAZZA and A. CIMMINO (Atti R. Accad. Lincei, 1933, [vi], 17, 1086—1091).—Stearic acid and, to smaller extents, oleic and palmitic acids are rapidly dehydrogenated by *B. coli*. As the mol. wt. increases in the aliphatic acid series, the velocity of the action falls up to the C_6 — C_9 members, and later increases. As regards the action of F' and CN', and the influence of p_H , the bacterial enzyme behaves similarly to that of the liver. The velocity is proportional to the no. of bacteria present. If the bacteria are killed by PhMe, the action ceases after a relatively short time (cf. Mazza and Stolfi, A., 1933, 747). T. H. P.

Bacterial production of histamine from *l*-histidine. K. HIRAI (Biochem. Z., 1933, 267, 1—5).

—Strains of *B. coli* which produce tyramine from tyrosine (and one strain which produced p -OH· C_6H_4 · C_2H_4 · CO_2H from tyrosine) produce small amounts of histamine (I) from *l*-histidine (II) [0.9 g. of (I) hydrochloride from 10 g. of (II)]. W. McC.

Production of hydrogen peroxide by *Bacillus bulgaricus*. C. FROMAGEOT and J. ROUX (Biochem. Z., 1933, 267, 202—203; cf. A., 1933, 1206; Bertho and Glück, A., 1932, 654).—In presence of O_2 , production of H_2O_2 accompanies the fermentation (I) of glucose by *B. bulgaricus*, the amount of H_2O_2 increasing with that of O_2 . (I) is brought to an end by accumulation of H_2O_2 . W. McC.

Enzymic formation of hydrogen sulphide by certain heterotrophic bacteria. H. L. A. TARR (Biochem. J., 1933, 27, 1869—1874).—Yields of H_2S > 75% are obtained from cultures of *Proteus vulgaris* (I) and *Serratia marcescens* (II) when cysteine (III), cystine, and compounds of these are used as substrates. Substituted (III) compounds and α -thiol-carboxylic acids yield only small amounts, other org. S compounds examined giving no H_2S . S as substrate gives small amounts of H_2S , neither SO_3^{2-} nor SO_4^{2-} is reduced, and $Na_2S_2O_3$ gives H_2S with (I), but not with (II). The production of H_2S from (III) is possible in the case of aërobes, facultative anaërobes, and strict anaërobes, but is not effected by *S. lutea*. A. L.

Nutrition of trypanosomides and hæmophilic bacteria: Baudisch's "active iron." M. LWOFF (Ann. Inst. Pasteur, 1933, 51, 707—713; cf. A., 1933, 983).—Protohæmin (or protoporphyrin) is indispensable for the multiplication of *Strigomonas fasciculata*; it cannot be replaced by deuterio- or meso-hæmin, by hæmato- or meso-porphyrin, or by Baudisch's "active Fe" (I). It seems doubtful if (I) can play any rôle in the nutrition of hæmophilic organisms. A. W.

Trypano-agglutinins and -lysins and their production with killed trypanosomes. L. REINER and S. S. CHAO (Amer. J. Trop. Med., 1933, 13, 525—534).—Rats immunised with vaccines prepared by the action of *p*-benzoquinone or neoarsphenamine on *T. equiperdum* (I) show a marked but not abs. immunity to (I). The serum of these immunised rats agglutinated, and if sufficient complement was present, dissolved, (I). A marked parallelism between agglutinating and sensitising (lytic) powers indicates that the same antibody is responsible for the two functions. A. W.

Fluorescence of synthetic pyocyanine. C. DHÉRE (Compt. rend., 1934, 198, 126—128).—Pyocyanine and its hydrochloride (I), which do not fluoresce in aq. or buffered solutions, develop intense green fluorescence (in violet or ultra-violet light) when reduced (various reagents), especially in alkaline solution, fluorescence in visible light being observed in the aq. layer after shaking with $C_6H_{11}OH$. α -Hydroxyphenazine behaves similarly. J. W. B.

Evidence of the particulate nature of bacteriophage. R. F. FEEEMSTER and W. F. WELLS (J. Exp. Med., 1933, 58, 385—391).—Bacteriophage closely

follows the laws of chance distribution of particles in suspension. CH. ABS.

Selective action of crystal-violet and of brilliant-green on bacteriophages. A. Y. WELLS and N. P. SHERWOOD (J. Infect. Dis., 1933, 52, 209—213). CH. ABS.

Refractometric examination of purified antitoxins. C. SIEBENMANN (Biochem. J., 1933, 27, 1745—1752).—Globulins (I) and total solids may be determined in antitoxins (II) by a single refractometer reading. (II) of diphtheria, tetanus, scarlet fever, and erysipelas did not alter the n of (I) solutions. H. G. R.

Lithium chloride media for preservation and recovery of the typhoid bacillus in faeces. L. C. HAVENS and C. R. MAYFIELD (J. Infect. Dis., 1933, 52, 157—166).—Advantages are described. CH. ABS.

Illuminated counting chamber for plate cultures. A. T. R. MATTICK and E. R. HISCOX (J. Sci. Instr., 1933, 10, 373—376).—"Daylight" electric lamps are used. C. W. G.

Germicidal action of 2-chloro-4-*n*-alkylphenols.—See this vol., 183.

Energetic basis of endocrine actions. IV. Rôle of the growth hormone in the metabolism of liver and kidneys. M. REISS, A. HOCHWALD, and H. DRÜCKREY (Endokrinol., 1933, 13, 1—4; Chem. Zentr., 1933, ii, 1696).—The O_2 requirement of liver- and kidney-tissue of young rats is diminished by hypophysectomy. Injection of growth hormone produces normal or high vals. Anaërobic glycolysis increases; in the liver aërobic glycolysis is observed. The prep. of the hormone is described. A. A. E.

Action of thyroxine, di-iodothyronine, and di-iodotyrosine on the gaseous metabolism of normal and castrated rats. L. DE CARO and M. GIANI (Arch. exp. Path. Pharm., 1933, 173, 398—404).—The differences between the actions of thyroxine and di-iodothyronine on gaseous metabolism (I) are most marked with small doses, the duration of action being more significant than the max. val. attained. Di-iodotyrosine produces a slight increase in (I) followed by a fall to subnormal vals. Negative variations in (I) are produced by all three substances, the effects of which are diminished by castration. F. O. H.

Influence of hormones on the metabolism of surviving thyroid tissue. H. PAAL (Arch. exp. Path. Pharm., 1933, 173, 513—525).—Thyroid tissue (I) of normally fed guinea-pigs (II) has an average val. of Q_{O_2} = 8.2—7.35, an R.Q. = 1.1, and exhibits neither aërobic nor anaërobic glycolysis. The metabolism of (I) is increased by approx. 200% with (II) previously treated with anterior pituitary (III) or thyroxine preps. (IV), whilst prolactin and preps. of œstrin, posterior pituitary gland, vitamin-A, and carotene are inactive. (III) and (IV) also increase the metabolism of (I) on addition *in vitro*. The metabolism of (I) once activated by (III) or (IV) *in vivo* is not changed by further treatment *in vitro*. F. O. H.

Standardisation of thyroid preparations. G. ROTTER and E. SOOS (Arch. exp. Path. Pharm., 1933, 173, 614—621).—The analytical method of Leland and Foster (A., 1932, 432) fails to give trustworthy vals.; that of Harington and Randall (A., 1930, 504) is satisfactory. F. O. H.

Detoxification of the thyroid hormone by metals and natural springs. E. HESSE (Klin. Woch., 1933, 12, 1060—1061; Chem. Zentr., 1933, ii, 1384).—Medicinal water from Bad Kudowa has a similar protective action to metallic salts in respect of thyroid intoxication in dogs. The effect is due chiefly to the Fe and As. A. A. E.

Total and thyroxine-iodine content of thyroid gland after injection of saline anterior pituitary extracts. G. L. FOSTER, A. B. GUTMAN, and E. B. GUTMAN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1028—1032).—Intraperitoneal injections of saline anterior pituitary extract cause decrease in total I content of the thyroid gland of the sheep, with a proportionate decrease in thyroxine. NUTR. ABS. (m)

Diabetes-producing effect of anterior pituitary extract. B. A. HOUSSAY (Klin. Woch., 1933, 12, 773—775).—Daily administration of 7 c.c. per kg. of alkaline extract (I) of the anterior lobe of the pituitary (1.5 g. fresh gland) produces, within 3—7 days, hyperglycæmia (II), glycosuria, and acetoneuria in fed dogs. The same effect is produced by (I) after the removal of the pituitary or the thyroid or both. Blood-sugar returns to normal within 2—3 days after stopping (I) or when the dogs fast. In fasting dogs (I) causes no (II). After partial pancreatectomy, smaller doses of (I) suffice to produce similar changes. NUTR. ABS. (m)

Standardisation of posterior pituitary extracts. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 633—641).—A method is described for the assay of extracts depending on the constancy of the min. dose per kg. necessary to produce contraction of the uterus (*in situ*) of cats 2—4 days *post partum*. A standard pituitary extract is not necessary and an accuracy of $\pm 15\%$ is claimed. F. O. H.

Assay of the oxytocic principle of commercial posterior pituitary preparations. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 642—651).—The assay (cf. preceding abstract) of eleven commercial preps. indicated only one of the strength claimed. F. O. H.

Complexes containing oxytocic principle. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 652—661).—Admixture of quinine (I) with pituitary extracts (II) approx. doubles the oxytocic activity, whilst the pressor action is inhibited, the complex slightly diminishing the blood-pressure. Combinations of "gravitol" with (I) or (II) exhibit no additive or synergising effects. The absorption of (I) appears to be accelerated by (II). F. O. H.

Lack of maturity hormone in the pituitary of the infantile rat. O. SWEZY (Nature, 1933, 132, 598).—A discussion. L. S. T.

Influence of a decrease or an increase in blood-calcium on the action of pituitrin, secacornin, and hydrastine on the uterus. F. YAGI (*Folia Pharmacol. Japon.*, 1933, 16, No. 2, 113—125).—The action is diminished; it is not similar to that of adrenaline.

CH. ABS.

Effects of adrenalectomy and cortico-adrenal extract on renal excretion and tissue-fluids. H. SILVETTE and S. W. BRITTON (*Amer. J. Physiol.*, 1933, 104, 399—411).—In bilaterally adrenalectomised rats (I) which lost wt. there was a normal phenol-sulphonaphthalein excretion, but lowered H_2O excretion (II), which was more striking after H_2O injections. Excretion of urea and chlorides ran parallel with that of H_2O ; small injections of urea proved fatal. The H_2O content (III) of the liver and muscles of (I) was $>$ that of controls, the (III) of the blood lower, and that of the skin and brain the same. Probably (II) is not renal in origin.

NUTR. ABS. (m)

Influence of protein amino-acids on adrenaline action. I, II. H. NISHIYAMA (*Folia Pharmacol. Japon.*, 1933, 16, No. 2, 141—158, 159—181).—The effect of various NH_2 -acids on the depressant action of adrenaline on the isolated mouse uterus is reported.

CH. ABS.

Effect of adrenal cortex on resorption of sugar. W. WILBRANDT and L. LENGYEL (*Biochem. Z.*, 1933, 267, 204—210).—In rats from which the adrenal glands (I) have been removed resorption (II) of glucose in the intestine is reduced to the level of that of xylose, (II) of which remains unaltered. The alteration is due not to the removal of adrenaline, but to that of a substance (or substances) found in extracts of cortex of (I) ("eucortone"). W. McC.

Effect of diet on response to parathyroid extract and vitamin-D. I. Relation of calcium and phosphorus of the diet to the response in rats. A. F. MORGAN and J. G. FIELD. II. Effect of high-calcium-low-phosphorus diets in dogs. A. F. MORGAN and E. A. GARRISON. III. Effect of low-calcium-high-phosphorus diets in dogs. A. F. MORGAN, E. A. GARRISON, and M. J. HILLS. IV. Effect of diets of normal calcium and phosphorus contents in dogs. A. F. MORGAN, E. A. GARRISON, F. GILLUM, and M. J. HILLS (*Amer. J. Physiol.*, 1933, 105, 585—595, 596—607, 608—620, 621—634).—I. On a high-Ca-low-P diet (Steinbock), only those rats receiving vitamin-D (I) show a rise in serum-Ca (II) after injection with parathyroid extract (III), whereas on a low-Ca-high-P diet the reverse is the case. On a diet with normal Ca the rise in (II) is greater for rats without (I) than for those receiving it. (III) treatment does not affect the ash content of the femora.

II. With high-Ca-low-P diets, (III) produces hypercalcaemia (V) only in those dogs receiving (I). Serum-inorg. P rises whether (I) is given or not. Dogs on these diets deprived of (I) have low val. for serum-Ca and -P. The first is raised by giving (I) and the second by giving (I) and PO_4^{4-} . Addition of Ca to the low-Ca-low-P diet decreases the response to parathormone (IV).

III. Severe bone deformity, tetany, and muscular

paralysis are produced in dogs on a low-Ca-high-P diet without (I). When cod-liver oil is given, the symptoms are similar, but less severe, although the Ca and inorg. P content of the serum is normal. First doses of (IV) give (V), but subsequent doses have no effect unless they are much increased in amount. There is increased retention of Ca when (I) is given. (III) reduces P retention, but does not affect Ca retention in the presence or absence of (I).

IV. Young dogs fed on a diet of normal Ca : P ratio respond to injection of (III) with (V) unless deprived of (I). NH_4Cl in the diet tends to reduce, and NaCl to increase, (V). (III) injection lowers the retention of P in dogs receiving (I). The response to (III) injection depends on the amount and availability of a Ca reserve, and is therefore affected by the ingestion of (I) and by the amount and ratio of Ca and P in the diet.

NUTR. ABS. (m)

Comparative pharmacology of calcinosis factor and parathyroid hormone. II. Observations on man. F. HOLTZ, J. GÜRSCHING, and H. KRAUT (*Arch. exp. Path. Pharm.*, 1933, 174, 51—62; cf. A., 1932, 1068).—Both oral administration of the calcinosis factor (I) and subcutaneous injection of parathyroid hormone' (II) produce calcification (III) of the tissues (especially of the kidneys), and increase the blood-Ca and -Si. The differences in the toxic symptoms and in (III) of tissue cultures indicate, however, that the action of (I) is independent of (II).

F. O. H.

Detection of a substance resembling acetylcholine in the blood of the portal vein. W. FELDBERG and P. ROSENFELD (*Pflüger's Archiv*, 1933, 232, 212—235; *Chem. Zentr.*, 1933, ii, 1700).—Portal venous blood from the dog which has received physostigmine (I) intravenously contains a substance which behaves like acetylcholine (II). The depressor and contractile (leech muscle) activities are rapidly lost when (I) is not employed. Arterial, or femoral or jugular venous, blood does not behave similarly. (II) appears to be formed continuously at the gastric and intestinal walls and to be hydrolysed to choline unless the hydrolysis is arrested by (I). A. A. E.

Crystalline insulin. I. Mode of application and duration of insulin action. M. BÜRGER and H. KOHL. II. Preparation and properties. E. BRUCH. III. Action of intrathecally injected insulin in rabbits. H. KOHL. IV. Action on the diabetic metabolism. M. BÜRGER and A. PATZOLD. V. Inactivation by blood. M. BÜRGER and H. KOHL (*Arch. exp. Path. Pharm.*, 1933, 173, 431—438, 439—451, 452—457; 174, 118—129, 130—142).—I. The extent of the diminution in blood-sugar (I) is not a sufficient criterion of the activity of insulin (II), which is more fully indicated by the area between the (I) curve and the abscissa through the fasting val. of (I). This "area of activity" indicates that intraperitoneal injection of either amorphous or cryst. (II) into rabbits is more effective than intravenous injection, and that with both routes cryst. (II) differs in activity from the amorphous (II) from which it was prepared.

II. Analytical data are given for various preps. of (II). (II) is oxidised by aq. NaOH + $K_3Fe(CN)_6$,

1 mg. of (II) being equiv. to 2.093 mg. of $K_3Fe(CN)_6$ [or to 0.0509 mg. of O_2 , only 0.0116 mg. of which is necessary for complete inactivation of (II)]. When heated at 96° in 0.01*N*-NaOH, the liberation of NH_3 and the decrease in reducing power of (II) are not related to the concomitant inactivation.

III. Following intrathecal injection into rabbits, both amorphous and cryst. (II) are absorbed and produce a fall in (I) (cf. A., 1927, 994), the onset being later and the duration longer than with intravenous injection. With the latter route, however, hypoglycaemic convulsions are less evident.

IV. Administration of cryst. (II) to diabetics produces a two-phase action. The first corresponds with a compensatory equalisation of lack of (II), resulting in a more rapid utilisation of the available carbohydrate and to an increase in O_2 consumption (III) which, after 30 min., returns to normal for approx. 1 hr. The second corresponds with a deficiency in the body-carbohydrate and is indicated by a rise in (III), in the CO_2 output, and in (I) and by a fall in the R.Q.

V. (II) is inactivated by anaerobic incubation for 10–20 hr. at 37° with blood and, to a smaller extent, with serum. The inactivation (IV) is especially marked with the leucocyte-rich blood of patients with leucæmia, the extent of (IV) decreasing with decreasing concn. of leucocytes. With blood or serum heated to 56° , however, (IV) does not occur. F. O. H.

Action of insulin. N. A. NIELSEN (Skand. Arch. Physiol., 1933, 66, 19–49; Chem. Zentr., 1933, ii, 1698–1699).—In order to exhibit activity in the liver, cryst. insulin requires an accessory substance present in muscle. A. A. E.

Influence of insulin on body-temperature. L. DÜNNER (Arch. exp. Path. Pharm., 1933, 173, 710–721).—Insulin-hypoglycaemia (I) in guinea-pigs and in men is accompanied by a fall in body-temp. (II), which persists when the blood-sugar (III) returns to normal, and hence is not a symptom of (I). The decrease is probably partly dependent on the utilisation of carbohydrate reserves. Administration of luminal or novocaine lowers (II) without changing (III). Exposure to cold produces hyperglycaemia ("cold diabetes"). Insulin inactivated by dil. NaOH or H_2O_2 has no action on (II). F. O. H.

Purification of insulin. A. V. MOGILSKI (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 111–113).—Known methods are applied. CH. ABS.

Callicrein. VIII. Identification and occurrence of callicrein in blood. H. KRAUT, E. K. FREY, and E. WERLE (Z. physiol. Chem., 1933, 222, 73–99; cf. A., 1932, 547).—Callicrein (I) forms, with a substance present in blood (II), two inactive compounds. From one (A), (I) is liberated quickly (in 2 min.) on acidification, from the other (B), slowly and incompletely. On mixing (I) with (II), A is first formed and passes slowly into B, which is therefore regularly present in (II). Treatment of serum or plasma with $COMe_2$ activates an enzymic reaction which liberates all the (I) in 24 hr. The velocity of the reaction is dependent on temp., substrate concn., and p_H , and is max. at p_H 7–9. The inactivator

present in lymphatic and salivary glands differs from that in (II), since the complex formed only liberates (I) on acidification, not on $COMe_2$ treatment. It is found in small amount in (II) of ruminants. Human serum contains 2.6 units of inactive (I) per c.c., pig serum more, ape, ox, horse, and dog sera less.

J. H. B.

Influence of the follicular hormone on blossom and yield of plants. H. GOEBEL (Arch. Pharm., 1933, 271, 552–558).—Addition of the hormone in H_2O hastens growth and improves the yield and quality of blossom (and fruit) of hyacinths, *Calla althiopica*, maize, tomatoes, and other plants.

R. S. C.

Action of folliculin and prolan on the reproductive organs of the bat during hibernation. B. ZONDEK (Lancet, 1933, 225, 1256–1257).—Prolan (I) can also produce rupture of the follicle in bats during winter. Folliculin and (I) produce all the phases of the generative process in winter.

L. S. T.

Endocrine factors concerned in the control of the ovarian cycle. II. *Rana temporaria* as test animal. III. Action of anterior pituitary extracts on the ovary. C. W. BELLERBY (Biochem. J., 1933, 27, 2022–2025, 2025–2030).—II. Ovulation without oviposition, which is never complete and occurs in only a few animals, can be induced by injection of saline suspensions of anterior pituitary (I) in *R. temporaria* (II). As the ovary remains undeveloped for several months (II) can be used to determine the effect of the extract on development of the ova.

III. Alkaline extracts of (I) in equiv. dosage are as effective as acid extracts in producing ovulation (III) in the toad. Keeping the animals at 23 – 31° reduces the time between injection and (III) from 18 to 9 hr. without any effect on the sensitivity.

H. G. R.

Mechanism of the metabolism-stimulating effect of ovarian hormone. A. VON ARVAY (Endokrinol., 1933, 13, 9–16; Chem. Zentr., 1933, ii, 1694–1695).—Injection of ovarian hormone increases the gaseous metabolism of female rats.

A. A. E.

Hormones in colostrum. S. KONSULOV (Endokrinol., 1933, 13, 27–29; Chem. Zentr., 1933, ii, 1694).—The effect of injection of colostrum of pregnancy into the infantile mouse is described; *post-partum* colostrum has no effect. It is presumed that the hormone is consumed during parturition.

A. A. E.

Vitamin-A and visual purple. F. HAUROWITZ (Med. Klinik, 1933, 29, 1148–1149; Chem. Zentr., 1933, ii, 1703).—The $SbCl_3$ reaction for vitamin-A is given by frog's retina before or after extraction of the visual purple (I). (I) and its decolorised products do not give the reaction.

A. A. E.

Carotene and vitamin-A (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932–1933, 19).—Manuring appears to have no effect on the carotene content (I) or vitamin-A activity of cumbu leaves, and under all conditions of growing, (I) decreases with the age of the crop. NUTR. ABS. (m)

Association of nutritional conditions for plants with nutritional factors for animals (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 17).—Different conditions of manuring appear to have no appreciable effect on the vitamin-A and -B content of cumbu grains, or on the digestibility of the protein.

NUTR. ABS. (m)

Production of vitamins in plants. I. A. I. VIRTANEN, S. VON HAUSEN, and S. SAASTAMOINEN (Biochem. Z., 1933, 267, 179—191).—The total amount of vitamin-A (I) (carotene) and -C (II) in plants (wheat, peas, clover, grasses) increases with growth until the time of flowering (III) and then decreases, the max. being attained at the time of most vigorous growth. For (I) the highest % content is attained when soil acidity is optimal and N supply most favourable. The decrease in the (II) content after (III) is less certain than that of (I).

W. McC.

Fat-soluble vitamins. XXXVIII. Micro-organisms and the synthesis of carotene and vitamin-A. C. A. BAUMANN, H. STEENBOCK, M. A. INGRAHAM, and E. B. FRED (J. Biol. Chem., 1933, 103, 339—351).—Certain micro-organisms (I) can synthesise carotene (II), which accounts for the whole of their vitamin-A (III) activity. Transformation of (II) into (III) by (I) failed, and it is improbable that (III) as such is present in bacteria. H. G. R.

Stability of carotene in ethyl esters of fatty acids and in liver and vegetable oils. F. G. McDONALD (J. Biol. Chem., 1933, 103, 455—460).—Carotene (I) decomposed rapidly in solution in Et butyrate, laurate, and palmitate and peanut oil under all conditions. The loss of (I) in cod-liver, maize, and Wesson oils was retarded at 5° and in absence of O₂ at 37°.

H. G. R.

Vitamins of Californian and Asiatic dates. A. F. MORGAN (J. Home Econ., 1933, 25, 603—611).—Both varieties (I) (grown in California) contain about 300 international units of vitamin-A (II) per lb., but very little vitamin-D. Antiscorbutic activity is absent from pasteurised (I), but pasteurisation decreases the (II) activity only slightly.

NUTR. ABS. (m)

Coastal movements of the cod and vitamin content of Norwegian cod-liver oil. E. POULSSON (Nord. med. Tidsskr., 1933, 6, 886—890).—The vitamin (A and D) content of the liver oil (I) of the cod depends on the state of nourishment of the fish, and hence on the season at which fishing takes place. (I) from Norwegian cod is as potent as, or more potent than, (I) from Newfoundland cod with respect to vitamin-D.

NUTR. ABS. (m)

Colorimetric determination and detection of vitamin-A. E. ROSENTHAL and J. ERDELYI (Biochem. Z., 1933, 267, 119—123).—For the detection and determination of vitamin-A (I) 1 c.c. of a freshly-prepared 0.5% solution of pyrocatechol in CHCl₃ and 3 c.c. of a saturated CHCl₃ solution of SbCl₃ are added to 1 c.c. of a CHCl₃ solution of the material and the mixture is immediately heated at 60° for 1—2 min. The intense reddish-violet colour (II) (initially blue) produced is compared with that of 0.01% aq. KMnO₄. (II), which is not given by carotene, lycopene,

zeaxanthin, capsanthin, physalene, ergosterol (III), irradiated (III), or (I) irradiated with X-rays or ultra-violet light, exhibits characteristic absorption bands (e.g., those with max. at 552 and 476 mμ).

W. McC.

Determination of vitamin-A. A. W. DAVIES (Biochem. J., 1933, 27, 1770—1774).—The alkali digestion method has been simplified for rapid working. Vitamin-A in liver preps. is more stable if stored in 5% KOH.

H. G. R.

Sterility in males on diets deficient in vitamin-A or -E. V. KORENCHESKY (Proc. Roy. Soc. Med., 1933, 26, 1187—1192).—Histological degenerative changes in the testes of rats on a vitamin-A-deficient diet closely resemble those in rats on a diet deficient in vitamin-E.

NUTR. ABS. (m)

Significance of the passage of vitamin-A into milk. H. FASOLD and H. PETERS (Munch. med. Woch., 1933, 80, 1427—1429).—Vitamin-A, administered to lactating rats, passes into the milk.

NUTR. ABS. (m)

Transmission of vitamin-A from parents to young in mammals. II. Carotene and vitamin-A content of cow's colostrum. W. J. DANN (Biochem. J., 1933, 27, 1998—2005; cf. A., 1932, 1175).—Carotene (I) and vitamin-A (II) may be separated from milk by heating with aq. KOH and extracting with Et₂O+EtOH. The concns. of (I) and (II) in colostrum are frequently 70 and 10—100 times, respectively, those in later milk from the same cows. The sources of (II) for the young calf are discussed.

F. O. H.

Cockroaches as test animals in the quantitative analysis of vitamins in foodstuffs. V. MOSKALENKO (Nutr. U.S.S.R., 1933, 2, No. 4, 28—32).—Vitamin-C is not essential for development of the cockroach larvæ which require, however, vitamin-A and the -B complex, the necessary part of the latter being probably vitamin-B₁. As a source of fat-soluble factors, Et₂O extract of wheat germ is most potent.

NUTR. ABS. (m)

Relation of serum-calcium to pathological calcifications of hypervitaminosis-D. A. HAM and B. C. PORTUONDO (Arch. Path., 1933, 16, 1—14).—In rats receiving single large doses of irradiated ergosterol, the serum-Ca (I) reaches its max. about 72 hr. later; deposition (II) of Ca in the tissues (aorta and coronary vessels) takes place as the level begins to decline. (II) in hypervitaminosis-D depends more on the state of (I) than on its abs. level, and is attributed to the release of Ca from the fraction controlled by the parathyroid hormone.

NUTR. ABS. (m)

Effect of sources of vitamin-D on storage of the antirachitic factor in the egg. G. M. DEVANEY, H. E. MUNSELL, and H. W. TITUS (Poultry Sci., 1933, 12, 215—222).—Cod-liver oil (I), fed to Rhode Island Red hens, produces its optimal effect on the vitamin-D content (II) of the egg-yolks when the dose is 2% of the basal feed. With viosterol (20D) (III) the (II) increases with increasing dosage (up to 2%). At the optimal level for (I) feeding (II) is stored more efficiently than from (III). As regards

storage of (II) in the egg, irradiation of the hen for 15 min. daily with a carbon arc lamp is equiv. to adding 1% of (I) to the feed. NUTR. ABS. (m)

Sparing action of fats on the vitamin-B of animal tissues. A. R. KEMMERER and H. STEENBOCK (J. Biol. Chem., 1933, 103, 353—362).—1 unit of vitamin-B (I) is present in 2 g. of rat or chicken muscle, 0.25—0.5 g. of rat or chicken liver, 0.25 g. of pork ham. (I) in dark chicken muscle was > in the light muscle. Rats on low-(I), high-fat diets maintained a higher caloric intake than those on a low-(I), low-fat diet. Muscle and liver of rats, chicken, and pigs on a low (I), high-fat diet contained no more (I) than those on a low-(I), low-fat diet; the better maintenance on the former diet may be due either to a better caloric nutrition or to a ketogenic effect. H. G. R.

Apparent increased resistance of vitamin-B-deficient rats to an acute infection. L. REINER and J. B. PATON (Proc. Soc. Exp. Biol. Med., 1932, 30, 345—348).—Albino rats fed on a vitamin-B-complex-free diet (I) lived longer than control animals after infection (II) with *Trypanosoma equiperdum*. This effect appears to be due to lack of B_1 , but some slight effect was observed with diets containing B_1 but no B_2 . No difference was observed in the development of the (II), and the delayed death of infected rats on (I) may be due to secondary changes in the intermediate metabolism of the animals. Subsequent feeding of the infected deficient rats with B complex did not change the course of (II), but cured polyneuritis. Rats on vitamin-A-deficient diet died earlier after (II) than did control animals. A. W.

Relation of vitamin-B requirement to metabolism. W. A. HENDRICKS (Amer. J. Physiol., 1933, 105, 678—683).—In growing chickens the metabolism is proportional to the $5/3$ power of the live wt. (I). Since Cowgill has suggested that the vitamin-B ($-B_1$) requirement (II) bears a similar relation to (I), it follows that (II) is proportional to the metabolism. NUTR. ABS. (m)

Effect of vitamin-B₁ on respiratory quotient of brain tissue. H. M. SINCLAIR (Biochem. J., 1933, 27, 1927—1934).—The R.Q. of normal pigeon brain-tissue (I) in $PO_4^{''}$ -buffered lactate was approx. 0.90. The R.Q. of (I) from birds in opisthotonus due to vitamin-B₁ (II) deficiency was approx. 0.68 and was raised nearly to normal by cryst. (II). The R.Q. of (I) from birds showing no symptoms but fed on polished rice is scarcely affected by the feeding of (II). In CO_2-HCO_3' media the R.Q. of normal brain is approx. 0.81. In avitaminous brain addition of $PO_4^{''}$ and (II) raises the R.Q. > does the addition of (II) alone. H. D.

Avian carbohydrate metabolism. Action of catatorulin in brain. R. A. PETERS and H. M. SINCLAIR (Biochem. J., 1933, 27, 1910—1925).—The effect on the O_2 uptake of avitaminous pigeon's brain of a no. of substances with and without vitamin-B₁ (I) was determined. Purified hexose diphosphate (II) has no great influence and the (I) effect is reduced. Impure (II) has a slightly greater effect. α -Glycerophosphate (III) raises the respir-

ation level with and without (I). $Na_4P_2O_7$ (IV) at p_H 7.3 produces a steady respiration for 2—3 hr. and enhances the (I) effect. From this it is concluded that the interaction of (IV), lactic acid, and (I) constitutes the basis for the catatorulin effect (V). Mixtures of (IV), (I), and (III) have a considerable effect; adenylyl pyrophosphate is without effect. The (V) is reduced from a max. at p_H 7.3 to a min. at p_H 6.6; (IV) restores the (I) effect at p_H 6.6, hence it is inferred that free $P_2O_7^{''''}$ is split off in surviving respiration at p_H 7.3. 0.01M-NaF inhibits (V). H. D.

Growth of blow-fly larvæ on blood and serum. I. Response of aseptic larvæ to vitamin-B₁. R. P. HOBSON (Biochem. J., 1933, 27, 1899—1909).—Blow-fly larvæ hatched from aseptic eggs show deficient growth on aseptic blood; addition of yeast extract or marmite or the use of unsterilised blood produces normal growth. The H_2O -sol. fraction of marmite, Peters' antineuritic concentrate, and at least two heat-stable growth factors in yeast are all required for growth. It is concluded that vitamin synthesis is carried out by symbiotic micro-organisms in blood-sucking insects. H. D.

Action of formaldehyde on a vitamin-B₁ preparation (tiki-tiki). J. MALCOLM (Quart. J. Exp. Physiol., 1933, 23, 83—88).— CH_2O destroys or inactivates the vitamin-B₁ of tiki-tiki. NUTR. ABS. (m)

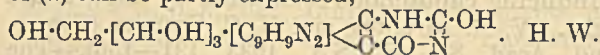
Does adenine sulphate have the action of vitamin-B₁ when irradiated by ultra-violet light? R. YAMAMOTO and T. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1933, 9, 749—751).—Avitaminosis-B₁ in pigeons was not cured. CH. ABS.

Irradiated adenine as a source of vitamin-B₁. B. SURE (Biochem. J., 1933, 27, 2043—2046).—Irradiated adenine sulphate, up to doses of 1 mg. per rat daily, does not exhibit vitamin-B₁ activity. H. G. R.

New nutritional factors required by chicks. J. A. KEENAN, O. L. KLINE, C. A. ELVEHJEM, E. B. HART, and J. G. HALPIN (J. Biol. Chem., 1934, 103, 671—685).—Chicks reared on a diet of caseinogen (24%), dextrin (63.5%), salt mixture (2.5%), yeast (8%), and cod-liver oil (2%) show defective growth and develop paralysis accompanied by brain degeneration, but not when the ration is supplemented by dried liver. Two factors are concerned: a H_2O -insol. heat-stable growth-promoting factor and a H_2O -sol. heat-labile antiparalytic factor (I), probably identical with vitamin-B₄ (cf. A., 1929, 1203; 1930, 380). Kentucky blue-grass and lucerne both contain (I). W. O. K.

Distribution of lyochromes and vitamin-B₂. E. ADLER and H. VON EULER (Svensk Kem. Tidskr., 1933, 45, 276—280).—The fraction of the $COMe_2$ extract sol. in light petroleum from animal organs, blood, and sarcoma tissue is shaken with H_2O ; the ultra-violet fluorescence of the aq. solutions determines the lyochrome content (I). Estimates of (I) per kg. include: fish-eyes, 13.5 mg.; ox-liver and kidney, 10 mg.; ox-blood, 0.025 mg. Vitamin-B₂ potency and (I) are parallel. R. K. C.

Lactoflavin (vitamin-*B*₂). R. KUHN, H. RUDY, and T. WAGNER-JAUREGG (Ber., 1933, 66, [B], 1950—1956; cf. A., 1933, 847).—Lactoflavin (I), m.p. 274° (corr., decomp.), $[\alpha]_D^{25} > -9.80^\circ$ in H₂O, after further purification through the *Tl* salt, is C₁₇H₂₀O₆N₄. The biological activity is unchanged and the identity of (I) with vitamin-*B*₂ appears established. The compound obtained from (I) and Ac₂O in C₅H₅N is an Ac₄ derivative; under like conditions lumilactoflavin (II) is unchanged. Comparison of the formulae C₁₇H₂₀O₆N₄ and C₁₃H₁₂O₂N₄ indicates that photolysis involves the removal of 4 acetylable OH distributed among 4 C atoms. Oxidation of (I) with Pb(OAc)₄ gives 0.775 mol. CH₂O, whereas (II) does not afford a volatile aldehyde. Hence the hydroxylated portion of the mol. has the structure $[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$. Treatment of (I) with Na₂S₂O₄, Pt+H₂, Zn dust in acid solution, or H₂S in Na₂CO₃ leads to leucolactoflavin, reconverted into (I) by agitation with air, whereas irradiation of (I) in H₂O in high vac. gives *deuteroleucolactoflavin*, converted by air into *deuterolactoflavin*, sharply differentiated from (I), since it becomes sol. in CHCl₃ after treatment with NaOH in the dark. Protracted irradiation of (I) in neutral aq. solution in presence of air leads to almost complete decolorisation and production of a *compound*, m.p. >360°, containing 26% N. (II) has the composition C₁₃H₁₂O₂N₄, m.p. 328° (corr., decomp.), $[\alpha] \pm 0^\circ$ (red *Ag* salt), contains 1 OH, and gives 1 mol. of AcOH when oxidised with CrO₃. It is sol. in H₂O and dil. AcOH to a yellow solution with intense green fluorescence; in dil. alkali the former remains, whilst the latter is lost, whereas the colour lightens and fluorescence disappears in dil. acid. Treatment with Ba(OH)₂ eliminates urea. Boiling 2*N*-NaOH yields pale yellow acidic *products*, the chief of which is C₁₂H₁₂O₃N₂ (III), sol. in NaHCO₃. When heated, (III) loses CO₂ and yields the *compound* C₁₁H₁₂ON₂ (IV), m.p. 174° (corr.). Distillation of (III) or (IV) with Zn dust affords a cryst. base of low m.p. which gives sparingly sol. ppts. with picric acid, AuCl₃, HgCl₂, and phosphotungstic acid. The constitution of (I) can be partly expressed,



Vitamin-*B*₂. I. **Yeast and liver preparations as source.** R. J. BLOCK and L. R. FARQUHAR (J. Biol. Chem., 1933, 103, 643—649).—Rats were fed on a basal diet containing sufficient of vitamins-*A*, -*B*₁, -*D*, and -*E*. The addition of liver or yeast concentrates, or heated or unheated yeast produced good growth. Digestion of a liver concentrate with gastric juice did not increase its growth-promoting activity. Another concentrate with a high content in pernicious anaemia factor contained no vitamin-*B*₂.

H. D.

Vitamin-*C* in the adrenal medulla. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, 27, 2006—2010).—The medulla (I) as well as the cortex (II) of the adrenal gland is very rich in vitamin-*C* (III), (I) being twice and (II) thrice as active (wt. for wt.) as standard lemon juice. When assayed biologically or by titration with 2:6-dichlorophenol-indophenol, ox (I) contains 1.1—1.2 mg. of (III)

per g. The staining with AgNO₃ is not a certain criterion of the presence or absence of (III). Rats, which synthesise their own (III), do not develop scurvy when adrenalectomised and fed on a (III)-free diet. The adrenal gland [which in rats contains approx. 0.6% of (III)] is not a storehouse for (III).

F. O. H.

Identification of vitamin-*C* and its derivatives. N. BEZSSONOFF and A. DELIRE (Compt. rend., 1933, 197, 1774—1776).—Ascorbic acid (vitamin-*C*) can be determined in biological media by means of the Bezssonoff colour reaction, after treatment with Pb(OAc)₂ at *p*_H 3.5. It is not present in vegetable juices as the free acid. In young males a considerable quantity is excreted in the urine.

P. G. M.

Distribution of vitamin-*C* in plant and animal tissues, and its determination. O. A. BESSEY and C. G. KING (J. Biol. Chem., 1934, 103, 687—698).—Vitamin-*C* may be determined by titration with 2:6-dichlorophenol-indophenol. For plant and animal tissues, extracts made with AcOH (8%) and CCl₃·CO₂H (8%), respectively, may be employed. In animals the highest concn. is in the adrenals and corpus luteum (1.4—2.3 mg. per g.). The distribution in the human body is similar to that in animals. In *C*-avitaminosis general tissue depletion occurs before symptoms of scurvy appear.

W. O. K.

Indophenol-reducing capacity and vitamin-*C* content of extracts of young germinated peas. S. W. JOHNSON (Biochem. J., 1933, 27, 1942—1949).—PO₄^{'''} (I), PO₄^{'''}-CN' (II), H₂SO₄, CCl₃·CO₂H, and aq. extracts of peas have similar reducing capacities (III) as determined by indophenol titration. The (I) and (II) extracts are less antiscorbutically active than the peas from which they are derived, and < would be expected from their (III). H₂S does not increase the titration of the extracts, indicating the absence of an active oxidised form of the vitamin. It is concluded that other substances are present in the extracts which reduce indophenol and that the methods of extraction were insufficient to remove the vitamin completely.

H. D.

Antiscorbutic potency of ascorbic acid. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, 27, 2016—2021).—Using the tooth-protection method, 3 c.c. of orange juice are equiv. to 2 mg. of ascorbic acid (I), agreeing with the val. obtained by titration. The (I) content of lemon juice varies from 0.19 to 0.69 mg. per c.c. (average, 0.47±0.11 mg. per c.c.).

H. G. R.

Antiscorbutic activity of compounds resembling ascorbic acid. O. DALMER and T. MOLL (Z. physiol. Chem., 1933, 222, 116—120).—“Maurer's acid” (A., 1933, 936), tested on guinea-pigs, has weak antiscorbutic properties, but 40 times and 20 times the ascorbic acid dose for oral and subcutaneous administration, respectively, are necessary for the same effect. Hydroxytetronic acid is inactive.

J. H. B.

Polyploidy and vitamin-*C*. F. W. SANSOME and S. S. ZILVA (Biochem. J., 1933, 27, 1935—1941).—The juice from tetraploid forms of the strains of tomato obtained by the induction of polyploid method is about twice as strongly antiscorbutic to

rats as that of the diploid forms. Similar results are obtained by indophenol titration. H. D.

Influence of vitamin-C on the gaseous metabolism of normal and scorbutic guinea-pigs. J. MOSONYI and L. RIGÓ (*Z. physiol. Chem.*, 1933, 222, 100—104).—The gaseous metabolism (I) of scorbutic guinea-pigs (II) is $>$ that of normal (II). After administration of ascorbic acid, the (I) of scorbutic (II) decreases and of normal (II) increases; the R.Q. rises in both cases, but in normal (II) only slightly. J. H. B.

Excretion of vitamin-C in human urine and its dependence on the dietary intake. L. J. HARRIS, S. N. RAY, and A. WARD (*Biochem. J.*, 1933, 27, 2011—2015).—Normal individuals excrete 30—33 mg. of vitamin-C (I) daily in the urine, but this increases 8- to 10-fold after ingestion of a massive dose of (I) and then rapidly falls to normal. This daily loss is slightly $>$ the reputed min. daily requirement for man. H. G. R.

Formation and decomposition of chlorophyll in the leaves of winter and spring cereals. M. S. TSCHAILACHJAN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 127—130).—The velocity of formation of chlorophyll in winter wheat and barley sprouts is $>$, and that of its decomp. is $<$, in spring cereals. R. T.

[H⁺] necessary for the germination of pollen and vital coloration of their vacuoles. HUREL-PY (*Compt. rend.*, 1934, 198, 195—197).—For a no. of plants in sucrose solution the p_{H} must be < 5 . R. S. C.

Ionising action of fresh pulp of vegetable tissues, and mitogenetic radiations. L. PETRI (*Atti R. Accad. Lincei*, 1933, [vi], 17, 1041—1043).—Pulped vegetable, especially embryonal, tissue determines slight ionisation of the air. Fresh potatoes, containing active oxidising enzymes, show this phenomenon, which, however, fails with cooked potatoes, in which oxidation processes are very slow. T. H. P.

Transpiration of tobacco plants in relation to radiant energy in the visible and infra-red. J. M. ARTHUR and W. D. STEWART (*Contr. Boyce Thompson Inst.*, 1933, 5, 483—501).—The effects of radiation of varying intensity, of temp., and of humidity on transpiration rates are examined. A. G. P.

Growth-differentiation balance versus carbohydrate-nitrogen ratio. W. E. LOOMIS (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 240—245).—Variations in the form, composition, and growth behaviour of a genotype are explained on the basis of variations in the growth-differentiation balance. CH. ABS.

Accumulation of carbohydrates in apple foliage, bark, and wood as influenced by moisture supply. J. R. MAGNESS, L. O. REGEIMBAL, and E. S. DEGMAN (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 246—252).—Carbohydrate synthesis in apple foliage is reduced under conditions of H₂O shortage. The starch content of storage tissues is reduced, but the sugar content of plant juices is increased. CH. ABS.

Starch in the young orange tree. S. H. CAMERON (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 110—114).—Only the root-bark shows marked fluctuations throughout the year. CH. ABS.

Relation between leaf area and size of fruit, chemical composition, and fruit-bud formation in Elberta peaches. J. H. WEINBERGER and F. P. CULLINAN (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 23—27).—Increasing the no. of leaves per fruit from 10 to 80 increased the total sugar from 7.2 to 12.3% (fresh wt.). Leaf-sugar and -starch, and twig-sugar, also tended to increase. CH. ABS.

Influence of leaf area on fruit growth and quality in the peach. I. D. JONES (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 34—38).—Increase in the no. of leaves per fruit increased the total solids, total sugars, acidity, and EtOH-sol. fraction. CH. ABS.

Relation of leaf area to fruit size and food reserves in apple seeds and branches. A. E. MURNEEK (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 230—234).—Carbohydrate storage in the branches increased with increasing area of foliage per fruit. Total N decreased in the new growth of twigs but increased in the older wood. CH. ABS.

Growth rate and composition of the Hiley peach from stone formation to flesh maturity. R. V. LOTT (*Proc. Amer. Soc. Hort. Sci.*, 1932, 29, 1—7).—Physiological maturity is reached in the order: stone, flesh, kernel. CH. ABS.

Assimilation and caoutchouc formation in the Tau-sagiz plant. V. A. NOVIKOV, A. I. GRETSCHUSCHNIKOV, J. P. BARMENKOV, and A. K. NOSOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 78—82).—The metabolism of the plant and the formation of caoutchouc (I) vary with the temp., the H₂O content of the leaves, and the intensity of incident light. (I) formation ceases completely in misty weather; under optimum conditions ($\pm 77\%$ H₂O in the leaves, in direct sunlight and at 28°) the daily production of (I) is 4 g. per 500 g. of leaves. R. T.

Inducing caoutchouc formation by ultra-violet light. V. A. NOVIKOV and E. C. GERBER (*Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 131—136).—The catalase activity of Tau-sagiz (I) seeds is increased 1600% by ultra-violet irradiation (II); the caoutchouc (III) content of the leaves of (I) and of *Asclepius* soaked in 3% aq. sucrose increases during 3 days after (II) from 0.8 to 2%, and from 1.6 to 4.5%, respectively. The (III) content of the roots of (I) grown from irradiated seeds is approx. 3 times that in normal plants, and the leaves are less subject to insect infestation. R. T.

Daily variations in weight and powder-volume of the dry substance of leaves. R. KOKETSU, T. FUJITA and K. HANADA (*Proc. Imp. Acad. Tokyo*, 1933, 9, 419—421).—The cellulose and ash contents of leaves vary but little from day to day and hence may be used as reference standards for wt. changes in other constituents. The powder-vol. of the dried leaves is less influenced than the dry wt. by changes in the rate of assimilation. F. O. H.

Iodine content of agar. A. ITANO (Proc. Imp. Acad. Tokyo, 1933, 9, 398—401).—Sea-weeds with 430—796 p.p.m. of I yielded agars with 24.5—101.9 p.p.m. Commercial preps. had 11.8—42.8 p.p.m. The I content can be controlled by the method of prep. whilst washing the agar with H₂O reduces it.

F. O. H.

South Indian pastures. I. Seasonal variation in the mineral and nitrogen content of spear-grass (*Andropogon contortus*). P. V. RAMIAH (Indian J. Vet. Sci., 1933, 3, 65—84).—The N, total ash, SiO₂, Ca, K, and P contents of the grass show considerable seasonal variations. The N and P curves are roughly parallel, whilst the Ca curve varies inversely. The main factor affecting the variation appears to be the period of growth. Max. and min. (dry-matter basis) are CaO 0.990, 0.234; K₂O 2.150, 0.568; P₂O₅ 0.588, 0.235; protein 11.48, 1.78%.

NUTR. ABS. (m)

Nitrogen, phosphoric acid, and potassium contents of different varieties of wheat. L. MAUME and J. DULAC (Compt. rend., 1934, 198, 199—202).—15 varieties of wheat growing under identical conditions have, at the time of efflorescence, N 0.54—1.26, P₂O₅ 0.28—0.49, and K₂O 1.13—3.32% (calc. on dry matter), a rough parallelism existing between the three vals.

R. S. C.

Determination of inorganic phosphate in vegetable substances. T. LITYŃSKI (Rocz. Chem., 1933, 13, 578—584).—The substance is shaken during 3 hr. with 1% HCl, the filtrate is deproteinised with CCl₃·CO₂H, inorg. P is pptd. as NH₄MgPO₄, which is dissolved in 25% HNO₃, and P is determined as phosphomolybdate.

R. T.

***Laurus camphora*, Nees. (*Cinnamomum camphora*).** V. E. VORONTZOV (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 88—93).—The tree (30 years) afforded the following percentages of camphor and essential oil, respectively: leaves and young branches 2.07, 0.13 (on dry substance); older branches 0.53, 0.13; trunk 2.14, 0.53; roots 1.65, 1.30. Storage only slightly affects the yields.

CH. ABS.

***Achillea millefolium*, Linné.** Constituents of the light petroleum extract of the blossoms. R. L. McMURRAY (Amer. J. Pharm., 1933, 105, 573—582).—The fatty oil (1.86% from the dry flowers) had: acid val. 37, sap. val. 112, I val. 57, unsaponifiable matter 22.75% (triacontane, ceryl alcohol, sterol, m.p. 135°), and fatty acids 52.5% (myristic, palmitic, cerotic, undetermined (? lignoceric), linoleic, and oleic).

E. H. S.

Isolation of *n*-triacontanol from lucerne wax. A. C. CHIBNALL, E. F. WILLIAMS, A. L. LATNER, and S. H. PIPER (Biochem. J., 1933, 27, 1885—1888).—The principal component of the wax from lucerne leaves is identified as *n*-triacontanol, m.p. 86.3—86.5°, by reduction to *n*-triacontane, m.p. 65.6—65.8°, and oxidation to *n*-triacontanoic acid, m.p. 93.6—93.9°. The wax also contains a mixture of paraffins, m.p. 65.6°, and fatty acids, no ketone being present.

A. L.

Isolation of *n*-octacosanol from wheat wax. A. POLLARD, A. C. CHIBNALL, and S. H. PIPER

(Biochem. J., 1933, 27, 1889—1893).—The principal component of the wax from blades of young wheat is identified as *n*-octacosanol, m.p. 83.2—83.4°, by reduction to *n*-octacosane, m.p. 61.3—61.5°, and by oxidation to *n*-octacosic acid, m.p. 90.8—91.1°. The wax also contains a mixture of paraffins, m.p. 66°, and fatty acids.

A. L.

Proteins of grasses. II. Method of preparation. A. C. CHIBNALL, E. J. MILLER, D. H. HALL, and R. G. WESTALL (Biochem. J., 1933, 27, 1879—1884).—The Et₂O—H₂O extraction method (A., 1932, 662) for the prep. of the proteins of leaves is modified, Et₂O—H₂O already used for cytotoxicity of leaf material being used in place of fresh Et₂O—H₂O. Improved yields of protein are obtained from several pure-strain grasses and forage crops.

A. L.

Occurrence of cyanogenetic glucosides in Nelson pasture plants. T. RIGG, H. O. ASKEW, and E. B. KIDSON (New Zealand J. Sci. Tech., 1933, 15, 222—227).—The proportion of HCN obtainable from red clover, alsike, subterranean clover, and *Lotus major* averaged 0.0001—0.0005% of fresh material and from white clover 0.0016—0.0124% (average 0.0045).

A. G. P.

Determination of hydrocyanic acid in white clover. H. O. ASKEW (New Zealand J. Sci. Tech., 1933, 15, 227—233).—Best results were obtained by grinding the fresh sample and steeping in H₂O for 20 hr. at room temp. or warming at 45° for 5 hr. Addition of acid to produce > 0.001N reduced the yield of HCN from the mixture but NaOH to give 0.01N had little effect. The extract is distilled and the distillate titrated with AgNO₃ in the presence of KI and aq. NH₃. The HCN content of stems is > that of leaves.

A. G. P.

Kuromamin, the colouring matter of "Kuro-mame." II. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1933, 9, 517—520; cf. A., 1933, 544).—The H₂O-sol. and -insol. portions of the seed-coat of Kuromame from many sources affords (improved prep.) a cryst. monoglucoside of cyanidin chloride.

J. L. D.

Phytochemistry. II. Carbohydrates of vegetable downs. E. VOROČEK and J. ZVONÍČEK (Coll. Czech. Chem. Comm., 1933, 5, 448—456).—The cleaned, degreased fibre is extracted with H₂O to remove sol. sugars (a), hydrolysed with 3% H₂SO₄ at 100° to remove hemicelluloses (b), and the residual cellulose hydrolysed. In each case a true cellulose giving glucose only on hydrolysis was obtained. The constituents of the other fractions are: flax (*Eriophorum angustifolium*), (a) 28% xylose (I), 72% galactose (II); (b) 83—91% (I), (II); thistle (*Carduus acanthoides*), (a), (I), fructose (III), (b) (I), (II); dandelion (*Taraxacum officinale*), (a) pentoses, (b), (I), and a little unidentified hexose; *Asclepius syriaca*, (a), (I), (III), (b), (I); poplar (*Populus nigra*), (a), mannose, (IV), and a little (I), (b), 85% (I), 15% (IV).

H. A. P.

Methods of staining plant tissues for differentiating natural plant oils from petroleum spray oils. P. W. ROHRBAUGH (Stain Tech., 1934, 9, 1—3).—A combination of Nile-blue sulphate and

"oil-red O" is used. This imparts a brownish-black colour to the plastids and to most natural oils whilst the petroleum is coloured red, after the sections have been treated with either KOH or Bouin's solution.

H. W. D.

Chromic fixation in alcoholic media. H. C. WATERMAN (Stain Tech., 1934, 9, 23—31).—I is suggested as a quick-killing adjuvant in chrome-alum-alcohol-acetic acid fixatives. The application of such mixtures to the study of chromosomes in the root-tips of *Vicia faba* is described.

H. W. D.

Inhibition of root-growth of *Lens esculenta* by radium. A. SARTORY, R. SARTORY, J. MEYER, and ERNST (Compt. rend., 1933, 197, 1760—1762).—Tubes of Ra were used either in contact with or at a distance of 10 mm. from the roots. The curve of mitosis shows a steady diminution on successive days of the treatment; the max. always occurs about mid-day. The effect \propto the time of application of the Ra.

P. G. M.

Inhibition of root-growth of *Lens esculenta* by radium; modification of the minimum inhibitory dose by antagonistic ions. A. SARTORY, R. SARTORY, J. MEYER, and ERNST (Compt. rend., 1934, 198, 197—199).—Isotonic KCl and, more so, MgSO₄ weaken the inhibitory action of Ra, doses of 10.16 and 11.015 millicuries, respectively, being needed to produce the effect of 7.8 millicuries in distilled H₂O.

R. S. C.

Death as the result of change of living matter within the plant cell. J. DUFRENOY (Science, 1933, 78, 494—500).—A lecture.

L. S. T.

Fever of *Arum*. L. BLARINGHEM (Compt. rend., 1933, 197, 1551—1554).—Absorption of O₂ by the whole inflorescence of *A. italicum* and *A. maculatum* is nearly doubled during the period when a higher temp. is observed. During ripening the male organs first consume 5—10 times the amount of O₂ absorbed by the (normal) female organs (the intensity and time of this crisis varying with individuals), then, later, a smaller increase occurs in the sterile papillae, and finally a two-fold increase in the O₂ absorption of the female organs.

J. W. B.

Biochemical changes accompanying curly top of tomato. F. B. WANN and H. L. BLOOD (Phytopath., 1933, 23, 929).—In comparison with healthy plants diseased specimens had higher proportions of dry matter in the pulp and of sugars and solids in the juice. The titratable acidity of the leaf juice was lowered and that of stem juice increased. In the leaves, sugar increased and total N declined. In stems the total sugars and starch increased and the total N decreased in some, but not all, varieties.

A. G. P.

Relationships between type of infection and the growth and course of metabolism of plants resulting from changes in mineral nutrition. K. BÖNING with E. BÖNING-SEUBERT (Zentr. Bakt. Par., 1933, II, 89, 85—106).—The influence of nutrient conditions and the composition of the sap of tobacco plants on infection by a no. of disease organisms indicate close relationships between plant metabolism and resistance to infection and injury.

A. G. P.

Possible chemical nature of tobacco mosaic virus. E. BARTON-WRIGHT and A. M. MCBAIN (Nature, 1933, 132, 1003—1004).—Vinson and Petre's work (A., 1931, 1201) has been confirmed and their conclusion that the virus disease of tobacco mosaic is a chemical compound and not an organism is supported. The mixed phosphate eluate is highly infectious, and contains protein. At p_H 5, COMe₂ ppts. a white, infectious material (I) containing protein. (I) can be separated into a white, cryst. solid (II) and a gelatinous protein portion (III). (III) produced disease and the virus could not be separated from protein. (II) consists mainly of phosphate with some org. matter. It contains no N, and is infectious. The addition of a 1% solution of safranin (IV) to the phosphate eluate produces a slow pptn. After removal of (IV) the aq. solution of the ppt. is infectious, but contained no N, P₂O₅, or protein.

L. S. T.

Accessory factor necessary for the growth of *Nematospora gossypii*. III. Preparation of concentrates of the second accessory factor. H. W. BUSTON and S. KASINATHAN (Biochem. J., 1933, 27, 1859—1868).—The second factor (I) (A., 1931, 1458) occurs in lentils combined with an inactive nitrogenous base or associated with proteins and is liberated on hydrolysis. (I), which is pptd. by Hg(OAc)₂ reagent and (when in the combined state) by phosphotungstic acid, appears to be a weak acid. With most active preps. 1.2 mg. per 100 c.c. of medium promotes full growth of the fungus. The first factor (*l*-inositol) cannot be replaced by quercitol, quebrachitol, *l*- or *d*-inositol, or sennitol.

Belling's green-light method for critical microscopy. H. C. WATERMAN (Stain Tech., 1934, 9, 21—22).—Practical advice is given.

H. W. D.

Continuous extraction apparatus. S. E. OWEN and W. L. OLSEN (J. Lab. Clin. Med., 1933, 18, 1072—1073).—An apparatus suitable for small quantities of biological material is described.

CH. ABS.

Micro-quinhydrone electrode. T. MIKAWA (Biochem. J., 1933, 27, 1829—1831).—The fluid (0.01—0.1 c.c.) is mixed with quinhydrone and sucked into a suitably insulated Au tube of 1 mm. diameter which serves as the metal electrode. The electrode is applicable to serum, urine, etc. but not to whole blood or tissue fluids *in vivo*.

F. O. H.

Micro-determination of gold. Application to gold therapy.—See this vol., 162.

Determination of furfuraldehyde-yielding constituents of plant materials. H. REYNOLDS, O. L. OSBURN, and C. H. WERKMAN (Iowa State Coll. J. Sci., 1933, 7, 443—451).—The sample is distilled with 100 c.c. (replenished) of 20% HCl, 200 c.c. being collected in 1 hr. The distillate, or a part thereof, is treated with excess of a saturated solution of 2 : 4-dinitrophenylhydrazine in cold 2N-HCl. After 3 hr. at room temp. or 2 hr. at 0° the ppt. is collected, dried for 1 hr. at 100°, and weighed. Arabinose (30—300 mg.) afforded 73—68% recovery; xylose (30—300 mg.) afforded 87.5—82.9% recovery.

CH. ABS.

