BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1932.

General, Physical, and Inorganic Chemistry.

Pressure effects in the secondary spectrum of hydrogen. W. G. Guthrie (Proc. Roy. Soc. Edin., 1931—1932, 52, 315—322).—The secondary spectrum of H_2 has been investigated at pressures between 30 cm. and 1 atm. The relative intensities of the lines are only slightly affected. W. R. A.

Absorption measurements for Balmer lines in a neon–hydrogen mixture subjected to condensed discharge. T. Takamine, L. S. Ornstein, and J. M. W. Milatz (Z. Physik, 1932, 78, 169—176).—A Ne discharge tube with traces of H_2 gives intensity of absorption measurements in agreement with Schrödinger's theory. A. B. D. C.

Excitation of continuous and line spectra in helium. J. S. Townsend and M. H. Pakkala (Phil. Mag., 1932, [vii], 14, 418—431).—The change in intensity of the yellow line and of the continuous spectrum with pressure and current in the high-frequency discharge in He has been measured. H. J. E.

Infra-red spectra of helium. W. F. Meggers and G. H. Dieke (Bur. Stand. J. Res., 1932, 9, 121—130).—Using xenocyanine-sensitised plates, 120 new lines from the infra-red spectrum of He, emitted by a Geissler tube, are recorded in the spectral range 8361—11,045 Å.; 32 belong to He I and 88 to the band spectrum of the He_2 mol. W. R. A.

Perturbations and rotation constants of some first negative nitrogen bands. W. H. J. Childs (Proc. Roy. Soc., 1932, A, 137, 641—661).—The 0,0 and 0,1 first negative N bands emitted from an arc have been examined under high dispersion. Vals. for the spin-doubling const. have been obtained. The bands were excited to such high rotational levels that a no. of large, hitherto unobserved perturbations were revealed. These are discussed in detail. L. L. B.

Recombination spectra in the positive column of metal vapours with doublet series. H. Kreefft (Z. Physik, 1932, 77, 752—773).—Recombination spectra were observed in positive columns of Na, K, Rb, Cs, In, and Tl. A. B. D. C.

Spectra of Na II, III, and IV in the extreme ultra-violet. B. B. Vance (Physical Rev., 1932, [ii], 41, 480—485).—New lines in the region 434,000—242,000 cm.$^{-1}$ are reported and classified. N. M. B.

New lines in the absorption spectra of the alkalis. S. Datta and B. Chakravarty (Indian J. Physics, 1932, 7, 273—282).—Data for K, Na, and Rb are reported. New lines were found on both sides of the absorption lines of the principal series. N. M. B.

Wood's method of separating the *D*-lines. E. Gaviola and P. Pringsheim (Z. Physik, 1932, 78, 211—219).—An investigation of the separation of the *D*-lines by means of interference bands due to a quartz plate. A. B. D. C.

Selective light absorption in thin layers of alkali metals. R. Fleischmann (Nachr. Ges. Wiss. Göttingen, 1931, 252—256; Chem. Zentr., 1932, i, 2293).—Experiments with Na, K, Rb, and Cs are described, and the conditions responsible for the selective absorption are discussed. A. A. E.

Nuclear moments of lighter elements. S. Tolansky (Z. Physik, 1932, 78, 71—73).—The curve giving $g(I)$ factors against at. no. for odd elements passes through a min. between the at. nos. 23 and 55. A relation between nuclear spin and mass defect is shown; protons contributing most to a positive mass defect possess nuclear spin. A. B. D. C.

Nuclear spin of arsenic. S. Tolansky (Proc. Roy. Soc., 1932, A, 137, 541—558).—The spectrum of As II has been observed in the region 6400—4300 Å., and the fine structures of the majority of the strong visible lines have been analysed. Most of the lines involve the $4p \times 5s$ and $4p \times 5p$ electron configurations. The structures can be explained by taking the nuclear spin as 3/2. The fine structure observations confirm the gross structure multiplet analysis (cf. Rao, this vol., 668). L. L. B.

Further investigation of the arc spectrum of arsenic. A. S. Rao (Proc. Physical Soc., 1932, 44, 594—607).—The spectrum of As obtained by the hollow-cathode discharge method in He and Ne has been investigated and about 100 new lines have been recorded. A new analysis of As I has been made. The first ionisation potential is approx. 10·5 volts. A. J. M.

Extinction of fluorescence of iodine vapour by intense magnetic fields. J. Genard (Z. Physik, 1932, 77, 791—794).—Study of the influence of magnetic fields on the rotation doublets and on the distribution of intensity in the resonance series indicates that only the excited state of the I_2 mol. is perturbed by a magnetic field. A. B. D. C.

Wave-lengths and Zeeman effects in lanthanum spectra. W. F. Meggers (Bur. Stand. J. Res., 1932, 9, 239—268).—Wave-length measurements and estimated relative intensities for 1535 lines of the arc and spark spectra of La between 2100 and 11,000 Å. are recorded. Zeeman effects for 476 lines between 2800 and 7500 Å. are also given. A new sequence for LaO (8423—9729 Å.) is appended. W. R. A.

Emission of glowing platinum in gases, especially in iodine vapour and chlorine. E. Müller (Ann. Physik, 1932, [v], 14, 831—855).—The emission of glowing Pt in O_2, N_2, H_2, I, and Cl_2 has been investigated. The vals. for O_2, N_2, and H_2 agree with those obtained by Richardson and Wilson. The emission in H_2, I, and Cl_2 decreases with time, and shows a decreasing sensitivity towards pressure changes. The high emission in these gases is therefore probably due to chemical processes. The carriers in I and Cl_2 are electrons. A. J. M.

Hyperfine structure and nuclear moment of mercury. K. Murakawa (Z. Physik, 1932, 77, 699—700).—Polemical, against Schüler and Jones (this vol., 440). A. B. D. C.

Hyperfine structure and nuclear moment of mercury. H. Schüler and E. G. Jones (Z. Physik, 1932, 77, 701—702).—A reply (cf. preceding abstract). A. B. D. C.

Perturbation of hyperfine structure terms of mercury. H. Schüler and E. G. Jones (Z. Physik, 1932, 77, 801—810).—Anomalies in the hyperfine structure of odd Hg isotopes are due to repulsion of levels with the same I and F vals., and the perturbation is dependent on these vals. A. B. D. C.

Isotope shift in hyperfine structure. (Miss) J. E. Rosenthal and G. Breit (Physical Rev., 1932, [ii], 41, 459—470).—The effect of deviations of the nuclear field from the inverse square law is calc., and considered in relation to the spectrum of Tl, Pb I, and Pb II. N. M. B.

Nuclear magnetic moments. S. Tolansky (Nature, 1932, 130, 402—403).—It is possible that both neutrons and protons contribute to the production of nuclear spin and if the spin g factors differ considerably, then anomalous $g(I)$ factors will arise (cf. A., 1931, 1345). Orbital motion and variable g factor may both be responsible in the case of the lighter elements (this vol., 439). L. S. T.

Characteristics of ultimate lines. A. T. Williams (Nature, 1932, 130, 313). L. S. T.

Multiplet splitting and intensities of intercombination lines. I. H. C. Wolfe (Physical Rev., 1932, [ii], 41, 443—458).—Mathematical. N. M. B.

Sum rules for atomic transition probabilities. J. P. Vinti (Physical Rev., 1932, [ii], 41, 432—442).—Mathematical. General rules, applicable to any discrete state of any atom, are deduced (cf. Dirac, this vol., 553). N. M. B.

Magneto-rotation between Zeeman components. W. Schütz (Z. Physik, 1932, 77, 437—445). A. B. D. C.

Optical investigation of spark ignition in air at atmospheric pressure by means of suppressed breakdown. W. Holzer (Z. Physik, 1932, 77, 676—694).—A study of the formation of electric arcs indicates that the primary mechanism is electron collision. A. B. D. C.

Electric discharges in gases at low pressures. I. Langmuir (J. Franklin Inst., 1932, 214, 275—298).—A review of published work on the properties of the plasma, and anode and cathode sheaths of discharge tubes. A. B. D. C.

Intensities of certain nebular lines and the mean lives of atoms emitting them. A. F. Stevenson (Proc. Roy. Soc., 1932, A, 137, 298—325).—Mathematical. The intensities and mean lives have been calc. for O III and N II. L. L. B.

Intensity of cosmic radiation in the high atmosphere. E. Regener (Nature, 1932, 130, 364).—There appears to be no γ-radiation from common radioactive bodies in outer space. L. S. T.

Effect of a secondary structure on the interference of X-rays. H. M. Evjen (Physical Rev., 1932, [ii], 41, 265—273). N. M. B.

Emission series in the ultra-soft X-ray region. J. A. Prins and A. J. Takens (Z. Physik, 1932, 77, 795—800).—New vals. are given for L, M, and N series of Ir, Zr, Y, and S. An unsuccessful attempt was made to obtain Li (K), Al (L), Fe (M), Cu (M), Zn (M), Au (N), and Bi (O). Available results for this region are given as a Moseley diagram. A. B. D. C.

X-Ray emission spectra and chemical binding. I. Fluorescence excitation of the $K\alpha_1\alpha_2$ doublets of sulphur. O. Lundquist (Z. Physik, 1932, 77, 778—787).—Displacement of the $K\alpha_1\alpha_2$ lines of S by chemical combination was studied for Cr_2S_3, CuS, ZnS, Ag_2S, Na_2SO_3, $CaSO_3$, $CuSO_3$, $BaSO_3$, Na_2SO_4, $CaSO_4$, $NiSO_4$, and $CuSO_4$. A. B. D. C.

Scattering of X-rays from solids. A. W. Coven (Physical Rev., 1932, [ii], 41, 422—431).—For Mo $K\alpha$ radiation the scattering from NaF and MgO and from KCl was approx. the same as that from Ne and A, respectively. The intensities of the diffracted part of the scattered ray and the sum of the diffracted and diffuse intensities are in agreement with theoretical relations for gases. N. M. B.

Scattering of X-rays by diatomic gases. Y. H. Woo (Sci. Rep. Tsing Hua Univ., 1932, 1, 177—180; cf. this vol., 892).—The Raman–Compton–Jauncey formula leads to an equation for electron scattering which is compared with the experimental results of Wollan (cf. A., 1931, 781). N. M. B.

Thermionic emission of metals in iodine vapour. S. Kalandyk (Spraw. Prace Polsk Towarz. Ficyz., 1930, 5, 141—156; Chem. Zentr., 1932, i, 3039).

Glow in photo-electric cells. (Lord) Rayleigh (Nature, 1932, 130, 365—366).—A "Mazda" thin-film Cs cell begins to glow at 15·8 volts, near the lower ionisation potential of A. L. S. T.

Normal gradient in gases. (Super-conductivity in inert gases.) A. Günther-Schulze and F. Keller (Z. Physik, 1932, 77, 703—712).—A discharge tube eliminating the influence of walls indicated that there is no potential gradient in the anode column of the gases He, Ne, and A; H_2 has a gradient 2·4 volts/cm. per mm. pressure. A. B. D. C.

Breakdown potential of nitrogen in the "restricted" discharge region for potentials up to 70 kv. H. Fricke (Z. Physik, 1932, 78, 59—70).—The breakdown potential of N_2 was studied for pressures near 0·01 mm., where this potential rises rapidly with decreasing pressure and electrode separation. A. B. D. C.

Discharge potential of helium, neon, and argon in presence of mercury vapour. B. Klarfeld (Z. Physik, 1932, 78, 111—122).—The presence of Hg vapour lowers the discharge potential, but addition of small quantities of non-inert gases greatly increases the discharge potential in A, and to a smaller extent in Ne and He; the effect might be used as a measure of the purity of A. A. B. D. C.

Effect of oxygen on thermal electron emission from platinum. H. Cassel and E. Glückauf (Z. physikal. Chem., 1932, B, 18, 347—359).—The electron emission voltage, E, into O_2 from glowing Pt previously treated with O_2 is const. for O_2 pressures of 10^{-5} mm. downwards at 8·46 volts. Treatment of the Pt with Hg vapour does not alter this val. If the Pt is heated in H_2, E falls below 5 volts, but as the H_2 is pumped off E rises and approaches a limiting val. of 6·45 volts. The theoretical implications of these results are discussed. R. C.

Surface potential for electrons emitted from metals. I. Tamm and D. Blochinzef (Z. Physik, 1932, 77, 774—777).—The work required to remove an electron from a metal surface is due to an image force rather than to a surface potential barrier. A. B. D. C.

Diffraction of electrons in mercury vapour. F. L. Arnot (Nature, 1932, 130, 438). L. S. T.

Pliable electron rays. E. Brüche (Z. Physik, 1932, 78, 177—195).—An electron beam in a discharge tube at 0·5 mm. H_2 pressure will follow a metal tube through 90° without loss of intensity; the pliability is due to space-charge effects, and the focussing of electron beams by residual gas is discussed. A. B. D. C.

Method of amplifying the energy of canal rays and its use in atomic disruption. C. Gerthsen (Naturwiss., 1932, 20, 743—744). W. R. A.

Experiments on potassium ions in potassium vapour. H. J. J. Braddick (Phil. Mag., 1932, [vii], 14, 450—464).—No K_2^+ ions are formed on leading K^+ ions into K vapour (cf. A., 1929, 735). H. J. E.

Slow mercury ion-rays. F. Beyerlein (Z. Physik, 1932, 77, 632—643).—Low-velocity rays of Hg ions were obtained by evaporating Hg through nozzles; the rays were electromagnetically analysed. A. B. D. C.

Energy distribution among the positive ions at the cathode of the glow discharge through gases. R. M. Chaudrhi and M. L. Oliphant (Proc. Roy. Soc., 1932, A, 137, 662—676).—The energy distribution among the positive ions which strike the cathode of the glow discharge through gases (air, H_2, and A) is independent of the current and the voltage across the dark space, and is, for any one gas, a function of pressure alone. The max. energy of the positive ions corresponds with the full potential on the discharge tube. At any given pressure the no. of ions possessing any one energy is proportional to the discharge current, but if the voltage is kept const. and the current varied by varying the pressure, then the no. of slow ions increases with the current more rapidly than the fast. L. L. B.

Diffraction of gas atoms. H. S. W. Massey and C. B. O. Mohr (Nature, 1932, 130, 276—277). L. S. T.

Dissociation by collision with positive ions. A. C. G. Mitchell (Z. Physik, 1932, 78, 138—140).—Polemical, against Schechter (this vol., 670). A. B. D. C.

Ionisation by positive ions. J. S. Townsend and F. L. Jones (Nature, 1932, 130, 398).—The energies of the positive ions in the collisions in which mols. of H_2 are ionised are of the same order as that of the electrons. L. S. T.

Reflexion of molecular beams. R. Frisch and O. Stern (Naturwiss., 1932, 20, 721).—Mol. beams of He and H_2 are reflected at cleavage surfaces of LiF and NaF with intensities which vary sharply as the reflecting surface is rotated in its own plane. A. C.

Existence of element 85. G. von Hevesy and R. Hobbie (Z. anorg. Chem., 1932, 208, 107—112).—X-Ray analysis of concentrates from pitchblende failed to reveal any lines due to element 85. It is inferred that, if the reactions of this element are similar to those of I, its concn. in pitchblende is < 1 in 10^9. E. S. H.

Fundamental at. wts. XI. At. wt. of iodine. II. O. Hönigschmid and H. Striebel (Z. anorg. Chem., 1932, 208, 53—58; cf. A., 1931, 1208).—Using AgI pptd. from aq. solution, the val. 126·917 is obtained for the at. wt. of I (from the ratio AgI : AgCl), in agreement with that obtained with synthetic AgI. E. S. H.

Radioactivity of potassium. D. Bocciarelli (Atti R. Accad. Lincei, 1932, [vi], 15, 686—693).—Further details are given showing the existence of a less intense, hard component of the β-radiation of K (cf. A., 1931, 1208). The radiation is more heterogeneous and harder than that of Rb. O. J. W.

Absorption of boron neutrons by lead. M. de Broglie and L. Leprince-Ringuet (Nature, 1932, 130, 315).—Neutrons emitted from B bombarded by α-rays from radon appear to possess less energy than neutrons from Be, and are more absorbed by Cu and paraffin wax than by Pb. Pb is transparent to neutrons from B, 5 cm. showing little or no absorption. L. S. T.

Excitation of neutrons in beryllium. F. Rasetti (Z. Physik, 1932, 78, 165—168).—The intensity of neutrons emitted from Be bombarded by Po α-rays was determined for various ranges of the α-rays. A. B. D. C.

Wave-mechanical classical model of the neutron. H. K. Kudar (Z. Physik, 1932, 78, 279—282).—Theoretical. A. B. D. C.

Range and total ionisation of α-rays in gases. M. Mäder (Z. Physik, 1932, 77, 601—615).—Ionisation in air, CO_2, and N_2 was determined for α-rays from Po; the half val. period for Po is 138 days.
A. B. D. C.

Scattering of α-particles at small angle by helium. P. Wright (Proc. Roy. Soc., 1932, A, **137**, 677—688).—The agreement between the observed scattering at 10°, 15°, and 27°, and that predicted by Taylor's theory (this vol., 106) is close enough to support the general explanation advanced by Taylor, *i.e.*, that the anomalous scattering is a consequence of the wave-mechanical scattering by the non-coulombian fields of force. L. L. B.

α-Rays of ionium. F. Soddy (Nature, 1932, **130**, 364—365).—Curves for the α-rays of ionium correlating differential ionisation current with distance show irregularities at present unexplained.
L. S. T.

Scattering of fast β-particles by electrons. F. C. Champion (Proc. Roy. Soc., 1932, A, **137**, 688—695).—In 650 m. of track of fast β-particles in N_2, photographed by the expansion method, 250 collisions with electrons have been obtained with angles of scattering $>10°$ and with β varying from 0·82 to 0·92. The abs. no. scattered and the distribution with angle were in good agreement with Möller's formula based on quantum mechanics (Z. Physik, 1931, 70, 786). L. L. B.

Absorption and scattering of hard γ-rays. C. Y. Chao (Sci. Rep. Tsing Hua Univ., 1932, **1**, 159—176).—A detailed account of work previously reported (cf. A., 1931, 142). N. M. B.

Selective transmission of γ-radiation by lead. F. L. Hopwood, T. E. Banks, and T. A. Chalmers (Nature, 1932, **130**, 506).—Experiments indicate that a substance is selectively transparent to some of the radiations emitted by its radioactive isotope.
L. S. T.

Energy exchange between inert gas atoms and a solid surface. J. M. Jackson and N. F. Mott (Proc. Roy. Soc., 1932, A, **137**, 703—717).—Theoretical. A theory of the accommodation coeff. for He on W is given, using an exponential field between the gas atom and a surface atom of the solid. Good agreement is obtained with the experimental results of Roberts (A., 1930, 1340).
L. L. B.

Conception of the chemical elements. F. Paneth (Schr. Königsberg Gelehr. Ges. Nat.-Wiss. Kl., 1931, 8, 101—125; Chem. Zentr., 1932, i, 3025).

Structure of nuclei. II. W. Heisenberg (Z. Physik, 1932, 78, 156—164).—The hypotheses previously advanced (this vol., 894) are applied to the stability of nuclei on β-ray disintegration and to the scattering of γ-radiation. An attempt to determine the "binding energy" of the electron in a neutron indicates that the neutron does not follow the laws of quantum mechanics. A. B. D. C.

Nuclear structure. H. C. Urey (Nature, 1932, **130**, 403).—A claim for priority (cf. this vol., 894).
L. S. T.

Absorption of Debye–Falkenhagen relaxation power in a neutral, partly-ionised gas (plasma, Kennely–Heaviside layer). K. F. Niessen (Physikal. Z., 1932, **33**, 705—718).—Mathematical.
W. R. A.

Molecular spectra and spectroscopic analysis. IV. Scandium. G. Piccardi and A. Sberna (Atti R. Accad. Lincei, 1932, [vi], **15**, 577—579; cf. this vol., 673).—As in the case of La and Y, Sc can be detected conveniently by means of the band spectrum of ScO. O. J. W.

Play of colours in leucite. F. Baier (Z. Krist., 1932, **83**, 141—144; cf. this vol., 359). C. A. S.

Intensity distributions in molecular spectra: Swan system (C_2). R. C. Johnson and N. R. Tawde (Proc. Roy. Soc., 1932, A, **137**, 575—591).—The difficulties of obtaining accurate measurements of the relative intensities of spectral lines or bands when these cover a wide wave-length range are discussed. The Swan system has been produced and studied from five sources, differing widely in temp. and in electrical conditions, and the peak intensities have been measured. L. L. B.

Absorption spectrum of photochemically coloured alkali halide crystals at various temperatures. E. Mollwo (Nachr. Ges. Wiss. Göttingen, 1931, 236—239; Chem. Zentr., 1932, i, 2137).—With rise of temp. the spectra are displaced towards longer wave-lengths. A. A. E.

Absorption spectra of chromium ammine hydrates. R. I. Colmar and F. W. Schwartz (J. Amer. Chem. Soc., 1932, **54**, 3204—3212).—Measurements in the visible spectrum have been made. On substitution of a H_2O mol. for an NH_3 mol. in either a Cr or Co complex (up to 4 substitutions) n, the wave no. at which max. absorption occurs, decreases by 610 $mm.^{-1}$ On substitution of a H_2O for an NH_3 mol. in a Cr complex the val. of the mol. extinction coeff., k, at the absorption max. decreases successively by 4·9 units. In Co complexes a decrease in k occurs with substitution of the first H_2O mol., but is followed by an increase for the second mol. entering. Substitution of a Co for a Cr atom in a complex reduces n by 510 $mm.^{-1}$ At the max. k is higher for Co than for the corresponding Cr compounds. Substitution of Cl for an NH_3 mol. reduces n by 1970 $mm.^{-1}$ C. C. K. (*c*)

Ultra-violet absorption of the ethylenic hydrocarbons $Ph\cdot[CH_2]_n\cdot CH{:}CH_2$. (Mme.) Ramart-Lucas and (Mlle.) P. Amagat (Bull. Soc. chim., 1932, [iv], **51**, 965—968).—Data are given for the compounds with $n=0$—5, and for $Ph\cdot CH{:}CH\cdot[CH_2]_7\cdot Me$, PhEt, and $CH_2{:}CH\cdot[CH_2]_2\cdot CH{:}CH_2$ (I). Compounds with the double linking adjacent to Ph give characteristic intense absorption bands. The other Ph compounds have absorption spectra similar to PhEt. (I) gives no bands. Compounds $Ph\cdot[CH_2]_n\cdot CH{:}CH_2$ were prepared by the action of allyl bromide on $Ph\cdot[CH_2]_{n-1}\cdot MgX$ in Et_2O at 0°. *η-Phenyl-Δ^α-heptene* has b.p. 236°/760 mm., 123°/24 mm. α-Phenylnonan-α-ol, prepared from $C_9H_{19}\cdot MgBr$ and PhCHO, gave *α-phenyl-Δ^α-decene*, b.p. 162—163°/14 mm., on warming with kieselguhr. D. R. D.

Spectral changes on ageing of mineral oils. II. Validity of Beer's law in the visible spectrum. E. Vellinger (Ann. Off. Nat. Combust. liq., 1931, 6, 225—228; Chem. Zentr., 1932, i, 2794).
A. A. E.

Absorption spectra of carbon dioxide, carbon monoxide, and water vapour in the range 600—900 A. H. J. Henning (Ann. Physik, 1932, [v], 14, 856).—Corrections to an earlier paper (this vol., 673).

Change in the infra-red reflecting power of bismuth in a magnetic field. J. C. McLennan, E. J. Allin, and A. C. Burton (Phil. Mag., 1932, [vii], 14, 508—512).—For cast Bi no change was observed between 5 μ and 8 μ. H. J. E.

New infra-red bands photographed in the absorption spectrum of acetylene. W. Lochte-Holtgreven and E. Eastwood (Nature, 1932, 130, 403).—Details of new bands at 10,164·8 and 10,369·8 Å. are recorded. L. S. T.

Molecular spectra and the effect on them of intermolecular forces. I. Strength of NH linking in gaseous, liquid, and dissolved ammonia. G. Jung and H. Gude (Z. physikal. Chem., 1932, B, 18, 380—400).—The fourth and fifth harmonics of a series of rotation–vibration bands starting from 3 μ for gaseous NH_3 are at 6474·0 and 5526·1 Å. The rotational fine structure of the fourth harmonic has been determined. In liquid NH_3 and solutions of NH_3 the third and fourth harmonics are displaced towards longer wave-lengths. With solutions the displacement, Δ, increases in a linear manner with the vol. concn., and is greater for the fourth than the third harmonic. There is no connexion between Δ and the dielectric const. of the solvent. Δ is attributed to a loosening of the N·H linking, which is most pronounced in liquid NH_3 and least in aq. NH_3.
R. C.

Infra-red region of the spectrum. VI. Absorption spectra of the dioxides of chlorine and sulphur. C. R. Bailey and A. B. D. Cassie (Proc. Roy. Soc., 1932, A, 137, 622—640).—The infra-red absorption spectrum of ClO_2 is found to be very similar to that of SO_2. The two substances are also physically alike and have similar structures. Two structures are possible, with vertices angles of approx. 60° and 120°; the available evidence is slightly in favour of the acute-angled form. The mol. characteristics for the acute-angled form are: SO_2: ν_1 1361, ν_2 524, ν_3 1152 cm.$^{-1}$ (fundamental frequencies); K_1 9·6 (S—O), K_2 1·7 (O—O) × 10^{-5} dynes/cm. (force consts.); ClO_2: ν_1 1109, ν_2 527, ν_3 946 cm.$^{-1}$; K_1 6·7 (Cl—O), K_2 1·8 (O—O) × 10^{-5} dynes/cm.; $\widehat{\mathrm{OSO}}$ 60°; S—O and O—O 1·37 Å.; $\widehat{\mathrm{OClO}}$ 60°; Cl—O and O—O 1·4 Å. For the obtuse-angled structure: SO_2: ν_1 1152, ν_2 524, ν_3 1361 cm.$^{-1}$; K_1 9·6 (S—O), K_2 3·3 (O—O) × 10^{-5} dynes/cm.; ClO_2: ν_1 946, ν_2 527, ν_3 1109 cm.$^{-1}$; K_1 6·7 (Cl—O), K_2 3·6 (O—O) × 10^{-5} dynes/cm.; $\widehat{\mathrm{OSO}}$ 122°; S—O 2·3 Å.; O—O 3·9 Å.; $\widehat{\mathrm{OClO}}$ 140°; Cl—O 2·4 Å., O—O 4·2 Å.
L. L. B.

Isotope separations in the infra-red absorption spectrum of HCl and the possible existence of a chlorine isotope of mass 39. J. D. Hardy and G. B. B. M. Sutherland (Physical Rev., 1932, [ii], 41, 471—479).—No trace of a Cl^{39} isotope was found (cf. Hettner, A., 1931, 1348); the relative abundance Cl^{35} to Cl^{39} cannot exceed 1—500. Accurate measurements of the isotope separations due to Cl^{35} and Cl^{37} are compared with theory. N. M. B.

A double band of solid hydrogen chloride. G. Hettner (Z. Physik, 1932, 78, 141—155).—The ordinary rotation–vibration doublet of HCl near 3·65 μ was investigated for the solid at 87° and 20° abs. At the lower temp. the longer wave-length branch almost vanishes; the actual shape of the doublet and sp. heat data fit neither the hypothesis of a rotating mol. in the solid, nor that of a mol. vibrating about some fixed direction, but suggest that the actual system is one intermediate between the two. A. B. D. C.

Absorption spectrum of benzene in the region of 6·75 μ. S. Silverman (Physical Rev., 1932, [ii], 41, 486—488).—The spectrum of the vapour showed three branches with evidence of unresolved fine structure. The liquid showed a less regular spectrum with a shift towards longer wave-lengths. New H_2O vapour lines in the 6·26 μ band are also reported. N. M. B.

Significance of infra-red characteristic vibrations for dielectric loss. M. Czerny and W. Schottky (Z. Physik, 1932, 78, 220—229).—The damping of infra-red characteristic vibrations (beyond 40 μ) can account quantitatively for the dielectric loss observed for very short electric waves.
A. B. D. C.

Are argon and methane molecules optically anisotropic? S. Parthasarathy (Indian J. Physics, 1932, 7, 243—249).—Transversely scattered radiations from A and CH_4 excited by polarised light were unpolarised, suggesting that the mols. oscillate as anisotropic electric dipoles in the field of the light wave. N. M. B.

Raman effect in salt solutions. A. da Silveira (Compt. rend., 1932, 195, 521—523; cf. this vol., 983).—In similar conditions the Raman spectra of saturated solutions of $(NH_4)_2SO_4$, NH_4NO_3, and NH_4Cl have been measured. New lines attributed to SO_4'' (possibly suppression of degeneration) are 553 and 683 cm.$^{-1}$, whilst three lines at or near 1116, 1300, and 1460 (1116 and 1351 only in the nitrate) are due to $NH_4^{\cdot}$. C. A. S.

Raman effect in aqueous nitrate solutions. P. Grassmann (Z. Physik, 1932, 77, 616—631).—A study of the Raman displacement near 1050 cm.$^{-1}$ due to aq. solutions of H, Li, Na, NH_4, K, Ag, Mg, Ca, Cu, Zn, Cd, Ba, and Pb nitrates, and of the displacement near 720 cm.$^{-1}$ due to Li, NH_4, Na, Ag, Mg, Ca, Cd, and Pb nitrates. A. B. D. C.

Spectroscopic evidence for the existence of the hydroxonium ion $(H_3O)^+$. Raman effect for perchloric acid and perchlorates. Z. Ollano (Z. Physik, 1932, 77, 818—822).—Raman displacements were obtained for $NaClO_4$, $KClO_4$, NH_4ClO_4, and $HClO_4$. The displacements 1118, 936, 627, and

461 cm.$^{-1}$ are ascribed to ClO_4^-. Displacements near 3580 cm.$^{-1}$ are ascribed to the ions $(H_3O)^+$ and $[H(H_2O)_n]^+$ in the aq. solutions. A. B. D. C.

Raman spectra of dimethyl ether, diethyl ether, and heptane. S. C. Sirkar (Indian J. Physics, 1932, 7, 257—272).—Full data and comparisons with infra-red absorption curves are reported. Me_2O shows new lines at 333 and 416 cm.$^{-1}$ N. M. B.

Raman spectrum of some aniline derivatives. G. B. Bonino and P. Cella (Atti R. Accad. Lincei, 1932, [vi], 15, 568—572).—The Raman spectra of benzylidene-, *p*-chlorobenzylidene-, and benzylidene-*p*-chloro-aniline, and of benz-anilide and -*p*-toluidide have been measured. The presence of a C:N linking in the mol. corresponds with the appearance of one or two lines between 1400 and 1500 cm.$^{-1}$ O. J. W.

Raman spectrum of Δ^2-dihydronaphthalene. G. B. Bonino and P. Cella (Atti R. Accad. Lincei, 1932, [vi], 15, 572—576).—The lines found in the Raman spectrum of the above substance are in complete accordance with its structural formula (cf. deca- and tetra-hydronaphthalene, this vol., 7). O. J. W.

Raman spectra of naphthalene derivatives. S. Ziemecki (Z. Physik, 1932, 78, 123—132).—The Raman spectra of naphthalene, 1- and 2-methyl-, -chloro-, and -bromo-naphthalene all show the characteristic displacement 1377 cm.$^{-1}$; they also show displacements 3058 and 1575 cm.$^{-1}$, although these vary in position with the derivative. A. B. D. C.

Raman effect with terpenes. II. Monocyclic terpenes. G. Dupont, P. Daure, and J. Lévy (Bull. Soc. chim., 1932, [iv], 51, 921—932).—Data are given for *p*-cymene, limonene, carvomenthene, menthane, sylvestrene, Δ^1-*m*-menthene, and α- and β-phellandrene. D. R. D.

[Ionic] emission of glasses of the composition $B_2O_3+Na_2O$. H. Bolling (Physikal. Z., 1932, 33, 625—632).—The emission of these glasses at 160—230° decreases at first with time, reaching finally an almost const. val. This variation is dependent on an internal lattice change and on a surface phenomenon which is modified by moisture, the latter increasing the emission. The emission rises with temp., but preheating to a higher temp. lowers the subsequent emission at a lower temp. Recovery is observed on keeping. Increased Na content raises the emission. J. W. S.

Line emission and absorption of chromium phosphors. I, II. O. Deutschbein (Ann. Physik, 1932, [v], 14, 712—728, 729—754).—I. The prep. of several phosphors is described. Their spectra were investigated. As a phosphor, Cr acts differently from the rare-earth elements, for emission and absorption spectra agree.

II. The light emission from many substances containing Cr, and the phosphorescence of some artificial and natural minerals were studied. Cr causes emission only if Cr_2O_3 is isomorphous with the principal substance, or if it occurs as a large mol. in the lattice. The emission and absorption spectra were determined at 20° and −195°. The Raman spectrum of a synthetic, colourless corundum was investigated. A. J. M.

Influence of carbon tetrachloride and of phosphorus oxychloride on the maximum oxygen pressure at which the chemiluminescence of white phosphorus commences. F. Schacherl (Gazzetta, 1932, 62, 610—621).—CCl_4 lowers, $POCl_3$ raises, the max. O_2 pressure (p) at which chemiluminescence of P begins. In presence of $POCl_3$ vapour alone, there is no chemiluminescence. The variation of p with the concn. of the added substance, x, is given by $p_{15^\circ}=533-835x$ and $p_{20^\circ}=678-1245x$ for CCl_4, and $p_{20^\circ}=16{\cdot}5/(0{\cdot}021-x)$ for $POCl_3$. The formation of P_4O by the action of P on $POCl_3$ may explain the favourable action of the latter. O. J. W.

Fluorescence. A. Kutzelnigg (Z. anorg. Chem., 1932, 208, 29—32).—Under the influence of ultra-violet light (with visible rays excluded) solid CO_2 has a bright bluish-violet fluorescence. A feeble effect is observed with MgO, but the MgO obtained by heating a solution in molten NH_4NO_3 (cf. this vol., 1099) gives a strong scarlet fluorescence. CuI in contact with the pptn. liquid fluoresces with a violet colour, but after washing the effect is red. Films of CuI on a Cu surface give a dark red fluorescence after a time or after mechanical working. Hydrosols of anthracene, prepared by pouring an EtOH solution into H_2O, show the fluorescence of massive anthracene. $ZnMe_2$ and $ZnEt_2$ have a weak bluish fluorescence. No effect was observed with pure As_2O_3 or Al_2O_3. E. S. H.

Necrobiotic rays. W. W. Lepeschkin (Science, 1932, 76, 168).—Ultra-violet rays emitted by dying cells are designated necrobiotic rays. Some of these rays, which are observed by means of a suspension of AgBr, have a wave-length shorter than that of any known ultra-violet rays. L. S. T.

Hallwachs effect in compounds of elements with double valency. A. Pochettino (Atti R. Accad. Lincei, 1932, [vi], 15, 505—509).—Measurement of the Hallwachs effect in many pairs of compounds containing an element with a variable valency shows that the effect is always greater, for a given pair of compounds, in that one in which the variable valency is lower, irrespective of the sign of the radical in which the element with variable valency is present, *e.g.*, $K_4Fe(CN)_6 > K_3Fe(CN)_6$, $FeCl_2 > FeCl_3$. The direct connexion between the Hallwachs effect and photo-chemical oxidation is not certain. O. J. W.

Life of excited NO_2. O. Heil (Z. Physik, 1932, 77, 563—566).—Excited NO_2 is shown to have a life period of 10^{-5} sec. A. B. D. C.

Photo-ionisation of the vapours of anthracene and diphenylamine. E. C. Allberry (Phil. Mag., 1932, [vii], 14, 400—404).—No evidence of photo-ionisation was found (cf. A., 1909, ii, 778). H. J. E.

Conditions necessary for production of an independent photo-electric potential. H. Teichmann (Z. Physik, 1932, 78, 21—25).—Becquerel, Hallwachs, internal photo-electric, barrier layer photo-electric, and crystal photo-electric potentials are ascribed to the potential barrier existing at an interface separating media with different distributions of possible electronic levels. A. B. D. C.

Influence of humidity and temperature on the characteristics of discharges in an electro-filter. S. P. Žebrowski (Physikal. Z., 1932, **33**, 727—729). W. R. A.

Use for the titanium photo-electric cell. J. W. Marden and K. O. Smith (Trans. Electrochem. Soc., 1932, **62**, 237—244).—Erythemogenic strengths of Hg discharge lamps can be closely estimated by means of the Ti photo-electric cell. H. J. T. E.

Chromium–selenium photo-voltaic cells. C. G. Fink and D. K. Alpern (Trans. Electrochem. Soc., 1932, **62**, 305—313).—A sensitivity of 150 micro-amp. per lumen has been obtained with commercial forms of the cells. The max. colour response depends somewhat on conditions of prep., but a typical val. is 5100 Å. The relationship between photo-voltaic cells and vac. and gas photo-electric cells is discussed. H. J. T. E.

Effect of a superimposed magnetic field on the dielectric properties of some solid, liquid, and gaseous bodies. R. Schmid (Ann. Physik, 1932, [v], **14**, 809—830).—The effect of a superimposed magnetic field on the dielectric current in liquids, the disappearance angle for solid insulators, and the breakdown potential of air at atm. pressure were investigated. A. J. M.

Electrolytic valve action. V. Properties of sparks. A. Günther-Schulze and H. Betz (Z. Physik, 1932, **78**, 196—210; cf. A., 1931, 546, 1130).—The size, duration, and spectral properties of the minute sparks formed with Al and Ta in borax solutions were studied, and estimates are given of the quantity of electricity transported by these sparks. A. B. D. C.

Electrical conductivity of barium oxide in relation to electron emission. W. Meyer and A. Schmidt (Z. tech. Physik, 1932, **13**, 137—144; Chem. Zentr., 1932, i, 2934).

Electric dipole moment of nickel carbonyl. L. E. Sutton and J. B. Bentley (Nature, 1932, **130**, 314).—The total and the electron polarisations of $Ni(CO)_4$ in CCl_4 at 0° are 39·5 and 37·3 c.c., respectively. The apparent orientation polarisation of 2·2 c.c. gives a max. val. of $0{\cdot}3\times10^{-18}$ e.s.u. for the electric dipole moment. As this is of the order expected for the atom polarisation of such a mol., the moment is taken to be zero. The structure, which must be symmetrical and not cyclic, is discussed. L. S. T.

Electric moments of acetone, acetaldehyde, acetyl chloride, chloroacetone, and chloroacetyl chloride. C. T. Zahn (Physikal. Z., 1932, **33**, 686—687).—Observed vals. for $COMe_2$, MeCHO, and AcCl are compared with vals. calc. by the method of Eucken and Meyer. Discrepancies are explained as arising from deformation of the tetrahedral symmetry. The val. obtained for CH_2ClAc is intermediate between the calc. vals. for a mol. with free rotation and a *trans* mol., and the val. depends on the temp. $CH_2Cl{\cdot}COCl$ gives a val. in good agreement with the theoretical val. Measurements were made on the vapours of these compounds at different temp.; except for CH_2ClAc, μ is independent of temp. W. R. A.

Dipole moments of unsaturated compounds. I. I. M. A. Bruyne, R. M. Davis, and P. M. Gross (Physikal. Z., 1932, **33**, 719—724).—Dipole moments of dichloropropylene, dichloro*iso*butylene, and trichloroethylene are 1·73, 2·01, and $0{\cdot}94\times10^{-18}$, respectively. Vals. calc. by a new method are compared with observed vals. and with vals. calc. by the method of Eucken and Meyer for 28 unsaturated hydrocarbon derivatives. W. R. A.

Electric moments of certain fatty acid esters. C. T. Zahn (Physikal. Z., 1932, **33**, 730—731).—Electric moments of the vapours of HCO_2Et, EtOAc, MeOAc, and amyl formate and acetate are uninfluenced by temp. Vals. calc. by different methods are compared with experimental results. W. R. A.

Dependence of measured dipole moments on the solution media. H. Müller (Physikal. Z., 1932, **33**, 731—732).—The polarisation at infinite dilution of PhCl for seven different solvents is given. Vals. of P_2 vary from 86·5 to 76. W. R. A.

Magnetic rotation dispersion of nickel tetracarbonyl. J. Verhaeghe (Bull. Acad. roy. Belg., 1932, [v], **18**, 532—539).—The variation of refractive index and magnetic rotation of $Ni(CO)_4$ between 4000 and 7000 Å. have been determined; the results indicate that the electrons effective in the magneto-optical rotation are the valency electrons of Ni. A. B. D. C.

Faraday effect in molecules. R. Serber (Physical Rev., 1932, [ii], **41**, 489—506).—Mathematical. The effect when the frequency of the incident light is near resonance or well removed from resonance with absorption lines of the mol. is examined. In the former case the mol. rotation, independence of spin, and magnitude of rotation and comparison with experiment, and in the latter case perturbation of energies by the magnetic field, with special reference to I vapour and the alkali metals, are considered. N. M. B.

Diamagnetic susceptibility of inorganic compounds. II. $Cu^{\cdot}$, $Ag^{\cdot}$, $Au^{\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, and $Hg_2^{\cdot\cdot}$ ions. K. Kido (Sci. Rep. Tôhoku, 1932, **21**, 288—297).—The vals. found for the ionic susceptibilities ($-\chi_{ion}\times10^6$) are: $Cu^{\cdot}$ 16·0, $Ag^{\cdot}$ 26·2, $Au^{\cdot}$ 44·8, $Zn^{\cdot\cdot}$ 12·8, $Cd^{\cdot\cdot}$ 20·3, $Hg^{\cdot\cdot}$ 36·6, $Hg_2^{\cdot\cdot}$ $2\times40{\cdot}3$ and CN′ 16·6. The relation between χ_{ion} and the no. of electrons in the ion (n) is $\chi_{ion}=-c\,.\,n\times10^{-6}$; the const. c is 0·6 for the Cu group and 0·46 for the Zn group. The difference in the susceptibilities of $Hg_2^{\cdot\cdot}$ and $Hg^{\cdot\cdot}$ is attributed to a diamagnetic effect of the shared electrons in $Hg_2^{\cdot\cdot}$. A. R. P.

Nature of ferromagnetism. F. Bitter (Physical Rev., 1932, [ii], **41**, 507—515).—Irregularities in the magnetisation of ferromagnetic crystals were studied by means of magnetic Fe_2O_3 particles suspended in EtOAc. The patterns of the particles on Fe, Ni, and Co crystals were observed. N. M. B.

Magnetic analysis of molecular orientations in crystals. K. S. KRISHNAN (Nature, 1932, 130, 313).—Correlation of magnetic consts. of a diamagnetic crystal with those of the individual mols. gives the mol. orientations in the crystal. This method is applied to diphenyl and dibenzyl. L. S. T.

Theory of induced polarity in benzene. A. LAPWORTH and R. ROBINSON (Nature, 1932, 130, 273).—A further discussion (cf. this vol., 795). L. S. T.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1932, [v], 18, 578—595; cf. A., 1930, 277, 853; 1931, 685, 1106, 1127, 1215, 1356).—Mathematical. J. W. S.

Surface tensions of ethyl ether, acetone, toluene, and methyl alcohol at low temperatures. T. TONOMURA and K. CHUJO (Bull. Chem. Soc. Japan, 1932, 7, 259—264).—The surface tensions between 30° and −100° of Et_2O, $COMe_2$, and PhMe were measured in a capillary tube. Results fit formulæ of the Eötvös type, $\gamma(M/d)^{2/3}=A(\tau+B)$. The surface tension of MeOH does not fit this expression, probably on account of association. A. G.

Quantitative measurements with the multiple interference spectroscope. P. GÖRLICH and E. LAU (Z. Physik, 1932, 77, 746—751). A. B. D. C.

Asterisms in X-ray diagrams. W. BERG (Z. Krist., 1932, 83, 318—322; cf. A., 1931, 782).—A qual. explanation of how these are caused in Laue diagrams by distortion of the crystals. C. A. S.

Influence of divergence [of radiation], thickness of substance examined, and depth of penetration on precision of lattice dimensions [determined] by the Debye–Scherrer method. F. LIHL (Z. Krist., 1932, 83, 193—221).—Corrections due to these causes in the localisation of the centre of the lines are calc. and practical applications given (cf. A., 1931, 1217). C. A. S.

Structure of polished solids. L. HAMBURGER (Nature, 1932, 130, 435—436).—A discussion. L. S. T.

Scattering of X-rays and cathode rays in free molecules. L. BEWILOGUA (Physikal. Z., 1932, 33, 688—692).—Theoretical. Experimental data on C_6H_6 and CCl_4 are discussed. W. R. A.

Method for deducing accurate values of the lattice spacing from X-ray powder photographs taken by the Debye–Scherrer method. A. J. BRADLEY and A. H. JAY (Proc. Physical Soc., 1932, 44, 563—579).—By the use of a calibration and an extrapolation process it is possible to eliminate many errors in deducing lattice spacing from X-ray photographs. A. J. M.

Closest spherical packing of higher orders. E. K. BROCH (Z. Physik, 1932, 78, 257—270).—Lattices of closest spherical packing with layer periodicities greater than the hexagonal 2, or cubic 3, and their possible interference patterns, are discussed. A. B. D. C.

Crystals as continuous media. A. V. SCHUBNIKOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 6, 799—815).—An exposition of the theories of the author (Z. Krist., 1929, 72, 271; 1930, 73, 430). R. T.

Crystallisation of thin films of salol and of benzophenone. I. V. KROTOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 6, 817—828).—The stability of supercooled liquid films of salol or $COPh_2$ is proportional to the smoothness of the supporting surface, but is independent of its nature (Cu, Ni, glass, wood, paper). The velocity of crystallisation of seeded films is independent of both the nature and the smoothness of the surface. R. T.

Applicability of the statistical method to ionic lattices. W. LENZ (Z. Physik, 1932, 77, 713—721).—Theoretical. The Thomas–Fermi method is applied to lattices of ions with many electrons. A. B. D. C.

Separation of the α-phase in β-brass. M. STRAUMANIS and J. WEERTS (Z. Physik, 1932, 78, 1—17).—The formation of the face-centred cubic α-phase from the body-centred β-phase subjected to various heat-treatments has been examined by X-ray and microscopical methods. A. B. D. C.

Determination of molecular structure by means of electron diffraction. III. Formaldehyde. IV, and V. Dimethyl ether and diethyl ether. L. BRÚ (Anal. Fís. Quím., 1932, 30, 483—485, 486—491).—III. The distance between the C and O atoms of the CO group of CH_2O is $1{\cdot}15\pm0{\cdot}05$ Å.

IV, V. The distance between the C and O atoms is $1{\cdot}34\pm0{\cdot}06$ Å. for Me_2O, and $1{\cdot}33\pm0{\cdot}08$ Å. for Et_2O. The angle formed by the two alkyl groups and the O atom is 100°. H. F. G.

X-Ray determination of size and form of crystals of carbon. U. HOFMANN and D. WILM (Z. physikal. Chem., 1932, B, 18, 401—416).—Examination of various forms of C, including technical activated C, has shown that each has the graphite lattice without essential modification. For a given variety the crystal size rises with the temp. of formation. The CO crystals of C obtained by decomp. of Fe carbide are, however, considerably greater even at 400° than C crystals formed by dissociation of benzine vapour at 950°. The crystals of highly active C are comparable in size with single large org. mols., so that the no. of mols. which can be adsorbed on a single crystal will often be small. With activated C, in which the surfaces of almost all the crystals are available for adsorption, the adsorbing surface calc. from the dimensions of the crystals agrees with the val. deduced from observations on the adsorption of dissolved substances. R. C.

Crystal structure of yttrium. L. L. QUILL (Z. anorg. Chem., 1932, 208, 59—64).—The following data have been determined: a $3{\cdot}663\pm0{\cdot}008$, c $5{\cdot}814\pm0{\cdot}012$ Å., c/a 1·588, d (calc.) 4·34. E. S. H.

Determination of lattice constant of titanium carbide. M. VON SCHWARZ and O. SUMMA (Z. Elektrochem., 1932, 38, 743—744).—TiC crystallises in the rock-salt type of the cubic system; the lattice const. is 4·311 Å. E. S. H.

Transformation of magnetite at a low temperature. T. OKAMURA (Sci. Rep. Tôhoku, 1932,

21, 231—241).—Sudden changes which occur in the thermal expansion, electric resistance, and magnetic properties of magnetite at −158° to −166° are attributed to an allotropic transformation. No change in the lattice structure can be detected.
A. R. P.

Lattice constants of α-Fe_2O_3 and of γ-Al_2O_3. R. Brill (Z. Krist., 1932, **83**, 323—325).—α-Fe_2O_3 [from $Fe(CO)_5$] has *a* 5·429 Å., α 54° 58′ (cf. A., 1930, 1361). γ-Al_2O_3 has *a* 7·91 Å., and like γ-Fe_2O_3 has the spinel structure (cf. this vol., 113). C. A. S.

Structure of hydroxides and hydrates. IV. Strontium peroxide octahydrate. G. Natta (Gazzetta, 1932, **62**, 444—456; cf. A., 1929, 244).—*X*-Ray analysis by the powder method shows that $SrO_2,8H_2O$ crystallises in the tetragonal system with a unit cell containing 1 mol. (*a* 6·32, *c* 5·56 Å., *c*/*a* 0·88), and belongs to the space-group D_4^1. The co-ordinates of the ions are: Sr$^{\cdot\cdot}$ (0,0,0), O_2'' of peroxide $(\frac{1}{2},\frac{1}{2},u')$ $(\frac{1}{2},\frac{1}{2},\bar{u}')$, O'' of H_2O (u,u,v) $(\bar{u},u,v)$ $(u,\bar{u},v)$ $(\bar{u},\bar{u},v)$ $(\bar{u},\bar{u},\bar{v})$ $(u,\bar{u},\bar{v})$, $(\bar{u},u,\bar{v})$ $(u,u,\bar{v})$, where $u' = 0·10$, $u = 0·20$, $v=0·25$. The radius of the O'' ion in H_2O mols. is calc. to be 1·30 Å. In the O_2'' ion of the peroxide the distance between the two O atoms is less than the diameter of the neutral atom. O. J. W.

Structure of lead chloride. H. Brækken (Z. Krist., 1932, **83**, 222—226; cf. A., 1929, 631).—Revised results are: for the unit cell *a* 4·525, *b* 7·608, *c* 9·030 Å.; each Pb atom is surrounded by 9Cl, which form a kind of double octahedron; Cl—Cl =3·4—4·1; Pb—Cl=2·8—3·5 Å. C. A. S.

Structures of potassium and rubidium dithionates. G. Hägg (Z. Krist., 1932, **83**, 265—273).—$K_2S_2O_6$ and $Rb_2S_2O_6$ crystallise in space-group D_3^2 with 3 mols. in the unit cell and, respectively, *a* 9·756, *c* 6·274, and *a* 10·144, *c* 6·409 Å. (cf. A., 1931, 1113); $Rb_2S_2O_6$ has *d* 2·89. The S_2O_6 group has a trigonal axis of symmetry, but the three such groups in the unit cell are not structurally equiv. $K_2S_2O_6$ and $Tl_2S_2O_6$ do not form mixed crystals (cf. A., 1905, ii, 390), nor was it possible partly to replace Rb by Cs in $Rb_2S_2O_6$. Huggins and Frank's proposed structure (cf. Amer. Min., 1931, **16**, 580) is not confirmed. C. A. S.

Crystal structure of double salts with different anions. H. Seifert (Z. Krist., 1932, **83**, 274—300).—A discussion on the structure and growth of crystals of such salts with special reference to the layer structure as found in compounds such as the humite, staurolite, chlorite, and parisite groups (cf. A., 1930, 280, 528, 1396; 1931, 1218); also on types transitional between these and the zeolites, *e.g.*, apatite, apophyllite, etc. (cf. A., 1931, 671; this vol., 494). C. A. S.

Structures of calcium chromate and its mono- and di-hydrates. J. H. Clouse (Z. Krist., 1932, **83**, 161—171).—$CaCrO_4$ is tetragonal, and not isomorphous with $CaSO_4$, but is so with $ZrSiO_4$ and YPO_4 (cf. A., 1881, 352). Its unit cell has *a* 7·25, *b* 6·34 Å., and contains 4 mols., space-group D_{4h}^1 (*I*4/*amd*); d^{20} 3·12. Each Cr is surrounded tetrahedrally by 4O at 1·64 Å., and each Ca by 8O at 2·45 Å. $CaCrO_4,H_2O$ is rhombic, *a* 7·99, *b* 12·77, *c* 8·11 Å., with 8 mols. in the unit cell, space-group V_h^{15} (*Pcab*). β-$CaCrO_4,2H_2O$ (prepared by evaporating at room temp. conc. aq. Na_2CrO_4 to which a little $CaCl_2$ has been added) is rhombic, *a* 16·02, *b* 11·39, *c* 5·60 Å., with 8 mols. in the unit cell, space-group V_h^{11} (*Pcmb*), *d* 2·50. C. A. S.

Isomorphism of borates and carbonates. V. M. Goldschmidt and H. Hauptmann (Nachr. Ges. Wiss. Göttingen, 1932, 53—72; Chem. Zentr., 1932, i, 2678).—$ScBO_3$, $InBO_3$, and YBO_3, space-group D_{3d}^6, have 2 mols. in the rhombohedral cell, and 12 in a larger (non-unit) hexagonal cell. Vals. of *a* (hexag.), *c* (hexag.), *a* (rhombohed.), α, $d_{calc.}$, and *H* are, respectively: 4·747±0·01, 4·766±0·01, 5·06±0·05 Å.; 15·274±0·04, 15·455±0·04, 17·21±0·15 Å.; 5·782±0·015, 5·841±0·015, 6·44±0·06 Å.; 48° 28′, 48° 10′, 46° 17′; 3·451, 5·576, —; 7, 6·5, —. $LaBO_3$ is rhombic; space-group V_h^{16}, with 4 mols. in the unit cell: *a* 5·10±0·01, *b* 8·22±0·02, *c* 5·83±0·01 Å.; $d_{calc.}$ 5·339, *H* 5. The structure of orthoborates of tervalent metals is very similar to that of carbonates of bivalent metals. A. A. E.

Structure of sillimanite and related materials. W. H. Taylor (J. Soc. Glass Tech., 1932, **16**, 111—120T).—The co-ordination no. of corresponding Al atoms is 4, 5, and 6 in sillimanite, andalusite, and cyanite, respectively. The close resemblance of sillimanite and mullite is due to the fact that one SiO_4 group per unit cell of sillimanite is replaceable by one AlO_4 group in mullite. The fibrous component of porcelain, "porcelainite," is distinct from mullite and sillimanite. J. A. S.

Crystal structure of bronzite from Chichi-jima in the Bonin islands. K. Takane (Proc. Imp. Acad. Tokyo, 1932, **8**, 308—311).—The dimensions of the unit cell are a_0 18·16, b_0 8·84, c_0 5·19 Å.; $a : b : c = 2·0543 : 1 : 0·5871$; the unit cell contains 16 mols. of $15·5FeSiO_3+84·5MgSiO_3$. P. W. C.

Equiline and folliculine. C. Gaudefroy (Compt. rend., 1932, **195**, 523—524; cf. this vol., 547).—The unit cell of equiline has *a* 6·42, *b* 9·06, *c* 23·5 Å., for folliculine *a* 7·84, *b* 10·0, *c* 10·2 Å. Corrected axial ratios (goniometric) are 0·720 : 1 : 2·61, and 0·776 : 1 : 1·826, respectively. C. A. S.

***X*-Ray study of prehnite and lawsonite.** B. Gossner and F. Mussgnug (Zentr. Min. Geol., 1931, *A*, 419—423; Chem. Zentr., 1932, i, 1874).—Prehnite has *a* 4·65, *b* 5·52, *c* 18·53 Å.; *d* 2·925; the unit cell contains 2 mols. of $Ca_2(SiO_3)_3(AlOH)\cdot AlO_2H$; space-group V_h^7 or C_{2v}^4. Lawsonite has *a* 5·87, *b* 8·85, *c* 13·22 Å.; the unit cell contains 4 mols. of $Ca(SiO_3)_2(AlO_2H_2)_2$; space-group probably V_h^{17}. A. A. E.

Crystal structure of pyrrhite. F. Machatschki (Zentr. Min. Geol., 1932, 33—37; Chem. Zentr., 1932, i, 2702).—Pyrrhite has *a* 10·41±0·02 or 10·37 Å.; it is classed with the pyrochlores, and its composition corresponds with $(Ca,Na,Fe)_2(Nb,Ta,Ti)_2(O,OH,F)_7$.
A. A. E.

Crystal structure of iodoform. M. L. Huggins and B. A. Noble (Amer. Min., 1931, **16**, 519—525).—The hexagonal unit cell has *a* $6·81_8$, *c* $7·52_4$ Å., and contains 2 mols.; space-group C_6. Ch. Abs.

[Crystal structure of] triphenylbismuthine dichloride. G. Greenwood (Amer. Min., 1931, 16, 473—483).—Holoaxial symmetry is confirmed; $a:b:c=0\cdot7743:1:0\cdot4115$; d 1·908; space-group V^2. The unit cell contains 8 mols. Ch. Abs.

***X*-Ray investigation of colour dimorphism among stilbene derivatives.** E. Hertel and K. Schneider (Z. physikal. Chem., 1932, **B**, 18, 436—440; cf. A., 1916, i, 24).—The unit cell of the stable red form of *o*-nitro-*p*-cyano-*p'*-methoxystilbene has I_a 8·50, I_b 7·45, and I_c 13·35 Å., and contains 2 mols. This form is to be regarded as a unimol. mol. compound without dipole association. The metastable yellow form has I_a 14·2, I_b 27·8, and I_c 7·6 Å., the constituent units of the lattice being double mols. formed by dipole association at the OMe groups. R. C.

Highly polymerised compounds. LXXI. *X*-Ray examination of polyoxymethylenes of high mol. wt. E. Sauter (Z. physikal. Chem., 1932, **B**, 18, 417—435).—Results previously reported for β-polyoxymethylene are confirmed (A., 1927, 647). The most probable space-groups are C_3^{2-3}. Examination of a γ-polyoxymethylene with an average degree of polymerisation of 100 has shown that it is impossible to determine the degree of polymerisation by *X*-ray examination. Polyoxymethylene glass, obtained by polymerisation of liquid CH_2O in O_2 at −80°, has a macromol. lattice (cf. A., 1930, 1241). R. C.

Paracrystalline and crystalline 1-anisylideneamino-4-benzeneazonaphthalene. F. Rinne (Z. Krist., 1932, 83, 227—242).—This compound melts to an isotropic fluid at 150°; on slow cooling it passes into a paracryst. phase at 110°, and then into α- and (below 75°) into β-spherulites, the individual crystals of which show respectively oblique and straight extinction. *X*-Rays show the α- and β-spherulites (m.p. 150·5—151°) to have identical structures, their relationship being that of mimetic isomerism, as boracite. The paracryst. phase has the ordinary nematic structure. The changes are well shown by reason of the different colours of the phases. C. A. S.

***X*-Ray interpretation of the molecular structure of feather keratin.** W. T. Astbury and T. C. Marwick (Nature, 1932, 130, 309—310).—Details of the mol. interpretation of feather keratin are given and its bearing on protein analysis is discussed. L. S. T.

***X*-Ray investigation of subcrystalline materials.** R. D. Miles (J.S.C.I., 1932, 51, 247—255T).—Suitable types of *X*-ray tubes are described and their efficient operation is discussed. An account is given of the various types of *X*-ray diagram which are yielded by the organised fibres, crystal powders, glasses, and liquids. The significance of these diagrams is indicated. Investigation has shown that the spiral structure of the cotton fibre is present in the fibre in the boll, before the convolutions are formed. Mercerisation of ordinary cotton under tension yields a fibre of which the *X*-ray diagram shows no sign of spiral structure. The main results of the *X*-ray examination of cellulose nitrate and rubber are reviewed.

Theory of association in dielectric liquids. M. Wolfke (Spraw. Prace Polsk. Towarz. Ficyz., 1930, 5, 157—167; Chem. Zentr., 1932, i, 3038).—A statistical theory is developed. Association of two dipolar mols. may occur with resulting zero moment, or with doubling of the electric moment. A. A. E.

Internal Barkhausen effect. S. Procopiu (Bull. Acad. Sci. Roumaine, 1932, 15, 84—86).—An explanation of the observations of von Hippel and Stierstadt (A., 1931, 790) is offered.

Hall effect in beryllium. A. Ciccone (Nature, 1932, 130, 315).—99·5% Be gave a val. +0·0024±0·0001 for the Hall coeff. L. S. T.

Influence of plastic deformation on the susceptibility of dia- and para-magnetic metals. A. Kussmann and H. J. Seemann (Z. Physik, 1932, 77, 567—580).—Plastic deformation influences the susceptibility of Cu, Ag, Bi, and Pb, but not that of Al, Au, Zn, W, Mo, and Cu–Zn–Ni alloys; the observed effects are due entirely to ferromagnetic impurities, which in the first series of metals can separate out as ferromagnetic particles. A. B. D. C.

Anomalous behaviour of the magnetic permeability of iron in high frequencies. G. R. Wait (Z. Physik, 1932, 77, 695—698).—Eddy currents may apparently change the permeability of Fe with frequency, but no real effect has been observed (cf. Malov, this vol., 449; Arkadiev, *ibid.*). A. B. D. C.

Change in electrical resistance of magnetostrictive metals in magnetic fields. II. T. Gnesotto (Atti R. Ist. Veneto Sci. Lett. Art., 1931, 90, 1153—1163).

Slipping and consolidation in single zinc crystals. M. Straumanis (Z. Krist., 1932, 83, 29—34). C. A. S.

Plasticity of rock-salt and sylvite. F. Rinne and W. Hofmann (Z. Krist., 1932, 93, 56—74; cf. A., 1930, 1243). C. A. S.

Relaxation period of the vibrational energies of CO_2 and N_2O. H. O. Kneser and J. Zühlke (Z. Physik, 1932, 77, 649—652).—The dispersion of sound waves in N_2O was measured, the relaxation period being 10^{-6} sec.; the dispersion curves indicate that the transverse vibration is the principal factor in the vibrational sp. heat. A. B. D. C.

Thermo-electric power of single-crystal bismuth near the m.p. A. Soroos (Physical Rev., 1932, [ii], 41, 516—522).—In the region from the m.p. to about 8° above it the thermo-electric power gradually changes from that characteristic of the solid to that characteristic of the final liquid state, indicating a persistence of a crystal structure into the liquid state. N. M. B.

Viscosity of molten sodium chloride. E. van Aubel (Bull. Acad. roy. Belg., 1932, [v], 18, 692—695).—Using the viscosity data of Dantuma, the internal friction of molten NaCl has been estimated between 816° and 997°. The crit. density is 0·509. W. R. A.

Viscosity of nitrobenzene. A. van Itterbeek (Nature, 1932, 130, 399—400; cf. this vol., 899, 905).—Viscosity curves for pure $PhNO_2$, determined by the oscillating-disc method, are linear with no discontinuous transition point. $PhNO_2$ containing H_2O as impurity gives 2 linear curves which intersect at approx. 9·6°, indicating that the results obtained by Mazur (A., 1931, 148) must be attributed to insufficient drying. Compared with other methods the oscillating-disc method provides, for relative measurements, very accurate results. L. S. T.

Influence of a magnetic field on the viscosity of oxygen. H. Engelhardt and H. Sack (Physikal. Z., 1932, 33, 724—727).—With the help of an "aërodynamic Wheatstone bridge" the influence of a magnetic field between 0 and 2000 gauss on the viscosity of O_2, air, and N_2 was studied. The viscosity of O_2 is influenced considerably by the pressure, of air only slightly, and of N_2 not at all. W. R. A.

Limiting values of physical observations. F. Ehrenhaft (Physikal. Z., 1932, 33, 673—682).—The determination of the wt. and charge of some submicroscopic bodies and experiments on photophoresis are discussed. W. R. A.

Precipitated sulphur. A. Nielsen (Dansk Tidsskr. Farm., 1932, 6, 177—181).—The solubility of pptd. S in C_6H_6, olive oil, and other org. solvents is identical with that of rhombic S; hence the particles in pptd. S consist of rhombic S in a microcryst. state. H. F. H.

Vapour pressure of rhenium heptoxide and vapour pressure and dissociation pressure of rhenium octoxide. E. Ogawa (Bull. Chem. Soc. Japan, 1932, 7, 265—273).—The following data have been obtained for Re_2O_7 and Re_2O_8. V.p. of solids: $\log P=-7217{\cdot}95/T+14{\cdot}83866$; $\log P=-1738{\cdot}74/T+5{\cdot}48512$. V.p. of liquids: $\log P=-3920{\cdot}13/T+9{\cdot}04668$; $\log P=-924{\cdot}18/T+3{\cdot}54384$. M.p. 297° and 145°, b.p. of Re_2O_7 363°. Heats of sublimation 33,050 g.-cal. (230—295°) and 7960 g.-cal. (100—140°). Heats of evaporation 17,950 g.-cal. (300—360°) and 4230 g.-cal. (160—220°). Heats of fusion 14,610 and 2500 g.-cal. Dissociation pressure of Re_2O_8, $\log P=-416{\cdot}08/T+1{\cdot}73877$. A. G.

F.p. of "*iso*octane" (ββδ-trimethylpentane). J. H. Bruun and M. M. Hicks-Bruun (Bur. Stand. J. Res., 1932, 9, 269—270).—The f.p. of pure *iso*octane is −107·41°; the purity of a commercial sample is given by $3{\cdot}86t_F+514{\cdot}8$, where t_F is the initial f.p. in ° C. W. R. A.

Latent heats and heat conductivities of some aqua-crystalline compounds. K. R. Sturley (J.S.C.I., 1932, 51, 271—273T).—The latent and sp. heats of $Na_2S_2O_3$, NaOAc, and K alum are given and the methods of obtaining them described.

Specific heats of ammonium salts. J. L. Crenshaw and I. Ritter (Z. physikal. Chem., 1932, B, 19, 84).—In a previous paper (this vol., 453) the data given for NH_4CN refer to NH_4CNS.

M.p. of benzene. A. W. Menzies and D. A. Lacoss (J. Physical Chem., 1932, 36, 1967—1968).—The val. 5·49±0·02° has been obtained (cf. A., 1920, i, 152; 1931, 1361; this vol., 452). Saturation with H_2, N_2, or air depresses the f.p. by 0·017°. The f.p. is not dependent on the rate of cooling. J. H. R. (*c*)

Equation for representation of high-temperature heat content data. C. G. Maier and K. K. Kelley (J. Amer. Chem. Soc., 1932, 54, 3243—3246). The equation $-Q_{273\cdot1}^{T}=[aT+\frac{1}{2}bT^2+c/T]_{273\cdot1}^{T}$ appears to represent such data better than the usual power-series expression. L. P. H. (*c*)

Constants of the higher aliphatic alcohols. C. H. Kao and S. Ma (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 181—183).—The b.p., *d*, and n_D at 15°, 20°, and 25° are recorded for the Et esters of the *n*-acids from valeric to decoic acid and for the primary *n*-alcohols from amyl to decyl alcohol. R. S. C.

Diffusion coefficients of bromine–hydrogen, bromine–nitrogen, bromine–oxygen, and bromine–carbon dioxide. J. E. Mackenzie and H. W. Melville (Proc. Roy. Soc. Edin., 1931—1932, 52, 337—344).—The observed diffusion coeffs. for Br are lower than the theoretical vals. and usually increase with time of diffusion. W. R. A.

Diffusion of alcohols. G. Franke (Ann. Physik, 1932, [v], 14, 675—682).—The diffusion coeffs. of EtOH and MeOH in H_2O and of C_6H_6 in CCl_4 have been determined by an optical method. A. J. M.

Diffusion of particles and the energy loss resulting from collision. W. de Groot (Physica, 1931, 11, 337—342; Chem. Zentr., 1932, i, 2299).

Humidity diagram for water vapour–air mixture. S. Kamei (Chem. Fabr., 1932, 337—339). E. S. H.

Formation of amalgams: its physico-chemical aspect. B. N. Sen (Chem. News, 1932, 145, 93).—Metals and metalloids form amalgams with Hg when the distance of closest approach of their atoms exceeds 2·5 Å. E. S. H.

***X*-Ray study of alloys of the iron–tungsten system and their carbides.** A. Ôsawa and S. Tadeka (Kinzoku-no-Kenk., 1931, 8, 181—196).—The system is distinguished by the compound Fe_3W_2 (ε-phase), trigonal, *a* 4·738, *c* 25·726 Å., the unit cell containing 8 mols. In the Fe-rich region of the system Fe–W–C there are three phases: WC, Fe_3C (η), and Fe_3W_3C (η). WC is hexagonal, *a* 2·910, *c* 2·838 Å.; Fe_3C is orthorhombic, *a* 4·626, *b* 5·107, *c* 6·633 Å. The double carbide is face-centred cubic with *a* 10·97—11·08 Å., according to the composition and heat treatment. Ch. Abs.

Structure of some copper–zinc phases. O. Carlsson and G. Hägg (Z. Krist., 1932, 83, 308—317).—The ε-phase (prepared by very slow cooling of an alloy containing 60 at.-% Sn) is rhombic, *a* 5·510, *b* 38·18, *c* 4·319 Å. The η-phase (about 45·5 at.-% Sn) is hexagonal, *a* 20·95, *c* 25·43 Å. The unit cells of these phases contain 32 and 500 atoms, and are hyperstructures of a hexagonal lattice, and of a NiAs structure with $a\times2$, $b\times8$, and $a\times5$ and $c\times5$, respectively (cf. A., 1928, 822). The γ′-phase (prepared by chilling an alloy of 21·8 at.-% Sn after 15 hr. annealing at 595°), is hexagonal, *a* 7·316, *c* 7·854 Å., with 26 atoms in the unit cell. The space-group is D_{3d}^{1}, but one atom of each group is absent, so that the lacunæ form a hexagonal lattice (cf. A., 1931, 1900, where the phase is denoted by ε). C. A. S.

Constitution of lead–tin alloys. D. Stockdale (Inst. Metals, Sept., 1932. Advance copy, 16 pp.).—The system has been re-examined by micrographic, electrical resistance, and two thermal methods. The eutectic point is placed at 61·86% Sn, and the solid solubility of Sn in Pb is 19·5% and of Pb in Sn 2·5% at the eutectic temp.; at room temp. the solubility of each metal in the other is very small. The evolution of heat which is observed at about 150° on cooling Pb-rich alloys varies in magnitude according to the previous history of the specimen; the temp. also varies somewhat with the composition and previous heat treatment. It is suggested that the phenomenon may be due to the separation of Sn from supersaturated solid solution in a form other than the ordinary white form, which is then converted into this form with the evolution of heat. A. R. P.

Hall effect and grating constants of alloys. E. van Aubel (Bull. Acad. roy. Belg., 1932, [v], 18, 696—699).—Cu–Ni alloys do not show the relation between the Hall effect and grating consts. which Ornstein and van Geel found for Ag–Au alloys. Au–Pd, Ag–Pd, and Au–Cu alloys are also discussed. W. R. A.

Magnetic properties of solid solutions. S. S. Bhatnagar and P. L. Kapur (J. Indian Chem. Soc., 1932, 9, 347—356).—Magnetic susceptibilities have been determined for $KMnO_4$–$KClO_4$, KCl–NaCl, KBr–KCl, and KBr–NaBr. In the first case, where the salts are true isomorphs, the mixture rule is obeyed and the susceptibility–composition graph is linear. For the three remaining systems curves are obtained, the max. deviation being at 50% for KCl–NaCl and KBr–NaBr and at 70% KBr for KBr–KCl, corresponding in each case with the min. m.p. In the last case the deviation from a straight line is slight. The solid solutions $KMnO_4$–$KClO_4$ have no heat of formation. The heat of formation of the 70% KBr solution in KBr–KCl is 220 g.-cal., whilst for the 50% KBr–NaBr and KCl–NaCl solutions, where the deviation is large, the heats of formation are 1400 and 2100 g.-cal. M. S. B.

Magnetic susceptibility and electrical resistance of the series of mixed crystals Pd–Ag and Pd–Cu. B. Svensson (Ann. Physik, 1932, [v], 14, 699—711).—The susceptibility of Ag–Pd and Cu–Pd alloys has been determined; in the Cu–Pd series the susceptibility changes on passing from the disordered to the ordered at. state. Electrical resistance determinations were also made with the alloys. These new observations afford further knowledge of the equilibrium states in their dependence on the previous heat treatment. A comparison of the resistance–concn. and susceptibility–concn. diagrams shows certain deviations that would not be expected for binary systems. A. J. M.

Electrical properties of dilute mixed-crystal alloys. II. Resistance of silver alloys. J. D. Linde (Ann. Physik, 1932, [v], 14, 353—366).—The effect of adding elements of at. no. 29—33, 46—51, and 78—83 to Ag on the electrical resistance has been determined. Some preliminary results on the effect of temp. on the resistance are given. The increase in resistance varies with the square of the horizontal distance of the element added from the chief metal of the alloy in the periodic table. A. J. M.

Magnetic moment and the chemical linking in alloys. J. Dorfman (Nature, 1932, 130, 506).—A re-interpretation of previously recorded data (cf. this vol., 679, 901) for Ni alloys. Calc. effective moments per atom are Ni^+ 1, Cu^+ 0, Zn^+ −1, Al^+ −2, Sn^+ −3 (M_B). L. S. T.

Aluminium–antimony alloys. J. Veszelka (Mitt. berg.-hüttenmann. Abt. Hochschule Sopron, 1931, 193—201; Chem. Zentr., 1932, i, 2230).—Equilibrium is reached very slowly in a mixture of fused Al and Sb. The liquidus has a max. at 1080°, corresponding with AlSb, which was present in all the alloys (Al 99 to <1·2%). AlSb is decomposed in moist air with formation of $Al(OH)_3$. A. A. E.

Equilibrium diagram of the copper–silicon system. K. Iokibé (Kinzoku-no-Kenk., 1931, 8, 433—456).—A homogeneous phase, X (Cu 89·4—89·3%), is formed at 800° by the peritectoid reaction $\delta+\varepsilon \rightleftharpoons X$. The δ–γ transformation occurs only in the alloys which contain a smaller amount of Si than X; the ε–ε' transformation occurs only in alloys of higher Si content than X. The ε-phase shows a transformation ε–ε'' (558—442°) besides ε–ε' (626—556°). Ch. Abs.

Liquation or "inverse segregation" in the silver–copper alloys. J. H. Watson (Inst. Metals, Sept., 1932. Advance copy, 12 pp.).—Chilling experiments with alloys having a wide solidification range have been made after soaking them for several hr. within this range; analyses of samples from various parts of the specimens and micrographic examination of the structure indicate that the primary crystals, whether Ag or Cu, are free to move under the influence of gravity while the metal is within the freezing range and may be repelled from their positions by severe local chilling in their vicinity. All liquation and segregation phenomena observed in these alloys can be explained by the formation of primary Ag- or Cu-rich crystals at the chilling surface of the mould during transition of the metal through the freezing range and their subsequent repulsion towards the hotter metal in the centre of the ingot. A. R. P.

Equilibrium of the ternary system tin–lead–antimony. K. Iwasé and N. Aoki (Kinzoku-no-Kenk., 1931, 8, 253—267).—The diagram, determined by means of total and differential thermal analyses and by microscopical examination, has three non-variant points corresponding with (1) $\beta \rightleftharpoons \beta'$ transformation of Sb–Sn, (2) eutectic crystallisation of α, β, and δ, (3) the peritecto-eutectic reaction $L+\beta \rightleftharpoons \gamma+\beta$. The solubilities of 4 solid solutions at each non-variant point have been accurately determined. Ch. Abs.

Intermetallic compounds formed in mercury. IV. Summary of work on the Sn–Cu, Sn–Fe,

Zn–Cu, Zn–Fe, Cd–Cu, Hg–Cu, Mn–Cu, and Zn–Mn systems. A. S. RUSSELL, T. R. KENNEDY, J. HOWITT, and H. A. M. LYONS (J.C.S., 1932, 2340—2342).—In addition to those described previously (this vol., 456), evidence has been obtained for a large no. of further binary and ternary compounds. D. R. D.

Specific gravity and vapour pressure of concentrated sea-water at 0—175°. R. HARA, K. NAKAMURA, and K. HIGASHI (Tech. Rep. Tôhoku, 1932, 9, 99—118).—Measurements at concns. ranging from the normal to approx. saturation with respect to NaCl have been made. The stable modification of $CaSO_4$ which is in equilibrium with the brine under varying conditions, and the effect of saturation with this salt on the sp. gr. are discussed. A graphic method is described whereby the v.p. of sea-H_2O may be readily obtained for any concn. and temp. within the range considered. M. S. B.

Vapour pressure of binary liquid mixtures. Benzene–toluene and benzene–*m*-xylene. W. VON HUHN (Forsch. Gebiet Ingenieurwesens, 1931, A, 2, 109—113, 129—138; Chem. Zentr., 1932, i, 1502).—Equilibrium data for 20° intervals between 100° and 300° have been obtained. Empirical relations connecting pressure, temp., and composition are given for each mixture. L. S. T.

Vapour pressures of aqueous solutions of lithium nitrate and activity coefficients of some alkali salts in solutions of high concentration at 25°. J. N. PEARCE and A. F. NELSON (J. Amer. Chem. Soc., 1932, 54, 3544—3555).—The v.p. of aq. solutions of $LiNO_3$ and of five alkali halides have been determined for concns. from 0·1*M* to saturation by Pearce and Snow's method (A., 1927, 302). The activity of the solvent, the mean activity coeffs. of the ions, and the free energy changes accompanying the transfer of solute and solvent are tabulated. CH. ABS. (*c*)

Calculation of the affinity of vaporisation on the plates of a rectifying column. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1932, [v], 18, 730—736).—Mathematical; an extension of de Donder's theory of affinity to the problem of distillation. Calculations have been made for a mixture of PhCl and PhBr. W. R. A.

Formation of molecular additive compounds from observations of ultra-violet absorption spectra. N. G. RUIZ (Anal. Fís. Quím., 1932, 30, 561—563).—The displacement of the absorption bands for solutions of $COPh_2$, camphor, PhOH, and resorcinol in $CHCl_3$, as compared with solutions in H_2O or EtOH, indicates that additive compounds are formed between the solute and $CHCl_3$. H. F. G.

Solvent influence. V. Dipole moment of solvents and rotatory power of dissolved menthyl dialkylmalonates. H. G. RULE and J. T. R. RITCHIE (J.C.S., 1932, 2332—2340).—Measurements have been made of the rotatory powers, *M*[α], of *l*-menthyl oxalate, phthalate, acetate, and malonates of the type $C_{10}H_{19}O_2C\cdot CR_2\cdot CO_2R'$, where R=H, Me, Et, Pr, or Bu, and $R'=C_{10}H_{19}O_2C$ or H, in 12 org. solvents, and of the Na salts (R'=Na) in EtOH. For the dimenthyl esters ($R'=C_{10}H_{19}O_2C$), *M*[α] falls as the alkyl chain R becomes longer, except when R=Pr, in which case exceptionally high vals. are obtained in liquids of low polarity. The variation of *M*[α] with change in the solvent is greatest when R is large. In the case of the phthalate, acetate, and dipropyl- and dibutyl-malonates, *M*[α] falls regularly with increase in the polarity of the solvent, but no such regularity is observed with the other compounds. Cryoscopic measurements of the mol. wt. of the oxalate and dibutylmalonate in C_6H_6 indicate that no association occurs. Di-*l*-menthyl oxalate was obtained in two forms. On cooling the molten substance in CO_2–Et_2O, an unstable *form*, m.p. 39°, separates. This form can be recryst. from light petroleum, but on keeping for 2 months reverts to the normal form, m.p. 68°, b.p. 222—224°/11 mm. Both forms give the same val. for *M*[α], so that the difference is attributed to dimorphism. The following compounds were prepared by the methods previously employed for their lower homologues (A., 1930, 1558): *di*-l-*menthyl dipropylmalonate*, m.p. 94°; l-*menthyl hydrogen dipropylmalonate*, m.p. 41—42°; *di*-l-*menthyl dibutylmalonate*, m.p. 58°; and l-*menthyl hydrogen dibutylmalonate*, a syrup. D. R. D.

Magnetic susceptibility of mixtures of acetone and chloroform and of trichlorobutyl alcohol. B. CABRERA and A. MADINAVEITIA (Anal. Fís. Quím., 1932, 30, 528—539).—The susceptibility of mixtures of $COMe_2$ and $CHCl_3$ is a linear function of the composition. Vals. are also recorded for trichlorobutyl alcohol, COMeEt, $Bu^{\alpha}OH$, *sec*.- and *tert*.-BuOH, and $Pr^{\alpha}OH$. For the first-named, the susceptibility is somewhat greater than that of an equimol. mixture of $COMe_2$ and $CHCl_3$; the cause of this difference is discussed. H. F. G.

Magnetic study of colour changes in cobalt chloride. S. S. BHATNAGAR and A. N. KAPUR (J. Indian Chem. Soc., 1932, 9, 341—346).—The val. of the Weiss magneton no. for the red $Co^{\cdot\cdot}$ in H_2O solution is 25, confirming Chatillon's conclusion (A., 1928, 454). When $CoCl_2,6H_2O$ is dissolved in EtOH the no. varies between 22 and 23, according to the concn. of the solution. Vals. below 25 are also found in MeOH and $C_5H_{11}\cdot OH$. These changes are probably related to the colour changes in Co solutions and indicate the presence of different ions. In HCl solutions the val. lies between 22 and 24. This is not due to the production of anhyd. $CoCl_2$ or $CoCl_2,2H_2O$, as the no. for these salts is practically 25 and is also high for $CoCl_2$ in H_2SO_4 (A., 1929, 862). The effect is attributed, therefore, to the formation of $(CoCl_3)'$ and $(CoCl_4)''$. M. S. B.

Solubility of praseodymium selenate in water. J. N. FRIEND (J.C.S., 1932, 2410—2413).—The solubility is almost const. up to 60°, above which temp. it falls abruptly, the *dodecahydrate*, $Pr_2(SeO_4)_3,12H_2O$, being formed. The existence of the octa- and pentahydrates has been confirmed. Addition of H_2SeO_4 has only a slight influence on the solubility. The solubility curve is closely similar to those of $La_2(SeO_4)_3$ and $Nd_2(SeO_4)_3$, and recrystallisation of the selenates cannot be recommended as a method for separating Pr, La, and Nd. D. R. D.

Solubility of the mixed crystals $m(NH_4)_2SO_4 + n(NH_4)_2CrO_4$ and mNi$(NO_3)_2,6H_2O + n$Mg$(NO_3)_2,6H_2O$. J. MARKOWSKA (Arch. Min. Soc. Sci. Varsovie, 1930, 6, 11—28).—The diagrams are of Roozeboom's types V and IV, respectively. CH. ABS.

Solubility of calcium gluconate in presence of sodium phosphate and arsenious acid. F. DE CARLI (Atti R. Accad. Lincei, 1932, [vi], 15, 579—583; cf. this vol., 16).—Data for 20° show that NaH_2PO_4 increases the solubility of Ca gluconate; the double salt $(C_6H_{11}O_7)_2Ca,NaH_2PO_4$ is formed. The solubility of the gluconate is also increased by As_2O_3. O. J. W.

Solubilities of amino-acids and proteins. E. J. COHN (Naturwiss., 1932, 20, 663—672).—The solubility of NH_2-acids and proteins in various solvents is considered with reference to the nature of the ions. A. J. M.

Micro-determination of reciprocal solubilities. System phenol–water. R. A. SMITH (Mikrochem., 1932, 11, 227—236).—Homogeneous mixtures of the two components are sealed within capillary tubes and the temp. at which turbidity appears on cooling are observed. Measurement of the temp. at which a heterogeneous mixture becomes clear is not recommended, owing to the difficulty of mixing in narrow tubes. Results are given for the system PhOH–H_2O. H. F. G.

Distribution of acids between water and several immiscible solvents. R. C. ARCHIBALD (J. Amer. Chem. Soc., 1932, 54, 3178—3185).—The distribution ratios at 25° of the normal fatty acids from HCO_2H to hexoic acid, and of HCl, $HClO_4$, H_2SO_4, and HNO_3 between H_2O and COMeEt or an aliphatic alcohol have been determined. B. E. T. (*c*)

Static adsorption isotherms. Adsorption of carbon dioxide by charcoal. L. J. BURRAGE (J. Physical Chem., 1932, 36, 2272—2283; cf. A., 1931, 558).—The isotherm at 25° has been determined between 0·04 and 81 mm. P. H. E. (*c*)

Modification of Freundlich adsorption isotherm. W. ROGERS, jun., and M. SCLAR (J. Physical Chem., 1932, 36, 2284—2291).—A form of equation is derived which is particularly suitable for the calculation of equilibrium concns. and pressures and the amount of adsorbent required for total adsorption. P. H. E. (*c*)

Adsorption of gases by glass. IX. Nitrous oxide. M. CRESPI (Anal. Fis. Quím., 1932, 30, 520—527).—The adsorption of N_2O on glass at 16° between 253 and 760 mm. has been measured. The correction to be applied to v.d. measurements in a 1-litre vessel is about 6×10^{-5} g. The adsorbed film is probably unimol. H. F. G.

Pressure to which adsorbed air is subjected on the surface of an adsorbent (charcoal or soil). M. V. CHAPEK (Pedology, Russia, 1931, 26, No. 3, 57—66).—The adsorbed air and H_2O form a multimol. layer on the surface of the adsorbent. The lower layers of the air adsorbed by C are under a pressure equiv. to 64·5 atm., whereas those of the soil are under a pressure of 5—18 atm. Adsorbed air is similar in composition to atm. air. CH. ABS.

Adsorption isotherm? S. CASPE (J. Chem. Educ., 1932, 9, 907—909).—Adsorption experiments with animal C before and after prolonged treatment with HCl are recorded. CH. ABS.

Sorption of alcohol vapours by cellulose and cellulose acetate. S. E. SHEPPARD and P. T. NEWSOME (J. Physical Chem., 1932, 36, 2306—2318).—The amount of alcohol adsorbed under the saturated v.p. at 30° increases, in general, with the Ac content of the primary acetates, which have a smaller adsorption capacity than *sec.* acetates. Higher alcohols are usually adsorbed and desorbed more slowly than lower alcohols. The no. of mols. adsorbed per g. of adsorbent decreases with the mol. wt. of the alcohol, but is practically const. from BuOH to octyl alcohol. P. H. E. (*c*)

Adsorption of cations from ammoniacal solution by silica gel. I. M. KOLTHOFF and C. A. STENGER (J. Physical Chem., 1932, 36, 2113—2126).—With increase in the NH_3 concn. the adsorption of $Ca^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$ passes through a max. $NH_4^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$ tend to reduce the adsorption of $Ca^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$. The adsorption of aq. Ca ions is similar in character to the adsorption of ammoniacal Cu ions. The ratio NH_3 : Cu in the adsorption of the latter is <4. P. H. E. (*c*)

Selective adsorption of metallic oxides and their auto-reduction in presence of glycogen. L. HUGOUNENQ and J. LOISELEUR (Bull. Soc. Chim. biol., 1932, 14, 1011—1016; cf. A., 1931, 1091).—The auto-reduction in alkaline solution of "pseudo-colloidal" metallic oxides in presence of glycogen is due to the hydrolysis of a minute part of the glycogen providing reducing sugars. In some cases (*e.g.*, Au) this takes place at room temp., whilst in others warming is necessary, the metal remaining in colloidal solution. A. A. L.

Adsorption and capillary condensation. G. LINDAU (Kolloid-Z., 1932, 60, 253—263).—The equiv. pressure curves of two vapours or of a vapour at two temp. are linear and independent of the adsorbent. The slope of the curves is not in accordance with the requirements of the capillary condensation theory, but agrees better with that calc. from the potential theory. As saturation is approached, systematic deviations from linearity appear, the curve eventually satisfying the Thomson equation. The deviations mark the beginning of capillary condensation. E. S. H.

Film which adsorbs atomic hydrogen and does not adsorb molecular hydrogen. K. B. BLODGETT and I. LANGMUIR (J. Amer. Chem. Soc., 1932, 54, 3781—3782).—Discussion of the behaviour of tungsten and Elinvar filaments towards H. C. J. W. (*c*)

Effect of *X*- and γ-radiation on adsorption. G. HARKER (J.S.C.I., 1932, 51, 314—316T).—*X*-Radiation has no effect on the direct union of C_2H_4 and H_2, but accelerates the reaction in presence of a Cu catalyst. The amount of H_2 adsorbed by Cu is increased by about 2% under the influence of

X-rays; a similar effect occurs with Pd. These effects are intelligible in the light of Nyrop's views (A., 1931, 1375). The adsorption of Congo-red and methylene-blue by filter paper is retarded by γ-radiation from Ra; in presence of electrolytes the retardation is increased with Congo-red and diminished with methylene-blue. E. S. H.

Adsorptive power of protein–cellulose membranes. J. Loiseleur and P. Morel (Compt. rend. Soc. Biol., 1931, 108, 484—486; Chem. Zentr., 1932, i, 1885).—The presence of casein or ovalbumin endows a cellulose acetate membrane with marked adsorptive power for dyes from dil. H_2SO_4 solution; the effect runs parallel with the ratio protein : cellulose. A similar phenomenon is observed with cellulose acetate–casein membranes in $BiCl_3$ solution. A. A. E.

Inhibition of chemical reactions. V. Influence of pyridine and other substances on the absorption of ethylene by sulphuric acid and on the surface tension of sulphuric acid. W. S. E. Hickson and K. C. Bailey (Sci. Proc. Roy. Dublin Soc., 1932, 20, 267—279; cf. A., 1928, 718; 1929, 151; 1930, 429; 1931, 438).—The absorption of C_2H_4 by H_2SO_4 is inhibited by $C_{10}H_8$, PhOH, piperidine, *m*-$C_6H_4Me_2$, C_5H_5N, $COMe_2$, $(NH_4)_2SO_4$, quinoline, NH_2Ac, C_6H_6, NH_2Ph, and H_2O, and is accelerated by $CHCl_3$ and SO_3. The effects of C_5H_5N, H_2O, and SO_3, which have been studied in detail, show no discontinuities, and the surface tensions of H_2SO_4 solutions of these compounds are consistent with the view that inhibition takes place in the surface layer of the liquid. J. W. S.

Interfacial tensions between hexane and aqueous salt solutions. M. Kidokoro (Bull. Chem. Soc. Japan, 1932, 7, 280—286).—Measurements by the capillary-tube and drop-no. methods show that the interfacial tension between H_2O and *n*-hexane from petroleum (b.p. 68·5°, *d* 0·6691) is raised by the addition of $BaCl_2$, $BaBr_2$, NaCl, KCl, KBr, KI, $CuCl_2$, $AgNO_3$, $Ba(NO_3)_2$, or $[Co(NH_3)_6]Cl_3$. A. G.

Gum surfaces. II. F. V. von Hahn (Kolloid-Z., 1932, 60, 247—253; cf. this vol., 691).—The spreading of a drop of aq. dye solution containing a surface-active substance increases with the available area of the gum surface on which it is placed up to a crit. val., beyond which increase in the gum surface has no effect. The crit. val. varies with the gum. The spreading is least when the contour of the surface is circular. E. S. H.

Theory of flotation. P. Siedler, A. Moeller, and T. Reddehase (Kolloid-Z., 1932, 60, 318—324).—Photomicrographs of the flotation of various minerals show that the particles are held at the surface of the air bubbles, not by edges or points, and do not penetrate the bubble. Ostwald's theory (this vol., 333) is criticised; flotation is not a linear, but a laminar, effect, and the ideal flotation agent is not tri-, but di-affine; it has essentially metallophilic and aërophilic groups, which serve as a union between the solid and gaseous phases. Reduction of surface tension aids the process by providing a large liquid–gas interface. E. S. H.

Theory of flotation. II. Wo. Ostwald (Kolloid-Z., 1932, 60, 324—340).—The theory of linear flotation formerly advanced (this vol., 333) is amplified. A reply is made to criticisms (cf. preceding abstract). E. S. H.

Properties of protein films. W. Y. Lee and H. Wu (Chinese J. Physiol., 1932, 6, 307—320).—The rate of spreading of films of protein over the surface of aq. solutions varies with the protein. Whilst hæmoglobin and serum-albumin spread to their max. areas on 0·1*N*-HCl in a few min., ovalbumin requires 8 hr. The protein remains entirely on the surface. The max. area occupied by carbamide-denatured ovalbumin is 10,400 sq. Å. per mol., whilst that of natural ovalbumin is 8400 sq. Å., the film thicknesses being 4·1 and 4·8, Å., respectively. For natural ovalbumin, the film area is a max. at p_H 4·8, the isoelectric point; that for carbamide-denatured ovalbumin is a max. at p_H 7·0, which would therefore seem to be the isoelectric point. The compressibility of the albumin film varies with p_H, being a max. at the isoelectric point, at which also the "film viscosity" is a min. The "film tension" of ovalbumin films, measured at varying p_H and pressure, is a linear function of the pressure. The slope $-\Delta\sigma/\Delta P$ varies with p_H, with a max. at the isoelectric point. The significance of these observations is discussed. R. N. C.

Rhythmic crystallisation of melts. I. Factors influencing the phenomenon. J. F. J. Dippy (J. Physical Chem., 1932, 36, 2354—2361).—Rhythmic crystallisation of thin films has been observed with various aromatic compounds. When supercooling is prevented rhythmic crystallisation stops. Unless an air interface is present, crystallisation is continuous. The thinner is the layer of melt, the more rapid are the pulsations of crystal growth; thick films crystallise continuously. 3 : 5-Dichloromethyldiphenyl crystallises rhythmically when a thin layer of an Et_2O solution evaporates at room temp. E. J. R. (*c*)

Method of counting particles. L. H. C. Tippett (Proc. Roy. Soc., 1932, A, 137, 434—446).—Counts are made only on zones with few particles, those zones with more than a certain no. of particles being classed together. The mean is estimated from the modified frequency distribution so formed. L. L. B.

True specific gravity of colloid-containing materials such as the bentonites. R. M. Woodman (J.S.C.I., 1932, 51, 327—328T).—An attempt is made to determine the true sp. gr. of the bentonites by submersion in liquids causing no swelling. The alkaline bentonites have the greatest densities.

Structure of colloidal particles. S. M. Liepatov (J. Appl. Chem., Russia, 1931, 4, 1023—1029).—Pauli's theory is criticised. Ch. Abs.

Dispersion of gases in liquids. H. Rudolph (Kolloid-Z., 1932, 60, 308—317).—The bubbles formed when air is passed into water through a porous diaphragm have been photographed. As the size of the pores decreases, the bubbles decrease in size, but increase in no. per unit vol., whilst the velocity of rise in the liquid decreases and the rotation and screw-like motion increase. With increasing pressure of gas the bubbles increase in size up to a const. max. val., whilst the velocity and rotation increase by reason of the expansion on release. The size of the bubbles increases with the height of the liquid column. Reduction of surface tension of the liquid leads to a decrease in size and an increase in the no. of bubbles per unit vol. Quant. relations between these effects are worked out. E. S. H.

Preparation of colloidal silver and gold by means of a continuous high-frequency electrical discharge. A. N. Fraser and J. Gibbard (Canad. J. Res., 1932, 7, 133—136).—Metal sols may be prepared by passing a high-frequency discharge, of sufficient intensity to produce a continuous spark, between electrodes of the metal under H_2O; the electrodes are preferably knife-edges 5 mm. long and 1—2 mm. apart. A high-frequency continuous-wave thermionic valve generator circuit is described. Stable yellow (2 mg. per litre) and black (16 mg. per litre) Ag sols free from $Ag^{\cdot}$, and purplish-red Au sols have been prepared by this method, without addition of a protective colloid. H. F. G.

Preparation and properties of highly concentrated sols. I. R. N. Mittra and N. R. Dhar (J. Indian Chem. Soc., 1932, 9, 315—327).—Highly conc. sols of Fe, Al, and Cr hydroxides, containing 0·5063, 0·5255, and 0·8356 mol. of the respective oxides per litre, have been prepared. The sols cannot be freed completely from peptising substances, even by hot dialysis, and when purification is carried beyond a certain point they set to a firm gel. The undialysed sol is more stable towards pptg. agents than the dialysed sol of the same concn., and the ratio of the pptg. concns. of uni- to bi-valent ions decreases as the purity of the sol increases. The viscosity is very high for conc. sols and increases with purity (cf. A., 1929, 506, 1234). The viscosity–concn. curves are very steep and resemble those obtained for lyophilic sols. The vals. of the surface tension of Fe and Cr sols are only slightly less than for H_2O, but for Al sol the val. is considerably less. The conc. sols of Al and Cr are reversible colloids, since the air-dried solids swell and pass into the colloidal condition again in contact with H_2O. The empirical formulæ for the solids are respectively, $Al(OH)_3,H_2O,AcOH$ and $Cr_5(OH)_{12}Cl_3,28H_2O$. M. S. B.

Emulsification. J. B. Speakman and N. H. Chamberlain (Nature, 1932, 130, 274).—Theoretical. In ordinary emulsification the cybotactic condition of an oil is as important as the magnitude of the interfacial tension and the adsorption at the interface; in scouring processes adhesion phenomena are exceptionally significant. L. S. T.

Mercury emulsions prepared by means of ultrasonic waves. H. B. Bull and K. Söllner (Kolloid-Z., 1932, 60, 263—268).—By the action of ultrasonic waves on Hg under H_2O or aq. solutions, emulsions having a particle size 0·5—1·0 μ are formed. The process is aided by multivalent and strongly adsorbable ions, such as citrate. The charge on the particles is positive in pure H_2O; the positive charge is increased by adding the effective cations, but the effective anions produce a negatively-charged emulsion. Dispersion also takes place in non-aq. media, the tendency to emulsify being very weak in C_6H_6, PhMe, and CCl_4, but strong in viscous liquids containing O, such as olive oil and turpentine. Ga is also dispersed in H_2O under the action of ultrasonic waves, forming positively-charged sols, which are more stable than those of Hg. It is not necessary to melt the Ga, for heat is developed at the surface of the metal under the influence of the waves. E. S. H.

Emulsions. IV. Systems of sodium oleate, phenol, and water. II. J. Weichherz and H. Saechtling (Kolloid-Z., 1932, 60, 298—306).—The viscosities and *d* of binary and ternary mixtures between 20° and 80° are tabulated. E. S. H.

Conductivity of sodium myristate solutions at various temperatures. P. Ekwall [with B. Otterström] (Z. physikal. Chem., 1932, 161, 195—210).—The equiv. conductivity, λ, of 0·0008—0·19*N* aq. solutions has been measured at 17—80°. The λ–concn. curves are anomalous between 0·0015*N* and 0·006*N* and between 0·08*N* and 0·19*N*. The former anomaly, which becomes less pronounced and shifts towards higher concns. as the temp., *T*, rises, is attributed to the variation with concn. of the proportions of acid soap and neutral colloid in the solution. As *T* rises the tendency to form acid soap and the formation of colloid by supersaturation diminish. The second anomaly, which is that investigated by MacBain, does not become less marked as *T* rises. It is suggested that the formation of neutral colloid in soap solutions may be caused either by supersaturation, which depends on *T*, or, in the more conc. solutions, by associative forces, which are independent of *T*. R. C.

Cryolysis of lyophilic colloids. H. B. Bull (Z. physikal. Chem., 1932, 161, 192—194).—Application of Einstein and von Smoluchowski's viscosity equations to existing data (this vol., 337) shows that the freezing of a homogeneous ovalbumin sol causes an increase in the total vol. of the suspended particles, presumably by increase in the amount of bound H_2O consequent on disaggregation of the particles. With a gelatin sol freezing seems to favour aggregation. R. C.

Viscosity of cellulose glycollate. T. Nakashima (J. Soc. Chem. Ind. Japan, 1932, 35, 352—355B).—Cellulose glycollate, prepared according to the method of Sakurada (A., 1929, 430), was rendered ash-free by dialysis, repptd. several times from EtOH, and neutralised with NaOH. The viscosity of an aq. solution of this ester with the addition of NaOH and/or neutral salts has been determined. The relationship between viscosity and concn. is represented by $\eta_s/\eta_0=1+ac$. The influence of the electrolyte on the viscosity is discussed. V. E. Y.

Variation of the rigidity of colloids with temperature. M. M. S. Vencov and O. Teodorescu (Bull. Acad. Sci., Roumaine, 1932, 15, 91—94).—A mathematical discussion. A. G. P.

Colloidal, ferromagnetic ferric oxide as a biological indicator. O. Baudisch and W. H.

Albrecht (Naturwiss., 1932, 20, 639).—Magnetic susceptibility measurements for colloidal H_2O solutions of γ-Fe_2O_3 have been made. The magnetisation varies linearly with Fe content. The ferromagnetism of the oxide is influenced by dilution. W. R. A.

Stability of negative and positive silver halide and thiocyanate sols. A. Basinski (Kolloid-Beih., 1932, 36, 257—349).—Sols of AgCl, AgBr, AgI, and AgCNS have been prepared by the interaction of aq. $AgNO_3$ and the corresponding K salt. Negative sols are formed when the K salt is in slight excess, and positive sols when $AgNO_3$ is in slight excess. The order of stability of both positive and negative sols is $AgI > AgBr > AgCl > AgCNS$. Positive AgCl sols are more stable than the negative AgCl sols at all concns. of electrolyte, but negative AgI sols are more stable than positive AgI sols. Negative AgI and AgBr sols are also stabilised by K salts having the anions Cl', Br', I', CN', CNS', $Fe(CN)_6'''$, $Fe(CN)_6''''$, but not by those containing HF_2', NO_3', ClO_4', MnO_4', C_2O_4'', CO_3'', SO_4'', CrO_4'', or Cr_2O_7''. The amount of Ag salt dispersed increases with increasing concn. of stabilising K salt up to a max., KCNS being the most effective. At higher concns. the K salts have a coagulating effect. The amount of sedimentation of the Ag salt is related to the time by an S-shaped curve; the rate of sedimentation is low at first, then increases rapidly, and again falls. As the excess of K salt present is increased, the sedimentation velocity rises in a short time to a max. The charge on the particles of positive Ag halide sols in excess of $AgNO_3$ falls gradually to 0 when the sol is diluted, and at great dilutions a const. negative val. is reached. The charge on the particles of both positive and negative sols is lowered by diluting the sol with the ultrafiltrate. In all the sols examined, the charge decreases with time, indicating the formation of secondary from the primary particles. E. S. H.

Lyophilic colloids. XV. Influence of high concentrations of electrolyte on sols of amylum and gum arabic. H. R. Kruyt and H. J. Edelman (Kolloid-Beih., 1932, 36, 350—384; cf. A., 1931, 796).—When progressively-increasing, small concns. of electrolyte are added to a sol of amylum, the viscosity of the sol is rapidly reduced. As more electrolyte is added, the viscosity generally passes through a min. and then rises at a rate which depends on the ions present. In the case of Li_2SO_4, $MgSO_4$, and $BeSO_4$ (which salt out the colloid) the viscosity continues to fall slowly, probably in consequence of dehydration. The increase of viscosity due to higher concns. of other electrolytes follows the lyotropic series and is apparently due to increasing hydration of the amylum particles. With gum arabic sols the addition of increasing quantities of electrolytes causes the viscosity to fall at first rapidly and then slowly to a const. val. E. S. H.

Influence of temperature on the coagulation of sols of silver halides and of arsenic trisulphide. T. Katsurai (Bull. Chem. Soc. Japan, 1932, 7, 257—259).—Sols of Ag halides are most stable to heat when prepared from an excess of halide, and increase in stability in the order AgCl, AgBr, AgI; the last is fully coagulated only at 200°. Sols of As_2S_3 freed from H_2S coagulate almost completely at 200°, whereas in presence of H_2S dissolution occurs at 180°. A. G.

Electrolyte coagulation of colloids. XII. Second phase of the coagulation of arsenious sulphide sols. A. J. Rabinovitsch and D. T. Vassiliev (Kolloid-Z., 1932, 60, 268—273; cf. A., 1929, 1143).—The first stage of coagulation of As_2S_3 sols consists of exchange of added cations with the $H^{\cdot}$ of the sol particles; the second stage is the visible clotting of particles. The action of dil. solutions of KCl, $BaCl_2$, and $AlCl_3$ on As_2S_3 sols was observed over periods of 4—9 months. The concn. of electrolyte required to coagulate the sols is not equiv. to $[H^{\cdot}]$ liberated from the sol; in the case of KCl this is due to feeble displacement of adsorbed $H^{\cdot}$, and with $AlCl_3$ it is due to hydrolysis. The second stage of coagulation is traced to an electrostatic compression. E. S. H.

Physico-chemical properties of sulphite–chromium complexes. E. Preis (Vestn. Kozhev. Prom. Torgov., 1929, 692—695).—The complex obtained by adding Na_2SO_3 to $Cr(OH)SO_4$ is most stable at p_H 7. Migration to the anode starts at 1·3 mols. SO_3 per mol. at p_H 8·4, or 2·0 at p_H 7. The point of change to negative charge corresponds with that of max. Cr fixation by hide powder; this max. is also shown by a solution 2 days old. SiO_2 gel and cellulose do not fix Cr, but reversibly adsorb a little; glutein adsorbs it irreversibly. Activated C gives a characteristic adsorption curve without max. Cr solutions containing 0·25—100 mols. SO_3'' give characteristic absorption spectra; at least two Na_2SO_3–Cr complexes are formed. Ch. Abs.

Volume relations in the system cellulose–water. E. Filby and O. Maass (Canad. J. Res., 1932, 7, 162—177).—The sp. vol. of cellulose has been determined by allowing He to expand into, or from, a vessel containing the specimen, the pressure changes being measured. The method is more accurate than gas injection methods and allows a correction to be made for adsorption of the gas. The sp. vol. of cellulose is 0·64 c.c. The sp. vol. of the system cellulose–H_2O vapour is much smaller than that calc. additively when the H_2O content is $<4\%$; with further increase of the H_2O content the apparent density of the H_2O falls, becoming normal at about 8%. It is suggested that the first H_2O adsorbed combines chemically, with contraction of the system, and that further addition of H_2O increases the cellulose surface and consequently the contraction, until finally normal liquid H_2O begins to fill the capillaries of the cellulose. The relation of the results to the difference between the adsorption and desorption isotherms, and to the process of paper-making, is discussed. H. F. G.

Heat capacity measurements in gelatin gels. I. W. F. Hampton and J. H. Mennie (Canad. J. Res., 1932, 7, 187—197).—The heat capacities of dry gelatin and of gelatin containing 12·5 and 24% H_2O have been determined. The problem of calculating from such data the amount of bound H_2O is discussed, and a new equation for this purpose is derived. In an 87·5% gel probably all the H_2O is bound, but in a

24% gel the bound H_2O (g. per g. of dry gelatin) falls continuously from 0·69 at –3° to 0·24 at –78·5°.
H. F. G.

Changes caused in isoelectric gelatin by the action of neutral salts. A. Scala (Annali Igiene, 1931, 41, 325—336; Chem. Zentr., 1932, i, 1639).—Changes in p_H caused by the addition of acids, bases, and neutral salts to isoelectric gelatin are recorded; the changes in swelling power are also described.
A. A. E.

Diffusion velocity in gelatin gels as a function of the viscosity of the dispersion medium. E. Hatschek (Kolloid-Z., 1932, 60, 273—276).—The velocity of diffusion of K_2CrO_4 in gelatin gels with aq. glycerol as dispersion medium deviates a little from the inverse sq. root viscosity relation and the deviation increases with the concn. of glycerol. It is suggested that the "solid" phase is hydrated to a smaller degree in presence of increasing amounts of glycerol, causing a widening of the channels for diffusion and a reduction of the viscosity of the original dispersion medium.
E. S. H.

Reversible sol–gel transformation, "crystallisation" of gelatin, and the fine structure of elastic gels, especially of gelatin and caoutchouc, in the light of Röntgen optics. O. Gerngross, K. Herrmann, and R. Lindemann (Kolloid-Z., 1932, 60, 276—288).—An apparatus is described by means of which *X*-ray interference photographs of gelatin can be taken during the sol–gel transformation. As the swelling and H_2O content increase the interference lines gradually disappear. This is due to distortion of the lattice by the H_2O taken up, for interference rings reappear when the swollen gelatin is stretched. The particles of gelatin are regarded as long polypeptide chains, three-dimensional in the middle and unidimensional towards the ends. When the gelatin is stretched the particles are brought into parallel positions and partial valency linkings come into operation, thus explaining the development of heat. An *X*-ray diagram can be obtained from the sol just above its setting point, showing that the three-dimensional micelles still exist, but at higher temp. these break up into single polypeptide chains. This state of disaggregation of the particles can be fixed by pouring the hot sol into a plate kept at 100°, so that H_2O evaporates; the dried gelatin then gives no interference figures. On the addition of H_2O a rearrangement takes place and *X*-ray interference is again obtained. The crystallinity of gels of gelatin and caoutchouc increases with the age of the gel consistently with the increase in solidity; the crystallinity is destroyed by vigorous stirring. The caoutchouc micelle is regarded as similar to that of gelatin, but the three-dimensional kernel is much smaller and accounts for the greater elasticity. When unstretched, the caoutchouc cannot give an interference diagram, by reason of its small kernel, but in the stretched condition the parallel orientation of micelles causes interference.
E. S. H.

Formation and decomposition of urate gels. E. G. Young and F. F. Musgrave (Biochem. J., 1932, 26, 941—953).—The optimal temp. for supersaturation is 80—90°. The degree of cooling required to produce gelation varies with the concn. of urate between 0° and 40°. The limiting concns. have been determined for different urates: for Na urate gels between p_H 5 and 8·5, K urate between p_H 6 and 11·5, and Li urate between p_H 6 and 12. There is a shift to the basic side in the formation of gels. The dissociation consts. for uric acid are $K_{a_1}=8\times10^{-6}$, $K_{a_2}=7\times10^{-10}$ and a possible $K_{a_3}=6\times10^{-11}$. Some org. bases form supersaturated solutions with uric acid which ultimately undergo gelation under the usual conditions; others form gels only in the presence of traces of NaCl or KCl. These gels crystallise, with one exception, in the course of a few min. to several weeks, depending on the nature of the base and the concn. of uric acid used. The cryst. deposits consist of 2 mols. of acid and 1 mol. of base.
S. S. Z.

Properties of proteins in organic solution. J. Loiseleur (Bull. Soc. Chim. biol., 1932, 14, 1088—1100).—Lipins, proteins, and some carbohydrates form true solutions in HCO_2H, AcOH (less effective), lactic and pyruvic acids either alone, or with the addition of certain auxiliary substances (NH_2-acids, simple aromatic compounds, HCl, etc.). Dissolution in some cases may also be obtained under sp. conditions with other solvents. Colloidal properties reappear on addition of H_2O. The solubility and stability of the solutions appear to depend on the hydrophilic nature of the solute. Dissolution is due to the formation of sol. complexes with the solvent. Proteins dissolved in anhyd. HCO_2H give a violet coloration on warming, and similar solutions of caseinogen and keratin give "nitro"-derivatives with HNO_3 and HCl at 40°.
A. A. L.

Denaturation of proteins. III. Reversibility of the changes which occur when serum-proteins are adsorbed and eluted. M. Spiegel-Adolf (Biochem. Z., 1932, 252, 37—55; cf. A., 1930, 101).—Complete adsorption of the proteins [serum-albumin (I), pseudoglobulin (II), euglobulin (III)] in 0·2—1·1% solution by $Al(OH)_3$ occurs only when 0·17 g. of the latter is produced from $AlCl_3$ in 10 c.c. of the protein solution by addition of alkali. As regards their adsorbability, the proteins form the ascending series (I), (II), (III). (I) and (II) entirely lose their H_2O-solubility on adsorption by $Al(OH)_3$ or mastic. For removal of the adsorbed proteins by elution 0·01*N*-NaOH is most suitable. (I) in concns. up to 1·6% can be almost completely removed by elution and (II) can be removed somewhat less completely. Only about 34% of (III) can be removed thus. For (I) and (II) part of the material removed by elution is H_2O-sol. and heat-coagulable, the amount depending on the ratio protein : alkali prevailing during elution. The partly reversible changes which occur on adsorption are similar to those caused by heat or treatment with EtOH.
W. McC.

Mobility of protein ions. P. König and W. Pauli (Biochem. Z., 1932, 252, 325—342).—The velocity of migration of protein ions (egg- and serum-albumin and pseudoglobulin) in electrolyte-free aq. solution on addition of varying amounts of strong acid and alkali has been measured and a series of curves indicates the variation of mobility with the amounts of combined acid and alkali.
P. W. C.

Physical chemistry of lipins. I. Swelling and specific anion action. M. SPIEGEL-ADOLF (Klin. Woch., 1932, 11, 185—186; Chem. Zentr., 1932, i, 2190).—Bromides reduce the viscosity of 1% lecithin and lecithin-protein (serum-albumin and -pseudoglobulin), but not of protein, sols; the effect exceeds that of Cl′, I′, CNS′, K *d*-tartrate, and $K_2B_4O_7$. The result is not a sp. ionic effect of Br, but appears to be associated with ease of oxidisability. A. A. E.

Colloidal pectin. S. A. GLIKMAN (J. Appl. Chem., Russia, 1931, 4, 1041—1059).—Pectin has no chemical action on sugar; the influence of sugar on the formation of pectin gels is due to the weakening of the association characteristics of H_2O mols. Cations have a considerable effect on the gel-forming properties of pectin. The dimensions of the micelles remain unchanged, and the differences must be due to changes in the composition of the dissolved pectin. The p_H is important; when the p_H is high the properties of different acids need separate investigation.

CH. ABS.

Union of biocolloids. VII. Protein and nucleic acid and their degradation products. S. J. VON PRZYLECKI and M. Z. GRYNBERG (Biochem. Z., 1932, 251, 248—265).—The combination between albumin and yeast-nucleic (Na salt), guanylic, adenylic, xanthylic, and cytidinic acids, adenosine, guanosine, guanine, xanthine, and KH_2PO_4 has been investigated. The formation of a salt (union of NH_3^+ and PO^-) with albumin and nucleic acid and phosphorylated nucleotides occurs at a p_H lower than the isoelectric point of the albumin. At the isoelectric point union with nucleic, adenylic, and cytidinic acids occurs only by double salt formation (union of CO_2H of albumin with NH_2 group of adenine and cytosine), the NH_3 group being still dissociated at p_H 5·6. All other combinations, *e.g.*, between protein and the free purines, nucleosides, and phosphorylated substances at a p_H greater than the isoelectric point of albumin, are non-chemical in nature. P. W. C.

Isoprene and caoutchouc. XL. Elasticity of caoutchouc. H. STAUDINGER (Kolloid-Z., 1932, 60, 296—298).—The double linking plays no part in the elasticity of caoutchouc, for hydrocaoutchouc is also elastic. The length of the mol. is probably the determining factor. E. S. H.

Free energy of water, carbon monoxide, carbon dioxide, and methane. Their metallurgical significance. J. CHIPMAN (Ind. Eng. Chem., 1932, 24, 1013—1017).—The following expressions are derived for the mol. heat capacities of substances over the range 300—2300° abs.: H_2 $6\cdot70+0\cdot0007T$, N_2, O_2, and CO $6\cdot50+0\cdot0010T$, H_2O $7\cdot20+0\cdot0027T$, CO_2 $7\cdot40+0\cdot0066T-1\cdot50\times10^{-6}T^2$, CH_4 $3\cdot60+0\cdot01807T-4\cdot20\times10^{-6}T^2$. The free energies obtained are: (1) $H_2+0\cdot5O_2=H_2O$ (gas) $-57{,}120+2\cdot75T\log T-0\cdot00075T^2-6\cdot65T$, (2) C (graphite) $+0\cdot5O_2=CO-27{,}070-2\cdot05T\log T+0\cdot00225T^2-0\cdot20\times10^{-6}T^3-7\cdot92T$, (3) C (graphite) $+O_2=CO_2-94{,}210+0\cdot30T\log T-0\cdot0003T^2+0\cdot05\times10^{-6}T^3-0\cdot94T$, (4) C (graphite) $+2H_2=CH_4-15{,}320+11\cdot00T\log T-0\cdot0058T^2+0\cdot50\times10^{-6}T^3-50\cdot94T$. E. S. H.

Dissociation constant of acetic acid. C. W. DAVIES (J. Amer. Chem. Soc., 1932, 54, 3776—3777).—Correction of MacInnes and Shedlovsky's conductivity data (this vol., 695) for viscosity gives nos. which agree with the "theoretical" vals.

C. J. W. (*c*)

Limiting mobilities of some univalent ions and the dissociation constant of acetic acid at 25°. A. I. VOGEL and G. H. JEFFERY (Nature, 1932, 130, 435).—The mobility of AcO′ is found to be 37·85. Conductivity measurements in SiO_2 cells with 0·0001—0·01*N*-AcOH give a val. of $1\cdot776\times10^{-5}$ for the thermodynamic dissociation const. of this acid (cf. this vol., 695). L. S. T.

Activity coefficients of barium chloride. R. F. NEWTON and E. A. TIPPETTS (J. Amer. Chem. Soc., 1932, 54, 3779).—E.m.f. data show that the activity coeff., γ, of $BaCl_2$ passes through a max. as the temp. rises (cf. this vol., 467). For a given concn. γ is about the same at 45° as at 0°, but at 25° is appreciably greater. C. J. W. (*c*)

Relations between structure and strength of certain organic bases in aqueous solution. N. F. HALL and M. R. SPRINKLE (J. Amer. Chem. Soc., 1932, 54, 3469—3485).—The ionisation consts. of 38 org. derivatives of NH_3 have been determined by H electrode measurements. The temp. coeff. of K_w/K_B varies regularly with the basic strength. The effect of substituents on the strength of bases is comparable with their effects on the strength of acids. Attention is directed to the effect of two Et groups in enhancing basic strength. CH. ABS. (*c*)

Affinity between asymmetric acids and bases. H. ERLENMEYER and K. G. HOFFMANN (Helv. Chim. Acta, 1932, 15, 1140—1157).—At 31·5° the solubilities in EtOH of *l*-strychnine *d*-αβ-dibromocinnamate (*l*B*d*A) and *l*-strychnine *l*-αβ-dibromocinnamate (*l*B*l*A) are equal, whilst at temp. above or below 31·5° *l*B*d*A is more sol. The separation of the latter from a mixture, sometimes observed at room. temp., is due to infection with cryst. nuclei and does not represent a true equilibrium. No resolution is effected by adsorption on animal C. It is concluded that in solution there are no forces affecting asymmetrically the affinity between asymmetric acids and bases. Solubility and conductivity data are given. *l*B*d*A has $d_4^{19\cdot5}$ $1\cdot536\pm0\cdot01$ and *l*B*l*A $1\cdot589\pm0\cdot01$. F. L. U.

Hydrolysis of mercurous sulphate. C. B. HAGER and G. A. HULETT (J. Physical Chem., 1932, 36, 2095—2098; cf. A., 1900, ii, 481; 1902, ii, 74; 1904, ii, 563).—A saturated solution of Hg_2SO_4 in pure H_2O at 25° contains 0·002 mol. per litre of $HgHSO_4$. The solubility curve of Hg_2SO_4 in aq. H_2SO_4 exhibits slight discontinuities at 0·27 and 0·025 and a marked discontinuity at $1M$-H_2SO_4. This last corresponds with the disappearance of $Hg(OH)_2,Hg_2SO_4$ from the solid phase, pure Hg_2SO_4 remaining. The e.m.f. of a Cd cell containing saturated Hg_2SO_4 in $0\cdot1M$-H_2SO_4 as a depolariser decreases slowly; this is attributed to slow hydrolysis of Hg_2SO_4. J. H. R. (*c*)

Metastability of elements and compounds as a consequence of enantiotropy or monotropy. XVI, XVII. Precipitation reactions. I, II. E.

Cohen and J. W. A. van Hengel (Z. physikal. Chem., 1932, 161, 161—178, 179—191).—I. The heat of the reaction $AgNO_3+KI=AgI+KNO_3$ in aq. solution is the same whether the $AgNO_3$ is added to the KI or the KI to the $AgNO_3$, and this is true even if impurities are present. Hence there is no evidence that metastable forms of AgI are pptd.

II. Calorimetric and dilatometric measurements and *X*-ray examination show that the $BaCO_3$ pptd. from a mixture of $BaCl_2$ and Na_2CO_3 is heterogeneous; the proportion of the metastable form diminishes on keeping. R. C.

Effect of pressure on the liberation of gases from metals, with special reference to silver and oxygen. N. P. Allen (Inst. Metals, Sept. 1932. Advance copy, 24 pp.).—When Ag saturated with O is allowed to cool in air two arrest points occur on the cooling curve, the first at 951° and the second at 930—940°; the latter coincides with the temp. at which "spitting" occurs. During solidification comparatively pure Ag separates at first and the liquid becomes enriched in O until the pressure of O which would be in equilibrium with it is $\nless$ the external pressure; at this stage bubbles of O_2 are evolved, but prior to this there is practically no loss of O_2. Escape of O_2 can therefore be prevented by the application of sufficient external pressure, in which case the liquid solidifies as a $Ag–Ag_2O$ eutectic. The rate of cooling has no effect on the temp. at which spitting occurs, but more O_2 is liberated at slow rates of cooling. The m.p. of Ag is lowered by the presence of O according to the expression $T°=961-22{\cdot}31P^{\frac{1}{2}}$, where P=pressure in atm. The $Ag–Ag_2O$ eutectic forms at 500—600°; by extrapolation of the m.-p. curve the eutectic point is 507° and 414 atm. Mathematical expressions are derived for calculating the pressure necessary to prevent gas evolution from liquid metals when the evolution is due to solubility changes and when it is due to reactions. For tough-pitch Cu this pressure is 0·5 ton per sq. in. A. R. P.

Irregularities in the behaviour of the systems $CaO–SO_2$ and $CaO–CO_2$. S. Bretsznajder (Rocz. Chem., 1932, 12, 551—556).—At partial CO_2 or SO_2 pressures which are relatively high or low in comparison with the equilibrium pressure, it is found that false equilibria supervene, in which the pressures are respectively > or < theoretical. This effect is ascribed to formation of systems possessing greater surface energy than at true equilibrium. R. T.

Equilibrium diagram of the system $PbO–SiO_2$. K. A. Krakau and N. A. Vakhrameev (Keram. i Steklo, 1932, 8, no. 1, 42—43).—The system has been examined up to 72 mol.-% SiO_2. $2PbO,SiO_2$ and PbO,SiO_2 are definite compounds, the temp. of crystallisation being 746° and 765°, respectively. The former undergoes polymorphic conversion at 600°. The orthosilicate–metasilicate eutectic temp. is 700°. $3PbO,SiO_2$ is metastable below 690°, and forms eutectics also. The $PbO,SiO_2–SiO_2$ eutectic is at about 700°. Tridymite and cristobalite are produced during crystallisation of silicates from glasses containing 60—70% SiO_2. Ch. Abs.

Influence of gaseous thermal diffusion on equilibrium measurements on iron–oxygen–hydrogen system. P. H. Emmett and J. F. Shultz (J. Amer. Chem. Soc., 1932, 54, 3780—3781).—Preliminary data are presented to show that the principal cause of discrepancy between the various steam equilibrium consts. for this system is thermal diffusion. This also applies to the Sn–H–O system. C. J. W. (c)

System iron–cobalt–carbon. R. Vogel and W. Sundermann (Arch. Eisenhüttenw., 1932—1933, 6, 35—38).—The system has been investigated by thermal analysis, magnetic measurements, and micrographic examination of alloys containing up to 5% C. Primary crystals which separate from the liquid may consist of ternary α, ternary γ, or graphite. The eutectic consists of ternary solid solution and either cementite or graphite; the fields in which the cementitic and graphitic eutectics solidify are separated by a narrow field in which both eutectics separate together in proportions which vary according to the rate of cooling and the pressure. In alloys containing up to 80% Co the γ-phase decomposes on cooling into pearlite composed of binary α and graphite or cementite; in alloys with 80—94% Co the γ-phase is stable at room temp. The magnetic transformation occurs in all alloys with $\ngtr$ 70% Co at a temp. which rises with increasing Co content and eventually with high C or > 12% Co coincides with the A3 point. With a rate of cooling of 65° per sec. a martensitic structure is obtained in alloys containing < 1·7% C, 2% Co; 1·5% C, 4% Co; 0·9% C, 8% Co, and 0·01% C, 9·5% Co; all alloys containing C and Co above these limits retain a pearlitic structure and none of the alloys shows an austenitic, sorbitic, or troostitic structure. A. R. P.

Equilibrium diagram of the $Fe–Fe_3C–FeS$ system. T. Satô (Tech. Rep. Tôhoku, 1932, 9, 119—159).—Primary crystallisation and transformation points have been determined by thermal analysis for 75 alloys containing 0—62·1% Fe_3C and 0—89·0% FeS. Isothermal diagrams for the primary crystallisation surfaces of the space model of the ternary system have been constructed. The results, combined with microscopical investigation, have confirmed the existence of the two liquid phases observed by Hanemann and Schildkötter (B., 1930, 242), the upper layer being rich in FeS, whilst the lower layer is rich in Fe and Fe_3C. A binary monotectic reaction takes place in the range covering the primary crystallisation surfaces of γ-Fe and cementite and a monotecto-eutectic reaction takes place at 1103°. Thermal analysis indicates two polymorphic transformations in FeS at 135° and 308°, and also in the alloys Fe–FeS and $Fe–Fe_3C–FeS$. The crit. points Ac1, Ac3, Ar3, Ar1, A2, and A0 have been determined. These are practically the same as for plain C steel, indicating that FeS can be only slightly sol. in γ- and α-Fe. The binary equilibrium diagram for the system Fe–FeS is similar to that found by other investigators. Section diagrams for const. FeS or Fe_3C content and also a projection diagram of the space model of the ternary system have been constructed. A qual. binary diagram for the system $Fe_3C–FeS$ has been deduced from the diagrams of the ternary system. The process of crystallisation for a no. of alloys belonging to the respective fields in the projection diagram has been deduced and changes in alloys have been confirmed by microscopic examination. S appears to be almost insol. in solid Fe. M. S. B.

Equilibria between potassium chloride, sodium chloride, and water from −23° to 190°. E. Cornec and H. Krombach (Ann. Chim., 1932, [x], 18, 5—31; cf. this vol., 339).—There is no evidence of the existence of mixed crystals. E. S. H.

Solubility of the carnallite system. N. S. Kurnakov, D. P. Manoev, and N. A. Osokoreva (Kali, Russia, 1932, No. 2, 25).—Solubility tables and diagrams are given for $KCl–NaCl–MgCl_2–H_2O$ (25° and 100°), $KCl–NaCl–H_2O$, $NaCl–MgCl_2–H_2O$, $KCl–MgCl_2–H_2O$ (25° and 100°), $KCl–H_2O$, $NaCl–H_2O$, and $MgCl_2–H_2O$ (10—110°). Ch. Abs.

System calcium chloride–magnesium chloride–water at 0°, −15°, and −30°. C. F. Prutton and O. F. Tower (J. Amer. Chem. Soc., 1932, 54, 3040—3047).—Solubility data give no indication of double-salt formation. Only one form of $MgCl_2,8H_2O$ has been observed. B. E. T. (*c*)

Equilibrium in the system $(NH_4)_2SO_4–Th(SO_4)_2–H_2O$. A. Rosenheim and J. Zickermann (Z. anorg. Chem., 1932, 208, 95—99).—The data for 25° reveal the existence of 3 double salts: $(NH_4)_6[Th(SO_4)_5],3H_2O$, $(NH_4)_4[Th(SO_4)_4],3·5H_2O$, and $(NH_4)_2[Th(SO_4)_3],5H_2O$. The stability increases with increasing proportion of $(NH_4)_2SO_4$. E. S. H.

System manganese sulphate–thorium sulphate–water at 30°. New type of double salt. R. M. Caven (J.C.S., 1932, 2417—2420).—The stable solid phases are $Th(SO_4)_2$, $MnSO_4,5H_2O$, and the double *salt* $MnSO_4,Th(SO_4)_2,7H_2O$; the last separates only from solutions containing a large excess of $Th(SO_4)_2$ and cannot be recryst. from H_2O. D. R. D.

Phase-rule studies on metallic thiocyanates. II. Systems $AgNCS–NaNCS–H_2O$, $AgNCS–KNCS–H_2O$, and $AgNCS–NH_4NCS–H_2O$ at 25°. V. J. Occleshaw (J.C.S., 1932, 2404—2410).—The following double salts are recorded: $3NaNCS,AgNCS$; $NaNCS,AgNCS,2H_2O$ (new); $KNCS,AgNCS$; $2KNCS,AgNCS$; $NH_4NCS,AgNCS$; $5NH_4NCS,AgNCS$ (I). Only (I) can be recryst. from H_2O. The rate of dehydration of $NaNCS,2H_2O$ (the stable phase at 25°) over $CaCl_2$ or H_2SO_4 affords no indication of the existence of a lower hydrate at this temp. D. R. D.

Ternary systems. W. F. Ehret (J. Amer. Chem. Soc., 1932, 54, 3126—3134).—The stable double salt $CaCl_2,Ca(NO_3)_2,4H_2O$ occurs in the system $CaCl_2–Ca(NO_3)_2–H_2O$ at 25°. There are no double salts in the systems $CaCl_2–Ca(ClO_3)_2–H_2O$ and $SrCl_2–Sr(NO_3)_2–H_2O$ at 25° or in the system $KNO_3–Pb(NO_3)_2–H_2O$ at 0°. B. E. T. (*c*)

Properties of solutions of calcium chloride and carbamide. F. de Carli (Atti R. Accad. Lincei, 1932, [vi], 15, 584—590).—Solubility data at 11° and 25° are recorded. The cryst. compound $CaCl_2,4CO(NH_2)_2,2H_2O$ can be obtained by slow evaporation of the corresponding solution. Viscosity and refractivity data indicate that there is no association between $CaCl_2$ and $CO(NH_2)_2$ in solution. O. J. W.

Specific heats of aqueous solutions of formic, acetic, propionic, and *n*-butyric acids. C. R. Bury and D. G. Davies (J.C.S., 1932, 2413—2417).—Data are given for concns. up to approx. 30%. For aq. HCO_2H, AcOH, and $EtCO_2H$ the sp. heat falls regularly with increase in concn., but with $Pr^{\alpha}CO_2H$ there is an abrupt change in slope at a concn. of 13%, due to the formation of micelles. The form of the curve indicates that the heat of micelle formation is small. D. R. D.

Heats of formation of [ternary] water–alcohol mixtures. P. Brun (J. Chim. phys., 1932, 29, 362—366; cf. A., 1928, 844).—Sp. heats and heats of mixing are recorded for H_2O–EtOH–*iso*amyl alcohol mixtures in the range of complete miscibility. The results are at variance with those of Mondain-Monval (*ibid.*, 1084) in the zone of crit. miscibility. J. G. A. G.

Heats of combustion and formation of carbon monoxide and methane. W. A. Roth and H. Banse (Arch. Eisenhüttenw., 1932—1933, 6, 43—46).—Combustion of CO and CH_4 in a brass bomb with an insulated ignition device gave the following results: $CO+0·5O_2=CO_2+67·70$ kg.-cal. at 20° and $CH_4+3O_2=CO_2+2H_2O$ (liq.)+213·0 kg.-cal. From these results it follows that the heat of formation of CO from graphite at 20° is 26·57 kg.-cal. and that of CH_4 17·97 kg.-cal. A. R. P.

Thermal calculations for determining the reactivity of carbon monoxide. I. A. Trefiliev and S. A. Kostro (Gorni Zhur., 1930, 13, No. 10—11, 11—17).—The "thermal difference" (heat of combustion—sum of heat effects of components) × 100/sum of heat effects of components, is: C_2H_6 −7·07% (−28·18 kg.-cal.), C_2H_4 +4·72% (+15·60 kg.-cal.), C_2H_2 +19·32% (+50·58 kg.-cal.), CO +19·69%. It is shown that the expected similarity in the reactivities of C_2H_2 and CO exists. On raising the temp. of distillation of hard coal the CO content of the gases decreases. When cellulose is heated with CO_2 at 30 atm. the pressure progressively decreases, the cellulose becoming extensively oxidised. Ch. Abs.

Heat of combustion of methylglyoxal. C. Neuberg and E. Hofmann (Biochem. Z., 1932, 252, 440—450).—The heats of combustion of AcCHO, its oxime, $BzCHO,H_2O$, its oxime and $BzCO_2H$ are 345·7, 402·9, 905, 970·4, and 843·5 kg.-cal. per mol. and the heats of dissolution +10·3, −3·9, −4·8, —?, and −2·44 kg.-cal. per mol., respectively. The bearing of these vals. on the mechanism of the degradation of sugar is discussed. P. W. C.

Heat of combustion of some mixtures of organic compounds. M. Milone and P. Rossignoli (Gazzetta, 1932, 62, 644—655).—Data are given for $C_{10}H_8$–phenanthrene, $C_{10}H_8$–α-$C_{10}H_7·NH_2$, salicylic acid–α- and β-$C_{10}H_7·NH_2$, BzOH–α-$C_{10}H_7·NH_2$, $C_{10}H_8$–picric acid, anthracene–picric acid. In general, when the equilibrium diagram shows the absence of compound formation, the heat of combustion of the mixtures is a linear function of the composition. Cases of compound formation are indicated by corresponding points of inflexion in the heat of combustion–composition curves. O. J. W.

Heat of formation of calcium metasilicate (wollastonite) and ferrous orthosilicate (fayalite). W. A. Roth and H. Troitzsch (Arch. Eisenhüttenw., 1932—1933, 6, 79—83).—A calorimeter is described by the aid of which the constituents of slags and cements can be readily dissolved in a mixture of 20% HCl and HF at 77°. From the vals. obtained for CaO, FeO, SiO_2 (α-quartz and amorphous SiO_2), $CaSiO_3$, and Fe_2SiO_4 the heats of formation of $CaSiO_3$ and Fe_2SiO_4 from the oxides and α-quartz are, respectively, +21·0 and +10·3 kg.-cal. at 77°, and +20·96 and +9·6 kg.-cal. at 500°. The heat of dissolution of amorphous SiO_2 in 20% HF is 36·44 and of α-quartz 32·93 kg.-cal., whence the heat of transformation of the former into the latter at 77° is 3·51 kg.-cal. A. R. P.

Thermochemistry of metasilicates of calcium and magnesium and of diopside. H. Wagner (Z. anorg. Chem., 1932, 208, 1—22).—The true sp. heats of α- and β-wollastonite have been determined from 10° to 300° abs., and the mean sp. heats of α-wollastonite, β-wollastonite, clinoenstatite, and diopside from 273° to 1600° abs. At room temp. the heat of dissolution of α-wollastonite in 2*N*-HCl is 21,270 g.-cal.; that of β-wollastonite is 20,010 g.-cal. No anomalies are shown by the sp. heat–temp. curves. The transformation of α- into β-wollastonite has been examined with reference to Nernst's heat theorem. E. S. H.

Transport number of gold in a gold amalgam. K. Schwarz (Z. physikal. Chem., 1932, 161, 231—232).—In 0·1% Au amalgam the Au migrates to the cathode, its transport no. at 25° being $2{\cdot}7_8\times10^{-7}$. R. C.

Transference of water. II. Its dependence on concentration and temperature in the electrolysis of sodium chloride solutions. G. Davies, N. J. Hassid, and M. Taylor (J.C.S., 1932, 2497—2503).—The transference of H_2O to the cathode during the electrolysis of aq. NaCl has been measured, using $CO(NH_2)_2$ as non-electrolytic reference substance. The quantity transferred increases with increasing dilution and with falling temp., the variation being too great to be due solely to changes in transport no. or degree of hydration. It is inferred that the ions transport a considerable quantity of H_2O which is not chemically combined. D. R. D.

Conductivity of alkali metal hydroxides in water, and the mobility of the hydroxyl ion. J. Goworecka and M. Hłasko (Rocz. Chem., 1932, 12, 403—415).—At 25° the limiting mol. conductivities are 239·55 for LiOH, 251·0 for NaOH, and 274·9 for KOH. The conductivity coeffs. (λ_r/λ_∞) of these hydroxides are for dil. solutions 1% smaller than the vals. given by Onsager's formula (cf. A., 1927, 517), and increase in the order Li<Na<K (cf. A., 1926, 906). R. T.

Conductivity of alkylated ammonium picrates in aqueous solution at 0°, 25°, and 90°. I. P. Ekwall (Z. physikal. Chem., 1932, 161, 211—226).—Measurements have been made over a wide concn. range. R. C.

Variation of the potential of a hydrogen electrode with pressure, in the low-pressure region. R. Romann and W. Chang (Bull. Soc. chim., 1932, [iv], 51, 932—938).—The e.m.f. of the cell $^+Hg|0{\cdot}1N$-KCl saturated with $HgCl|0{\cdot}1N$-$HCl|(H_2+xN_2)^-$ at 1 atm. and 25° has been measured for partial pressures of H_2 from 1 to 0·001 atm. Down to 0·005 atm. the observed results agree well with theory. D. R. D.

Electrode potentials of iron–manganese alloys. C. Wells and J. C. Warner (Trans. Electrochem. Soc., 1932, 62, 233—236).—The electrode potential of Fe–Mn alloys in 0·1*M*-$MnSO_4$ when plotted against alloy composition gives a smooth curve over the whole range from 1·8 to 100% Mn. This result is discussed in relation to *X*-ray and metallographic data. H. J. T. E.

Electrometric studies of the precipitation of hydroxides. V. Tervalent gold chloride solutions. H. T. S. Britton and N. E. Dodd. **VI. Sexavalent uranium chloride solutions.** H. T. S. Britton and A. E. Young (J.C.S., 1932, 2464—2467, 2467—2469).—V. Measurements of p_H (by means of a glass electrode) and of conductivity during the titration of aq. $HAuCl_4$ with NaOH indicate that the former behaves as a mixture of HCl and partly hydrolysed $AuCl_3$. The HCl is neutralised immediately, whilst the $AuCl_3$ reacts slowly with NaOH, forming $NaAuO_2$.

VI. Similar data for a solution of $U(OH)_6$ in aq. HCl, using both glass and quinhydrone electrodes, indicate that the original solution contains UO_2Cl_2, which does not react appreciably with HCl, and that the ppt. produced by NaOH is $U(OH)_6$. D. R. D.

Deposition potential of some complex oxalates. A. Mazzucchelli and U. Bacci (Gazzetta, 1932, 62, 764—774).—Measurements have been made of the deposition potential and of the static potential of the deposited metal for Cr, Fe, Co, Ni, and Cu deposited electrolytically from solutions of their complex NH_4 oxalates. The deposition potentials show a considerable overvoltage, decreasing from Cr to Cu; passivity phenomena are associated with the static potential. O. J. W.

Kinetics of electrode processes. I. Depolarisation effects by hydrogen and oxygen at platinum electrodes. J. A. V. Butler and G. Armstrong (Proc. Roy. Soc., 1932, A, 137, 604—621).—On anodic polarisation of a Pt electrode, which has previously been cathodically polarised in a solution saturated with H_2, using c.d. between 0·5 and 30×10^{-3} amp. per sq. cm., two depolarisation processes are observed at potentials more negative than that at which steady liberation of O_2 occurs. They are attributed respectively to electrolytic dissolution of adsorbed or dissolved H_2 and to the formation of a layer of adsorbed O_2. Only one such process, which marks the disappearance of a layer of adsorbed O_2, is observed in the cathodic polarisation of an electrode which has previously been anodically polarised. L. L. B.

Polarographic studies with the dropping mercury cathode. I. Determination of decomposition potential. G. Semerano (Gazzetta, 1932, 62, 518—538).—A theoretical discussion of the polarisation curves, obtained by the method of Heyrovský and Shikata, at a dropping Hg cathode. The decomp. potential is taken to be the point of max. curvature on the curve. A method for calculating the resistance of the polarised circuit and the order of the electrolytic process from the polarisation curve is described. O. J. W.

Polarographic studies with the dropping mercury cathode. XXV. Solutions of Ga, Ti, V, Nb, and Ta. S. Zeltzer (Coll. Czech. Chem. Comm., 1932, 4, 319—334).—Current–voltage curves with a dropping Hg cathode show that reduction occurs at the following voltages compared with the normal HgCl electrode. Ga^{III} to metal at −1·08 volts in acid solutions and at −1·5 volts in aq. NH_3; no reduction in aq. alkali hydroxides. Ti^{IV} to Ti^{III} at −0·8 volt in acidic, no reduction in alkaline, solutions. V^{IV} or V^{III} to V^{II} at −0·84 volt in acid solutions, at −1·50 volts in aq. NH_3, and at −1·80 volts in aq. alkali hydroxides; V^{V} oxidises Hg. Nb^{V} at −0·83 volt in aq. HNO_3 but not in aq. HCl or in alkaline solutions. Ta^{V} is not reduced. Ga can be detected in the presence of excess of Al and of equal amounts of In or Zn. Ti can be approx. determined in the presence of Cr, Fe, and Al. V is distinguished from Ti in alkaline solutions. By examination in aq. HCl, aq. HNO_3, and aq. NH_3 mixtures of Ti, V, Nb, and Ta can be approx. analysed. A. G.

Polarographic studies with the dropping mercury cathode. XXVI. Decrease of hydrogen over-potential effected by traces of platinum. I. Šlendyk (Coll. Czech. Chem. Comm., 1932, 4, 335—349).—Current–voltage curves with a dropping Hg cathode show a current increase at −1·0 volt compared with the normal HgCl electrode in aq. HCl containing traces of $PtCl_4$. For this purpose a cell is used in which the Hg anode is in a separate compartment. That the current increase is not due to Pt deposition is shown by the voltage at which it occurs, by its excessive amount, and by its increase with increasing $[H^{\cdot}]$. It is ascribed to catalysed H_2 deposition, and this large effect of traces of Pt is said to be the cause of irregular results in measurements of H_2 over-potential. In $2N$-HCl a concn. of $10^{-7}M$-$PtCl_4$ can be detected. Many commercially "pure" salts are shown to contain traces of Pt not present in the natural crude compounds. A. G.

Anodic behaviour of nickel. II. K. Georgi (Z. Elektrochem., 1932, 38, 714—731; cf. this vol., 1000).—The p.d.–time curves in aq. salt solutions have been determined. Three states of the Ni anode are recognised. The active state is favoured by a low c.d., a small anion, high $[H^{\cdot}]$, and temp.; the reverse conditions favour an impoverished diffusion layer next to the anode and cause a transition to a state of higher p.d. At the lowest c.d. the change $Ni\longrightarrow Ni^{\cdot\cdot}$ takes place at certain active centres on the electrode, whilst H collects on the greater (passive) portion and may be removed by oxidation or other depolarising influences. The second state is characterised by an invisible film of $Ni(OH)_3$ and the third state by a porous diaphragm of $Ni(OH)_3$. The effect of the easily-penetrating ions Cl′ and Br′ on the transition from one state to another has been examined; in some cases periodic effects are noted. E. S. H.

Passivity of metals. VII. Specific function of chromates. T. P. Hoar and U. R. Evans (J.C.S., 1932, 2476—2481).—The inhibiting effects of different oxidising agents on the corrosion of Fe in H_2O or aq. KCl have been compared. $K_2CrO_4 > NaVO_3 > KMnO_4 > H_2O_2$; the last-mentioned accelerates corrosion under certain conditions. The sp. inhibiting action of CrO_4'' is due to the fact that it ppts. $Fe^{\cdot\cdot}$ completely, the ppt. consisting of hydrated Fe_2O_3 and Cr_2O_3, which has considerable protective action owing to its gelatinous nature, high sp. vol., close adhesion to the Fe, etc. The sp. protective action of Cr in steel and of Cr pigments is due to the formation of similar films. D. R. D.

Relation between the two constants of the Arrhenius equation. M. J. Polissar (J. Amer. Chem. Soc., 1932, 54, 3105—3111).—The simple collision hypothesis cannot account for all known bimol. reactions. Gas-collision formulæ probably do not apply to reactions in liquid solution. An explanation of the linear relation between the consts. in Arrhenius' equation for bimol. reactions in solution is given. S. L. (*c*)

Spontaneous inflammability and chemical constitution. C. Zerbe and F. Eckert (Angew. Chem., 1932, 45, 593—598).—The temp. of spontaneous ignition have been determined for hydrocarbons and compounds containing O in the aromatic, aliphatic, and naphthene series. For each ignition temp. there is a crit. concn. of O_2 and for a given concn. of O_2 there is a min. temp. required. The rule breaks down above the spontaneous inflammability temp. in the case of aliphatic compounds and naphthenes which contain no conjugated double linking. This linking definitely reduces the tendency to spontaneous inflammability. The no. of H atoms is unimportant, except in so far as the general constitution is altered, but the presence of O lowers the temp. of spontaneous ignition of aromatic compounds and raises that of aliphatic compounds. E. S. H.

Inflammation of air–hydrocarbon mixtures by heated substances. M. Aubert and A. Pignot (Ann. Off. Nat. Combust. liq., 1931, 6, 819—828; Chem. Zentr., 1932, i, 2435).—In contact with Pt heated at a sufficiently high temp., mixtures of 400 c.c. of air with 0·02—0·09 c.c. of hydrocarbon (hexane, *cyclo*hexane, C_6H_6) explode. The lowest ignition temp. of hexane– and heptane–air mixtures is about 300°. The time taken by a mixture to reach the max. temp. depends on the temp. of the Pt wire and on the composition of the mixture. A. A. E.

Influence of foreign gases on the lower critical oxidation pressure of carbon disulphide. A. Ritchie, R. R. H. Brown, and J. J. Muir (Proc. Roy. Soc., 1932, A, 137, 511—519).—The lower crit. oxidation pressure for $CS_2 : 3O_2$ mixtures in presence of A, N_2, CO_2, and SO_2 is given by the expression

$p_{CS_2}p_{O_2}[1+(fD_x^{-1}p_x)/(p_{CS_2}+p_{O_2})]$=const., where p_{CS_2} and p_{O_2} are the lower crit. explosion pressures in the presence of pressure p_x of inert gas. D_x is the diffusion coeff. of the chain propagator into the foreign gas. H_2, CCl_4, and C_6H_6 do not behave as inert gases and give abnormal results. With H_2, the main reaction appears to be the H_2 : O_2 explosion, with CS_2 acting as an explosion sensitiser.

L. L. B.

Decomposition of diethyl ether at low pressures. O. K. Rice and D. V. Sickman (J. Amer. Chem. Soc., 1932, 54, 3778—3779).—In the decomp. at 525° and 462°, with initial pressures of 0·15—200 and 0·8—450 mm., respectively, the graph of the logarithm of the velocity coeff., k, against the logarithm of the pressure falls much less rapidly in the region of the lower pressure than would be expected from the usual theory; the very slight concavity upwards suggests that a second unimol. region is approached at low pressures. The increase in k by H_2 has been verified. C. J. W. (*c*)

Homogeneous first-order gas reactions. III. Decomposition of paraldehyde. C. C. Coffin (Canad. J. Res., 1932, 7, 75—80).—The decomp. of paraldehyde to MeCHO is a homogeneous gas reaction of the first order. Between 209° and 270° and initial pressures of 1·18 and 52·0 cm. the velocity is unaffected by the pressure and only slightly by the presence of Hg, H_2O, or tap grease or by the area of glass surface. The influence of temp. is given by the equation $\log_e k=34·83-(44,160/RT)$, the energy of activation being thus 44,160 g.-cal. per mol.

A. G.

Kinetics of reaction between hydrogen peroxide and potassium permanganate in acid solutions. I. W. Limanowski (Rocz. Chem., 1932, 12, 519—535).—The velocity of reduction of $KMnO_4$ by excess of H_2O_2 in acid solution is $dx/dt=k_1b(1-x)+k_2ax(1-x)$, where a and b are the initial concn. of $KMnO_4$ and H_2O_2, and x is the relative concn. of $Mn^{\cdot\cdot}$. R. T.

Differing velocity of esterification of the optical antipodes of a racemate using optically active catalysts. R. Wegler (Annalen, 1932, 498, 62—76).—Treatment of *dl*-α-phenylethyl alcohol (I) with Ac_2O in presence of CCl_4 and brucine gives an optically active acetate. The rotation of the ester increases with the reaction time to a max. and then decreases (to approx. 0), is always smaller at higher temp., is max. when approx. 0·25 mol. of brucine per mol. of (I) is used, and varies with the solvent and the order of addition of the reagents. The velocity of esterification of (I) is 20 times as great in presence of brucine as in its absence. The results are ascribed to the more rapid esterification of one antipode of (I). The use of AcCl (for Ac_2O) leads to a product which has a final rotation; in this case, one antipode is esterified, whilst the other is partly converted into styrene and α-phenylethyl chloride. (+)-α-Phenylethyl alcohol is esterified more readily with AcOH in presence of CCl_4 and brucine than the (−)-form. *dl*-α-Phenylpropyl alcohol and "brucine acetate" (from brucine hydrate and Ac_2O in CCl_4) in pyridine or CCl_4 give dextrorotatory esters. *dl*-α-Phenylethylamine (II) and $ClCO_2Et$ in CCl_4 containing brucine afford a urethane (α +3·64°); the unreacted amine had α −3·1°. The unreacted amine from (II) and PhNCO in pinene (α −33·25°) had α +0·25°. H. B.

Phenomena accompanying the hydrolysis of sucrose. S. Bezzi (Gazzetta, 1932, 62, 745—755).—In HCl solutions $[H^{\cdot}]$ increases with the amount of added glucose or invert-sugar, and also during the hydrolysis of sucrose. The increase, therefore, of the velocity not only during the inversion of sucrose but also with increasing sugar concn. is explained by the increase in the catalyst concn., which can be attributed to hydration of $H^{\cdot}$ and of the sugars. The calc. degree of hydration of the latter agrees well with the vals. obtained in other ways. O. J. W.

Rate of decomposition of the normal diazotates. Z. E. Jolles and W. Camiglieri (Gazzetta, 1932, 62, 720—726).—Curves are given showing the rate of evolution of N_2 at 20° in the decomp. of diazotates of the following bases: NH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$, *o*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$, *o*- and *p*-$NH_2{\cdot}C_6H_4{\cdot}OEt$, α-$C_{10}H_7{\cdot}NH_2$, and phenylazoxycarbonamide. The rate of decomp. is increased by the presence of alkoxy-groups in the *o*- and *p*-positions and of Me in the *p*-position with respect to the diazo-group, whereas the opposite is the case with diazonium salts. O. J. W.

Oxidation rates of silicon carbide and graphite powders. A. H. Ballard and R. R. Ridgway.—See B., 1932, 841.

Mass rate of reactions in solids. R. S. Bradley, J. Colvin, and J. Hume (Proc. Roy. Soc., 1932, A, 137, 531—541).—An attempt is made to evaluate the effect of progressive nucleation in the reactions $CaCO_3,6H_2O \rightarrow CaCO_3+6H_2O$ and $KHC_2O_4,0·5H_2O \rightarrow KHC_2O_4+0·5H_2O$ by means of an analysis of the form of the mass decomp. curves. L. L. B.

Temperature increment of reaction velocity in heterogeneous reactions. IV. Reactions of cadmium carbonate. K. Fischbeck and K. Schnaidt (Z. Elektrochem., 1932, 38, 731—737; cf. this vol., 577).—The temp. increments of the reactions of $CdCO_3$ with H_2 and with liquid S are each 20 kg.-cal. This val. is < that obtained for CdO, which is more reactive. E. S. H.

Velocity of dissolution of metals in bromine water. A. Basiński (Rocz. Chem., 1932, 12, 536—550).—The velocities of dissolution of Cd, Zn, and Ni in aq. Br are, under similar conditions of temp. and stirring, identical; the temp. coeff. for the interval 15—25° is in all cases 1·43. In the case of Sn and Cu the reactions are: $Sn+Br_2 \longrightarrow SnBr_2 \xrightarrow{Br_2} SnBr_4 \xrightarrow{Sn} SnBr_2$ and $Cu+Br \longrightarrow CuBr \xrightarrow{Br} CuBr_2 \xrightarrow{Cu} CuBr$, the first and third reactions taking place at the metal surface, and the second in solution. Assuming the velocity of the second reaction to be great relatively to that of the first and third, the velocity of the process is given by $K_1-K_2=2·303V\log\{K_1a-(K_1-K_2)\}/S(t_2-t_1)\times\log\{K_1a-(K_1-K_2)x\}$, where K_1 and K_2 are the velocity coeffs. of the first and third reactions, respectively, V is the vol. of aq. Br, S

the area of the metal surface, a the initial Br concn., and x is the concn. of reaction products after t min. R. T.

Reactions between gas and solid. V. Azotation of calcium carbide and the effect of size of grain on its velocity. T. Aono (Bull. Chem. Soc. Japan, 1932, 7, 274—280).—At 1140° the rate of nitrogenation of grains of CaC_2 is proportional to the surface area of the unchanged part and is unaffected by the outer layer of nitride; at 950° and below the rate is also inversely proportional to the thickness of this layer. A. G.

Kinetics of reaction NH_3(gas)$\rightleftharpoons$N (dissolved in α-Fe) + $1{\cdot}5H_2$(gas). G. Engelhardt and C. Wagner (Z. physikal. Chem., 1932, B, 18, 369—379).—The rate is given by $dc/dt=kp(c_e-c)$, where c is the N concn. in the Fe at time t, and c_e the equilibrium concn. when the partial pressure of H_2 in the gas phase is p. Both forward and backward reactions seem to occur in stages, the rate of nitriding probably being determined by the rate of decomp. of NH_2 formed as an intermediate product in the adsorbed film, and the rate of denitriding by the rate of formation of NH_2. R. C.

Corrosion and Tammann's resistance limits. *X*-Ray study of gold–copper single crystals. L. Graf (Metallwirt., 1932, 11, 77—82, 91—96; Chem. Zentr., 1932, i, 2379).—Strongly oxidising reagents produce a corrosion pattern of pure Au; slightly oxidising, S-containing, or gaseous reagents produce one of mixed crystals rich in Au. The mechanism of the process is discussed. A. A. E.

Kinetics of the acetylation of cellulose. II. I. Sakurada.—See B., 1932, 880.

Kinetics of the nitration of cellulose. I. Sakurada and M. Shojino.—See B., 1932, 880.

Dynamics and catalysis of the thermal decomposition of hydrogen carbonates in aqueous solution. VI. Hydrogen carbonate decomposition in the gas stream. VII. Hydrogen carbonate decomposition in boiling calcium, strontium, and barium hydrogen carbonate solutions. R. Stumper (Z. anorg. Chem., 1932, 208, 33—45, 46—52; cf. this vol., 234, 703).—VI. The velocity of decomp. of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in aq. solution depends partly on the rate at which the CO_2 can be removed. Experiments on passing various gases through $0{\cdot}005N$ and $0{\cdot}01N$ solutions at 100° show that the acceleration of the decomp. increases with increasing streaming velocity for all the gases and also increases specifically in the order $H_2<O_2<$ air. The sp. effect is related to various physical properties of the gases. In a stream of CO_2 the decomp. is retarded in the case of $Ca(HCO_3)_2$, whilst $Mg(HCO_3)_2$ does not decompose even at 100°. A sufficient stream of CO_2 serves to separate a boiling mixed solution of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, $CaCO_3$ being pptd. and $Mg(HCO_3)_2$ remaining in solution. When CO_2 is removed by a stream of indifferent gas, the decomp. of $Ca(HCO_3)_2$ is bimol.; the decomp. of $Mg(HCO_3)_2$ is complicated by hydrolysis of $MgCO_3$.

VII. The decomp. of boiling 0·0025, 0·005, and $0{\cdot}010N$-$Ca(HCO_3)_2$, -$Sr(HCO_3)_2$, and -$Ba(HCO_3)_2$ with or without the aid of a gas stream decreases in the order Sr > Ca > Ba, bearing a relation to the solubilities of the carbonates. The general course can be represented by $dx/dt=k_2[HCO_3']^2-k_1C$, in which the second term is practically negligible. E. S. H.

Ozone as an oxidation catalyst; ozonation of benzaldehyde. E. Briner, A. Demolis, and H. Paillard (J. Chim. phys., 1932, 29, 339—361; cf. A., 1931, 1016; this vol., 235).—The oxidation of PhCHO and its solutions in hexane, petrol, CCl_4, and C_2HCl_5 by O_2 containing 0·9—8% O_3 and 0—90% N_2 has been investigated by a dynamic and a static method at temp. between −20° and 60°. The additional yield of BzOH produced in a fixed time by a const. gas flow due to catalysis by the O_3: (*a*) increases rapidly with O_3 concn. to a max. and then decreases slowly, (*b*) decreases regularly with falling O_2 concn. (but O_3 consumption increases), and (*c*) passes through a max. with increasing concn. of PhCHO. O_3 lowers the temp. at which autoxidation of PhCHO becomes appreciable. The yield of BzO_2H increases rapidly during an experiment and tends to a const. val. which, in general, varies concomitantly with that of BzOH. The catalysis is explained on the basis of reaction chains initiated by the interaction of O_3 with PhCHO, and not BzOH, to produce activated BzO_2H capable of reacting with PhCHO, and O atoms which propagate the chains by regenerating O_3 from O_2. J. G. A. G.

Spontaneous oxidation of cysteine. E. G. Gerwe (Science, 1932, 76, 100).—A reply to criticism (this vol., 129). The autoxidation of cysteine is not due to the presence of Cu, which was shown to be absent by means of Yoe's $K_4Fe(CN)_6$ test and by the failure of cyanide to reduce the rate of oxidation. Oxidation is also unaffected by the addition of pyrophosphate, which inhibits the catalytic activity of Fe and Mn, but not of Cu. L. S. T.

Autoxidation of fatty acids. I. W. Franke.—See this vol., 1112.

Relation of adsorption to catalysis. Catalytic union of ethylene and hydrogen. G. Harker (J.S.C.I., 1932, 51, 323—326T).—Experiments on the adsorption of C_2H_4 and H_2 and catalysis of their union at a surface of Cu distributed on diatomaceous earth show that the activity of the catalyst is promoted by the adsorption of H_2 and degraded by adsorption of C_2H_4. The reaction occurs at active centres, representing about 1/2000 of the total metal. The active centres are more readily oxidised than the bulk of the metal; admission of a trace of air destroys the activity of the catalyst. E. S. H.

Catalytic properties of rhenium. H. Tropsch and R. Kassler (Mitt. Kohlenforsch.-Inst. Prag, 1931, 13—15; Chem. Zentr., 1932, i, 2420).—Re catalyses the hydrogenation of ethylenic linkings. A. A. E.

Non-metallic catalysts for hydrogenation and dehydrogenation. II. Catalytic properties of chromium oxide. W. A. Lazier and J. V. Vaughen (J. Amer. Chem. Soc., 1932, 54, 3080—3095).—Amorphous Cr_2O_3, prepared by pptn. as $Cr(OH)_3$ or by igniting $(NH_4)_2Cr_2O_7$ in a vac. or in thin layers in air, is an active catalyst for the hydrogenation of C_2H_4, C_3H_6, and C_8H_{16} and the dehydrogenation of C_6H_{12} (cf. A., 1931, 1376). Cr_2O_3 prepared by igniting the nitrate or oxalate or by reducing higher oxides yields an *X*-ray diffraction pattern and is inactive. Any treatment inducing the glow phenomenon results in crystallisation of Cr_2O_3, and destroys its activity towards hydrocarbons, but not to the same extent for MeOH synthesis or alcohol decomp. The capacity of amorphous Cr_2O_3 for activating hydrocarbons is not in harmony with Balandin's mechanism of hydrogenation and dehydrogenation (A., 1929, 519). J. V. V. (*c*)

Catalytic oxidation of *n*-propyl alcohol. A. R. Day and A. Eisner (J. Physical Chem., 1932, 36, 1912—1915).—In the oxidation by air at 350—500°, using mixtures of Ag and Sm_2O_3 as catalysts, the max. yield of EtCHO (76·4%) is obtained with a small rate of flow of the gas mixture and a catalyst containing 0·25% Sm_2O_3. J. H. R. (*c*)

Electrolytic oxidation. I. Electrolytic oxidation of sodium thiosulphate at a platinum anode. S. Glasstone and A. Hickling (J.C.S., 1932, 2345—2356).—The main product of the electrolytic oxidation of S_2O_3'' at a Pt anode in buffered solutions is S_4O_6''. A small amount of SO_4'' is also formed, and this increases with the p_H of the solution. The curve obtained by plotting anode potential against amount of electricity passed indicates that the oxidation apparently takes place at two different potentials, but, although the relative amounts of electricity passing at the two stages can be altered by varying the current, the nature and amounts of the products remain practically const. The addition to the electrolyte of catalysts for the decomp. of H_2O_2 results in a marked decrease in current efficiency for the oxidation and in the quantity of electricity passing at the initial lower potential stage. $Hg(CN)_2$, which is not a catalyst for H_2O_2 decomp., suppresses the lower potential stage, but does not affect the oxidation efficiency. The results may be explained by supposing that OH′ discharged at the anode forms H_2O_2 and part of this is decomposed spontaneously, the rate determining the relative extent of the two potential stages, whilst part reacts with S_2O_3'' to form S_4O_6'' and SO_4''. The anodic oxidation of S_2O_3'' thus appears to be a secondary chemical reaction and not an electrochemical process involving the discharge of S_2O_3''. M. S. B.

Avoidance of the loss of anodic platinum in the electrolysis of alkaline, especially ammoniacal, solutions. E. Reichel (Z. anal. Chem., 1932, 89, 411—421).—Loss in wt. of a Pt–Ir gauze anode, observed in solutions containing aq. NH_3 with or without $(NH_4)_2SO_4$, KOH, or KCN, is due to transference of Pt to the cathode. This is prevented by the addition of N_2H_4,H_2SO_4 or NH_2OH,H_2SO_4. More accurate results were obtained by adding these substances in the electrolytic determination of Zn, Ni, or Ga in presence of aq. NH_3 and its salts. M. S. B.

Electrochemical production of sodium hyposulphite. I. M. A. Rabinovitsch and A. S. Fokin. **II.** P. B. Shivotinski, A. P. Maschovetz, and A. S. Fokin. **III.** P. B. Shivotinski.—See B., 1932, 840.

Electrolytic oxidation of iodine and of iodic acid. H. H. Willard and R. R. Ralston (Trans. Electrochem. Soc., 1932, 62, 249—263).—Well-stirred suspensions of I in dil. HCl were electrolysed in a diaphragm cell with a Pt anode in the suspension, and a H_2O-cooled Au-plated Cu coil as cathode in $2N$-HNO_3, until the anolyte was free from I. HIO_3 was produced with current efficiencies >90%, but to avoid loss through reduction by HCl it is advantageous to continue electrolysis until anodic evolution of Cl_2 ceases; the total current efficiency of HIO_3 production was then 75—88% at 0·11 amp. per sq. cm. At this or higher c.d. the HCl concn. must not be <0·3*N* or else I is not dissolved as rapidly as it is oxidised. If, after completion of Cl_2 evolution, the Pt anode is replaced by one of PbO_2 electrodeposited on Pt gauze, further electrolysis converts HIO_3 almost completely into periodic acid at a current efficiency which approaches 50% if the c.d. is below about 0·2 amp. per sq. cm. Anode potential measurements show that although higher polarisations may be obtained at a Pt anode, scarcely any periodic acid is formed, probably because Pt catalyses its decomp. Commercial I may be used for both of the above prep., for the HIO_3 and H_5IO_6 obtained by evaporation of the anolytes are easily recryst. from conc. HNO_3. H. J. T. E.

Deposition of copper in presence of gum arabic. R. Taft and O. R. Bingham (J. Physical Chem., 1932, 36, 2338—2353; cf. A., 1931, 1249).—The mass of cathode deposit, both in neutral and acid solutions of $CuSO_4$, increases with the gum concn. to a limiting val. Deposits in neutral solutions contain more Cu than is obtained in the Cu coulometer placed in series, the proportion of excess increasing with rising temp. The results are interpreted as indicating that Cu oxides and gum are simultaneously adsorbed on the newly-deposited Cu crystals obtained on electrolysis of neutral $CuSO_4$ solutions. From acid solutions gum alone is adsorbed. C. L. R. (*c*)

Electrodeposited ε-brass. H. Kersten and J. Maas (J. Physical Chem., 1932, 36, 2175—2177).—Solutions containing 40 g. $Zn(CN)_2$, 50 g. NaCN, 30 g. Na_2CO_3, and 1·5—1·7 g. CuCN per litre, electrolysed at 50° using stainless steel electrodes and a c.d. of 2 amp. per sq. dm., give ε-brass. The deposit contains 11·4—21·4% Cu. The lines of the *X*-ray diagram of the electrodeposited material are not as sharp as those for fused ε-brass. C. L. R. (*c*)

Electrodeposition of cadmium from cadmium sulphate solutions. I. S. Wernick.—See B., 1932, 846.

Cathodic disintegration of metallic alloys. III, IV. L. Belladen (Gazzetta, 1932, 62, 493—496, 497—503; cf. this vol., 237).—III. Data similar to those obtained previously are given for Bi–Sb and Cu–Sn alloys.

IV. The results of previous papers are discussed. If atoms of a second metal, which increases the unit cell of the alloy, are introduced into a given metallic lattice, the ease of disintegration of the resulting alloy increases, whether mixed crystals or intermetallic compounds are formed. Alloys which crystallise in the hexagonal system, with $a=2{\cdot}70$ Å. approx., are not easily disintegrated and correspond with minima in the disintegration–composition curve. Compounds which crystallise in other systems different from those of the constituents give either a max. or a point of inflexion in the curve. The metal which is disintegrated from definite compounds has the same composition as the alloy. A relation is given between the ease of disintegration and the dimensions of the unit cell of pure metals which are of the same lattice type. O. J. W.

Electrodeposition of chromium, molybdenum, and tungsten. L. F. YNTEMA (J. Amer. Chem. Soc., 1932, 54, 3775—3776).—Preliminary note. C. J. W. (*c*)

Electrodeposition of chromium from tervalent chromium salt solutions. II. Chromium acetate, oxalate, and tartrate baths. H. T. S. BRITTON and O. B. WESTCOTT.—See B., 1932, 893.

Control of operations in chromium-plating baths. A. WOGRINZ; J. KORECKY.—See B., 1932, 845.

Electrolysis of red ammonium chromioxalate. A. MAZZUCCHELLI and U. BACCI (Gazzetta, 1932, 62, 756—763; cf. this vol., 236).—Investigation of the electrolysis of solutions of $[(H_2O)_2Cr(C_2O_4)_2]NH_4,3H_2O$ under varying conditions of temp., c.d., and time of electrolysis show that this compound is not so suitable as the blue complex salt previously described for the deposition of Cr. O. J. W.

Electrochemical oxidation of molybdenum in potassium hydroxide solutions. M. DEK. THOMPSON and A. L. KAYE (Trans. Electrochem. Soc., 1932, 62, 271—281).—KOH solutions of various concn. were electrolysed in a diaphragm cell with Fe cathode and Mo sheet anode at 25° and various c.d. At low c.d. molybdate is formed with 100% current efficiency, but at higher c.d., especially in more dil. KOH solutions, increasing amounts of oxide mud in which the valency of Mo is 4—5·4 are produced. No O_2 is liberated even at 0·4 amp. per sq. cm. C.d.–anode potential curves for the separate anode reactions are recorded. Curves showing the relation between anode potential at given c.d. and KOH concn. resemble those for Fe-Mn anodes, but no min. is obtained when current efficiency is plotted against KOH concn. (cf. B., 1924, 907). H. J. T. E.

Electrodeposition of tin. J. J. COLLINS.—See B., 1932, 846.

Electrolytic oxidation of leuco-bases of the triphenylmethane series of dyes. G. H. WHITE, jun. [with A. LOWY].—See B., 1932, 848.

Electric discharges in liquids. II. Arc discharge in water (continued). H. D. CARTER and A. N. CAMPBELL (Trans. Faraday Soc., 1932, 28, 634—644; cf. this vol., 580).—The heat evolved by the arc running at known p.d. and current is about 88% of the energy input as determined by the const.-flow calorimeter described. The rate of evolution of gas increased with the current, and the C cathode was worn away at a rate inappreciable compared with the C anode. Fe or Cu cathodes had little effect, but with Fe or Cu anodes the rate of gas evolution decreased and hydrated metallic compounds were produced. The $CO:CO_2$ ratio in the evolved gases decreases with increase of current and rise of temp. of the H_2O surrounding the arc; the concn. of O_2 is diminished by metallic anodes. The results are discussed and are at variance with the "thermal" theory. J. G. A. G.

Chemical action in glow discharge. IX. Reaction in Crookes dark space and negative glow. A. K. BREWER and P. D. KUECK (J. Physical Chem., 1932, 36, 2133—2140; cf. this vol., 130).—The rate of synthesis of NO_2 is practically zero throughout the Crookes dark space, and is a max. at the beginning of the negative glow and decreases exponentially with the distance from the Crookes dark space. Under 1 mm. pressure the average path over which electrons from the cathode are capable of initiating reaction is 0·36 cm., which shows the no. of positive ions formed per electron in the negative glow to be 3·3. P. H. E. (*c*)

Influence of stirring on the velocity and temperature coefficient of photochemical reactions. W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1932, 9, 335—340).—An expression has been deduced which indicates that when the ratio between the light absorption and velocity of a photochemical reaction deviates appreciably from unity, stirring leads to increased velocity and decreased temp. coeff. When the ratio is 1, stirring should have no effect. M. S. B.

Photochemical fission of metallic salts dissolved in organic solvents. E. PUXEDDU (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 26; Chem. Zentr., 1932, i, 2293—2294).—In abs. EtOH, $HgCl_2$ dissociates into HgCl+Cl; in $COMe_2$ cryst. Hg_2Cl_2 is formed, whilst in C_5H_5N there is no ppt., the cryst. mass which remains after distillation of the solvent containing $2C_5H_5N,2HgCl_2$, m.p. 179°, and $2C_5H_5N,3HgCl_2$, m.p. 194—195°. HgI_2 dissociates in $COMe_2$, and $CuCl_2$ in Et_2O. A. A. E.

Action of oxides on silver nitrate and gold chloride in light. C. RENZ (Helv. Chim. Acta, 1932, 15, 1077—1084; cf. this vol., 821).—Photoreduction of aq. $AgNO_3$ is sensitised by oxides of Al, Y, La, Sm, Er, Pr+Nd, Ce, Zr, Ti, Nb, Bi, W, Cd, and, less strongly, by those of Be, Ta, Th, and In. With Sb_2O_3 the $AgNO_3$ is unchanged, whilst Sb is formed. Aq. $AuCl_3$ is photolysed in presence of only some of the above, including Sb_2O_3. F. L. U.

Destruction of the latent image by monochromatic light from the whole visible spectrum. J. NARBUTT (Z. wiss. Phot., 1932, 31, 146—151; cf. A., 1930, 1385).—The latent image in photographic plates, exposed, and subsequently desensitised with pinacryptol-yellow, is partly destroyed by exposure to blue light, and to a smaller extent by yellow or red light; undesensitised plates also show the effect weakly. If the desensitiser is removed from treated plates by washing, the emulsion regains some of its sensitivity to light. J. L.

Nature of the latent image for physical development. III. H. Arens (Z. wiss. Phot., 1932, 31, 125—130; cf. this vol., 821).—The amount of Ag developed in unit time on unit surface of Ag nuclei is not const. The rule that the amount of Ag developed is dependent only on the no. of nuclei per sq. cm. is correct only for nuclei of average wt. $<10^{-15}$ g. (which is about the size of nuclei of photographic plates). J. L.

Evaluation and production of orthoactinic radiation. H. Bertling (Z. wiss. Phot., 1932, 31, 107—124).—The energy vals. of the light from various types of discharge tubes are compared. The abs. vals. can be calc. from photometric results using the mechanical equiv. of light according to Brodhun and Hoffmann, or Ives. Suitable combination of different discharge tubes can be used to give a required orthoactinic radiation. J. L.

Action of light on thallous chloride in presence of ammonia or oxalic acid. E. Baur and C. Renz (Helv. Chim. Acta, 1932, 15, 1085—1088).—When illuminated by a quartz lamp, TlCl in presence of aq. NH_3 gives a "photochloride" and HNO_3, and in presence of aq. $H_2C_2O_4$ a similar photochloride and CO_2. In neither case is any Tl^{III} compound formed. F. L. U.

Degradation of protein by ultra-violet light. J. P. Becker and P. Szendrö (Pflüger's Archiv, 1931, 228, 755—763; Chem. Zentr., 1932, i, 2959).—On irradiation of dialysed ovalbumin solutions free from globulin the characteristic max. at 280 mμ disappears; the presence of O_2 is necessary. The products do not give pptn. reactions. A. A. E.

Azeotropy and the preparation of pure compounds. I. Rabcewicz-Zubkowski (Rocz. Chem., 1932, 12, 567—575).—Theoretical. R. T.

"Triatomic" hydrogen. C. Naegeli and B. Lambert (Helv. Chim. Acta, 1932, 15, 1137—1139).—In experiments on the production of active ("triat.") H by electrical discharge under conditions used by previous workers, positive results (formation of H_2S from S) were obtained only when parts of the apparatus adjacent to the S became electrically charged. F. L. U.

Direct preparation of hydrogen peroxide in a high concentration. J. H. Walton and G. W. Filson (J. Amer. Chem. Soc., 1932, 54, 3228—3229).—When O_2 is bubbled into an EtOH solution of hydrazobenzene autoxidation occurs, $NHPh{\cdot}NHPh+O_2\longrightarrow NPh{:}NPh+H_2O_2$. About 97% of the theoretical yield of H_2O_2 can be obtained. E. G. V. B. (*c*)

New form of H_2O_2. K. H. Geib and P. Harteck (Ber., 1932, 65, [*B*], 1551—1555).—The action of H atoms on O_2 at low temp. gives a colourless, glassy solid with the at. ratio H : O : : 1 : 1. At −115° it is partly decomposed with production of normal H_2O_2. It is regarded as a new *form* of H_2O_2, possibly $\begin{matrix}H\\H\end{matrix}\!>\!O{:}O$. H. W.

Lithium cyanide. A. Perret and R. Perrot (Helv. Chim. Acta, 1932, 15, 1165—1171).—Observations previously recorded (cf. this vol., 238) have been confirmed and extended. Anhyd. LiCN can be prepared by the action of a mixture of HCN and C_6H_6 (1 : 1) on Li foil. LiCN is very hygroscopic and is readily hydrolysed; m.p. 160°, d_4^{18} 1·0755. Conversion of LiCN into Li_2CN_2 above 300° is measurably rapid only in presence of Fe as catalyst. LiCN is formed when a mixture of LiCl, C, and $CaCN_2$ is heated at 850°. F. L. U.

Metal cyanamides. A. Perret and A. M. Krawczynski (Helv. Chim. Acta, 1932, 15, 1009—1022).—Na_2C_2 reacts with NH_3 at 300° to give Na_2CN_2, with intermediate formation of $NaNH_2$ and C_2H_2. Above 300° the Na_2CN_2 is slowly converted into NaCN. Up to 68% $CaCN_2$ was obtained by interaction of $CaCO_3$ and NH_3 (with or without CO_2) for 6 hr. at 750°; $SrCO_3$ and $BaCO_3$ behave similarly, but not $MgCO_3$. $CaCN_2$ was also obtained from CaO by the action of a mixture of NH_3 and CO at 750°. None of these methods offers any advantage over the usual procedure. F. L. U.

Gurwitsch radiation in simple chemical reactions. L. K. Wolff and G. Ras (Biochem. Z., 1932, 250, 305—307).—The radiation arises during neutralisation of NaOH with HCl. P. W. C.

Carbonates of copper (Mlle.) S. Hémar (Bull. Soc. chim., 1932, [iv], 51, 969—974).—The products described as $6CuO,CO_2$ (J.C.S., 1862, 14, 70) and $8CuO,CO_2$ (Ann. Chim. Phys., 1851, [iii], 33, 75) are mixtures of variable composition (cf. J.C.S., 1909, 95, 1409). D. R. D.

Simple and double carbonates of copper. (Mme.) E. Poulenc-Ferrand (Bull. Soc. chim., 1932, [iv], 51, 883—902).—The existence of the compounds $K_2Cu(CO_3)_2$ and $K_2Cu(CO_3)_2,H_2O$ (A., 1907, ii, 620) has been confirmed. The compound described as $K_2Cu(CO_3)_2,4H_2O$ has the formula $2CuCO_3,3K_2CO_3,9H_2O$, whilst Gröger's $K_6Cu(CO_3)_4$ is really $K_2Cu(CO_3)_2$ contaminated with K_2CO_3. The results obtained by Benrath (A., 1926, 695) could not be confirmed. D. R. D.

Sulpho-salts of copper and iron. L. Cambi and L. Szegö (Atti R. Accad. Lincei, 1932, [vi], 15, 599—602).—The substance $K_2FeCu_3S_4$ described by Schneider consists of a series of solid solutions with a tetragonal lattice, *c*/*a* 1·182. They are paramagnetic and contain Fe^{III}. The sulpho-salts of Cu, *e.g.*, KCuS, KCu_4S_3, and $KCuS_4$, are diamagnetic. O. J. W.

Formation of ammines in aqueous solution. IX. R. Ripan (Bul. Soc. Stiinte Cluj, 1931, 6, 286—298; Chem. Zentr., 1932, i, 2003).—The following hexamethylenetetramine (X) *compounds* have been prepared: $Cu_2(OAc)_4,X$; $Cu_3(C_6H_4{\cdot}CO_2)_6,X$; $Cu_3(C_6H_5{\cdot}CH_2{\cdot}CO_2)_6,X$; $Cu_2(o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2)_4,X$; $Cu_3(o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2)_6,X$; $Cu_2(m\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2)_4,X$; $Cu_2(p\text{-}NO_2{\cdot}C_6H_4{\cdot}CO_2)_4,X$. A. A. E.

Magnesium sulphide and polysulphides. A. Tettamanzi (Gazzetta, 1932, 62, 597—600).—The labile sulphides of Mg can be fixed by means of hexamethylenetetramine (cf. A., 1914, i, 1125). The latter acts on a solution of $Mg(OAc)_2$ and $(NH_4)_2S$ to give white crystals of the *compound* $Mg(SH)OH,2C_6H_{12}N_4,10H_2O$. By using solutions of

$MgSO_4$ and NH_4 polysulphides the orange-yellow *compounds* $MgS_4,2C_6H_{12}N_4,10H_2O$ and $MgS_5,2C_6H_{12}N_4,10H_2O$ are obtained. O. J. W.

Hydrates of magnesium chloride and preparation of the anhydrous salt from the hexahydrate. W. D. Treadwell and T. Zürrer (Helv. Chim. Acta, 1932, **15**, 1271—1280).—When $MgCl_2,6H_2O$ is slowly dehydrated in a circulating stream of dry HCl, it loses H_2O in stages corresponding with hydrates containing 5, 4, 3·5 (new), 2, and $1H_2O$. Anhyd. $MgCl_2$ is rapidly formed at 200° in dry HCl. V.p. of the monohydrate between 100° and 170° are given. Heats of hydration are calc. and discussed theoretically. F. L. U.

Preparation of anhydrous magnesium chloride by action of chlorine on magnesium oxide in presence of carbon. J. G. Schtscherbakov and A. K. Raspopina (Techn. Urals, 1931, **7**, No. 5—6, 16—20; Chem. Zentr., 1932, i, 1939).—Reaction begins at 200° and is nearly complete at 300°, when a product containing 1—1·5% MgO may be obtained. At 500°, with a small excess of Cl_2, the product contains <0·5% MgO. The reaction is $2MgO+2Cl_2+C=2MgCl_2+CO_2$, but the gas contains about 12% CO. A. A. E.

Oxidisability of zinc. I. Influence of nickel on the oxidation of zinc. A. Oliverio and O. Belfiori (Annali Chim. Appl., 1932, **22**, 484—493).—The Zn–Ni couple, derived from the action of Zn on solutions of $NiSO_4$ or $NiCl_2$, or from contact of the two metals, liberates H_2 from cold H_2O. If the metals are finely divided, and if the temp. is raised to the b.p., the reaction with H_2O is very vigorous. The couple may be of use for the reduction of org. compounds in neutral media. E. W. W.

Brick-red form of zinc oxide. A. Kutzelnigg (Z. anorg. Chem., 1932, **208**, 23—28).—ZnO dissolves in molten NH_4NO_3, liberating NH_3 and forming basic Zn nitrate. When the product is heated it deflagrates, leaving brick-red ZnO. The colour is not affected by repeated boiling with H_2O, but it becomes cream after ignition. The brick-red form fluoresces under the influence of ultra-violet light; *X*-ray analysis does not distinguish it from the white form. E. S. H.

Ammines. Simple selenocyanoammines. VI. G. Spacu and C. G. Macarovici (Bul. Soc. Stiinte Cluj, 1932, **6**, 401—410; Chem. Zentr., 1932, i, 3044).—The following *compounds* of tolidine (*T*) and $NHPh{\cdot}NH_2$ are described: $[CdT(C_5H_5N)_4](SeCN)_2$, $[ZnT_2(C_5H_5N)_4](SeCN)_2$, $[MnT'_2(C_5H_5N)_4](SeCN)_2$, $[X(NHPh{\cdot}NH_2)_6](SeCN)_2$, where X=Co, Ni, Cd, Zn, and Mn. A. A. E.

Solid mercury hydride. K. H. Geib and P. Harteck (Ber., 1932, **65**, [*B*], 1550—1551).—The interaction of Hg vapour and activated H at the temp. of liquid air and 0·5 mm. yields *mercury hydride*, HgH. Decomp. commences at −125° and is complete at −100°. H. W.

Solubility of mercuric sulphide in dilute hydrochloric acid. M. Dorenfeldt-Holtan (Z. anorg. Chem., 1932, **208**, 76—80).—Black HgS is perceptibly attacked by hot or cold 5% HCl. Red HgS is attacked by hot but not by cold dil. HCl. E. S. H.

Chlorination of aluminium oxide with chlorine and carbon. W. D. Treadwell and L. Terebesi (Helv. Chim. Acta, 1932, **15**, 1053—1066).—The main reaction in the chlorination of Al_2O_3 at 550—980° is: $Al_2O_3+3C+3Cl_2\rightleftharpoons 2AlCl_3+3CO$, the concurrent reaction: $Al_2O_3+3CO+3Cl_2\rightleftharpoons 2AlCl_3+3CO_2$ proceeding much more slowly. A mechanism is suggested. The heat and free energy of the reaction are calc. F. L. U.

Carbon prepared by thermal decomposition of benzine in the gaseous phase. U. Hofmann and E. Groll (Ber., 1932, **65**, [*B*], 1257—1267).—Light petroleum, b.p. 60—70°, is allowed to drop slowly through a vertical quartz tube filled with H_2 and electrically heated, so that the temp. of the gas space is 950°. The "liquid benzine soot" is freed from tar by prolonged, successive extractions with C_6H_6 and $COMe_2$. The product formed on the walls of the quartz tube is lustre C. The crude "soot" contains appreciable amounts of H which is not removed by heating in tetrahydronaphthalene or at 500°/high vac.; ignition in H_2 at 950° or oxidation with CO_2 at 950° effects removal, but the former process is accompanied by enlargement of the crystals. The adsorptive power of "liquid benzine soot" as freshly prepared is immeasurably small, but after activation in CO_2 at 950° or, preferably, 850°, it becomes more than half as potent as the best specimens of technical active C. The catalytic activity also approximates to that of the technical product. Controlled degradation accompanied by measurement of absorptive power and size of crystals proves the material to consist uniformly of cryst. particles, so that adsorption is not conditioned by admixed amorphous C. The adsorptive power of lustre C is too small to be measured, but becomes appreciable after grinding with quartz powder and subsequent activation in CO_2; retort graphite behaves similarly. Adsorptive power is regarded as a surface property of C, and the differences shown by "liquid benzine soot" and lustre C are attributed to the production of the former in minute, independent crystals, whereas the lustre C crystals are deposited closely together and grow to thick plates. H. W.

Simple and complex iodates of titanium. P. R. Rây and H. Saha (Z. anorg. Chem., 1932, **208**, 100—106).—The prep. and properties of the following *compounds* are described: $H_2[Ti(IO_3)_2(OH)_4]$, $H_2[Ti(IO_3)_4(OH)_2]$, $H_2[Ti(IO_3)_6],2H_2O$, and $X_2[Ti(IO_3)_6]$, where X=Li, Na, K, Rb, Cs, NH_4, $NHMe_3$, or NMe_4. These are analogous to the corresponding compounds of Sn (cf. A., 1926, 1015). *d* has been measured at 32° in each case. The mol. vols. are in general smaller than the sum of the mol. vols. of the components, the contraction being 8·4% in the K compound. The contraction is smallest in $Na_2[Ti(IO_3)_6]$, but $Li_2[Ti(IO_3)_6]$ shows a slight increase of mol. vol. E. S. H.

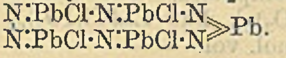
Germanium. X. Aluminium germanates. R. Schwarz and G. Trageser (Z. anorg. Chem., 1932, **208**, 65—75; cf. this vol., 584).—Neutral aq. $AlCl_3$

and Na_2GeO_3 react with pptn. of $Al_2O_3,2GeO_2,xH_2O$. The composition of the ppt. is independent of the ratio of the reactants, and its properties are analogous to those of the corresponding Si compound. The nature of binding of the H_2O is zeolitic. At 100° the compound $Al_2O_3,2GeO_2,3H_2O$ is formed. Permutitic compounds are formed by treatment with NaOH. Ge permutites are also formed by reaction between the solutions or melts of Na_2GeO_3 and Na aluminates. In these the H_2O is zeolitic; the cation can be exchanged for $Ag^{\cdot}$. E. S. H.

Hydrated stannic oxides and sulphides [and basic chlorides]. P. Sisley and L. Meunier (Bull. Soc. chim., 1932, [iv], **51**, 939—946).—The formula $Sn_5O_9Cl,2H_2O$ for parastannyl chloride (A., 1898, ii, 29) is correct, but metastannyl chloride is $Sn_5O_8Cl_4,3H_2O$, confirming Weber's results (Pogg. Ann., 122, 358). Structural formulæ are suggested. The conditions of pptn. and redissolution of SnS_2 have been investigated, and the existence of SnS_2,H_2O and H_2SnS_3 has been confirmed. On passing H_2S into aq. $Sn_5O_8Cl_4,3H_2O$ and leaving for 12 hr., a ppt. is formed of metastannyl sulphide, of approx. composition $Sn_5O_6S_4,6H_2O$, which is probably a mixture. *Parastannyl sulphide*, prepared similarly, is a definite compound, $Sn_5O_7S_2,9H_2O$, which at 120° is converted into the *hexahydrate*. D. R. D.

Action of hydriodic acid on stannic oxide. E. R. Caley (J. Amer. Chem. Soc., 1932, **54**, 3240—3243).—With conc. HI the reaction is $SnO_2+4HI\longrightarrow SnI_4+2H_2O$. It commences at about 90—95° and is rapid at the b.p. Under similar conditions HBr does not react. E. G. V. B. (*c*)

Ammonolysis of tin and lead tetrachloride. R. Schwarz and A. Jeanmaire (Ber., 1932, **65**, [*B*], 1443—1448).—$SnCl_4$ is converted by liquid NH_3 into a compact, colourless substance and thence into a white powder, whereby somewhat more than 8 mols. of NH_3 are absorbed without production of definite ammonates. Exhaustive extraction with liquid NH_3 leaves a *compound*, $2Sn(NH_2)_3Cl,NH_4Cl$, which, when heated at 100° and again washed with liquid NH_3, passes into the *triaminochloride*, $Sn(NH_2)_3Cl$, readily hydrolysed by H_2O. It darkens when heated, becoming brown at 270° and yielding a white sublimate, $SnCl_4,2NH_3$, and the *nitrilochloride*, SnNCl. The small amount of gas evolved at 360° is almost exclusively N_2, which continues to be slowly evolved to 600°. At this temp. the residue consists of globules of Sn mixed with the unstable *tin nitride*, Sn_3N_4, which commences to decompose as soon as formed.

$(NH_4)_2PbCl_6$ is converted by liquid NH_3 into *Pb nitrilochloride*, PbNCl, obtained, mixed with NH_4Cl, as a spongy, brown powder. Prolonged extraction of this product with liquid NH_3 gives $PbCl_2$ and a very explosive powder regarded as derived from the hexameric nitrilochloride by loss of $PbCl_2$ and thus having the constitution  $\left.\begin{matrix}N{:}PbCl{\cdot}N{:}PbCl{\cdot}N\\N{:}PbCl{\cdot}N{:}PbCl{\cdot}N\end{matrix}\right>Pb$. H. W.

Existence of lead suboxide, Pb_2O. R. Fricke and P. Ackermann (Z. physikal. Chem., 1932, **161**, 227—230).—*X*-Ray examination has shown that the supposed Pb suboxide is not Pb_2O, but a mixture of Pb with other Pb compounds (cf. this vol., 823). R. C.

Reaction between phosphorus pentachloride and metallic fluorides. W. Lange and G. von Krueger (Ber., 1932, **65**, [*B*], 1253—1257).—NH_4F and PCl_5 react violently at 80—110°, yielding NH_4PF_6 in max. yield of 67% calc. on PCl_5 used. The product is dissolved in cold H_2O and the nitron salt is pptd. by nitron acetate and converted into the NH_4 salt by addition of aq. NH_3 and extraction of the org. base with $CHCl_3$. The alkali salts resemble the perchlorates chemically and the chlorides crystallographically. NH_4Cl and PCl_5 afford the compound $(PNCl_2)_x$. Anhyd. KF reacts with PCl_5 more quietly than NH_4Cl; reaction is never quant., but by use of a large excess of KF, the yield of KPF_6 is raised to 80% (calc. on PCl_5 used). The salt is isolable by fractional crystallisation. With NaF reaction is much slower and, in consequence of loss of PCl_5 by sublimation, the yield of $NaPF_6$ is only 5—6%. With CaF_2, BaF_2, ZnF_2, or PbF_2 reaction proceeds slowly, leading to evolution of PF_5 without production of salts of HPF_6. H. W.

Selenium and selenium dioxide and the oxides of nitrogen. E. Barnes (J. Indian Chem. Soc., 1932, **9**, 329—333).—SeO_2 and NO do not react between 30° and 315° nor Se and NO below 330°. Se slowly reacts with gaseous NO_2 at 30° forming SeO_2 and NO, and with liquid N_2O_4 at 0° forming SeO_2 and N_2O_3. SeO_2 is insol. in liquid N_2O_4. Pure HNO_3 reacts rapidly with Se and does not appear to require the presence of NO_2 as a catalyst. M. S. B.

Fourth degree of oxidation of molybdenum. II. W. F. Jakób and C. Michalewicz (Rocz. Chem., 1932, **12**, 576—588).—Red $[Mo(CN)_4(OH)_4]''''$ undergoes hydrolysis to $[Mo(CN)_4(OH)_3]'''$, which is further hydrolysed to blue $[Mo(CN)_4(OH)_2]''$, a no. of salts of which are described. Acids convert this ion into $Mo(CN)_2(OH)_2$, and this is irreversibly converted by alkalis into $Mo(OH)_4$, which can also be obtained directly by adding alkali to the product of reaction of the red hydroxycyanide with acids. The reduction potential of $Mo(OH)_4$ solutions is $<$ that of $Mo(OH)_3$ or $Mo(OH)_5$ solutions. Mo^{IV} is converted without the intermediate stage of Mo^{V} into Mo^{VI} on treatment with $KMnO_4$. R. T.

Peruranates. A. Rosenheim and H. Daehr (Z. anorg. Chem., 1932, **208**, 81—94).—By treating $UO_2(NO_3)_2$ with alkali hydroxides and H_2O_2 the following *peruranates* have been isolated: $Na_2U_2O_{10},4H_2O$, $Na_4UO_8,8H_2O$, $Na_4UO_8,9H_2O$, $K_2UO_6,3H_2O$, $K_6U_2O_{13},10H_2O$, $(NH_4)_2U_2O_{10},5H_2O$, $(NH_4)_2U_2O_{10},3H_2O$, $(NH_4)_6U_2O_{13}$. Guanidine gives $(CN_3H_6)_4UO_8$. Structural formulæ are suggested for these compounds. E. S. H.

Preparation of chemically pure hydrofluoric acid. V. Y. Tartakovski (Min. Suir., 1931, **6**, 853—869).—HF solution is distilled with NaF (1·5—2 pts. > that required for neutralisation of H_2SiF_6 and H_2SO_4). The solubility of Na_2SiF_6 in HF in presence of much NaF is negligible. Cl is removed with $PbCO_3$ as PbFCl, which is insol. in 40% HF. Ch. Abs.

Synthesis of hydrogen chloride. I. G. Schtscherbakov and E. A. Nikonova (Techn. Urals, 1931, 7, No. 5—6, 20—24; Chem. Zentr., 1932, i, 1939).—Cl_2 (0·4—1·8 pts.) and H_2O vapour (60—100% excess) were passed over C (1 pt.) at temp. up to 350°. The yield of HCl (0·4—0·5% H_2O) varies considerably owing to adsorption of Cl_2 by the C. Experiments were also performed in presence of Fe_2O_3 and at 600° without this catalyst. A. A. E.

Lower degrees of oxidation of rhenium. E. Turkiewicz (Rocz. Chem., 1932, 12, 589—597).—Re^{VII} ($KReO_4$) is reduced by Cr^{II} to Re^{IV}; the reaction is catalysed by I′. ReO_2,xH_2O, pptd. by alkalis from the reduced solutions, yields $K_3[ReO(CN)_4OH]$ on boiling with conc. aq. KCN; in acid solutions this salt yields the ion $[Re(CN)_4(OH)_2]''$. R. T.

Complex salts. IV. G. Spacu and P. Spacu (Bul. Soc. Stiinte Cluj, 1932, 6, 384—395; Chem. Zentr., 1932, i, 3025).—The following *compounds* were obtained: $[Ni\,en_2][Hg(CN)_2(CNO)]_2$, $[Cr\,en_3]I[AgI_2]_2$, $[Co\,en_2Cl_2]_3[BiBr_6]$, $[Co\,en_2Cl_2]_2[SnBr_6]$, $[Co\,en_3]_2[PbI_4]_3$, $[Cr\,en_3][PbI_3]_3$, $[Cd\,en_2][PbI_3]_2$, $[Zn\,en_2][PbI_4]$, $[Ni\,en_3][PbI_3]_2$, $[Cu\,en_2][PbI_3]_2$. A. A. E.

Optically active inorganic salt. F. G. Mann (Nature, 1932, 130, 368).—Evidence is given for the presence of the *cis*-isomeride in Na diaquorhodium-disulphamide, $Na[(H_2O)_2Rh(NH{\cdot}SO_2{\cdot}NH)_2]$. L. S. T.

Behaviour of chelate groupings attached to platinum and palladium. H. D. K. Drew (J.C.S., 1932, 2328—2331).—The diammine, $Pt\,en\,Cl_2$, and the tetrammines $[Pt\,en_2]Cl_2$ and $[Pt\,en\,(NH_3)_2]Cl_2$, are all of the β-types, the chelate grouping being unable to span the α-position, contrary to the behaviour of Pd compounds (this vol., 824). The opening and closing of the chelate group in the Pt compounds by HCl and NaOH, respectively, is in accordance with the theory previously developed, and it can be shown that the positive charges of the cations of the plato-salts and the tetrammines must be located on N atoms in α-positions and not on Pt. Werner's theory of the *trans*-elimination of groups cannot hold for both plato- and pallado-tetrammines at the same time. M. S. B.

Extraction analysis with two unknowns. H. Jessen-Hansen (Z. anal. Chem., 1932, 89, 422—425).—The factors to be taken into account in the determination of a substance by extraction with a solvent from an insol. medium are discussed mathematically. M. S. B.

Analysis of the anions. F. J. Welcher and H. T. Briscoe (Chem. News, 1932, 145, 161—170).—A systematic treatment for the separation of ions is based on a preliminary separation into (*a*) ions of which the Ba and Ca salts are insol. in H_2O–$COMe_2$ mixtures; (*b*) ions with insoluble Zn salts; (*c*) ions with insoluble Ag salts; (*d*) the remainder. J. W. S.

Application of the polarographic method in micro-analysis. J. Heyrovský (Mikrochem., 1932, 64, 25—64).—A summary of published work. E. S. H.

Direct titration method on a new principle. I. S. Saitō (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 43—48).—A new principle of direct titration takes advantage of two quant. reactions, one producing a less-ionising or insol. two-component compound, the other giving a more stable and much less ionising or more insol. compound of the same two components with a further component. J. W. S.

Stability of certain volumetric solutions. E. P. Hedley (Proc. VI Congr. S. Afr. Sugar Tech. Assoc., 1932, 6—8).—0·1*N*-$KMnO_4$ retained its original titre for about 6 months. 0·1*N*-$Na_2S_2O_3$ showed the same factor for nearly 3 months. 0·1*N*-As_2O_3 solution, prepared by Kolthoff's directions ("Volumetric Analysis," II, 363), is stable for a long time, and is superior to $Na_2S_2O_3$ as a primary standard. J. P. O.

Applicability of the antimony electrode. W. Böttger and L. von Szebellédy (Z. Elektrochem., 1932, 38, 737—742).—Existing forms of Sb electrodes give variable results in measuring the p_H of standard buffer solutions. A cast Sb electrode, polished in one direction with emery, and having deposited on it a greyish-black coat of Sb from a solution containing 10% $SbCl_3$ and 2*N*-HCl, rapidly acquires its final potential and gives a linear relation with p_H. It is suitable for acid–alkali titrations. E. S. H.

Theory of error of acid–base titration. P. S. Roller (J. Amer. Chem. Soc., 1932, 54, 3485—3499).—Equations are formulated by which the accuracy and limiting conditions of titration can be predicted when the end-point is determined colorimetrically or potentiometrically. The error is a simple function of the known error of the colour indicator, or of the potentiometer, and of the concns. and ionisation consts. For an unsymmetrical titration, the error is proportional to the square root of the concn. of the product at the end-point, so that the accuracy may be enhanced by artificially diminishing this concn. W. T. H. (c)

Poirrier-blue. J. M. Olsen and F. Reimers (Dansk Tidsskr. Farm., 1932, 9, 161—177).—The colour change of Poirrier-blue occurs over the p_H range about 11—12 in H_2O, 10·0—11·0 in 50% EtOH, and 10·3—11·3 in 75% EtOH. The absorption curves in various media have been determined with the Pulfrich photometer; those in presence of 0·1*N*-HCl show a marked change from aq. to EtOH solution. Solutions in different concns. of EtOH containing 0·1*N*-$Na_2B_4O_7$ show a continuous colour progression. Commercial preps. of Poirrier-blue are very impure, but the change occurs at the same p_H val.; there is no relation between colour strength and content of ash, H_2O, S, or N. Poirrier-blue can be used as an indicator in the titration of several alkaloid salts in EtOH with 0·1*N*-NaOH, but it cannot be used for strychnine nitrate. E. S. H.

Determination of alkalinity in boiler waters. F. G. Straub.—See B., 1932, 819.

Determination of hydroxide and carbonate in boiler waters. I, II. E. P. Partridge and W. C. Schroeder. **III.** L. F. Collins and W. C. Schroeder.—See B., 1932, 819.

Detection and determination of hydrochloric acid in presence of hydrobromic acid as perchromic acid, chromic oxide, and barium chromate. G. G. Longinescu and I. I. Prundeanu (Bul. Chim. Soc. Române, 1931, 34; 5 pp.).—Distillation of the sample with conc. H_2SO_4 and $K_2Cr_2O_7$ and subsequent oxidation of the CrO_2Cl_2 to the blue perchromic acid provides a very sensitive test for Cl′ even in presence of Br′. Determination of the CrO_2Cl_2 as Cr_2O_3 or $BaCrO_4$ or iodometrically leads to rather high vals. of Cl′ content. J. W. S.

Volumetric assay of chlorates. I. Reduction by hydriodic acid in presence of ferrous sulphate. II. Reduction by hydriodic acid in presence of concentrated hydrochloric acid. G. J. W. Ferrey (Pharm. J., 1932, 129, 242—243).—I. Contrary to Harvey (A., 1925, ii, 1197), the method (B.P., 1932) gives theoretical results. Either the time or temp. of the reaction may be reduced if the $FeSO_4$ solution is made more conc. and more strongly acid.

II. Chlorates can be quantitatively reduced by a min. excess of HI in the presence of conc. HCl. Under suitable conditions the action of air on HI is inappreciable. W. S.

Determination of chlorate in nitrates. K. Lesničenko.—See B., 1932, 840.

Determination of the oxygen evolved by certain peroxides. R. Poggi (Annali Chim. Appl., 1932, 22, 493—496).—A single vessel contains a tap funnel of dil. H_2SO_4, a chamber for peroxide, and a trap of conc. H_2SO_4 through which the O_2 evolved can pass. The whole is weighed full of air, the peroxide decomposed, and the O_2 displaced by dry CO_2-free air; the loss in wt. is the wt. of O_2+CO_2 evolved. The CO_2 is trapped and weighed in a second vessel. For testing respirator fillings this method is more suitable than that involving titration by $KMnO_4$ (cf. A., 1924, ii, 568), which reacts with per-salts. E. W. W.

Automatic apparatus for the determination of small concentrations of sulphur dioxide in air. III. M. D. Thomas.—See B., 1932, 841.

Determination of sulphur dioxide when present in low concentration in air. S. W. Griffin and W. W. Skinner.—See B., 1932, 914.

Reduction indicator. L. Michaelis (Biochem. Z., 1932, 250, 564—567).—1 : 1-*Dimethyl*-4 : 4′-*dipyridylium chloride*, from 4 : 4′-dipyridyl and Me_2SO_4 by way of the picrate, is normally colourless, but becomes deep blue on reduction, and on titration in alkaline solution with $Na_2S_2O_4$ gives readily reproducible potential curves. The normal potential is sufficiently negative to enable the measurement of reduction intensity of cells to be made under anaërobic conditions. P. W. C.

Determination of selenium in selenious compounds by means of hydrazine and its salts. V. Hovorka (Coll. Czech. Chem. Comm., 1932, 4, 300—318).—When H_2SeO_3 is reduced to Se by N_2H_4 in acid solution there is always a small loss, partly as H_2Se and partly mechanical. The amount of H_2Se is min. in the presence of citric acid; in the presence of mineral acids the reaction is faster and the loss greater. A. G.

Detection of nitric acid as fuschin. G. G. Longinescu and T. I. Pirtea (Bul. Chim. Soc. Române, 1931, 34; 3 pp.).—The $PhNO_2$ method of detecting HNO_3 is extended by reducing the $PhNO_2$ to NH_2Ph and converting the latter into fuschin. J. W. S.

Micro-determination of phosphoric acid by means of strychnine molybdate. E. Rauterberg (Mikrochem., 1932, 12, 116—117).—Polemical (cf. this vol., 354, 587). E. S. H.

[Micro-determination of phosphoric acid by means of strychnine molybdate.] H. Kleinmann (Mikrochem., 1932, 12, 118).—A reply (cf. preceding abstract). E. S. H.

Separation of phosphoric acid from calcium and magnesium by means of ammonium molybdate. Z. Perkowski (Przemysł Chem., 1932, 16, 160—161).—PO_4''' is pptd. by Woy's method, and excess of Mo is removed from the filtrate by addition of excess of aq. NH_3 and 3—5 c.c. of $(NH_4)_2S_x$. The solution is then made acid with HCl, when MoS is quantitatively pptd. R. T.

Detection of arsenate and phosphate ions. A. I. Sheinkman and N. A. Galetzki (Farm. Zhur., 1932, No. 3—4, 120—121).—The NH_4 molybdate ppt. is boiled until colourless with aq. NH_4OAc; arsenate produces a white ppt. or turbidity on cooling, and phosphate is tested for in the filtrate. Ch. Abs.

Rapid determination of boron. W. W. Scott and others.—See B., 1932, 841.

Determination of silicon in aluminium. L. H. Callendar.—See B., 1932, 844.

Volumetric determination of silica in presence of aluminium and iron compounds. V. Tartakovski (Min. Suir., 1931, 6, No. 12, 1075—1087).—(1) The silicate or quartz (0·02—0·2 g. SiO_2) is evaporated to dryness with 2*N*-NaOH (10—20 c.c.) and HF (5—6 c.c.); 1 g. HCO_2Na is added for every 5 c.c. NaOH (to decompose $NaHF_2$), the solution is evaporated, and the residue dried at 120—130°, and the Na_2SiF_6 titrated hot with 0·5*N*-NaOH (phenolphthalein). Alkali or alkaline-earth metals, Th, and Pb do not interfere. (2) If other metals (Ce, Ta, Zr, W) or Ti are present the Na_2SiF_6 must first be separated from the residue by adding KCl to 20% concn., then aq. 20% KCl, filtering, and washing the residue with 20% KCl before titration. In presence of Al and Fe, neutral NaF (3—4 g.) is added to the solution (100 c.c.), whereby the action of NaOH on the cryolite-like compounds formed by AlF_3 and FeF_3 is checked. Ch. Abs.

Determination of argon. H. Copaux (Bull. Soc. chim., 1932, [iv], 51, 989—992).—A method is described for the rapid determination of A in mixtures with O_2, N_2, H_2, etc., these gases being absorbed by means of Li. D. R. D.

Volumetric determination of potassium by the sodium cobaltinitrite method. C. B. Maw and K. R. Miller (Proc. Utah Acad. Sci., 1931, 8, 61—64).—To obtain a ppt. of uniform composition for treatment with $KMnO_4$ followed by $H_2C_2O_4$ a 3% aq. solution of the reagent should be used and the solution saturated with NaCl. Ch. Abs.

Determination of sodium in aluminium. I. Chemical analysis. R. W. Bridges and M. F. Lee. **II. Spectrographic analysis.** A. W. Petrey.—See B., 1932, 844.

Direct gravimetric determination of sodium in commercial aluminium. E. R. Caley.—See B., 1932, 844.

Determination of sodium in aluminium. K. Steinhäuser and J. Stadler.—See B., 1932, 892.

Distinction between lithium and strontium by means of their flame colorations. E. Macciotta (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 55—56; Chem. Zentr., 1932, i, 3324).—A small quantity of the substance on a Pt wire is introduced into the lower part of a Bunsen flame; in presence of Li the whole flame immediately assumes an intense red coloration. If the substance is then moistened with HCl and again heated in the lower part of the flame, in presence of Sr a red spray is produced. Na and Ba must be absent. A. A. E.

Application of spectrum analysis to the determination of alkali and alkaline-earth metals. I. W. H. Jansen and J. Heyes (Z. physiol. Chem., 1932, **211**, 75—87).—The solution is placed in a special form of atomiser whence the vapour passes into a non-luminous C_2H_2 flame. The spectra are photographed and by photometric comparison of the blackening due to the appropriate spectral lines with those obtained from standard solutions, the metal is determined. The results for Na, Li, K, and Ca in a mineral spring water agree well with those obtained by chemical analysis. J. H. B.

Separation and identification of the alkaline-earth metals. P. E. Williams and H. T. Briscoe (Chem. News, 1932, **145**, 177—184).—The alkaline-earth metals, including Mg, can be separated from the alkali metals as carbonates by addition of $COMe_2$ instead of EtOH. Sr can be separated from Ca and Mg as $SrCrO_4$ or $(p\text{-}C_6H_4Me\cdot CO_2)_2Sr$ in presence of $COMe_2$. $Ca(NO_3)_2$ is much more sol. in $COMe_2$–H_2O mixtures than are $Ba(NO_3)_2$ and $Sr(NO_3)_2$. J. W. S.

Gravimetric determination of beryllium and its separation from $Fe^{\cdot\cdot\cdot}$, $UO_2^{\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$, $Zr^{\cdot\cdot\cdot\cdot}$, $Tl^{\cdot}$, CrO_4'', MoO_4'', $Cu^{\cdot\cdot}$, AsO_3''', SbO_3''', VO_4''', and WO_4'' by means of guanidine carbonate. A. Jílek and J. Koťa (Z. anal. Chem., 1932, 89, 345—354).—The method is similar to that used in the separation of Be from Al except that when VO_4''' and WO_4'' are present the solution must be made exactly neutral (Me-red) before adding the guanidine (cf. A., 1931, 1024). A. R. P.

Colorimetric determination of small amounts of magnesium in pure magnesium salt solutions and in presence of calcium. J. Tischer (Mikrochem., 1932, 12, 65—86).—Mg is pptd. as $MgNH_4PO_4$ and the PO_4 content of the ppt. is determined colorimetrically by a suitable modification of Parker and Fudge's method (B., 1927, 758). The procedure allows the determination of $1—5000\times10^{-6}$ g. Mg in 1 c.c. with a max. error of ±2%. When $Ca^{\cdot\cdot}$ is also present, its pptn. is prevented by adding NH_4 citrate. The amount of NH_4 citrate required to form a stable complex with $Ca^{\cdot\cdot}$ increases with the amount of both $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ and it is necessary to allow more time for complete pptn. of $MgNH_4PO_4$. E. S. H.

Titration of zinc salts by means of ferrocyanide solution, and a sensitive reaction for iron. J. Guéron (Ann. Chim. Analyt., 1932, [ii], 14, 393—397).—The slightly acid $Zn^{\cdot\cdot}$ solution, containing a trace of $Fe_2(SO_4)_3$, is titrated at 60—70° with aq. $K_4Fe(CN)_6$ until the blue colour disappears. The results agree with those obtained potentiometrically, and are less affected by the presence of salts of alkali metals, except acetates. Addition of $ZnSO_4$ makes the $Fe(CN)_6''''$ test for $Fe^{\cdot\cdot\cdot}$ more sensitive; 1 mg. of $Fe^{\cdot\cdot\cdot}$ per litre produces a transient blue colour. The solubility products of $K_2Zn_3[Fe(CN)_6]_2$ and $K_2Cd[Fe(CN)_6]$ are approx. 10^{-14}; that of $Mn_2[Fe(CN)_6]$ is $2—3\times10^{-13}$. D. R. D.

Rapid determination of volatile constituents in small samples of copper–zinc alloys by a distillation method. L. I. Weinstein and A. A. Benedetti-Pichler.—See B., 1932, 892.

Determination of traces of lead and copper in presence of iron, with special reference to iron ammonium citrate. N. L. Allport and G. H. Skrimshire (Pharm. J., 1932, 129, 248—249).—After destruction of org. matter by oxidation with H_2O_2, the Cu and Pb are extracted by means of a $CHCl_3$ solution of diphenylthiocarbazone and determined colorimetrically, the Pb in the usual way with Na_2S, and the Cu with dithio-oxamide. W. S.

Application of Spacu's reaction in the micro-determination of copper. J. Golse (Bull. Soc. Pharm. Bordeaux, 1931, 69, 247—269; Chem. Zentr., 1932, i, 3090).—Details of the application of this method (A., 1931, 454) to micro-analysis are given. A. A. E.

Microchemical contributions. VII. L. Rosenthaler (Mikrochem., 1932, 12, 98—101; cf. A., 1930, 881).—The microscopical appearance of the ppts. formed by $Hg_2(NO_3)_2$ with numerous org. and inorg. substances is described. E. S. H.

Volumetric determination of mercuric chloride by Rupp's method. H. Brindle (Pharm. J., 1932, 129, 245).—The sole drawback of the method (B.P., 1932) is the difficulty of dissolving the Hg ppt. in the I solution, and this is overcome by the addition of a small quantity of a mixture of 1 vol. $CHCl_3$ and 2 vols. Et_2O. W. S.

Titrimetric determination of aluminium in presence of iron and free hydrochloric acid. E. Erdheim and E. Benesch (Przemysł Chem., 1932, 16, 128—130).—$Fe^{\cdot\cdot}$ is oxidised to $Fe^{\cdot\cdot\cdot}$ by H_2O_2, and Fe and Al are pptd. as Na_3FeF_6 and Na_3AlF_6 by NaF; free HCl is titrated with 0·5*N*-NaOH. Fe is determined in another portion of solution by titration with $KMnO_4$. Excess of 0·4*N*-Na_2CO_3 is added to a third portion, which is then boiled and filtered from $Fe(OH)_3$ and $Al(OH)_3$, and an aliquot part of the filtrate is titrated with 0·5*N*-HCl. The Al content is calc. from the difference between the amount of alkali used and that necessary for pptn. of Fe and neutralisation of free HCl. R. T.

Determination of manganese as dioxide. E. Wohlmann (Z. anal. Chem., 1932, 89, 321—338).—Mn is quantitatively deposited on a gauze anode by electrolysis of aq. $MnSO_4$ containing (*a*) EtOH and NaOAc or (*b*) HCO_2H and HCO_2Na. The deposit in both cases contains H_2O and more or less MnO, but after heating to const. wt. at 250° the true MnO_2 is obtained by the use of the factors (*a*) 0·9459 and (*b*) 0·9085. In the volumetric determination of Mn by Fischer's modification of Volhard's method, boiling with AcOH after the first end-point appears is essential for correct results; in this way adsorbed MnO is converted into MnO_2 during the subsequent addition of $KMnO_4$ to obtain the second and true end-point. A. R. P.

Spectroscopic determination of nickel, manganese, and chromium in steels. F. Twyman and A. Harvey.—See B., 1932, 891.

Analysis of cations of the ammonium sulphide group. A. I. Sheinkman (Farm. Zhur., 1932, No. 3—4, 119—120).—The NH_4OH-$(NH_4)_2S$ ppt. is treated with hot AcOH to dissolve Fe, Cr, Al, and Mn. ZnS is extracted from the residue with 2*N*-HCl. Ch. Abs.

Determination of small amounts of iron in copper. B. Park.—See B., 1932, 844.

Use of α-benzoinoxime in the determination of molybdenum. H. B. Knowles (Bur. Stand. J. Res., 1932, 9, 1—7).—Mo is completely pptd. from solutions containing 5 vol.-% H_2SO_4, HCl, or HNO_3 by addition of an EtOH solution of α-benzoinoxime at 5—10°, provided that enough aq. Br is added to colour the solution yellow after addition of the reagent. The ppt. on ignition at 500—525° affords MoO_3 for weighing. WO_3 must subsequently be removed by pptn. with cinchonine. V_2O_5 and CrO_3 must first be reduced by boiling with an excess of SO_2 or by addition of $FeSO_4$. The method provides an accurate separation of Mo from Sb and gives good results in the analysis of steels and Mo ores in a much shorter time than any other procedure. A. R. P.

Microchemical reaction for the detection of molybdenum, vanadium, and tungsten. A. Martini (Mikrochem., 1932, 12, 112—113; cf. A., 1928, 387).—Characteristic cryst. ppts. are formed when a drop of $CH_2Ph{\cdot}NH_2$ is added to a drop of 1% aq. solution of a compound of Mo, V, or W containing pyrocatechol, and aq. AcOH is then added. The ppts. formed are of the type $H_2[(C_6H_4O_2)_2OM^{V}OH]OAc,CH_2Ph{\cdot}NH_2$, where M is Mo, V, or W. E. S. H.

Colorimetric determination of vanadium in titanomagnetites. K. Bolshakov (Tzvet. Met., 1931, 487—493).—The finely-ground ore (1 g.) is evaporated to dryness with HNO_3 (15 c.c.) and HCl (45 c.c.); the residue is treated with conc. HNO_3 (20—30 c.c.), evaporated to small vol., diluted with hot dil. HNO_3, and filtered. The filtrate is again evaporated to dryness and then heated with 20 c.c. of 6*N*-HNO_3 until dissolved. The solution is treated with 10% $AgNO_3$ solution (1—2 c.c.), Cl is removed by boiling, and the solution filtered. The filtrate is diluted to 100 c.c.; 10 c.c. of this, 18 c.c. HNO_3 (*d* 1·2), and 10 c.c. H_3PO_4 are diluted to 80 c.c., 10 c.c. of fresh NH_4 molybdate solution then being added. The solution is then compared colorimetrically with a solution containing 0·002 g. V_2O_5, 20 c.c. HNO_3 (*d* 1·2), 10 c.c. H_3PO_4, and 10 c.c. of NH_4 molybdate solution in 100 c.c. The presence of Ti does not interfere. Ch. Abs.

Use of manganese sulphate in the determination of antimony by Low's method. W. G. Leemann (J.S.C.I., 1932, 51, 284T).—The difficulty of determining the end-point when the method is applied to Sb in white bearing alloys, owing to the rapid disappearance of the colour of $KMnO_4$, is overcome by adding $MnSO_4$ solution before titrating with $KMnO_4$. The solution is prepared by dissolving 110 g. cryst. $MnSO_4$ in 500—600 c.c. H_2O, adding 138 c.c. H_3PO_4 (*d* 1·7) and 130 c.c. H_2SO_4 (*d* 1·84), and diluting to 1000 c.c. E. S. H.

Potentiometric determination of platinum and gold with cuprous chloride solution. E. Müller and K. H. Tänzler (Z. anal. Chem., 1932, 89, 339—344).—The reduction of $AuCl_3$ to Au and of $PtCl_4$ to $PtCl_2$ by Cu_2Cl_2 in dil. HCl at 50° is made the basis of potentiometric titrations for Au and Pt. Simultaneous determinations of both metals in the same solution are not accurate, as the Au end-point is not sharp in the presence of Pt; the sum of Au and Pt may, however, be ascertained accurately in this way. A. R. P.

Precision aperiodic thermostat. O. H. A. Schmitt and F. O. Schmitt (Rev. Sci. Instr., 1932, [ii], 3, 467—473).—Constructional details are given. The temp. variation is <0·001°. C. W. G.

Isothermic titration microcalorimeter. I. V. Krotov (Bull. Acad. Sci. U.R.S.S., 1932, No. 5, 669—680).—The temp. is kept const. by addition of aq. NH_4NO_3 to H_2O, the heat of reaction being proportional to the vol. of NH_4NO_3 added. In the case of endothermic reactions H_2SO_4 is used in place of NH_4NO_3. An accuracy of 1% is obtained. R. T.

Modification of Lewis–Thomson calorimeter. E. Casati (Annali Chim. Appl., 1932, 22, 566—570).—A tube conveying O_2 runs along the usual vertical tube and the bell, and enters the base of the combustion chamber. Either an oxidising mixture or a current of O_2 may be used. In the latter case the usual cartridge is replaced by the grate and burner designed for the purpose. O. F. L.

Hydrogen discharge tube for the continuous ultra-violet spectrum. H. C. Urey, G. M. Murphy, and J. A. Duncan (Rev. Sci. Instr., 1932,

[ii], **3**, 497—498).—A Pyrex tube with SiO_2 windows is cooled sufficiently to permit the use of currents of 2 amp. C. W. G.

Improved Laue camera. H. Kersten and W. Lange (Rev. Sci. Instr., 1932, [ii], **3**, 493—496).—A specially shaped rotating disc is fitted to equalise the exposures of different parts of the plate when the crystal-to-film distance is small. C. W. G.

Spectrophotometer for the visible region in the rapid analysis of alloys. G. Scheibe and G. Limmer (Metall-Wirt., 1932, **11**, 107—110; Chem. Zentr., 1932, i, 2977).

Device for demonstrating Brownian movement in gases. D. A. Wells and W. Lange (Rev. Sci. Instr., 1932, [ii], **3**, 474—475).—Three 5/16-in. cavities are drilled in a brass block and are joined by a 1/8-in. hole perpendicular to their axes. Intense light passes through a simple collimator (a pair of slits) in the first cavity, illuminates smoke in the second one, and is absorbed by the blackened walls of the third. A magnification of 100 is desirable.
C. W. G.

Control of ultra-violet ray lamps. W. E. Hammond (Science, 1932, **76**, 125).—The power of the lamp can be judged by the amount of I liberated from "Lipiodol" after 5 min. irradiation. L. S. T.

Simplified minimum deviation method of measuring refractive indices. P. Rossier (Arch. Sci. phys. nat., 1932, [v], **14**, 226—227).—A small-angle prism-objective is introduced. N. M. B.

Limitations of a blanket calibration chart for reading dispersions on the Abbe refractometer. L. E. Dodd (J. Opt. Soc. Amer., 1932, **22**, 477—487). —The exact and approx. forms of the basic Abbe formulæ, and their derivation, are given in detail. The errors involved in using the blanket calibration chart in the measurement of dispersions with a refractometer having compensating prisms are checked by direct calculations. The consts. β, N, ΔN, k should be known precisely for each instrument. J. L.

Determination of refractivity temperature coefficients for liquids. J. J. Manley (Proc. Physical Soc., 1932, **44**, 556—562).—An improved form of the Jamin interferometer is described by means of which the variation of refractive index of a liquid with temp. can be determined with accuracy.
A. J. M.

Portable thermionic electrometer for the determination of glass electrode potentials. C. Morton (J. Sci. Instr., 1932, **9**, 289—293).—Potentiometer current, grid bias, filament current, anode voltage, and compensating current are derived from a common source and are standardised in one operation. Within limits the instrument is self-adjusting for fluctuations in the battery voltage. C. W. G.

Automatic control and recording of hydrogen-ion concentration by means of the glass electrode. C. Morton (J.C.S., 1932, 2469—2475).—A potentiometric regulator has been constructed for automatic p_H recording or control in conjunction with the glass electrode. Its accuracy is of the order of ±1 mv. and is unaffected by oxidising or reducing agents, suspended ppts., colloids, or any electrode "poisons." Electric currents up to 10 amp. at 250 volts may be made or broken without the use of an intermediate relay. Thermionic valves are employed for amplification, but the calibration of the instrument is permanent and unaffected by changes in the battery voltages and valve characteristics. It will function continuously for many months without attention. Photo-electric or other minute leakage currents may also be controlled or recorded, the current sensitivity being approx. 10^6 times that of the standard thread recorder. A simple recording cell, suitable for use with a glass electrode in continuously flowing solutions, is also described.
M. S. B.

Multiple-unit electrodialysis apparatus. A. Löddesöl (Science, 1932, **76**, 83—84). L. S. T.

Simple apparatus for thermoelectric determination of f.p. H. C. S. Snethlage (Chem. Weekblad, 1932, **29**, 557—559).—Constructional details and typical results are given. H. F. G.

Vacuum or circulating pump. E. L. Harrington (Rev. Sci. Instr., 1932, [ii], **3**, 476—481).—An inclined helical tube, partly immersed in a suitable liquid, is caused to rotate (by direct drive, or electromagnetically). Gas trapped by the lower end of the helix is forced out of the upper end, together with liquid, which is returned to the main supply.
C. W. G.

High-speed high-vacuum diffusion pumps. I. Estermann and H. T. Byck (Rev. Sci. Instr., 1932, [ii], **3**, 482—487).—The construction of glass-metal pumps is described. C. W. G.

Mercury vapour pumps for vacuum distillations. R. H. Munch (Science, 1932, **76**, 170—171).—A Pyrex glass Hg-vapour diffusion pump, designed to work against an aspirator used as a force pump capable of producing a pressure reduction of 30 mm., is described. The apparatus can advantageously replace pumps of the Cenco Hyvac type.
L. S. T.

Cryoscopic mol. wt. determination. F. B. Straub (Biochem. Z., 1932, **252**, 378—379).—A simple apparatus and method are described which permit the determination of the lowering of f.p. of $0{\cdot}5M$ aq. solutions with an accuracy of ±4%.
P. W. C.

Device for adding saturated alkali solution in the Kjeldahl method for nitrogen determination. F. T. Adriano (Univ. Philippines Nat. Appl. Sci. Bull., 1932, **2**, 27—32).—Alkali is contained in a funnel connected by a rubber tube and pinchcock to a glass tube entering the steam inlet immediately above the stopper of the Kjeldahl flask, and is added during temporary removal of the flame from the boiler.
Ch. Abs.

Method of constructing slits of fixed width. W. L. Buxton (J. Sci. Instr., 1932, **9**, 297).—The edges of two metal strips are machined straight, and rectangular notches of depth equal to half the required width of the slit are cut in them. The slits are then formed by mounting the two strips with their machined edges touching. C. W. G.

[Laboratory] sieving machine. E. Berl and A. Schmidt (Chem. Fabr., 1932, 299).—Shaking machines of the type in which a spring is given impulses by a rotating pulley loaded on one side can be adapted to screening, the sieves being clamped in the position occupied by the article to be shaken. Comparative tests with hand-screening for 25 min. show slightly smaller residues in the case of machine-screening. C. I.

Standardisation of weights. F. C. Eaton (J. Amer. Chem. Soc., 1932, 54, 3261—3263).—Richards' method of calibration gives vals. identical with those found by substituting in algebraic formulæ, such as those of Kohlrausch. E. G. V. B. (*c*)

Apparatus for filtration at high temperatures. A. Stadler (Mitt. Kohlenforsch.-Inst. Prag, 1931, 80–81; Chem. Zentr., 1932, i, 2488).

Apparatus for filtration at low temperatures, particularly for the determination of paraffin. B. G. Simek (Mitt. Kohlenforsch.-Inst. Prag, 1931, 74–79; Chem. Zentr., 1932, i, 2488).

Adjustable apparatus stand and truck. R. W. Shaw (Science, 1932, 76, 259). L. S. T.

Automatic control for vacuum apparatus. C. I. Swayze (Science, 1932, 76, 196—197). L. S. T.

Improved sodium burner. F. L. Humoller and W. C. Austin (Science, 1932, 76, 105—106). L. S. T.

Micro-balances of the Kuhlmann type. L. Ramberg (Svensk Kem. Tidskr., 1932, 44, 188—191).—The error due to irregularities in the position of the usual type of rider is pointed out, and an improved form of rider is described. H. F. H.

Lubricant insoluble in organic solvents. C. C. Meloche and W. G. Fredrick (J. Amer. Chem. Soc., 1932, 54, 3264—3266).—A mixture of 25 g. anhyd. glycerol, 7 g. dextrin, and 3·5 g. *d*-mannitol is heated until the solid is dissolved and the solution begins to boil. In general, H_2O, alcohols, aliphatic acids, and certain amines and heterocyclic N compounds prevent the use of the lubricant. E. G. V. B. (*c*)

Combustion of hydrocarbons. Volumetric composition of the gaseous products. J. Rimbaut (Ann. Off. Nat. Combust. liq., 1931, 6, 835—873; Chem. Zentr., 1932, i, 2491).—Calculations for the construction of two nomograms are given. A. A. E.

History of red phosphorus. R. Wegscheider (Oesterr. Chem.-Ztg., 1932, 35, 169—171).

Geochemistry.

Natural gases. III. Methane and its homologues in Polish natural gases. K. Kling, E. Beckówna, and K. Kirschbaum (Przemysł Chem., 1932, 16, 97—108).—The CH_4 content of Galician natural gases varies from 74·5 to 89%, that of C_2H_6 from 1·73 to 11·63%, of C_3H_8 from 1·37 to 6·07%, and of higher homologues from 0·83 to 6·97%. R. T.

Iodine in the air. H. Cauer (Umschau, 1931, 35, 991—992; Chem. Zentr., 1932, i, 1506).—The atm. in Bad Kreuznach is rich in I; 50×10^{-6} g. can be inhaled in 24 hr. Mountain air has a normal I content. The incidence of goitre is discussed. A. A. E.

Formaldehyde in rain water. N. R. Dhar and A. Ram (Nature, 1932, 130, 313—314).—CH_2O occurs in distilled and undistilled rain H_2O obtained from high altitudes at Allahabad. It appears to be obtained from the union of CO_2 and H_2O vapour in presence of solar ultra-violet light and not from the decomp. of vegetable matter. L. S. T.

Analysis of Acquarossa mineral water. P. Bertolo and S. Lanza (Annali Chim. Appl., 1932, 22, 469—478).—H_2O from this spring, in Belpasso (Catania), contains much CO_2, with Na, K, Ca, Mg, Al, and Fe; these have been determined, also Cl', SO_4'', NO_3', HCO_3', and SiO_2. The solid residue (at 105°) is 1·2828 g., and the total dissolved gas 451 c.c. (at 0° and 760 mm.) per litre. E. W. W.

Mineral water from Madesimo. R. Marconi (Annali Chim. Appl., 1932, 22, 574—577).—The results of the chemical and physico-chemical examination of this H_2O are given. O. F. L.

Genesis of dolomite. O. Bär (Zentr. Min. Geol., 1932, A, 46—62; Chem. Zentr., 1932, i, 2155).—Solubilities of $CaCO_3$ and $MgCO_3$ in H_2O of varying CO_2 content are recorded. The composition of the solution resulting from magnesite+dolomite and from calcite+dolomite in CO_2+H_2O was also determined; other solubilities in CO_2+H_2O determined were those of $FeCO_3$, $ZnCO_3$, and $MnCO_3$. A. A. E.

Beryl from Erythræa. G. Liberi (Annali Chim. Appl., 1932, 22, 544—554).—From the result of two analyses the formula appears to correspond with $4BeO,Al_2O_3,7SiO_2$, *i.e.*, $4BeSiO_3,Al_2(SiO_3)_3$. O. F. L.

Microscopical characters of natural manganese oxides and manganite. J. Orcel and S. Pavlovitch (Bull. Soc. Franç. Min., 1931, 54, 108—179; Chem. Zentr., 1932, i, 2444).

Sodalite from Cerro Sapo, Bolivia. W. Brendler (Zentr. Min. Geol., 1932, A, 42—46; Chem. Zentr., 1932, i, 2154).—The large, ultramarine-coloured crystals, *d* 2·290, contained Na_2O 24·53, K_2O 1·13, Fe_2O_3 0·70, Al_2O_3 31·17, SiO_2 36·72, Cl 7·22, H_2O (110°) 0·23%; MgO, CaO, BaO, FeO, and SO_3 were absent. A. A. E.

Granite, vesuvianite, ilmenite, and titanite from Monte Roseo di Verra (Monte Rosa group). I. Granite and vesuvianite. II. Ilmenite and titanite. T. Carpanese (Atti R. Accad. Lincei, 1932, [vi], 15, 591—595, 694—699).—Analysis of the granite gave: SiO_2 37·66; TiO_2 0·77; Al_2O_3 15·50; Fe_2O_3 9·47; FeO 2·00; CaO 34·51; MnO 0·53=100·44%. This agrees well with the general formula $M^{II}_3M^{III}_2(SiO_4)_3$. Crystallographic data are given for all these minerals. O. J. W.

Geology of the Roundstone district, County Galway. L. R. WAGER (Proc. Roy. Irish Acad., 1932, 41, B, 46—72).—Analyses are given of picrite, altered allivalite, and a completely altered anorthite-rock. The rocks of the area have been altered by a later intrusion of granite. L. J. S.

Composition of meteorites and of the earth. I. I. SASLAVSKY (ZASLAWSKY) (Tsch. Min. Petr. Mitt., 1932, 43, 144—155; cf. A., 1931, 1389).—A speculative deduction of the average composition of meteorites and the earth as a whole. The results obtained differ considerably from those of previous estimates. L. J. S.

Dacite in the Börzsöny Mts., Hungary. L. JUGOVICS (Tsch. Min. Petr. Mitt., 1932, 43, 156—174).—Description of the occurrence and petrography of the dacite. A chemical analysis of the rock is compared with analyses of dacites from other parts of Hungary and Transylvania. It was derived from a quartz-dioritic to granitic magma. L. J. S.

Rocks from the Austrian Alps. F. ANGEL and K. METZ (Tsch. Min. Petr. Mitt., 1932, 43, 175—181).—Analyses are given of granite from Carinthia and of spessartite from Styria. L. J. S.

Parasepiolite from magnesite deposits of the Veitsch type. H. MEIXNER (Tsch. Min. Petr. Mitt., 1932, 43, 182—193).—"Mountain leather" occurs with quartz and dolomite in crevices in magnesite deposits at several places in Styria. That from Sunk gave SiO_2 48·93, Al_2O_3 0·43, Fe_2O_3 1·12, FeO 0·24, MnO 0·04, MgO 24·05, CaO 2·96, CO_2 4·21, H_2O >110° 9·57, H_2O <110° 8·35=99·90. Deducting dolomite and limonite, this corresponds with parasepiolite. The reactions of sepiolite, parasepiolite, and palygorskite are compared. L. J. S.

Garnet-cordierite-gneiss from Mogok [Burma]. J. A. DUNN (Rec. Geol. Survey, India, 1932, 65, 445—456).—The rock consists of cordierite, biotite, hypersthene, garnet, plæonaste, and sillimanite with quartz and zircon inclusions, the latter surrounded by haloes. It shows arrested metamorphic diffusion, having been formed by the permeation of an original rock high in MgO, Fe, and Al_2O_3 by an acid granite high in Na_2O according to the equations: 4 garnet + $6SiO_2$ = 8 hypersthene + cordierite; 3 biotite + garnet + $3SiO_2$ = 5 hypersthene + cordierite + $3(KH)_2O$; and 2 garnet + 4 sillimanite = 2 spinel + cordierite; cordierite acting in all cases as a common solid solvent. C. A. S.

Granitic intrusions and associated rocks in Ranchi and Singhbhum, Bihar and Orissa [India]. L. A. N. IYER (Rec. Geol. Survey, India, 1932, 65, 490—533).—The nature and interrelations of these are discussed, and 23 complete analyses of granites, gneisses, aplites, hornblende and mica schists, dolerites, and perknite given. C. A. S.

Green mica. S. K. CHATTERJEE (Rec. Geol. Survey, India, 1932, 65, 536—539).—A green mica occurs in quartzite near Mahalgaon (Bhandara district, Central Provinces, India), in clusters up to 1/4×1/8 in. It contains SiO_2 47·35, Al_2O_3 30·99, Cr_2O_3 2·74, V_2O_3 0·48, Fe_2O_3 0·94, FeO 0·64, MgO 1·27, CaO 1·16, Na_2O 1·71, K_2O 9·26, H_2O >110° 3·96, H_2O <110° 0·02%, with traces of TiO_2, MnO, BaO, and (from its spectrum) Cs; *d* 2·904, n_β 1·612, n_γ 1·615. It is strongly pleochroic (bluish- and olive-green), and appears to be intermediate between fuchsite and roscoelite. C. A. S.

Osmiridium. O. E. ZVJAGINTSEV and B. K. BRUNOVSKI (Z. Krist., 1932, 83, 172—192).—Previous analyses are discussed. Fresh analyses by a modification of Leidié and Quennessen's method (cf. A., 1903, ii, 576) of eight samples from Newjansk, and one each from Syssertsk, Miass, and Transbaikalia show (in % in this order), respectively, Ir, Os, Pt, Rh, Ru, Au, Fe, and S: 34·7—44·7, 30·6—41·9, 1·8—13·6, 0·1—2·3, 3·0—14·1, 0—1·5, 0—3·5, 0—0·3; 42·2, 24·8, 8·3, 0, 19·1, 0, 0, 0; 44·8, 35·5, 6·6, 0·2, 13·4, 0, 0, 0; and 24·5, 46·0, 7·4, 0, 18·3, trace, 2·6, 0. The samples are classified as newjanskite, Ru-, Rh-, and Pt-newjanskite, syssertskite, and Ru-syssertskite as they contain predominant or at least considerable amounts of Ir (46·8—77·2), Ru (4·7—13·4), Rh (11·25—12·3), Pt (10·1—13·6), Os (67·9), and Os+Ru (46·0+18·3%), respectively. Ru is not present as laurite, nor is there any definite combination between the metals; all are present in solid solution, the transition from newjanskite to syssertskite being continuous. These conclusions are confirmed by *X*-ray examination, which shows a hexagonal lattice, *a* 2·620—2·710, *c* 4·235—4·282 Å., with no connexion between variations and composition. Pure Os has *a* 2·716, *c* 4·331 Å. (cf. A., 1926, 664). Low density (17·0—18·6) is due to gaseous inclusions. C. A. S.

Composition of roeblingite. R. BLIX (Amer. Min., 1931, 16, 455—460).—Roeblingite from Franklin Furnace contained SiO_2, 23·57, CO_2 0·61, SO_3 10·81, PbO 30·04, MnO 2·49, CaO 23·12, SrO 2·79, H_2O+ 6·15, H_2O− 0·45, total 100·03%, corresponding with $2PbSO_4,R_7H_{10}(SiO_4)_6$, where R=Ca, Sr, or Mn. CH. ABS.

Presence of beryllium in milarite. C. PALACHE (Amer. Min., 1931, 16, 469—470).—Be is an essential constituent of milarite, $K_2Ca_4(Be_4Al_2Si_{24})O_{60},H_2O$. One sample contained 5·24% BeO; a complete analysis is given. CH. ABS.

Zinc-bearing chromite. M. DONATH (Amer. Min., 1931, 16, 484—487).—Ramberget chromite, *H* 6—7, *d* 4·5, contains ZnO 2·42, Cr_2O_3 41·66%; the ZnO is present as an isomorphous mixture together with MgO, FeO, and Fe_2O_3. CH. ABS.

Biology and coal. F. FISCHER (Proc. III Int. Conf. Bit. Coal, 1932, 2, 809—819).—Bacterial decomp. of wood cellulose proceeds actively prior to coalification. Bacteria produced CH_4 from brown coal in a H_2 atm. *B. methanicus* produces CO_2 and H_2O from CH_4; *B. oligocarbophilus* oxidises CO, and putrefying bacteria, in absence of air, formed CH_4 from CO_2+H_2, AcOH being an intermediate product. Sewage sludge contained bacteria which produce CH_4 from $CO+H_2$. Small amounts of brown coal stimulate the growth of plants. CH. ABS.

Mineral oil and potassium radiation. F. Schwarz (Petroleum, 1932, 28, No. 40, 8—10).—A review.

Physical and chemical characteristics of soils from the erosion experiment stations. H. E. Middleton, C. S. Slater, and H. G. Byers (U.S. Dept. Agric. Tech. Bull., 1932, No. 316, 50 pp.).—Numerous analyses are recorded and discussed. A. G. P.

Mechanical composition of podsol soils. A. A. Rode (Trans. Dokuchaiev Soil Inst., 1932, 6, 153—189).—Mechanical and aggregate analyses on five podsol and podsol-gley soils showed a tendency to aggregate formation in the humus horizons. In lower horizons the tendency is weaker. Particles of diam. 0·0063 mm. mark a boundary between larger particles which are relatively accumulated and smaller particles which are removed. The velocity of disintegration of particles of diam. close to 0·0063 mm. is the same as the velocity of disintegration of the rock as a whole. A. M.

Age and evolution of soils in connexion with the age of the parent rock and the relief. N. N. Sokolov (Trans. Dokuchaiev Soil Inst., 1932, 6, 1—55).—A discussion of the abs. and relative age of soils. Three methods are appropriate for determining the relative age of soils; (*a*) the stratigraphical (buried soils), (*b*) the palæographical (where the soil does not correspond with present-day conditions), (*c*) the geographical method (for soils corresponding with present-day conditions). A. M.

Microflora of soil from the delta of the Lena. N. N. Sushkina (Trans. Dokuchaiev Soil Inst., 1932, 6, 191—196).—In the profile investigated bacterial activity was very slight. Nitrifying, cellulose-decomposing, and aërobic putrefying bacteria are absent. Microbiological life is concentrated in *A* horizon (2—5 cm.). Protein decomp. is caused by moulds or anaërobic putrefying bacteria. A. M.

Classification of soil colours. N. A. Archangelskaya (Trans. Dokuchaiev Soil Inst., 1932, 6, 197—306).—A full account of an attempt to determine soil colour using Ostwald's colour disc. Examples are given from all the main soil groups. A. M.

Soil protozoa in the Austrian Schneeberge. L. Varga (Zentr. Bakt. Par., 1932, II, 86, 254—259).—The H_2O content of these mountain soils increases and the p_H decreases with height. The no. of active protozoa is greatest at the highest levels. A. G. P.

Organic Chemistry.

Thermal decomposition of organic compounds from the point of view of free radicals. II. Experimental evidence of decomposition of organic compounds into free radicals. F. O. Rice, W. R. Johnston, and B. L. Evering (J. Amer. Chem. Soc., 1932, 54, 3529—3543; cf. A., 1931, 819).—Numerous org. compounds decompose into free radicals when heated at 800—1000°, and by chilling the products the free radicals can be combined with metals. From $COMe_2$ Me only is obtained, but C_3H_8 yields 80% Me and 20% Et and C_4H_{10} gives 70% Me and 30% Et. The half-life of the free radicals so obtained is about $1—2\times10^{-3}$ sec. The rate of their disappearance does not exactly follow either the uni- or the bi-mol. law. The temp. coeff. of the decomp. into free radicals of $COMe_2$ is practically the same as that of the ordinary thermal decomp. Free radicals in C_4H_{10} at 40—70 mm. pressure do not show the Paneth effect on a metallic mirror a few mm. from their point of origin. C. J. W. (*c*)

Hydration of solid and liquid hydrocarbons under pressure in the laboratory. II. Procedure and methods of expressing the results. F. Laupichler (Chem. Fabr., 1932, 327—331).—A general but detailed review of research methods. H. F. G.

Synthesis of *n*-hexane from *n*-propyl bromide by Würtz' method. E. Erdheim (Rocz. Chem., 1932, 12, 631—634).—*n*-Hexane is obtained in 47·6% yield by the action of Na on $Pr^{\alpha}Br$ in the presence of MeCN. βγ-Dimethylbutane cannot be prepared analogously from $Pr^{\beta}Br$. R. T.

Selenium dioxide, a new oxidising agent. II. Reaction with some unsaturated hydrocarbons. H. L. Riley and N. A. C. Friend (J.C.S., 1932, 2342—2344).—Oxidation of C_2H_4 or $CHMe{:}CH_2$ with SeO_2 occurs exothermally at 45—55°, the temp. rising to 200° with the production of $(CHO{\cdot}CHO)_3$ and $COMe{\cdot}CHO$, respectively: $3SeO_2+2C_2H_4=2(CHO)_2+3Se+2H_2O$. When the SeO_2 is mixed with P_2O_5 monomeric $(CHO)_2$ is formed in small yield. Reduction of SeO_2 with C_2H_2 (at 40—50°) occurs less readily than with C_2H_4, $(CHO)_2$ (6%) and much CO_2 being formed. With C_2H_6 at 350—400°, AcOH, CO_2, and a little $(CHO)_2$ are formed, but no reduction occurs with β-amylene, $CMe_2{:}CHMe$, $CHPh{:}CH_2$, $CHMe{:}CH{\cdot}CHO$, or $CHPh{:}CH{\cdot}CHO$ at their b.p., complex products being obtained at higher temp. By passage of C_2H_4 or $CHMe{:}CH_2$ saturated with HCl through a saturated solution of SeO_2 in fuming HCl aq. ββ′-dichloro-diethyl and -dipropyl selenide dichloride, respectively, are obtained, the dibromide being prepared similarly in HBr aq.: $2C_2H_4+4HX+SeO_2=(CH_2X{\cdot}CH_2)_2SeCl_2+2H_2O$. J. W. B.

Preparation of pure ethylene from ethyl alcohol. H. Tropsch and R. Kassler (Mitt. Kohlenforsch.-Inst. Prag, 1931, 43—44; Chem. Zentr., 1932, i, 2159).—Newth's method (J.C.S., 1901, 79, 915) affords C_2H_4 containing varying proportions of hydrocarbons such as hexane; these may be removed at −80°. A. A. E.

Production of isoprene from rubber. H. L. Bassett and H. G. Williams (J.C.S., 1932, 2324—2328).—Max. yields of isoprene (overall yield 23%; cf. below) are obtained by dropping small pieces of solid rubber (smoked sheet or crêpe) into an Fe retort (described) at 600°, and rapid cooling of the distillate (87%). Fractionation gives (1) b.p. up to 60° (19·9% containing 84% of isoprene), (2) b.p. 60—110° (6·5%, C_6H_6 etc. from secondary changes), (3) b.p. 110—200° (27·9%), and (4) residue (32·5%). By cracking (3) using a modification of the isoprene lamp of Harries and Gottlob (A., 1911, i, 798) a further 17·2% of isoprene is obtained. An improved method for the determination of isoprene based on the Diels–Alder reaction with maleic anhydride in C_6H_6 at 100° (cf. this vol., 141) gives accurate results in the absence of other butadienes, and is unaffected by the presence of amylenes. J. W. B.

Isomerides in "di*iso*butylene." II. C. O. Tongberg, J. D. Pickens, M. R. Fenske, and F. C. Whitmore. **III. Determination of their structure.** F. C. Whitmore and J. M. Church (J. Amer. Chem. Soc., 1932, **54**, 3706—3710, 3710—3714; cf. A., 1931, 1148).—II. Di*iso*butylene is separated into βδδ-trimethyl-Δ^{α}- (I), b.p. 101·2°/760 mm., f.p. −93·6±0·1°, and -Δ^{β}-pentene (II), b.p. 104·5°/760 mm., f.p. −106·5±0·1° (an isomorphic form, m.p. −108·3°, is sometimes obtained), by a single distillation through the columns described by Fenske *et al.* (B., 1932, 826). The following m.p. are reported: octane, −56·9°; heptane, −90·7°; βδδ-trimethylpentane, −107·7°.

III. Details are given for the ozonolysis of (I) and (II). (I) gives CH_2O, Me neopentyl ketone, and a trace of $CMe_3\cdot CH_2\cdot CO_2H$, whilst (II) affords $COMe_2$, $CMe_3\cdot CHO$, and $CMe_3\cdot CO_2H$. C. J. W. (*b*)

Formation of methylene iodide by oxidation of iodoacetic acid and analogous reactions. L. Panizzon (Helv. Chim. Acta, 1932, **15**, 1187—1194).—$CH_2I\cdot CO_2H$ (10 g.) and $K_2S_2O_8$ (I) (1 mol.) give CH_2I_2 (II) (81·9%), succinic acid (0·3 g.), and a little CO_2 and CH_2O, whereas use of less (I) gives less (II) (cf. A., 1930, 735). $CH_2I\cdot COCl$, 3% H_2O_2, and pyridine at 0° give *iodoacetyl peroxide*, $(CH_2I\cdot CO_2)_2$, m.p. 50—52°, decomp. 70—80°, which in boiling H_2O yields (II) (76·5%), MeOH, CO_2, and a little CO. $CH_2Cl\cdot CO_2H$ and (I) give CH_2Cl_2 and a little CH_2O and $H_2C_2O_4$. *Chloroacetyl peroxide*, m.p. 35°, decomp. 70—80°, is stable to boiling H_2O, but in 15% HCl gives about 10% of CH_2Cl_2. $(CH_2Cl\cdot CO_2)_2O$, H_2O, and cold, conc. H_2SO_4 give *perchloroacetic acid*, b.p. 33—34°, which on decomp. by HCl gives O_2 and $CH_2Cl\cdot CO_2H$. The peroxides are considered to be an intermediate product in the formation of methylene halides by electrolysis or action of (I). R. S. C.

Substances analogous to graphite. III. F. Bellino (Gazzetta, 1932, **62**, 795—798).—Thermal decomp. of CI_4 yields C which after being heated at 700° has *d* 1·46 and a much higher *R* than $(C_6)_n$ from C_6I_6 (A., 1928, 721). E. W. W.

Preparation of ethylene chlorohydrin from ethylene, chlorine, and water. H. Tropsch and R. Kassler (Mitt. Kohlenforsch.-Inst. Prag, 1931, 16—42; Chem. Zentr., 1932; i, 2159).—The $CH_2Cl\cdot CH_2\cdot OH$ concn., x, obtained when C_2H_4 and Cl_2 are passed into H_2O, is related to the ratio, y, in which $CH_2Cl\cdot CH_2\cdot OH$ and $(CH_2Cl)_2$ have been formed, by $y=-1\cdot312x+0\cdot182p+8\cdot66$, where $p=100p_{C_2H_4}/(p_{C_2H_4}+p_{Cl_2})$, $p_{C_2H_4}$ and p_{Cl_2} being the partial pressures of the reacting gases. With increasing x more $(CH_2Cl)_2$ is formed; the greater is the excess of C_2H_4, the more is the formation of $(CH_2Cl)_2$ repressed. Working conditions and the course of the reaction are discussed. A. A. C.

Catalytic oxidation of *n*-propyl alcohol. A. R. Day and A. Eisner.—See this vol., 1096.

Halides from Δ^{ι}-octadecenol. W. Seck and F. Dittmar (Chem. Umschau, 1931, **39**, 169—171).—Treatment of oleyl alcohol in EtOH with HCl at 0° yielded *κ-chloro-octadecanol*, from which *ακ-dichloro-octadecane* was prepared by reaction with PCl_5 in the cold. Direct treatment of oleyl alcohol with HBr, in the cold or at 140°, furnished *ακ-dibromoctadecane*; reaction with PBr_3 in $CHCl_3$ gave mixtures of Br- and Br_2-derivatives. The halides were yellow or brown liquids, which decomposed on distillation at 11 mm. E. L.

Optical properties of derivatives of lower aliphatic alcohols and aldehydes. W. M. D. Bryant (J. Amer. Chem. Soc., 1932, **54**, 3758—3765).—Optical methods can be used to differentiate between closely related substances, particularly when used in conjunction with the m.p. Complete optical data are reported for the 3 : 5-dinitrobenzoates of MeOH, EtOH, PrOH, $Pr^{\beta}OH$, BuOH, $Bu^{\beta}OH$, *sec.*- and *tert.*-BuOH, and $CMe_2Et\cdot OH$ and for the 2 : 4-dinitrophenylhydrazones of CH_2O, MeCHO, EtCHO, $Pr^{\alpha}CHO$, and $Pr^{\beta}CHO$. C. J. W. (*b*)

Configuration of methyl*iso*propylcarbinol: racemisation. P. G. Stevens (J. Amer. Chem. Soc., 1932, **54**, 3732—3738).—Correlation of *l*-CHMePr·OH and *l*-$CHMePr^{\beta}\cdot OH$ is accomplished by synthesis from Et *d*-lactate, $[\alpha]_D^{27}$ +0·52°. The ester with EtI and Ag_2O gives Et *d*-α-ethoxypropionate, b.p. 152·7—152·8°/730 mm. $[\alpha]_D^{23\cdot5}$ +1·69°, converted by MgMeI into l-β-*ethoxy-γ-methylbutan-γ-ol* (I), b.p. 140—140·5°, $[\alpha]_D^{20\cdot5}$ −1·84°; another sample showed $[\alpha]_D^{30\cdot3}$ −0·83°. The carbinol, dehydrated by Tschugaev's xanthate method, affords d-β-*ethoxy-γ-methyl-Δ^{γ}-butene*, b.p. 97·1—98·1°/730 mm., $[\alpha]_D^{25\cdot5}$ +1·85°, reduced catalytically to l-β-*ethoxy-γ-methylbutane*, b.p. 100°, $[\alpha]_D^{26}$ −1·19°. *d*-$CHMePr^{\beta}\cdot OH$ is ethylated to d-β-*ethoxy-γ-methylbutane*, b.p. 99—99·4°, $[\alpha]_D^{25}$ +0·60°. The K derivative of (I) does not racemise when heated at 190° for 10 hr. This supports Hückel's mechanism (A., 1931, 1286) of racemisation and rearrangement of alcoholates. C. J. W. (*b*)

Dehydration of secondary carbinols containing a neopentyl system. I. *iso*Propyl*tert.*-butylcarbinol. F. C. Whitmore and A. L. Houk (J. Amer. Chem. Soc., 1932, **54**, 3714—3718).—None of the normal dehydration products is obtained either by dehydration of the carbinol or by thermal decomp. of the Grignard complex from which it is prepared; about 5% of βδδ-trimethyl-Δ^{α}-pentene is isolated. C. J. W.

Properties of pure decatetraenol. T. Reichstein and G. Trivelli (Helv. Chim. Acta, 1932, **15**, 1074—1076).—$\Delta^{\beta\delta\xi\theta}$-Decatetraenal, m.p. 107—108° (corr.) (cf. this vol., 496), and $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ afford $\Delta^{\beta\delta\xi\theta}$-decatetraenol, m.p. 171—172·5° (corr.) (much lower when determined microscopically), hydrogenated (PtO_2) in Et_2O to pure *n*-decyl alcohol.

The alcohol has an absorption band from 2500 to 3300 Å., with max. at 2985 and 3110 Å. R. S. C.

Reduction of glycidic esters of αγ-glycols and transformation of the latter into unsaturated primary alcohols. A. S. Pfau and P. Plattner (Helv. Chim. Acta, 1932, 15, 1250—1267).—Reduction of glycidic esters with Na and abs. EtOH gives good yields of αγ-glycols, some glycidic acid, and (sometimes) a little saturated alcohol, whilst a small amount of the ester undergoes ketonic fission. The stability of the glycols, particularly of *γζ-dimethyl-*Δ^{ζ}*-octadiene-αγ-diol* (I) (geraniol or nerol hydrate), which undergo only partial decomp. when distilled at atm. pressure, is not in agreement with the view that (I) is an intermediate in the geraniol–linalool change, nor is the fact that cautious dehydration of the glycols gives only βγ-unsaturated alcohols (and, with Ac_2O, 10—25% of hydrocarbon). Substances of the type $R\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot OH$ yield mixtures of the isomerides $R\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot OH$ and $R\cdot CH_2\cdot C({:}CH_2)\cdot CH_2\cdot CH_2\cdot OH$. The glycidic ester from Me heptenone (II) and $CH_2Cl\cdot CO_2Et$ with Na and EtOH gives some glycidic acid, some (II), and (I) b.p. 149—150°/10 mm. When amyl alcohol is used, (II), (I), and only a trace of citronellol are obtained (cf. A., 1924, i, 865). Distillation of (I) with I, $POCl_3$, $ZnCl_2$, PBr_3, $H_2C_2O_4$, Na_2SO_4, or H_3BO_3, and of its Ac_2 derivative with pyridine, NH_2Ph, or $NPhMe_2$, gives a mixture (III) of *γη-dimethyl-*$\Delta^{\gamma\zeta}$*-octadien-α-ol* (IV) and *η-methyl-γ-methylene-*Δ^{ζ}*-octen-α-ol* (V), varying amounts of hydrocarbon (probably a mixture of myrcene and ocimene), and an oxido-alcohol (not isolated). With Ac_2O at 120° (I) gives a mixture of Ac and Ac_2 compounds, which, when distilled at atm. pressure, loses AcOH to yield the *Ac* derivative, b.p. 122—123°/10 mm., hydrolysed to (III), b.p. 109·5—110°/10 mm., unstable (*dibromide*, m.p. 185—186°). Quant. ozonolysis of (III) yields $COMe_2$ (85%), CH_2O (10%), and HCO_2H (40%). Et methylnonylglycidate gives similarly some glycidic acid, methylnonylcarbinol, and Me nonyl ketone, and (as main product) *γ-methyldodecane-αγ-diol* (VI), b.p. 180—182°/10 mm. (*benzal*, b.p. 157—158°/0·1 mm.). With Ac_2O (VI) gives a mixture of the *Ac*$_2$, b.p. 172°/4 mm., and *Ac* derivatives of a mixture (VII), b.p. 145°/10 mm., of *γ-methylenedodecan-α-ol* and *γ-methyl-*Δ^{γ}*-dodecen-α-ol*. Oxidation of (VII) by $KMnO_4$–CrO_3 gives nonoic and decoic acids, by O_3 in $CHCl_3$ CH_2O and nonoic acid, and by O_3 in AcOH nonaldehyde, *hydroxynonyl peroxide*, m.p. 72°, and a *substance*, m.p. 43—44°, hydrogenated (Ni) to Et nonyl ketone; Me nonyl ketone was not formed, Quant. ozonolysis of (VII) showed the presence of 48% of the methylene compound. Ozonolysis of the *phenylurethane*, m.p. 55·5—56°, of (VII) gives CH_2O. With Na_2SO_4 at 220°/15 mm. (VI) gives partly (VII) and a *hydrocarbon*, $C_{13}H_{24}$, b.p. 108°/10 mm., unstable, which, although it gives only nonoic acid when oxidised, is probably a mixture of *γ-methylene-*Δ^{α}*-dodecene* and *γ-methyl-*$\Delta^{\alpha\gamma}$*-dodecadiene*. Et methylethylglycidate affords similarly *γ-methylpentane-αγ-diol*, b.p. 115°/10 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 43°/10 mm., of *γ-methylenepentan-α-ol* and *γ-methyl-*Δ^{γ}*-penten-α-ol*. Et methyl*iso*hexylglycidate gives *γη-dimethyloctane-αγ-diol*, b.p. 155—156°/10 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 109°/10 mm. (*diphenylurethane*, m.p. 66·5°), of *γη-dimethyl-*Δ^{γ}*-octen-α-ol* and *η-methyl-γ-methylene-octan-α-ol*. Tetrahydro-ψ-ionone gives the *glycidic ester*, b.p. 184—186°/10 mm., which with Na and EtOH affords *γηλ-trimethyl-*Δ^{κ}*-dodecene-αγ-diol*, b.p. 160—162°/1 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 161—163°/10 mm., of *ηλ-dimethyl-γ-methylene-*Δ^{κ}*-dodecen-α-ol* and *γηλ-trimethyl-*$\Delta^{\gamma\kappa}$*-dodecadien-α-ol*. Et phenylglycidate affords a little benzyl alcohol, much *γ-phenylpropyl alcohol*, b.p. 112—113°/10 mm., and γ-phenylpropane-αγ-diol, b.p. 165°/10 mm., the di-*p*-nitrobenzoate of which, when distilled, gives BzOH and *trans*-cinnamyl benzoate. Et phenylmethylglycidate gives a little phenylmethylcarbinol and impure *γ-phenyl-*n*-butyl alcohol*, b.p. 130—133°/10 mm., and much *γ-phenyl-*n*-butane-αγ-diol*, b.p. 130°/1 mm., changed by refluxing with Ac_2O and AcOH and subsequent hydrolysis to *γ-phenyl-*Δ^{γ}*-buten-α-ol*, b.p. 123°/10 mm., which with O_3 in AcOH gives CH_2O, but only traces of COPhMe derived from the αβ-isomeride. Et (β-phenylethyl)methylglycidate gives a little δ-phenyl-*n*-butan-α-ol and much *ε-phenyl-γ-methylpentane-αγ-diol*, b.p. 149—150°/1 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 153°/10 mm. (*diphenylurethane*, m.p. 82·5—83°), of *ε-phenyl-γ-methylenepentan-α-ol* and *ε-phenyl-γ-methyl-*Δ^{γ}*-penten-α-ol*. R. S. C.

Preparation of pure *iso*amyl ether. P. Schorigin and J. Makarov-Semlianski (Ber., 1932, 65, [*B*], 1293—1295).—Fermentation amyl alcohol is purified by $H_4FeC_6N_6$ and distilled with H_2SO_4,H_2O; H_2O is separated from the distillate, which is returned to the flask, the operation being repeated until the temp. of the liquid in the flask is 140°, after which the product is distilled with steam. Further purification is effected by distillation with the calc. amount of H_3BO_3 and use of C_6H_6 to entrain H_2O vapour. The product is distilled under diminished pressure and finally over Na. Alternatively, the alcohol is heated with p-$C_6H_4Me\cdot SO_2Cl$ under a reflux condenser arranged so that the volatilised H_2O can be drawn off, whereas condensed alcohol returns to the flask. After formation of H_2O has ceased, the product is worked up as described above. The respective yields are 65—70% and 70—75%. H. W.

Dehydration of β-hydroxy-esters. G. A. R. Kon and K. S. Nargund (J.C.S., 1932, 2461—2463).—The relative proportions of αβ- and βγ-unsaturated esters obtained by dehydration of Et β-hydroxy-β-methyl- and -β-ethyl-valerate, -β-propylhexoate, and -αβ-dimethylvalerate, Et *cyclo*hexanol- and *cyclo*pentanol-acetate with P_2O_5 (39·5, 23·5, 24·0, 28·0, 19·0, and 30·0%), $POCl_3$ (62·0, 68·0, 45·5, 47·5, 55·5, and 58·5%), $SOCl_2$ (53·5, 50·0, 31·5, 33·0, 32·0, and 50·0), and $KHSO_4$ (57·5, 63·5, 51·0, 28·0, 45·0, and 38·0), have been determined by the iodometric method. Best yields (60—80%) of the unsaturated ester are obtained with P_2O_5 and $SOCl_2$, the former giving a mixture of max. βγ-content, whilst $POCl_3$ affords the min. proportion of this form, the respective proportions of αβ-ester being given in parentheses. COMeEt, $COEt_2$, and $COPr^{\alpha}_2$ readily condense with

$CH_2Cl\cdot CO_2Et$ in the presence of Mg powder and a trace of I to give 40—48% yields of the OH-ester.

J. W. B.

Chemistry of the three-carbon system. XXIX. Tautomerism of unsaturated esters. G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan (J.C.S., 1932, 2454—2461).—The proportions of αβ-ester and the mobility of the system, on equilibration, under standard conditions, for the following esters are given in parentheses. *Et* β-*hydroxy*-α-*methyl*-n-*hexoate*, b.p. 110°/19 mm. (*acid*, m.p. 50°), dehydrated by P_2O_5 in boiling C_6H_6 gives, after fractional hydrolysis and esterification, *Et* α-*methyl*-Δ^{β}-*hexenoate*, b.p. 68—69°/16 mm. (95%; 151) (better prepared as in preceding abstract), whence, after equilibration, the corresponding Δ^{α}-*ester*, b.p. 72°/10 mm. (*acid*, b.p. 118°/11 mm.), is obtained. *Et* αβ-*dimethyl*-Δ^{α}-*pentenoate*, b.p. 68°/10 mm. (94·5%; 2), and the Δ^{β}-*ester*, b.p. 63°/12 mm., were similarly prepared from the acids (A., 1928, 1218), purified by partial esterification; Et *cyclo*pentylidene- (I), b.p. 96°/15 mm. (60%; 835), and Et *cyclo*pentenyl- (II), b.p. 85°/15 mm., -acetate; Et α-methyl*cyclo*pentylidene-, b.p. 96°/12 mm. (88%; 84), and Et α-methyl*cyclo*pentenyl-, b.p. 79°/6 mm.; Et α-methyl*cyclo*hexylidene-, b.p. 109°/10 mm. (5%; 0·15), and Et α-methyl*cyclo*hexenyl-, b.p. 104°/13 mm., -acetate were similarly obtained from the corresponding acids. Et Δ^{α}- (75%; 26) and Δ^{β}-β-methylpentenoate (preceding abstract), and Et Δ^{α}- (92%; 153) and Δ^{β}-hexenoate were similarly equilibrated, but in the last case the equilibrium proportion of αβ-ester is only approx. owing to the rapid addition of EtOH to this form to give *Et* β-*ethoxyhexoate*, b.p. 94°/14 mm. The proportions of αβ- and βγ-isomerides were determined by Linstead's iodometric method and checked by determinations of n_D^{20} and d_4^{20}. The results are discussed and it is concluded that they cannot be correlated with structure on any simple electronic theory. Contrary to expectations based on the high mobility of the system (I) $\rightleftharpoons$ (II), no evidence of alkylation of these esters, under conditions effective in the case of *cyclo*hexenylacetone (a system of similar mobility), could be detected.

J. W. B.

α-Methylhexenoic and αβ-dimethylpentenoic acids. G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan (J.C.S., 1932, 2452—2454).—In the equilibration of the pairs of acids $CH_2Et\cdot CH{:}CMe\cdot CO_2H$ (I) (88—90%) $\rightleftharpoons$ $CHEt{:}CH\cdot CHMe\cdot CO_2H$ (II), and $CH_2Me\cdot CMe{:}CMe\cdot CO_2H$ (III) (72—73%) $\rightleftharpoons$ $CHMe{:}CMe\cdot CHMe\cdot CO_2H$ (IV) under the standard conditions previously used (A., 1927, 1167) the equilibrium vals. for the αβ-form are given in parentheses, the mobility of the systems being 18·8 and 0·12, respectively. (II) is obtained by thermal decarboxylation of α-*carboxy*-α-*methyl*-Δ^{β}-*hexenoic acid*, m.p. 130° (decomp.), which is obtained by hydrolysis of the ester, b.p. 130—140°/18 mm., resulting from the methylation of Et butylidenemalonate: [for (I), (III), and (IV) see preceding abstract]. An α-Me substituent stabilises the αβ-phase, but greatly depresses the mobility of the system only if there is also a substituent in the β-position (A., 1931, 935, 934).

J. W. B.

Micro-determination of *iso*propylidene groups. Constitution of dehydrogeranic acid. R. Kuhn and H. Roth (Ber., 1932, 65, [*B*], 1285—1292).—The substance (5—10 mg.) is ozonised in 99—100% AcOH at 0°, the solution is diluted, partly neutralised with NaOH, and oxidised by boiling with $KMnO_4$ under reflux. $COMe_2$ is removed by distillation. The distillate is rendered alkaline, treated with 0·05*N*-I at room temp. for 10—15 mm., then acidified with conc. HCl and titrated with 0·05*N*-$Na_2S_2O_3$. Very pure H_2O must be used. $COMe_2$ is scarcely affected by successive treatments with O_3 and $KMnO_4$. The no. of mols. of $COMe_2$ thus obtained from each substance is given in parentheses; acetonephenylhydrazone (0·95); methylheptenone, geraniol, and citral (0·9). Only under exceptional conditions can treatment with O_3 be omitted. Other Me ketones react with KOI to give CHI_3. COMeEt and COPhMe quantitatively give $EtCO_2H$ and BzOH, respectively, and can thus be determined iodometrically. The presence of the CMeEt: or CPhMe: groups interferes with the $CMe_2{:}$ determination, since the corresponding ketones are only slightly decomposed by $KMnO_4$. $CH_2Ac\cdot CO_2Et$ yields no $COMe_2$, very small amounts of which are produced from amylene or *iso*valeraldehyde. $COMe_2$ is also obtained from compounds containing Pr^{β} (thymol, terpin hydrate, $Pr^{\beta}OH$).

Dehydrogeranic acid affords 0·61—0·65 mol. of $COMe_2$ or less if ozonisation is omitted. The conclusion that it contains the forms $CH_2{:}CMe\cdot CH_2\cdot CH{:}CH\cdot CMe{:}CH\cdot CO_2H$ and $CMe_2{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CO_2H$ is not in harmony with its absorption spectrum in hexane or EtOH and that of its Na salt in H_2O, which resembles closely that of octatrienoic acid, $Me\cdot[CH{:}CH]_3\cdot CO_2H$, and indicates that all double linkings are in conjugation. Preference is accorded to the optical evidence and doubts are expressed as to the validity of calculating the relative proportions of α- and β-forms from the quantity of $COMe_2$ obtained.

H. W.

Interconversion of *cis*- and *trans*-modifications of monoethylenic higher fatty acids by nitrogen trioxide (elaidin reaction). H. N. Griffiths and T. P. Hilditch (J.C.S., 1932, 2315—2324).—Isomerisation of oleic, petroselic (Δ^{ϵ}-octadecenoic), and erucic (Δ^{ζ}-docosenoic) acids with Poutet's reagent (Hg in HNO_3, *d* 1·42) or oxides of N from As_2O_3 and HNO_3, at 10—20°, results in the production of an equilibrium mixture of *cis*- and *trans*-acids containing approx. 66, 60, and 60%, respectively, of the latter form. Small amounts of additive products are also obtained, and since the same equilibrium is attained starting from the *trans*-acids, isomerisation probably occurs through the reversible addition of oxides of N. The gases prepared from $NaNO_2$ and H_2SO_4 are slightly less effective, whilst those from Cu and HNO_3 give only poor yields (about 25%) of the *trans*-acid and a much greater proportion of additive products, the proportion of the latter being increased by rise of temp. or excess of the reagent. Rankoff's method (A., 1930, 65; 1% S at 220°) effects 55—60% conversion into elaidic acid. Me oleate and triolein undergo isomerisation to the same extent as oleic acid in so far as the total transformation to elaidic groups is concerned, but only 30% of triolein (separated by crystallisation from $COMe_2$) is formed, the remaining 35% of elaidic acid being in the form of mixed elaidic–oleic glycerides. Thus the reaction is not suitable for the quant. determination of triolein in natural fats, but may be used for the approx. evaluation of oleic acid in its mixtures with linoleic and linolenic acids, and for differentiation and characterisation of some natural fats. The proportion of *cis*- and *trans*-acids was determined by fractional crystallisation of the Pb salts from EtOH–ligroin and determination of the I val. or thermal analysis of the acids so obtained. J. W. B.

Probable non-existence of normal tribasic aluminium soaps such as aluminium tripalmitate. J. W. McBain and W. L. McClatchie (J. Amer. Chem. Soc., 1932, 54, 3266—3268).—Normal tribasic Al soaps have never been prepared, even in completely anhyd. media. In the prep. of oleates, stearates, and palmitates nothing more than the dibasic soap is ever obtained. Al soaps are commonly a mixture of free fatty acid with either monobasic or mono- and di-basic soaps. E. G. V. B. (*c*)

Autoxidation of unsaturated fatty acids. I. W. Franke (Annalen, 1932, 498, 129—165).—Autoxidation of linoleic acid (I) occurs more rapidly in basic (NH_2Ph, $NPhMe_2$, pyrrole, C_5H_5N, piperidine) than in neutral solvents (PhMe, $C_6H_4Me_2$, amyl alcohol and acetate). The catalytic effect of NH_2Ph (in EtOH) is observed at a concn. of $1{\cdot}2\times10^{-7}$ mol. per c.c. of (I); the effect increases slightly and then decreases (probably owing to the formation of quinonoid oxidation products) with rise in the concn. o-$C_6H_4Br{\cdot}NH_2$, m- and p-$NH_2{\cdot}C_6H_4{\cdot}OH$, p-$C_6H_4(NH_2)_2$, NHPhMe, $NPhMe_2$, and $NHPh_2$ are less effective, whilst m-$C_6H_4Br{\cdot}NH_2$ and p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ are more effective, than NH_2Ph. Of the heterocyclic bases studied, 2 : 2′-dipyridyl and pyrazine are the best catalysts; histamine shows a catalytic effect in concns. of $1{\cdot}2\times10^{-5}$ mol. per c.c. of (I). The catalytic effect of the following substances increases in the order quoted: $CO(NH_2)_2$ (small), KOH, $NHEt_2$, acetylcholine, NH_3, lecithin, $C_2H_4(NH_2)_2$. Proline is more effective than any of the above compounds. Autoxidation of oleic acid is catalysed [to a smaller extent than with (I)] by C_5H_5N, piperidine, $NHEt_2$, $C_2H_4(NH_2)_2$, proline, and 2 : 2′-dipyridyl, but is inhibited by NH_2Ph, NHPhMe, and $NPhMe_2$. The O_2-uptake of (I) is increased by addition of an equal vol. of aq. 0·2*M*-solutions of the following NH_2-acids (in the order quoted): glycine (little effect), valine, proline, leucine, tryptophan, lysine, arginine, and histidine. Aq. $({\cdot}S{\cdot}CH_2{\cdot}CO_2H)_2$ has little effect, but cysteine and $SH{\cdot}CH_2{\cdot}CO_2H$ are good catalysts; cysteine is also effective in the homogeneous mixture with (I). Autoxidation of (I) is catalysed by glyceraldehyde (small effect), $CO(CH_2{\cdot}OH)_2$, and AcCHO; cholic and deoxycholic acids and cholesterol have little or no effect, whilst ergosterol is active. Carotene and related compounds (except bixin) have approx. the same activity as ergosterol. Autoxidation of (I) is inhibited by the following substances (concn. $1{\cdot}2\times10^{-5}$ mol.) in the homogeneous state (in the order quoted): p-benzoquinone (initial activation), quinol (slight initial activation), o-$C_6H_4(OH)_2$ (I has approx. the same effect), PhOH, m-$C_6H_4(OH)_2$, and adrenaline (max. inhibition).

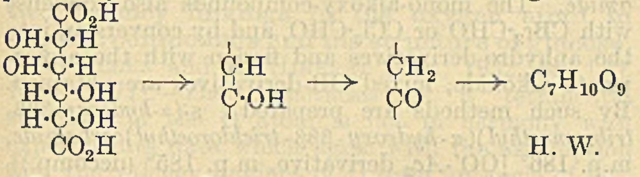
Of the metal chloride catalysts used [in concns. of 8×10^{-7} and $1{\cdot}2\times10^{-5}$ mol. per c.c. of (I)], $Co^{\cdot\cdot}$ is infinitely more active than $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, or $Cu^{\cdot\cdot}$; smaller concns. are relatively more active. The activity of dihydroxymaleic acid is increased by Cu, Ni, Co, and $Fe^{\cdot\cdot}$ (max.); the influence of $SH{\cdot}CH_2{\cdot}CO_2H$ is either not affected or retarded by the above and Mn. The activity of 2 : 2′-dipyridyl is increased by Cu, Co, $Fe^{\cdot\cdot}$, and Mn (max.) and retarded by Ni. Autoxidation of (I) is accelerated by hæmin, mesohæmin, and deuterohæmin ester [used in C_5H_5N (which also causes an activation by comparison with EtOH-hæmin)]; hæmin is relatively more effective in small concns. Chlorophyll, α-methylchlorophyllide, bilirubin, biliverdin, and ætioporphyrin have little or no effect, but hæmato-, meso-, and deutero-porphyrins show increasing activity. Hæmin (in C_5H_5N) is more effective than hæmoglobin (for the same amount of Fe) with (I)+H_2O. H. B.

Cleavage of αα-diacyl and of β-keto-α-monoacyl derivatives of diethyl succinate, glutarate, and adipate. R. N. Isbell, B. Wojcik, and H. Adkins (J. Amer. Chem. Soc., 1932, 54, 3678—3687).—The ratio of cleavage products in the alcoholysis and hydrolysis of five αα-diacyl-succinic and -glutaric esters and of two β-keto-α-acetyl-α-alkyladipic esters is not determined by the relative acidity of the acids produced by cleavage; the ratio of AcOH to BzOH is 2 : 1 for the hydrolysis of Et α-benzoyl-α-acetylsuccinate and 4 : 1 for the corresponding glutaric ester. Similarly, the ratio of AcOH to $PrCO_2H$ is approx. 2 : 5 for Et α-acetyl-α-butyrylsuccinate, whilst AcOH is not produced from Et α-acetyl-α-butyrylglutarate. The size of the alkyl group has a pronounced effect, since the Ac cleavage is only two thirds as much with Et β-keto-α-acetyl-α-lauryladipate as with Et β-keto-α-acetyl-α-butyladipate. Various conclusions previously deduced regarding the cleavage of simple αγ-diketones also hold for these more complex αγ-diketones which are also β-keto-esters. *Et α-acetyl-α-butyrylsuccinate*, b.p. 144—150°/4 mm., results in 53% yield from Et α-acetylsuccinate, PrCOCl, and Na. *Et α-benzoyl-α-acetylsuccinate* (I), b.p. 178—182°/1 mm., is formed similarly in 55% yield and in 54% yield from Et α-benzoyl-α-acetylacetate and $CH_2Cl{\cdot}CO_2Et$. *Et α-benzoyl-α-acetylglutarate* (II), b.p. 184—187°/1 mm.; *Et α-acetyl-α-butyrylglutarate*, b.p. 156—159°/3 mm.; *Et α-acetyl-α-trimethylacetylsuccinate*, b.p. 143—146°/4—5 mm.; *Et α-acetyl-α-trimethylacetylglutarate*, b.p. 148—153°/4—5 mm.; *Et β-keto-α-acetyl-α-butyladipate* (III), b.p. 147—150°/1 mm.; and *Et β-keto-α-acetyl-α-lauryladipate* (IV), b.p. 234—239°/1 mm., are prepared. Hydrolysis of (I) with H_2O at 200° and 100 atm. for 25 hr. gives 69% of $CH_2Bz{\cdot}CH_2{\cdot}CO_2H$, 64% of AcOH, and 31% of BzOH; (II) affords 79% of $CHBzMe{\cdot}CH_2{\cdot}CO_2H$, 80% of AcOH, and 21% of BzOH; (III) yields 18% of γ-ketononoic acid, 45% of AcOH, and 59% of heptan-β-one; (IV) gives 33%

of γ-ketomargaric acid, 30% of AcOH, and 66% of tridecan-β-one. C. J. W. (*b*)

Electrolytic preparation of *d*-galactonic acid. H. Kiliani (Ber., 1932, 65, [*B*], 1269—1272).—Detailed directions are given for the electrolytic oxidation of galactose to Ca *d*-galactonate according to the modified method of Isbell and Frush (A., 1931, 1038). H. W.

Action of potassium cyanide on potassium mannosaccharate. H. Kiliani (Ber., 1932, 65, [*B*], 1272—1274).—New analyses of the Ca and Zn salts (A., 1928, 741; 1931, 1274) establish the respective constitutions $C_7H_6O_8Ca$ and $C_7H_6O_8Zn$. They are derived from a monolactone, $C_7H_8O_8$, corresponding with the tribasic acid $C_7H_{10}O_9$ instead of $C_7H_{10}O_{10}$ previously recorded. The course of the change is :



H. W.

Isomerism phenomena of *d*-mannosaccharic acid. K. Rehorst (Ber., 1932, 65, [*B*], 1476—1486).—*d*-Mannosaccharodilactone is converted through the corresponding Na and Ag salts into cryst. *d*-mannosaccharic acid (I), m.p. 128·5°, $[\alpha]_D$ +3·6° to +50·0° in H_2O (for method, cf. A., 1928, 272). After neutralisation, the solution does not reduce Fehling's solution or react with I and alkali according to Willstätter and Schudel. During the earlier stages of mutarotation, the titratable acidity of the solution diminishes, but reducing products are not formed; after long preservation at room temp., I is absorbed and Fehling's solution reduced to an increasing extent. Neutralisation of cryst. (I) by NaOH or KOH gives the Na salt, $[\alpha]_D$ −17·2°, and K salt $[\alpha]_D$ −14·1° (identical with Kiliani's salt from the diamide); the solutions have no reducing properties and do not become discoloured at 100°. If cryst. (I) is kept in aq. solution for 5—6 hr. at 100°, *d*-mannosaccharodilactone (II) is formed with the properties described by Kiliani and Fischer, which can scarcely be attributed to the presence of a ·CHO or :CO group. The aq. solution of (II) gradually becomes acid, whereas the consumption of Fehling's solution and of alkaline I diminishes to about 10% of its initial val. (I) is converted instantaneously by a moderate excess of NaOH into (II) and the excess can be titrated accurately after a few min. (I) prepared from (II) through the Na salt and an equiv. amount of acid differs widely from the cryst. acid, since it has $[\alpha]_D$ −10·8° to +26·4°, reduces Fehling's solution, and ppts. CHI_3 from alkaline I. Gradual increase of $[\alpha]_D$ is accompanied by diminution of directly titratable acid and of the consumption of I to about 34% of that of the recently liberated acid. Alkali salts derived from (II) by an excess of alkali followed by neutralisation differ from those obtained from cryst. (I) in exhibiting reducing properties. These diminish more rapidly than in the case of the free acid, and at equilibrium the consumption of I is only about 10% of the initial amount. $[\alpha]_D$ changes very rapidly, the vals. recorded being −32·8° to +7·5° and −31·6° to +8·5° for the K_2 and Na_2 salts, respectively. It is suggested that the valencies of the atoms involved in the formation of the two furan rings and consequently of the C atoms are distorted from their normal position and that, after opening of the rings, the C skeleton, now capable of rotation about a common C–C axis, assumes a labile condition, thus explaining the enhanced reactivity and consequent loosening and readier fission of the C chain. The stable modification of *d*-mannosaccharic acid is coupled with the gradual transition to the normal form of the C chain. H. W.

Preparation of methyl-*d*-galacturonide. K. P. Link (Nature, 1932, 130, 402).—When heated with MeOH+HCl commercial polygalacturonide from citrus pectin yields the Me ester of methyl-*d*-galacturonide as $C_6H_{11}O_5·CO_2Me,H_2O$, m.p. 138—140°, $[\alpha]_D^{25}$ +124·1°, no mutarotation. This gives methyl-*d*-galacturonide by way of the Ba salt as $C_6H_{11}O_5·CO_2H,2H_2O$, m.p. 112—114°, $[\alpha]_D^{25}$ +127·6°, no mutarotation. L. S. T.

Methylation of monocarboxylic acids derived from aldoses. Structure of pentamethyl-α-glucoheptono-γ-lactone. W. N. Haworth, E. L. Hirst, and M. Stacey (J.C.S., 1932, 2481—2485).—The OH groups in positions 4 and 5 in galactonic acid, certain hexoses, and α-glucoheptose resist methylation either by Ag_2O+MeI or Me_2SO_4+NaOH, and such methylation of the sugar acid frequently affords the best method for the prep. of the fully methylated γ-lactone. Thus Na α-glucoheptonate with Me_2SO_4 and 30% NaOH in H_2O–$COMe_2$ at 55° (or the γ-lactone with AgO–MeI) gives 2 : 3 : 5 : 6 : 7-*pentamethyl-α-glucoheptono-γ-lactone*, m.p. 104°, $[\alpha]_D^{20}$ (initial) −13° in H_2O, +69° in Et_2O, hydrolysed extremely slowly in aq. solution and oxidised by HNO_3 (*d* 1·42) to *i*-dimethoxysuccinic acid unaccompanied by trimethoxyglutaric or higher acids. γ-Mannonolactone is similarly methylated to its 2 : 3 : 5 : 6-Me_4 derivative, whilst γ-galactonolactone +H_2O (I) gives 2 : 3 : 4 : 6-tetramethylgalactonic acid and 2 : 3 : 5 : 6-tetramethyl-γ-galactonolactone (II). After dehydration (I) with Ag_2O and MeI (four treatments) and subsequent esterification gives (?) 2 : 3 : 6-*trimethylgalactonolactone*, m.p. 99°, $[\alpha]_D^{17}$ −40° to −28° in H_2O in 14 days, further methylated to (II) and oxidised with HNO_3 (*d* 1·2) to *d*-dimethoxysuccinic acid, no methylated mucic acid being detected. Under the same conditions γ-arabono- and -glucono-lactones give completely methylated products. J. W. B.

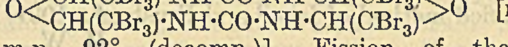
Catalytic hydrogenation of ozonides. F. G. Fischer, H. Düll, and L. Ertel (Ber., 1932, 65, [*B*], 1467—1472).—Ozonisation should be effected in dil. solution at a low temp. and an excess of O_3 must be strictly avoided, since oxozonides and perozonides are reduced to acids. To avoid "acid isomerisation" of ozonides, hydrogenation (Pd–$CaCO_3$) is effected with careful cooling. The yields of aldehyde or ketone are 50—90%. Markedly polymerised ozonides are hydrogenated in warm solution under pressure, the use of MeOH or EtOH as solvent also protecting the aldehyde by production of the sluggish acetals. Ozonisation in EtOAc is not accompanied by the production of insol. polymerised ozonides. The following schemes are suggested for the degradation of aldehydes and acids or esters: $CH_2R{\cdot}CHO \xrightarrow{MgPhBr} CH_2R{\cdot}CHPh{\cdot}OH \longrightarrow CHR{:}CHPh \xrightarrow{O_3+H_2} R{\cdot}CHO+PhCHO$; $CH_2R{\cdot}CO_2H \xrightarrow{MgPhBr} CH_2R{\cdot}CPh_2{\cdot}OH \longrightarrow CHR{:}CPh_2 \longrightarrow R{\cdot}CHO+COPh_2$; MgEtBr may replace MgPhBr. The following examples are recorded: methylheptenone to lævulaldehyde (yield 70%), mesityl oxide to methylglyoxal, oleic acid to nonaldehyde and azelaic acid semialdehyde; *cyclo*pentene to glutardialdehyde, *cyclo*hexene to adipdialdehyde (*dioxime*, m.p. 183—184°) and its Me_4 acetal, *cyclo*heptene to pimeldialdehyde (*dioxime*, m.p. 153°), nonoic acid to *αα-diphenyl-Δ^{α}-nonene*, b.p. 200—210°/13 mm., and thence to octaldehyde. H. W.

Additive compounds of mercaptans with aldehydes during the formation of mercaptals. T. G. Levi (Gazzetta, 1932, 62, 775—780).—CH_2O combines in MeOH with EtSH, $Pr^{a}SH$, *iso*-$C_5H_{11}{\cdot}SH$, and PhSH to form liquid additive *compounds*, and with 2-thiolbenzthiazole to a *compound* (I), m.p. 125—130°. In presence of $ZnCl_2$, *di*-n-*propylthiolmethane*, b.p. 216°, *di*iso*amylthiolmethane*, b.p. 265°, and $CH_2(SPh)_2$ are formed. 2-Thiolbenzthiazole is converted by MeI into *methylene dibenzthiazyl sulphide*, m.p. 98°, not obtainable from (I). E. W. W.

Microchemical detection of formaldehyde in presence of hexamethylenetetramine. C. Kollo and F. Polychroniade (Pharm. Zentr., 1932, 73, 578—582).—Hexamethylenetetramine (I) is removed from the solution either as the picrate or as the $BiCl_3$ compound and CH_2O is detected in the residue with dimethyldihydroresorcinol (II) (A., 1928, 1117). (I), which reacts with (II) on heating, is completely pptd. by either reagent and no CH_2O is formed by hydrolysis. E. H. S.

System amino-substance–aldehyde–hydrogen acceptor. F. Lieben and V. Getreuer (Biochem. Z., 1932, 252, 420—433).—The hydrogenation of methylene-blue, malachite-green, and cysteine in a system containing an NH_2-compound, PO_4''' buffer, and an aldehyde is examined. By variation of the NH_2-compound and the aldehyde, it is shown that introduction of CO_2H and Me groups, especially on the C atom adjacent to the N, decreases, whereas that of Ph and OH groups increases, the rate of hydrogenation. Both a free NH_2 and the NH group of proline and hydroxyproline react in this way. The PO_4''' buffering may be replaced by BO_3'''. EtCHO reacts more slowly than MeCHO. Unsaturated aldehydes (acraldehyde, crotonaldehyde) considerably accelerate the reaction. Decrease of concn. of NH_2-compound and of aldehyde retards, and increase of concn. accelerates, hydrogenation. P. W. C.

Condensation of bromal with carbamide. F. D. Chattaway and E. J. F. James (Proc. Roy. Soc., 1932, A, 137, 481—488).—$CO(NH_2)_2$ condenses with $CBr_3{\cdot}CH(OH)_2$ in H_2O to give *α-hydroxy-βββ-tribromoethylcarbamide*, m.p. 136° (decomp.) [*Ac_2* derivative $CBr_3{\cdot}CH(OAc){\cdot}NH{\cdot}CO{\cdot}NHAc$, m.p. 184° (decomp.)], which, fused with more $CBr_3{\cdot}CH(OH)_2$, gives s-*di-(α-hydroxy-βββ-tribromoethyl)carbamide*, m.p. 178° (decomp.) [OO′-*Ac_2* derivative, m.p. 180° (decomp.)]. These with *N*-NaOH and Ac_2O at 0° afford, respectively, bis-(α-carbamido-βββ-tribromoethyl) ether, decomp. 211° [*Ac_2* derivative $[NHAc{\cdot}CO{\cdot}NH{\cdot}CH(CBr_3)]_2O$, m.p. 219° (decomp.)], and the anhydro-compound



$$O{<}\begin{matrix}CH(CBr_3){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH(CBr_3)\\CH(CBr_3){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH(CBr_3)\end{matrix}{>}O$$

[not pure, m.p. 92° (decomp.)]. Fission of these ethers with NaOR in ROH gives the alkoxy-derivative, $CBr_3{\cdot}CHO$, HCO_2Na, and $CO(NH_2)_2$, and thus are obtained: α-*methoxy*-, m.p. 184° (decomp.), α-*ethoxy*- (I), m.p. 162° (decomp.) (N′-*Ac* derivative, m.p. 177° (decomp.)], and α-n-*propoxy*-, m.p. 144° (decomp.), -βββ-*tribromoethyl*-, s-*di*-(α-*methoxy*-βββ-*tribromoethyl*)-, m.p. 215° (decomp.), and s-*di*-(α-*ethoxy*-βββ-*tribromoethyl*)-, m.p. 196° (decomp.), -*carbamide*. The mono-alkoxy-compounds also condense with $CBr_3{\cdot}CHO$ or $CCl_3{\cdot}CHO$, and by conversion into the anhydro-derivatives and fission with the appropriate alkoxide, mixed OR-derivatives are obtained. By such methods are prepared: s-(α-*hydroxy*-βββ-*tribromoethyl*)(α-*hydroxy*-βββ-*trichloroethyl*)*carbamide*, m.p. 186° [OO′-*Ac_2* derivative, m.p. 185° (decomp.)], from the anhydro-derivative of which the corresponding (α-*OEt*)$_2$-derivative, m.p. 203° (decomp.), is obtained. (I) and $CCl_3{\cdot}CHO$ give s-(α-*ethoxy*-βββ-*tribromoethyl*)(α-*hydroxy*-βββ-*trichloroethyl*)*carbamide*, m.p. 144° (decomp.) [O-*Ac* derivative, m.p. 192° (decomp.)], the anhydro-derivative (not characterised) of which gives s-(α-*ethoxy*-βββ-*tribromoethyl*)(α-*ethoxy*-βββ-*trichloroethyl*)*carbamide*, m.p. 203° (decomp.). s-(α-*Methoxy*-βββ-*tribromoethyl*)(α-*hydroxy*-βββ-*trichloroethyl*)-, m.p. 193° (decomp.), and the isomeric s-(α-*methoxy*-βββ-*tribromoethyl*)(α-*ethoxy*-βββ-*trichloroethyl*)-, m.p. 206° (decomp.), and s-(α-*ethoxy*-βββ-*tribromoethyl*)(α-*methoxy*-βββ-*trichloroethyl*)-, m.p. 197° (decomp.), -*carbamide*, are similarly obtained. J. W. B.

Alkyl peroxides. IX. Perparaldehyde. A. Rieche and R. Meister (Ber., 1932, 65, [*B*], 1274—1279).—MeCHO is added to 3% ethereal H_2O_2 at 0° in presence of anhyd. Na_2SO_4 and, after 2 days at 0°, the product is filtered and treated with P_2O_5. After removal of the solvent at 20°/15 mm., "*synthetic dimeric butylene ozonide*," $C_8H_{16}O_6$, remains as an unstable, mobile liquid. It is hydrolysed by warm dil. H_2SO_4 to MeCHO and H_2O_2, slowly by cold H_2O, whereby the active O is slowly utilised in the production of AcOH; utilisation is immediate in the presence of $FeSO_4$. When preserved or placed in vac. at 40°, it appears to yield ethylidene peroxide. When cautiously distilled under diminished pressure, the synthetic ozonide is transformed into *monoperparacetaldehyde*, $C_6H_{12}O_4$, b.p. 45—46°/12 mm., m.p. about 9°, $d^{19\cdot6}$ 1·0672. It is hydrolysed by warm, dil. H_2SO_4 to MeCHO (3 mols.) and H_2O_2 (1 mol.) and by alkali with formation of AcOH (1 mol.). H. W.

Oxidation of methylglyoxal by molecular oxygen in presence of hydrocyanic acid. C. V. Smythe (Ber., 1932, 65, [*B*], 1268—1269).—AcOH, CO_2, and a small quantity of HCO_2H are the main ultimate products formed when methylglyoxal is shaken with O_2 in presence of an excess of HCN. H. W.

Iodometric determination of acetone. K. Lesničenko (Chem. Obzor, 1932, 7, 2—4; Chem. Zentr., 1932, i, 2743).—The error is ±0·5%, the results usually being too high. A. A. E.

Colorimetric determination of sugars. A. Castiglioni (Annali Chim. Appl., 1932, 22, 570—574).—To 0·3—5·0 c.c. of solution, containing 0·003—0·05 g. of sucrose, glucose, or lactose, 10 drops of 20% alcoholic resorcinol are added, then 2 vols. of HCl (*d* 1·19), and the mixture is boiled for 1 min. After cooling the ppt. is dissolved in EtOH and the solution is diluted to 20 c.c. with H_2O. The coloration is compared with a standard (1 c.c. of 1% sugar solution) in a Duboscq colorimeter. O. F. L.

Reactions of carbohydrates and polysaccharides. XL. Magnitude of the angle between the two valency linkings of the oxygen atom in organic compounds and the structure of glucose. J. S. Allen and H. Hibbert (Ber., 1932, 65, [*B*], 1362—1371).—The hypothesis of a tetrahedral structure of the O atom is not in harmony with experimental data which agree with the assumption that the valency linkings of O form an angle of 90°. The data cannot be regarded as final, but as mean vals. for the particular compounds. The systems are to be regarded as kinetic, not static, although the cyclic compounds exhibit a definite, geometrical structure. 2-*Hydroxy*-2′-*dichloromethyl*-1 : 3-*dioxalan* is described. H. W.

5-Methylglucose of Ohle and von Vargha. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1932, 97, 751—761).—The 5-methylglucose of Ohle and von Vargha (A., 1929, 1279) (improved prep.) is shown to be 6-methylglucose, m.p. 153—154° (rapid heating, softens 150°) [osazone, m.p. 183° (sinters 180°, decomp. 192°); Ac_4 derivative, m.p. 95—96°; *Ba* salt of the gluconic acid] (cf. A., 1931, 939). A. A. L.

Carbohydrates. XIII. Benzylidene and benzoyl derivatives of glucose. P. Brigl and H. Grüner (Ber., 1932, 65, [*B*], 1428—1434).—4 : 6-Benzylidene-α-*d*-glucose, m.p. 172°, $[\alpha]_D$ +39·6° to +4·3° in EtOH (cf. Zervas, A., 1931, 1275), is converted by BzCl in C_5H_5N or aq. alkali into 4 : 6-*benzylidene*-α-d-*glucose* 1 : 2 : 3-*tribenzoate* (I), m.p. 193°, $[\alpha]_D$ −10·6° in $CHCl_3$, hydrolysed by 2*N*-HCl in $COMe_2$ at 50° to *glucose* 1 : 2 : 3-*tribenzoate* ($+\frac{1}{3}C_6H_6$) (II), m.p. 107—108° after softening at 104°, $[\alpha]_D$ +30·8° in $CHCl_3$ or, solvent-free, $[\alpha]_D$ +33·1° in $CHCl_3$, which is re-converted into (I) by PhCHO and $ZnCl_2$. (I) is transformed by Ac_2O and $ZnCl_2$ at room temp. or, preferably, by Ac_2O and a little conc. H_2SO_4 into 1 : 4 : 6-*triacetylglucose* 2 : 3-*dibenzoate* (III), m.p. 168°, $[\alpha]_D$ +130·7 in $CHCl_3$ (glucose pentabenzoate is similarly converted by Ac_2O and $ZnCl_2$ into 1-acetylglucose tetrabenzoate, m.p. 160—161°, $[\alpha]_D$ +90·6°). (I) and HBr–AcOH afford β-*methylglucoside* 4 : 6-*diacetate* 2 : 3-*dibenzoate*, m.p. 133°, $[\alpha]_D$ +78·8° in $CHCl_3$, also obtained from (III) or from *glucose diacetate* 1 : 2 : 3-*tribenzoate* (III) by means of HBr–AcOH and Ag_2CO_3–MeOH. Treatment of (II) with Ac_2O–C_5H_5N at room temp. gives (IV), m.p. 174°, $[\alpha]_D$ +36·6° in $CHCl_3$, and with BzCl and C_5H_5N yields *glucose* 1 : 2 : 3 : 6-*tetrabenzoate* (V), m.p. 153—154°, $[\alpha]_D$ +27·0° in $CHCl_3$. *Glucose* 4-*acetate* 1 : 2 : 3 : 6-*tetrabenzoate*, m.p. 149—150°, $[\alpha]_D$ +55·0° in $CHCl_3$, is derived from (V) and Ac_2O–C_5H_5N. *iso*Propylideneglucose, PhCHO, and $ZnCl_2$ give 1 : 2-iso*propylidene*-3 : 5-*benzylideneglucofuranose*, m.p. 149°, $[\alpha]_D$ +23·4° in $CHCl_3$, identical with the "1 : 2-*iso*propylidene-5 : 6-benzylideneglucofuranose" of Levene and Meyer (A., 1923, i, 92). The constitution is established by conversion of the substance into 1 : 2-iso*propylidene*-3 : 5-*benzylideneglucose* 6-*benzoate*, m.p. 124°, $[\alpha]_D$ +3·5° in $CHCl_3$, and 6-*acetate*, m.p. 126—127°, $[\alpha]_D$ +11·8° in $CHCl_3$, identical with the products derived by the action of PhCHO and $ZnCl_2$ on 1 : 2-*iso*propylideneglucose 6-benzoate and 6-acetate. *iso*Propylideneglucose 3-acetate could not be condensed with PhCHO and $ZnCl_2$. H. W.

Action of titanium tetrachloride on tetracetyl-β-*d*-glucosidoglycollic ester. (Miss) T. M. Reynolds (J. Proc. Roy. Soc. New South Wales, 1932, 66, 167—170; cf. A., 1928, 1118).—$TiCl_4$ and Et tetra-acetyl-β-*d*-glucosidoxyacetate afford acetochloroglucose and not the α-glucoside. J. L. D.

Phenomena accompanying the hydrolysis of sucrose. S. Bezzi.—See this vol., 1094.

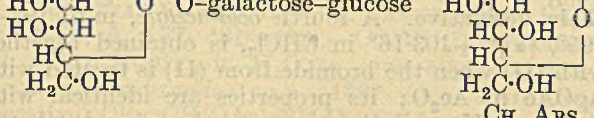
Characteristic decompositions of sucrose and employment of the decomposition products for the preparation of colloidal solutions of metals. A. H. Erdenbrecher (Z. ver. Deut. Zucker-Ind., 1932, 82, 718—741).—Decomp. of molasses or sucrose under pressure in presence of alkali gives an *acid* resembling humic acid. Oxidation of this with HNO_3 gives an *acid* containing N (*Na*, *K*, NH_4, *pyridine*, and N_2H_4 salts; *anilide*, and *naphthylamide*; *Cl*, *Br*, and *I* derivatives). The NH_4 salt gives up only part of its NH_3 with NaOH. Intermediate oxidation products are obtained with varying concn. of HNO_3. The substances, especially the oxidation products, possess strong protective colloid properties. A. A. L.

Ketone sugar series. I. Novel form of stereoisomerism in the sugar group. Acetyl and halogenoacetyl derivatives of turanose. E. Pacsu (J. Amer. Chem. Soc., 1932, 54, 3649—3661).—Three octa-acetates are obtained by acetylation of cryst. turanose (I) with Ac_2O and $ZnCl_2$ at room temp. instead of the two required by the theory of oxo-cyclo-desmotropy of the reducing sugars. The first *octa-acetate* (II), m.p. 216—217°, $[\alpha]_D^{20}$ +20·5° in $CHCl_3$, is a derivative of the semi-orthoacetic anhydride type. All such sugar derivatives contain a new asym. C atom in the mol. and can, therefore, exist in two diastereoisomeric forms. The second *octa-acetate* (III), m.p. 158°, $[\alpha]_C^{20}$ +85·4°, $[\alpha]_{HgI}^{20}$ +125·75° in $CHCl_3$, is assigned the 2 : 6-ring structure. The third *octa-acetate* has m.p. 96°, $[\alpha]_D^{20}$ +126·2°, $[\alpha]_C^{20}$ +98·14°, $[\alpha]_{HgI}^{20}$ +151·65° in $CHCl_3$, and is probably an open-chain derivative. A fourth *octa-acetate*, m.p. 194—195°, $[\alpha]_D^{20}$ +103·16° in $CHCl_3$, is obtained together with (II) when the bromide from (II) is treated with AgOAc in Ac_2O; its properties are identical with those of (II) and it represents the second (above) possible diastereoisomeride. (II) and $TiCl_4$ in $CHCl_3$ give the *Cl* derivative, m.p. 165° (decomp.), $[\alpha]_D^{20}$

—0·44° in $CHCl_3$; the *Br* derivative, m.p. 133—134° (decomp.), $[\alpha]_D^{20}$ —30·5° in $CHCl_3$, is prepared from (II) and HBr in AcOH–$CHCl_3$ or from (I) and Br in Ac_2O, whilst the *I* derivative, m.p. 105—106°, $[\alpha]_D^{20}$ —54·2° in $CHCl_3$, is obtained from (II) and HI in AcOH–$CHCl_3$. (III) yields a *Cl* derivative, syrupy, $[\alpha]_D^{20}$ +92·9° in $CHCl_3$, and a *Br* derivative, $[\alpha]_D^{20}$ +117·4° in $CHCl_3$. The stable halides from (II) are orthoacetyl halide derivatives; thus, the bromide and pyridine give a ketenacetal. The unstable halides from (III) have the regular structure of the α-halogenoacetylturanoses. Since the properties of these substances differ from those of the "α-chloroacetylfructose," it is concluded that the latter cannot be the stereoisomeride of the unstable β-chloroacetylfructose. C. J. W. (*b*)

Cellotriose. K. Dziengel, C. Trogus, and K. Hess (Ber., 1932, 65, [*B*], 1454—1457).—Cellotriose (Zechmeister and others, A., 1929, 544; 1931, 716) gives a Röntgen diagram which differs from those of hydrocellulose and cellobiose and is not altered by dissolution of the substance in H_2O, MeOH, or 95% EtOH and evaporation of the solutions or by fractionation from EtOH. It is therefore regarded as a chemical individual. Concn. of a solution in MeOH at room temp. yields a most sparingly sol. fraction which gives the interferences of hydrocellulose, whereas the other fractions are amorphous. Marked variations in $[\alpha]_D$ or I val. among the different fractions are not observed. Gradual addition of Et_2O to the substance dissolved in C_5H_5N yields fractions with interferences of an amorphous substance and marked variation in $[\alpha]_D$ and I val. Cellotriose is regarded as a mol. compound of hydrocellulose and an unknown reducing component other than cellobiose. H. W.

Constitution of stachyose. I. M. Onuki (J. Agric. Chem. Soc. Japan, 1932, 8, 445—462).—Stachyose, $(C_{24}H_{42}O_{21})_2,3H_2O$ (anhyd. at 115° in vac.), crystallised on addition of EtOH to the purified [$Pb(OAc)_2$, $Hg(OAc)_2$, $Ba(OH)_2$, phosphotungstic acid] juice of the bulb of *Stachys tuberifera*, Nd. *Tetradeca-acetyl-*, $C_{24}H_{28}O_7(OAc)_{14}$, m.p. 95—96°; *tetradeca*-p-*nitrobenzoyl-*, m.p. 166°; and *tetradecamethyl-stachyose*, a syrup, $[\alpha]_D^{24·5}$ +133·3° (C_6H_6), hydrolysed (HCl) to 1 : 3 : 4 : 6-tetramethyl-*d*-fructose and 2 : 3 : 4 : 6-tetramethyl-*d*-galactose, were prepared. Stachyose was hydrolysed by 20% AcOH to manninotriose, which was converted by way of Ca manninotrionate, and undecamethylmanninotrionic acid into 2 : 3 : 5 : 6-tetramethyl-*d*-gluconic acid lactone and 2 : 3 : 4 : 6-tetramethylgalactose. Stachyose is assumed to have the structure:



Ch. Abs.

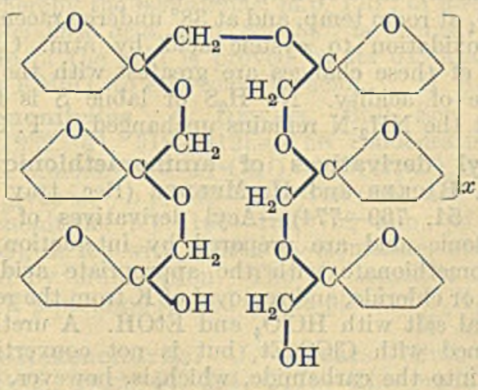
Polysaccharides. XII. Acetolysis products of cellulose. W. N. Haworth, E. L. Hirst, and O. Ant-Wuorinen (J.C.S., 1932, 2368—2371).—In agreement with Meyer and Mark (A., 1929, 51) and Freudenberg (*ibid.*, 430) cellobiosan acetate (I) obtained by acetolysis of cellulose under Hess' conditions (A., 1927, 44) is not homogeneous, but is a mixture of cellodextrin acetates of high mol. wt. (>3000 in camphor. Acetolysis of (I) (AcOH–Ac_2O–H_2SO_4 at 60°) affords a mixture of cellodextrin acetates (mol. wt. about 1600) and unchanged biosan, whilst under more drastic conditions (105°) there results a mixture of dextrin acetates, separated by crystallisation from EtOH into fractions differing in m.p. and $[\alpha]_D$, and of mol. wt. ranging from 640 to 1300. Methylation of (I) with Me_2SO_4–NaOH in H_2O–$COMe_2$ gives methylated cellobiosan, m.p. 213—215°, mol. wt. 1600, increased to 2100 after removal of partly degraded material by fusion with camphor. Acetolysis of cellulose under Bertrand and Benoist's conditions (A., 1923, i, 756) gives procellose free from admixture with cellobiose octa-acetate, the Ac derivative, m.p. about 120°, $[\alpha]_D^{19}$ +5° in C_6H_6, mol. wt. 690, of which with Me_2SO_4–30% NaOH in H_2O–$COMe_2$ gives a fully methylated procellose, b.p. about 300°/0·04 mm., $[\alpha]_D^{17}$ +27° in $CHCl_3$, hydrolysed by 5% HCl to tetramethylglucopyranose and 2 : 3 : 6-trimethylglucopyranose. The rate of hydrolysis is similar to that of a methylated trisaccharide (A., 1931, 941). Hence procellose is a trisaccharide and Ost's cello*iso*biose (A., 1920, i, 423) is probably a mixture of this with cellobiose. J. W. B.

Polysaccharides. XIII. Chain-length of methylated cellodextrins. W. N. Haworth and H. Machemer (J.C.S., 1932, 2372—2374).—By repeated fractional pptn. (cf. Bergmann and Machemer, A., 1930, 457) the products of the acetolysis of cellulose (Hess and Friese, A., 1927, 44) are separated into eight fractions ($[\alpha]_D$ in $CHCl_3$, decomp. point, and % OAc determined) of approx. chain-lengths of 21—12 glucose residues (by I. val.). Each fraction was converted into the corresponding Me derivative (A., 1931, 941; this vol., 1022), again fractionated, and each fraction ($[\alpha]_D$, decomp. point, and % OMe determined) hydrolysed and the yield of tetramethylglucose determined. Calc. from the latter, the estimated average no. of glucose residues varies from 26 to 11, a val. in agreement with that of other workers. Cellodextrins are long extended mols. consisting of mutually linked glucopyranose units. J. W. B.

Polysaccharides. XIV. Molecular structure of amylose and amylopectin. E. L. Hirst, (Miss) M. M. T. Plant, and (in part) (Miss) M. D. Wilkinson (J.C.S., 1932, 2375—2383).—Separation of potato starch by Ling and Nanji's method (*ibid.*, 1923, 123, 2666) gives amylose (I), $[\alpha]_D^{20}$ +190° in H_2O, and amylopectin (II), $[\alpha]_D^{20}$ +151° in 5% NaOH, which have the same P content (0·2%) as the original starch. Acetylation of (I) gives the Ac_3 derivative, charring at 173°, $[\alpha]_D^{19}$ +170° in $CHCl_3$, which is deacetylated and methylated without mol. degradation. Hydrolysis of the methylated amylose, m.p. 143° (previous softening), $[\alpha]_D^{21}$ +207° in $CHCl_3$, affords 5% of tetramethylglucopyranose (+80% of trimethylglucose), corresponding with a chain-length of 22—24 glucose units. According to conditions, acetylation of (II) gives products varying continuously from the sol. (I) acetate to the insol. (II) acetate, a similar gradation being encountered in the fractions obtained from the deacetylated and methylated product. Hydrolysis of either the viscous or the mobile methylated fractions with fuming HCl at 0° gives 5% of tetramethylglucose, corresponding with the same chain-length of 22—24 glucose units. Both (I) and (II) are probably built up of 24 glucopyranose units linked as in maltose, the presence of α-glucosidic linkings preventing the formation of long straight chains and favouring interlocked, aggregated mols. It is suggested that (II) consists of aggregates of these interlocked macromols. which in H_2O undergo hydration with the formation of a micellar structure. In solutions of (I) there is a less interlocked and more highly hydrated condition. Thus there is a continuous range of products with properties intermediate between those of (I) and (II) and it is found that (I) retrogrades through intermediate stages to the condition of (II).

J. W. B.

Polysaccharides. XV. Molecular structure of inulin. W. N. Haworth, E. L. Hirst, and E. G. V. Percival (J.C.S., 1932, 2384—2388).—Ac_2O and C_5H_5N convert inulin into its Ac derivative, $[\alpha]_D^{20}$ —33° in $CHCl_3$, converted in the usual manner (cf. preceding abstracts) into methylated inulin (I), m.p. 140°, $[\alpha]_D^{20}$ —54° in $CHCl_3$, both products being homogeneous and formed without appreciable degradation of the inulin mol. Hydrolysis of (I) with $MeOH–H_2O–H_2C_2O_4$ affords 3 : 4 : 6-tri- (II) and 3·7% of 1 : 3 : 4 : 6-tetra-methylfructofuranose (isolated as the methylfructosides), together with 3% of a hexamethyldifructose anhydride [hydrolysed to (II); cf. following abstract]. Contrary to Irvine (this vol., 502), only a trace of ω-methoxy-5-methylfurfuraldehyde is formed under the mild conditions used. These results support the suggestion that (I), and hence inulin itself, is composed of continuous chains of about 30 fructofuranose residues united through positions 1 and 2 (cf. A., 1928, 510). The annexed formula has a mol. wt. of 5000 in agreement with the val. previously deduced (*ibid.*, 1360).



J. W. B.

Polysaccharides. XVI. Molecular structure of inulin and of the derived difructofuranose anhydride. E. W. Bodycote, W. N. Haworth, and C. S. Woolvin (J.C.S., 1932, 2389—2391).—The substance $C_{13}H_{18}O_9$, m.p. 123°, obtained by Irvine and Stevenson (A., 1929, 1046) by the action of HNO_3 in $CHCl_3$ on inulin acetate, was impure. It is actually the Ac_6 derivative $C_{24}H_{32}O_{16}$, m.p. 128° (137° on remelting), $[\alpha]_D^{16}$ +0·65° in $CHCl_3$, of difructose-1 : 2-anhydride (this vol., 724) which is obtained by deacetylation with $NHMe_2$ or $Ba(OH)_2$. It is formed by rupture of the primary valency linkings of the fructofuranose units in inulin (preceding abstract) and their reunion to the more stable difructose anhydride.

J. W. B.

Dependence of the viscosity of cellulose solutions on temperature. K. Hess and B. Rabinowitsch (Ber., 1932, 65, [*B*], 1407—1411).—Staudinger's formula, $\eta_{sp}=K_mcM$, based on the behaviour of complex paraffins of known constitution, is valid only when the suspension has the properties of an ideal, dilute solution and η_{sp} is independent of the temp. Since these conditions are not fulfilled by cellite or limit dextrin 2 in AcOH or $COMe_2$, the relationship is inapplicable to cellulose solutions.

H. W.

Cellulose. XLVI. Osmometric investigations with dilute solutions of polymeric carbohydrates. II. Mol. wt. of "hendecamethylcellotriose" and its importance for the constitution of cellulose. K. Hess and M. Ulmann (Annalen, 1932, 498, 77—100).—Mol. wt. determinations [by measurement of osmotic pressures by isothermal distillation (cf. Ulmann, A., 1931, 1367)] of "hendecamethylcellotriose" (I) in aq. solution show that the reversible changes triose $\rightleftharpoons$ biose+monose and biose $\rightleftharpoons$ monose+monose occur. The changes are autocatakinetic and depend on concn. and p_H. Calculation of the mol. wt. by van 't Hoff's law is possible only when the concn. is <0·3% (above this, the increase in osmotic pressure is less than that required by theory). The original must be consulted for details.

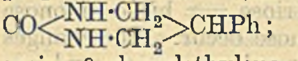
(I) should prove useful for the study of the relationship between colloidal properties and chemical constitution, the O linking in the C_6 group, and the properties of cellulose and its derivatives in solution.

H. B.

Behaviour of methylcellulose when melted. K. Hess, E. Garthe, and C. Trogus (Cellulosechem., 1932, 13, 156—157).—If methylcellulose is kept at the m.p. a new *X*-ray diagram is obtained which is ascribed to a double compound, but heating at a higher temp. restores the original lattice. A. G.

Methylenecellulose. M. Schenk (Helv. Chim. Acta, 1932, 15, 1088—1102).—Previous results (A., 1931, 717) are confirmed and extended. The max. CH_2O-content of methylenecellulose (I) is 8%, corresponding with the formula $(C_6H_{10}O_5)_2CH_2O$, but most of the immunity to swelling and adsorption of alkali is conferred by the first 1·5—2% of CH_2O introduced. It is considered that the product is of the type $(:C\cdot O\cdot)_2:CH_2$. The importance of regarding this and other cellulose reactions as taking place on the surface of the micelles is emphasised. (I), prepared by $CH_2(OPr^\beta)_2$, Ac_2O, and AcOH at 100°, contains also Ac groups (up to 5·73%) which can be removed by NaOH–EtOH. The hydrolysed product is also resistant to swelling and alkali. (I) is unaffected by $NaOH–CS_2$ and Schweitzer's reagent, and is harder, more brittle, less elastic, and tougher than the untreated cellulose. Small amounts (2%) of CH_2O greatly decrease the facility of acetylation of cellulose. (I) is sensitive to acids; its CH_2O-content can be determined by hydrolysis with cold, conc. HCl to glucose and CH_2O, the latter being then determined by combination with phloroglucinol (cf. A., 1931, 1401). R. S. C.

Reinecke's acid applied to some tests on organic bases. A. Dansi, L. Mamoli, and B. Ciocca (Annali Chim. Appl., 1932, 22, 561—565).—This acid is used in the detection of NMe_3 in presence of NH_2Me, $NPhMe_2$ in presence of NHPhMe, and in the gravimetric determination of HCO_2NMe_4. The bases are pptd. as salts of Reinecke's acid. NMe_4 Reineckate may be determined by taking advantage of its relative insolubility (0·0030 g. in 100 c.c. at 15°). O. F. L.

Reactivity of sodium azide with acid chlorides. J. Nelles (Ber., 1932, 65, [*B*], 1345—1347).—The passivity of technical NaN_3 towards acid chlorides is due to an unidentified impurity which can be removed by trituration with a trace of N_2H_4,H_2O, dissolution in a little H_2O, and pptn. with $COMe_2$. Examples of its use are: BzCl to NH_2Ph (yield 69%) and diphenylcarbamide; heptoyl chloride to hexylamine and dihexylcarbamide (total yield, 80%); β-phenylglutaryl chloride to αγ-diamino-β-phenylpropane (yield 48%) and the cyclic *carbamide*  $CO<\begin{matrix}NH\cdot CH_2\\NH\cdot CH_2\end{matrix}>CHPh$; cinnamoyl chloride to α-amino-β-phenylethylene, b.p. 115—120° (yield 77%). H. W.

Sugars containing nitrogen. IV. Catalytic reduction of azides. A. Bertho and J. Maier (Annalen, 1932, 498, 50—61).—Amines are obtained in good yield by catalytic reduction (usually PtO_2) of azides in MeOH, EtOAc, or H_2O. Benzyl azide gives $CH_2Ph\cdot NH_2$ (93% yield); PhN_3 affords NH_2Ph; Et azidoacetate furnishes $NH_2\cdot CH_2\cdot CO_2Et$; the *Et* ester, m.p. 57°, of dl-α-*azidoacetamido*-β-*phenylpropionic acid*, m.p. 104°, yields *Et* dl-α-*aminoacetamido*-β-*phenylpropionate* (*hydrochloride*, m.p. 161°), hydrolysed by cold 2*N*-NaOH to *N*-glycyl-*dl*-phenylalanine and a little of its anhydride; αα'-*diazidoadipic acid*, m.p. 147° (decomp.) (from Et αα'-dibromoadipate and NaN_3 in EtOH with subsequent alkaline hydrolysis), gives αα'-*diaminoadipic acid*, m.p. 280°; N-*azidoacetylglucosamine*, m.p. 187° (decomp.), $[\alpha]_D^{21}$ (in H_2O) +61·8° (7 min.) $\rightarrow$ +31·8° (3 hr.) (from glucosamine and azidoacetyl chloride in dil. NaOH), affords *N*-glycylglucosamine (*hydrochloride*, darkens 180—190°); β-azidoacetoglucose yields β-*aminoacetoglucose*, m.p. 126° (*hydrochloride*, m.p. about 170°), which with HNO_2 gives glucose tetra-acetate; β-*azidoacetogalactose*, m.p. 96°, $[\alpha]_D^{20}$ −16·2° in $CHCl_3$ (from β-acetochlorogalactose and NaN_3 in MeCN), furnishes β-*aminoacetogalactose*, m.p. 139°, $[\alpha]_D^{20}$ +26·7° in MeOH. H. B.

Preparation of aliphatic amino-alcohols. H. E. Glynn and W. H. Linnell (Pharm. J., 1932, 129, 250—251).—α-*Nitro*-β-*hydroxy*-n-*hexane* (b.p. 120°/20 mm.), obtained by condensing valeraldehyde with $MeNO_2$ in presence of KOH, is reduced by $SnCl_2$ and HCl to the corresponding NH_2-alcohol (O-*Bz* derivative, m.p. 137°). The anæsthetic inactivity of this NH_2-ester and of ON-*dibenzoyl*-δ-*aminopentanol* is discussed with reference to cocaine and to several well-known synthetic local anæsthetics. W. S.

Amino-hydroxy-compounds which show the biuret reaction. VIII. Stereoisomerism of *iso*serine. M. Tomita, J. Karashima, Y. Nakamura, and M. Nakashima (Z. physiol. Chem., 1932, 211, 38—46; cf. A., 1931, 1428).—Resolution of *dl*-benzoyl*iso*serine by means of brucine gives a mixture of two dextrorotatory components, benzoyl-*l*-*iso*serine (I), $[\alpha]_D^{20}$ +11·31° (*Ba* salt, m.p. 276°), and a *substance* (II), $C_{20}H_{24}O_7N_2$, m.p. 75°, $[\alpha]_D$ +29·46°, and two lævorotatory components, benzoyl-*d*-*iso*serine (III), m.p. 110°, $[\alpha]_D$ −11·26°, and a *substance* (IV), $C_{20}H_{24}O_7N_2$, m.p. 75°, $[\alpha]_D^{20}$ −30·03°. Both (I) and (II) give *l*-*iso*serine and BzOH on hydrolysis, (III) and (IV) give *d*-*iso*serine. From the benzoylated *dl*-*iso*serine a racemic compound of (II) and (IV), m.p. 75°, can be obtained. J. H. B.

μ-Amino-*n*-tridecoic acid. A. Müller and P. Krauss (Ber., 1932, 65, [*B*], 1354—1358).—αμ-Dibromo-*n*-dodecane is transformed by K phthalimide at 155—160° into μ-*bromo*-α-*phthalimido*-n-*butane*, m.p. 63·5—64° (corr.), whence by NaI in boiling EtOH μ-*iodo*-α-*phthalimido*-n-*butane* (I), m.p. 68—68·5° (corr.), is obtained. (I) and KCN in EtOH afford μ-*cyanododecamethylenephthalamic acid*, converted by HCl (*d* 1·19) at 170—180° into μ-amino-*n*-tridecoic acid hydrochloride, m.p. 153° (corr.) [free acid, decomp. about 177°; *chloroplatinate*, decomp. about 207°; *benzenesulphonyl*, m.p. 102·2° (corr.), and apparently dimorphous, m.p. 110·5—111° (corr.) and about 105°, respectively, and *Bz* derivatives]. H. W.

Oxidation of cystine in acid solution. J. C. Andrews (J. Biol. Chem., 1932, 97, 657—662).—Solutions (0·5—1·0%) of *l*-cystine (initially partly racemised) in 0·5, 2·5, and 6*N*-HCl and in 2·5*N*-H_2SO_4 at room temp. and at 38° undergo racemisation and oxidation to cysteic acid by atm. O_2. The rates of these changes are greatest with the higher degree of acidity. No H_2S or labile S is formed, whilst the NH_2-N remains unchanged. F. O. H.

Acyl derivatives of aminomethionic acid. H. J. Backer and H. Mulder (Rec. trav. chim., 1932, 51, 769—774).—Acyl derivatives of aminomethionic acid are prepared by interaction of K_2 aminomethionate with the appropriate acid anhydride or chloride, and removal of K from the resulting neutral salt with $HClO_4$ and EtOH. A urethane is obtained with $ClCO_2Et$, but is not convertible by NH_3 into the carbamide, which is, however, formed by interaction of K H aminomethionate with KCNO. The following are described: *acetamido*- (+$2H_2O$), m.p. 180° (decomp.) [K_2 salt (+$2H_2O$) (+$1HNO_3$, decomposed by H_2O)], *propionamido*- (as K_2 salt), *benzamido*- (as K_2 salt), *carbamido*- (+$2H_2O$) (K_2 salt), *carboxyethylamino*- (+$2H_2O$) [K_2, Tl_2, and *Ba* (+$2H_2O$) salts], and *carboxypropylaminomethionic acid* (as K_2 salt); also *strychnine* (+$3H_2O$), *Ba*, and Na_2 *aminomethionates*. H. A. P.

Unsaturated amides. M. Vossen (Bull. Soc. chim. Belg., 1932, 41, 331—332).—The following isomeric amides are prepared by slow hydrolysis of the corresponding nitriles (A., 1930, 75) with conc. H_2SO_4 at room temp. (to prevent isomerisation): *cis*-, m.p. 94° (cf. Macq, A., 1927, 652), and trans-*α-methyl-Δ^{α}-pentenoamide*, m.p. 82°, and α-methylene-*n*-valeramide, m.p. 63° (Macq, *loc. cit.*). Interconversion of these amides does not take place in $COMe_2$ in ultra-violet light. H. A. P.

[Butenonitriles and hexenonitriles.] P. Bruylants (Bull. Soc. chim. Belg., 1932, 41, 309—313).—Polemical (cf. this vol., 371). Contrary to Letch and Linstead, the bromometric method of Heim is readily applicable to the hexenonitriles; *n*-valeraldehyde gives a cyanohydrin by Ultée's method, and $Pr^{\alpha}CHO$ and $CN\cdot CH_2\cdot CO_2H$ condense normally in C_5H_5N to give two stereoisomeric αβ- and one βγ-isomeride. Dry-distillation of α-cyano-acids gives a mixture of αβ- and βγ-unsaturated nitriles, the latter preponderating. The purity of Letch and Linstead's αβ-*iso*- (cf. this vol., 258), βγ-*iso*-, αβ-*n*-, and βγ-*n*-hexenonitriles is questioned. H. A. P.

Condensation of cyanoacetic acid with acetaldehyde. G. Heim (Bull. Soc. chim. Belg., 1932, 41, 320—323).—The products of higher b.p. from the interaction of equimol. amounts of $CN\cdot CH_2\cdot CO_2H$, MeCHO, and C_5H_5N (A., 1931, 832) are proved by fractionation and hydrolysis to contain the dimeride of crotononitrile, b.p. 130—132°/14 mm. (cf. A., 1923, i, 1188), and β-methylglutarimide, m.p. 145—147°. H. A. P.

Dimeride of pentenonitrile. A. Dewael (Bull. Soc. chim. Belg., 1932, 41, 324—326).—The products of higher b.p. from the prep. of *n*-pentenonitrile (this vol., 257) contain about 50% of dimeric pentenonitrile (β-*ethyl-α-propenylglutaronitrile*), b.p. 150°/10 mm. (impure), identified by alkaline hydrolysis, distillation of the acid product at 10 mm., and treatment of the resulting syrupy anhydride with aq. NH_3, whereby the *monoamide*, m.p. 175°, of β-*ethyl-α-propenylglutaric acid*, m.p. 85—86°, is formed. The structure of the acid is proved by its oxidation by alkaline $KMnO_4$ to ethylsuccinic acid. H. A. P.

Hexenonitriles. A. Dewael (Bull. Soc. chim. Belg., 1932, 41, 318—319).—The condensation of equimol. amounts of $Pr^{\alpha}CHO$, $CN\cdot CH_2\cdot CO_2H$, and C_5H_5N gives *cis*-, b.p. 149—150°/756 mm., and *trans*-Δ^{α}-hexenonitrile, b.p. 164—165°/752 mm. (cf. this vol., 258), mixed with a little βγ-isomeride, which is removed by bromination. The *cis*-isomeride is not formed if piperidine is used in the place of C_5H_5N. H. A. P.

βγ-*iso*Hexenonitrile. J. Baerts (Bull. Soc. chim. Belg., 1932, 41, 314—317).—The product of interaction of equimol. quantities of $Pr^{\beta}CHO$, $CN\cdot CH_2\cdot CO_2H$, and C_5H_5N (cf. A., 1923, i, 661) is separated by fractional distillation at 1 atm. and 20 mm. into *cis*-, b.p. 137—138°, and *trans*-β-methyl-Δ^{β}-pentenonitrile, b.p. 156—157°, and *γ-methyl-Δ^{β}-pentenonitrile*, b.p. 64·6—65·6°/20 mm. It is possible to measure the separation of βγ- from the αβ-isomerides by Heim's bromometric method, with an accuracy of approx. 1%. H. A. P.

β-Propylcrotononitrile. G. Festraete (Bull. Soc. chim. Belg., 1932, 41, 327—330).—β-Methylamyl alcohol, formed in 30% yield, accompanied by δε-dimethyl-*n*-octane, b.p. 160—161°/754 mm., by interaction of $(CH_2O)_3$ with Mg *sec.*-amyl bromide (cf. A., 1909, i, 449), could not be oxidised to the corresponding aldehyde with $K_2Cr_2O_7$ and H_2SO_4. Condensation of chloroacetone with $MgPr^{\alpha}Br$, and treatment of the crude product with KCN in EtOH gives β-*hydroxy*-β-*methylhexonitrile*, b.p. 112·5—113°/10 mm., converted by distillation with a few drops of conc. H_2SO_4 into trans-β-*methyl*-Δ^{α}-*hexenonitrile*, b.p. 178—179°/760 mm. [*amide*, m.p. 44—45° (cold conc. H_2SO_4)], and its βγ-isomeride (approx. 39% of the total nitrile). H. A. P.

Ethylenic nitriles. Δ^{α}-Heptenonitrile. P. Bruylants (Bull. Soc. chim. Belg., 1932, 41, 333—336).—*n*-Hexaldehyde, b.p. 128—128·2°/760·6 mm., is prepared by catalytic oxidation of *n*-hexyl alcohol (cf. A., 1931, 1404). Dehydration of its *cyanohydrin*, b.p. 126—127°/12 mm., gives a mixture of cis-, b.p. 171—172°/761 mm., and trans-Δ^{α}-*heptenonitrile*, b.p. 186·6—187·4°/759 mm., and a little βγ-isomeride (removed by Br in $CHCl_3$ at −10° to −5°). The corresponding *amides*, prepared by slow hydrolysis with cold conc. H_2SO_4 (6 months), have m.p. 74—74·4°, and 124—124·6°, respectively. H. A. P.

Catalytic replacement of nitrogen by hydrogen in diazo- and triazo-(azido)compounds. H. Wienhaus and H. Ziehl (Ber., 1932, 65, [*B*], 1461—1467).—The following examples are cited, change being effected in presence of Paal's colloidal Pd: $CH_2N_2\cdot CO_2Et$ to EtOAc; NaN_3 to $NaNH_2+N_2$ and thence to NaOH and NH_3; MeN_3 to NH_2Me; PhN_3 to NH_2Ph+N_2; carbamideimidoazide to guanidine; cyanuric triazide to melamine; N_2O to H_2O+N_2. H. W.

Physical properties of *tert*.-arsines. W. J. Jones, W. J. C. Dyke, G. Davies, D. C. Griffiths, and J. H. E. Webb (J.C.S., 1932, 2284—2293).—By interaction of the appropriate Grignard reagent and substances of the type $AsRI_2$ or AsR_2I the following arsines are prepared. *Methyl-di*-n-*propyl*-, b.p. 42°/10 mm. (*chloromercurate*, m.p. 82°; *methochloromercurate*, m.p. 95°); -*di*-n-, b.p. 77°/10 mm. (*chloromercurate*, m.p. 87°; *methiodide*, m.p. 148°; *methoiodomercurate*, m.p. 68°), and -*di*iso-, b.p. 57°/10 mm. (*chloromercurate*, m.p. 123°; *methoiodomercurate*, m.p. 93°) -*butyl*-; -*di*-n-*amyl*-, b.p. 104°/10 mm. (*chloromercurate*, m.p. 66°; *methiodide*, m.p. 45—47°); -*di*-n-*hexyl*-, b.p. 134°/10 mm. (*chloromercurate*, m.p. 56°); -*dicyclohexyl*-, b.p. 127°/4 mm. (*chloromercurate*, m.p. 162°; *methiodide*, m.p. 185°; *methoiodomercurate*, m.p 149°); -*di-p-tolyl*-, b.p. 163°/6 mm. (*chloromercurate*, indefinite m.p.; *methiodide*, m.p. 177°); -*dibenzyl*-, b.p. 169°/5 mm., m.p. about 36° (*chloromercurate*, m.p. 158°); and -*di*-β-*phenylethyl*-, b.p. 190°/4 mm. (*chloromercurate*, m.p. 165°; *methiodide*, m.p. 151°), -*arsine*: *dimethyl-ethyl*-, b.p. 86°/760 mm. (*chloromercurate*, m.p. 154°; *methoiodomercurate*, m.p. 92°); -n-*propyl*-, b.p. 27°/17 mm. (*methiodide*, m.p. 211°); (-*n*-butyl-, -*n*-amyl-, and -*dl*-amyl-compounds isolated only as the derivatives *trimethyl*-n-*butylarsonium iodide*, m.p. 163°, and *iodomercurate*, m.p. 120°; *dimethyl*-n-*amylarsine chloromercurate*, m.p. 87°; *trimethyl*-n-*amylarsonium iodide*, m.p. 172°, and *iodocadmate*, m.p. 186°; *trimethyl*-dl-*amylarsonium iodide*, m.p. about 145°); -cyclo*hexyl*-, b.p. 65°/19 mm. [*methiodide*, m.p. 259° (decomp.); *methoiodomercurate*, m.p. 138°; *methoiodocadmate*, m.p. 198°], -p-*bromophenyl*-, b.p. 134—136°/9 mm.; -o-, b.p. 93°/10 mm. (*dibromide*, m.p. 104°; *hydroxybromide*, m.p. 182°; *methiodide*, m.p. 290°; *methoiodocadmate*, m.p. 179°; *methoiodomercurate*, m.p. 164°), and -m-, b.p. 88°/10 mm. (*dibromide*, m.p. 120°; *methiodide*, m.p. 240°; *methoiodocadmate*, m.p. 119°; *methoiodomercurate*, m.p. 127°), -*tolyl*-; -m-, b.p. 101°/10 mm. (*methiodide*, m.p. 203°; *methoiodomercurate*, m.p. 108°), and -p-, b.p. 113°/7 mm. (*dibromide*, m.p. 106°; *methiodide*, m.p. 223°; *methoiodomercurate*, m.p. 129°), -*xylyl*-; -β-*phenylethyl*-, b.p. 103°/10 mm. (*hydroxybromide*, m.p. 118°; *methiodide*, m.p. 202°; *methoiodocadmate*, m.p. 158°; *methoiodomercurate*, m.p. 116°; *bis*-β-*phenylethyltrimethylarsonium iodomercurate*, m.p. 155°); and -β-*naphthyl*-, b.p. 177°/10 mm. (*methoiodomercurate*, m.p. 154°), -*arsine*; *tri*-β-*phenylethylarsine*, b.p. 281°/10 mm. (*methiodide*, m.p. 115°; *methoiodomercurate*, m.p. 90°; *dibromide*, m.p. 117°); *ethyl-di*-n-*butyl*-, b.p. 93°/10 mm. (*oxide*, m.p. 133°; *methiodide*, m.p. 168°); -*di*-n-*amyl*-, b.p. 119°/10 mm. (*oxide*, m.p. 74°); and -*di*cyclo*hexyl*-, b.p. 161/10 mm. (*methiodide*, m.p. 135°): *diethyl*-, b.p. 64°/10 mm. (*oxide*, m.p. 103°; *methiodide*, m.p. 128°), and *di*-n-*propyl*-, b.p. 88°/10 mm. (*oxide*, m.p. 106°; *methiodide*, m.p. 190°; *ethiodide*, m.p. 192°) -n-*butyl*-; *phenyl-di*-n-*propyl*-, b.p. 125°/10 mm., and -*di*-n-*amyl*-, b.p. 174°/10 mm.; *diphenyl*-n-*propyl*-, b.p. 177°/10 mm. (*chloromercurate*, m.p. 152°; *methiodide*, m.p. 153°), -n-, b.p. 183°/10 mm. (*methiodide*, m.p. 140°), and -iso-, b.p. 185°/10 mm. (*hydroxybromide*, m.p. 116°; methiodide, m.p. 152°), -*butyl*-; -n-*amyl*-, b.p. 194°/10 mm., and -dl-*amyl*-, b.p. 195°/10 mm., -*arsine*. The b.p. and vals. of *d*, mol. vol., and $[R_L]$ are determined for these arsines and equations given whereby these consts. can be calc. for any particular case. From the $[R_L]$ vals. the mean at. refractivity of As is for *F* 12·30, for *D* 11·96, and for *C* 11·83. All m.p. are corr. J. W. B.

Organogallium compounds. Gallium trimethyl etherate. G. Renwanz (Ber., 1932, 65, [*B*], 1308—1309).—The *etherate*, $GaMe_3,Et_2O$, b.p. 99°/762 mm. (corr.), is prepared by addition of $GaBr_3$ in Et_2O to ethereal MgMeBr. It inflames on contact with air and appears to lose 1Me as CH_4 when treated with H_2O. H. W.

Behaviour of *cyclo*paraffins in the Friedel–Crafts reaction. N. D. Zelinski and E. M. Tarassova (Ber., 1932, 65, [*B*], 1249—1252).—Quant. isomerisation of *cyclo*hexane to methyl*cyclo*pentane does not invariably occur during the Friedel–Crafts reaction; the extent depends on experimental conditions. Mol. quantities of *cyclo*hexane, $AlCl_3$, and AcCl at 70° do not yield a homogeneous ketone. If excess of $AlCl_3$ is used, the product contains about 8·7% of unsaturated ketone, whereas in presence of excess of *cyclo*hexane at 35° about 53·7% of unsaturated ketone is formed. If technical, sublimed $AlCl_3$ (containing 3% of $FeCl_3$) is used, the proportion of unsaturated ketone is higher, reaching 85·1% when the complex compound of $AlCl_3$ and AcCl is employed, and 100% in presence of $AlBr_3$. Excess of $AlCl_3$ restricts the dehydrogenation of *cyclo*hexane. In all reactions of *cyclo*hexane with acid chlorides in presence of $AlCl_3$ there is liberation of H which partly reduces the chloride to aldehyde. There is no fundamental difference between the behaviour of C_6H_6 and of *cyclo*hexane in the Friedel–Crafts reaction, but the yields of ketone are widely different. *cyclo*Hexane appears to react in two isomeric forms in the sense of the theory of Sachse and Mohr. The initial change is dehydrogenation leading in the one case to the formation of a *meta* bridge followed by contraction of the ring and in the other case to the production of *cyclo*hexene, whence tetrahydroacetophenone, which is partly reduced to hexahydroacetophenone. H. W.

ψ-Halogens. XXI. Reaction of the silver salts of monobasic acids with iodine in presence of *cyclo*hexene. L. Birckenbach, J. Goubeau, and E. Berninger (Ber., 1932, 65, [*B*], 1339—1344; cf. this vol., 933).—The first product of the action of I on the Ag salts of monobasic acids is the iodide of the respective anion; the mixed halogen adds to *cyclo*hexene. I does not react appreciably with *cyclo*hexene in presence of AgI and Et_2O. $AgClO_4$, I, *cyclo*hexene, and Et_2O afford unstable 2-*iodo*cyclo*hexyl perchlorate*, hydrolysed to 2-iodo*cyclo*hexanol, m.p. 41—42°. $AgClO_4$, Et_2O, and *cyclo*hexene give the *compound* $AgClO_4,2C_6H_{10}$. Similarly, 1-chloro-2-iodo*cyclo*hexane, b.p. 108°/8 mm., and 2-*iodo*-1-*nitro*cyclo*hexane*, b.p. 120—124°/8 mm., are obtained with AgCl and $AgNO_2$. $AgNO_3$ scarcely reacts, probably by reason of lack of additive capacity of INO_3. $AgIO_3$, I, *cyclo*hexene, and Et_2O give a *compound* $C_{11}H_{18}O_2I_2$, b.p. 200°/8 mm.; omission of Et_2O or replacement of it by C_6H_6 leads to non-distillable liquids. $AgIO_4$ affords ill-defined products, whereas AgCN rapidly yields ICN. AgCNS gives 1-*iodo*-2-*thiocyano*cyclo*hexane*. 2-Iodo*cyclo*hexyl acetate, b.p. 120°/12 mm., is obtained from AgOAc in 80% yield (also obtained by allowing AgOAc and I to react in Et_2O at −80°, filtering, and adding *cyclo*hexene to the filtrate). 2-Iodo*cyclo*hexyl benzoate, b.p. 185°/10 mm., is prepared in 60% yield. H. W.

Hydrogenation and dehydrogenation as coupled reactions. R. Vesterberg and W. Braun (Ber., 1932, 65, [*B*], 1473—1476).—For the transference of H from one compound to another in presence of a suitable catalyst, it is essential that the maximal useful work (*Am'*) obtained by hydrogenation of the acceptor is greater than the work necessary for dehydrogenation of the donator. The calculation for a no. of org. compounds is based on the Lewis–Gibson equation from Nernst's theorem, $\Delta F = \Delta H - \Delta ST = -Am'$ (ΔF=free energy, ΔH=heat of formation, and ΔS=entropy of the particular compound). S is not a particularly powerful dehydrogenating agent, being greatly inferior to most org. acceptors. The use of Ca is suggested. H. W.

Decomposition of iodobenzene dichloride. VI. Action of sodium ethylmercaptide. E. V. Zappi and P. Egea (Bull. Soc. chim., 1932, [iv], 51, 748—751).—Interaction of $PhICl_2$ with EtSNa in Et_2O is substantially in accordance with the equation $PhICl_2 + 2EtSNa = 2NaCl + PhI + Et_2S_2$. PhIO is also formed in small amount, and is regarded as a product of secondary decomp. of an unstable intermediate compound $PhI(SEt)_2$. H. A. P.

Orienting power of the nitroso-group and the formula of nitrosobenzene. R. J. W. Le Fèvre (Nature, 1932, 130, 400—401).—A discussion. L. S. T.

Attempts to prepare a compound containing the group $\cdot N(\dot{:}O)\longrightarrow S$. R. J. W. Le Fèvre (J.C.S., 1932, 2503—2504).—Treatment of PhNO with H_2S_x, Na_2S_x, nascent S from $Na_2S_2O_3$ and acids, HgS, S at 100°, or S in C_5H_5N failed to effect condensation between PhNO and S to give the thio-analogue $Ph\overset{+}{N}(\dot{:}O)\longrightarrow S\}^{\ominus}$ of $PhNO_2$, whilst S is also without action on RO·NO. Hence PhNO is inadequately represented as a tercovalent N compound. C_5H_5N reacts with amyl and *cyclo*hexyl nitrites to give C_5H_5N,HNO_3. J. W. B.

General synthesis of diaryl compounds. F. Mayer and R. Schiffner (Ber., 1932, 65, [*B*], 1337—1338).—The product of the action of an aromatic Grignard reagent on a hydroaromatic ketone is dehydrated and dehydrogenated. Thus, Mg naphthyl bromide and 2-methyl*cyclo*hexanone afford 1-1′-*naphthyl*-2(or 6)-*methyl*-Δ^1-cyclo*hexene*, m.p. 55—56°, converted by S into 1-o-*tolylnaphthalene*, m.p. 63°. *cyclo*Hexanedione and 2MgPhBr without further dehydrogenation give triphenyl, m.p. 211°, whilst MgPhBr and phenyldehydroresorcinol yield an oil, b.p. 240—280°, dehydrogenated by S to 1 : 3 : 5-$C_6H_3Ph_3$. H. W.

Fractions of higher b.p. of coal-tar heavy oil. O. Kruber (Ber., 1932, 65, [*B*], 1382—1396).—The initial material is the residue, b.p. 273—295°, from the acenaphthene fraction. A portion, b.p. 272—275°, is subjected to successive treatments with 98% H_2SO_4 at 40—45°, whereby a paraffin fraction containing *n*-nonadecane, b.p. 328°/770 mm., m.p. 33°, remains unattacked. The initial sulphonated mixtures appear highly complex, whereas the later ones afford *K* 3-*methyldiphenyl*-4(?)-*sulphonate* (I) (corresponding *amide*, m.p. 174—175°). (I) is converted by molten KOH into 4(?)-*hydroxy*-3-*methyldiphenyl*, m.p. 114° (*Me ether*, m.p. 75—76°; *benzeneazo*-4(?)-*hydroxy*-3-*methyldiphenyl*, m.p. 128—129°), and by 70% H_2SO_4 at 160—170° into 3-*methyldiphenyl*, b.p. 269°/748 mm., which is oxidised by $KMnO_4$ to diphenyl-3-carboxylic acid, m.p. 165°. The fractions from the final sulphonations yield *K* 4-*methyldiphenyl*-2′(?)-*sulphonate* (II) (corresponding *Na* salt and *amide*, m.p. 236—237°), converted into 2(?)-*hydroxy*-4-*methyldiphenyl*, m.p. 155—156° (*Me ether*, m.p. 109°, oxidised by $KMnO_4$ to terephthalic acid), which, with PhN_2Cl, gives the *dye* $C_{19}H_{16}ON_2$, m.p. 117°. (II) and 70% H_2SO_4 at 190—200° afford 4-*methyldiphenyl*, b.p. 271—272°/752 mm., m.p. 48°, oxidised to diphenyl-4-carboxylic acid, m.p. 222°.

The neutral fraction, b.p. 296—299°, is subjected to successive sulphonations and from the intermediate treatments is isolated *K* 4 : 5-*benzoindanesulphonate* (*Na* salt; *amide*, m.p. 204—205°), transformed by 70% H_2SO_4 at 100—110° into 4 : 5-*benzoindane* (III), b.p. 294—295°/757 mm. (*picrate*, m.p. 110°). Oxidation of (III) with $K_3FeC_6N_6$ and KOH at 60° yields 1 : 2-$C_{10}H_6(CO_2H)_2$ (anhydride, m.p. 163—164°; Me_2 ester, m.p. 85°). (III) is oxidised by $Na_2Cr_2O_7$ in AcOH to 4 : 5-benzoindan-3-one, m.p. 105° (*oxime*, m.p. 175—176°) (cf. Mayer and Sieglitz, A., 1922, i, 740). 6-*Hydroxy*-4 : 5-*benzoindane*, m.p. 122°, with PhN_2Cl yields the *dye* $C_{19}H_{16}ON_2$, m.p. 145°. The later fractions of the sulphonation give a very difficultly separable mixture from which, by fractional treatment with 70% H_2SO_4, 4 : 4′-dimethyldiphenyl, b.p. 292—293°, m.p. 121—122°, is isolated. The non-hydrolysed portion yields *Na* 3 : 4′-*dimethyldiphenylsulphonate* (corresponding *amide*, m.p. 204°), converted into 3 : 4′-*dimethyldiphenyl*, b.p. 288—289°/752 mm., oxidised by dil. HNO_3 to a monocarboxylic *acid*, $C_{14}H_{12}O_3$, m.p. 193—194°, and thence by $KMnO_4$ to diphenyl-3 : 4′-dicarboxylic acid, m.p. 332° (Me_2 ester, m.p. 98—99°). The bulk of the fraction is not readily adapted to the sulphonation treatment. The action of KOH at 340—350°/15·20 atm. on the fraction b.p. 296—299° causes fission of the diphenylene oxides leading to the isolation of 2 : 2′-*dihydroxy*-3-*methyldiphenyl* (IV), b.p. 326—327°/762 mm., m.p. 101—102° (*Me_2 ether*, m.p. 107—108°, oxidised by $KMnO_4$ to 2 : 2′-*dimethoxydiphenyl*-3-*carboxylic acid*, m.p. 122—123°, and thence to 2-methoxy*iso*phthalic acid, m.p. 225° after softening at 215°). (IV) and $ZnCl_2$ at 265—270° give 1-*methyldiphenylene oxide*, b.p. 298°/760 mm., m.p. 45° (*picrate*, m.p. 94°, also directly isolable from the tar oil fraction), oxidised to 1-*carboxydiphenylene oxide*, m.p. 209—210°. Evolution of NH_3 during treatment with KOH and isolation of α- and β-naphthoic acids establishes the presence of the corresponding nitriles in this fraction.

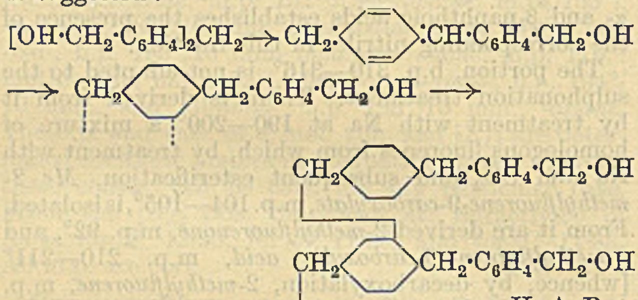
The portion, b.p. 310—316°, is not adapted to the sulphonation treatment. There is derived from it by treatment with Na at 190—200° a mixture of homologous fluorenes from which, by treatment with Na and CO_2 and subsequent esterification, *Me* 2-*methylfluorene*-9-*carboxylate*, m.p. 104—105°, is isolated. From it are derived 2-*methylfluorenone*, m.p. 92°, and 2-*methylfluorene*-9-*carboxylic acid*, m.p. 210—211° [whence, by decarboxylation, 2-*methylfluorene*, m.p. 104°, oxidised to fluorenone-2-carboxylic acid (V), m.p. 332°]. Oxidation of the homologous mixture (above) establishes in it the presence of 3-*methylfluorene*. (V) and molten KOH afford diphenyl-2 : 4′-dicarboxylic acid, m.p. 272° after softening at 266°, decarboxylated to Ph_2 and oxidised by $KMnO_4$ to terephthalic acid. H. W.

Orientation effects in the diphenyl series. XII. Mono- and di-nitration of 4 : 4′-dimethyldiphenyl. (Miss) E. E. J. Marler and E. E. Turner (J.C.S., 1932, 2391—2394).—With HNO_3 (*d* 1·42) in AcOH, 4 : 4′-dimethyldiphenyl (I) affords only the 2-*nitro*-derivative (II), b.p. 200—225°/29 mm., m.p. 69—70°, identical with a specimen synthesised from *p*-C_6H_4MeI, 4-bromo-3-nitrotoluene, and Cu-bronze at 220°, but different from the 3-*NO_2*-compound (III), b.p. 220—230°/20 mm., m.p. 80—81°, synthesised similarly. Reduction of (II) and (III) with $SnCl_2$–AcOH–HCl affords, respectively, 2-, m.p. 62—63° (*Ac* derivative, m.p. 118—119°), and 3-, m.p.

104—105° [*Ac* derivative, m.p. 156—157°; hydrochloride, m.p. about 230° (decomp.)], *-amino-*4 : 4'-*dimethyldiphenyl.* With HNO_3 (*d* 1·47) in AcOH at 50—60° (I), (II), and (III) all yield the 2 : 3'-$(NO_2)_2$ derivative, m.p. 119—120° [m.p. depressed by either the 2 : 2'- or 3 : 3'-$(NO_2)_2$-compounds]. The theoretical implications of these results are discussed.

J. W. B.

Derivatives of *pp'*-ditolylmethane, and mechanism of their polymerisation. E. Connerade (Bull. Soc. chim. Belg., 1932, 41, 337—348).—4 : 4'-Di(chloromethyl)diphenylmethane (I), m.p. 111° (cf. A., 1875, 151), is obtained from CH_2PhCl, $(CH_2O)_3$, and AcOH–H_2SO_4 at 50°; it is accompanied by the 2 : 4'- and 2 : 2'-isomerides, identified by oxidation of the derived $(OH)_2$-compounds by CrO_3–AcOH to the corresponding diphenylmethanedicarboxylic acids. (I) is converted by KI in EtOH into the corresponding I_2-compound, m.p. 169°, and by AgOAc–AcOH (but not NaOAc or KOAc in EtOH) into the *diacetate*, m.p. 51°, of 4 : 4'-*di*(*hydroxymethyl*)-*diphenylmethane*, m.p. 124° {*Et₂ ether* [(I) and NaOEt], b.p. 232°/12—14 mm.}, which with $KMnO_4$–AcOH gives benzophenone-4 : 4'-dicarboxylic acid, and with HNO_3–aq. AcOH at the b.p. gives *diphenylmethane*-4 : 4'-*dialdehyde*, m.p. 84° [*diphenylhydrazone*, m.p. 229° (photosensitive); *dioxime*, m.p. 177°]. $AgNO_3$–EtOH converts (I) into a polymeric (mono)*nitrate*, $(C_{15}H_{13}O_3N)_x$, hydrolysable to a polymeric alcohol; NH_3–EtOH, similarly, gives the polymeric *amine*, plastic at 118—145°. Similar behaviour is observed with alkalis and aq. KCN, and the following mechanism is suggested:



H. A. P.

Absorption spectrum of αα-diphenylethyl chloride plus stannic chloride. Preparation of 9 : 10-diphenylphenanthrene from tetraphenylethylene dichloride. C. S. Schoepfle and J. D. Ryan (J. Amer. Chem. Soc., 1932, 54, 3687—3694).—Absorption spectra curves of $CPh_2:CH_2$, αα-diphenylethyl alcohol, αα-diphenylethyl chloride in absence and presence of $SnCl_4$, and $CPh_3Cl+SnCl_4$ are given. The curves for the alcohol and its chloride show marked similarity to those of $CPh_3·OH$ and CPh_3Cl. The curve for the chloride $+SnCl_4$ is very similar in some respects to the curve for $CPh_3Cl+SnCl_4$. 9 : 10-Diphenylphenanthrene (I) results in 90—95% yield from *s*-tetraphenylethylene dichloride and $SnCl_4$ in $CHCl_3$, $C_2H_4Cl_2$, $PhNO_2$, or PhCN; a trace of (I) results in C_6H_6, CS_2, or CCl_4. (I) is also obtained in 25% yield from $(:CPh_2)_2$, Br, and $SnCl_4$ in $CHCl_3$. ααγγ-Tetraphenylbutyl alcohol, saturated with HCl in C_6H_6 at −5° in presence of $CaCl_2$, gives ααγγ-tetraphenyl-Δ^{α}-butene, also formed from the alcohol and AcOH–H_2SO_4; the alcohol and conc. H_2SO_4 give 1 : 1 : 3-triphenyl-3-methylhydrindene in 25% yield, the butene not being an intermediate. A reaction mechanism involving a quinonoid change is postulated to explain the formation of (I) and also the formation of triphenyl-*p*-diphenylylethylene from tetraphenylethylene dichloride and MgPhBr.

C. J. W. (*b*)

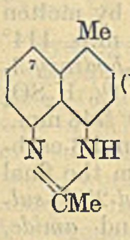
Preparation of benzamide, tetraphenylmethane, and tetraphenylethylene in liquid ammonia. P. M. Dean, G. Berchet, and L. Barnum, jun. (J. Colo. Wyo. Acad. Sci., 1930, 1, No. 2, 43).—BzCl, $CHPh_2Cl$, and CPh_2Cl_2 were condensed in liquid NH_3; in the last two cases Na and Et_2O were employed.

Ch. Abs.

Simple method of complete transformation of *cis*-decahydronaphthalene into the *trans*-form. N. Zelinski and M. Turova-Pollak (Ber., 1932, 65, [*B*], 1299—1301; cf. A., 1925, i, 1053).—Quant. isomerisation of *cis*- into *trans*-decahydronaphthalene is effected by $AlCl_3$ at room temp.; at higher temp., more complex isomerisation is observed.

H. W.

Orientation in substitution reactions of alkylnaphthalenes. II. Nitration of 1-methylnaphthalene. H. W. Thompson (J.C.S., 1932, 2310—2315).—By chemical separations of the isomerides suitable to each case it is found that nitration of 1-$C_{10}H_7Me$ with HNO_3 (*d* 1·42) at room temp. or HNO_3 (*d* 1·52) in Ac_2O, AcOH, or $MeNO_2$ at 0°, affords 4- (I) (70%), some 5-, and less 2-NO_2-derivatives. Reduction of (I) with S in boiling NaOH in H_2O–EtOH gives 4-*amino*-1-*naphthaldehyde*, m.p. 163°. Further nitration of (I) with HNO_3 (*d* 1·52) affords 4 : 5- (II) (45%), some 2 : 4- (III), a little 4 : 8- (IV) -$(NO_2)_2$-compounds, and a trace of 4 : *x*-*dinitro*-1-*methylnaphthalene*, m.p. 176° (cf. Veselý *et al.*, A., 1930, 593). Reduction of (II) with PI_3 and H_2O gives the 4 : 5-$(NH_2)_2$-derivative, m.p. 64° [*dihydrochloride*, m.p. 260° (decomp.)], converted by Ac_2O into 2 : 6-*dimethylperimidine* (V), m.p. 210—220°, the 7-*Cl*-derivative, m.p. 228°, of which is obtained by the action of $TiCl_3$ in AcOH on (II). Reduction of (IV) (H_2–PtO_2) and acetylation of the product gives 4 : 8-*diacetamido*-1-*methylnaphthalene*, m.p. 320—323°. The $(NO_2)_3$-derivative obtained by Lesser (A., 1914, i, 33) is 2 : 4 : 5-*trinitro*-1-*methylnaphthalene* (VI), m.p. 170° (*loc. cit.*, m.p. 180—181°), since it is obtained by nitration of either (II) or (III). Characteristic colour reactions are given (only) by (III) and (VI) with 2*N*-NaOH or -NH_3 in EtOH or $COMe_2$ (cf. Rudolph, A., 1921, ii, 604). Et sodioacetylsuccinate and *m*-$OMe·C_6H_4·COCl$ give Et α-*m*-methoxybenzoyl-α-acetylsuccinate (not characterised), hydrolysed by KOH aq. to β-m-*methoxybenzoylpropionic acid*, m.p. 111°, reduced by Zn–Hg and conc. HCl to γ-*m*-methoxyphenylbutyric acid, b.p. 200—205°/20 mm. (not characterised), which with conc. H_2SO_4 at 70° affords 5-*keto* - 2 - *methoxy* - 5 : 6 : 7 : 8-*tetrahydronaphthalene*, m.p. 82°, isolated as its *semicarbazone*, m.p. 235° (cf. Schroeter, A., 1930, 1039).



(V.)

J. W. B.

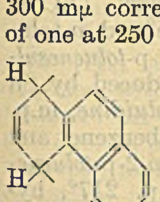
Separation of 1 : 8- from 1 : 5-dinitronaphthalene. M. Gallotti and P. Galimberti (Annali Chim. Appl., 1932, 22, 600—601).—The mixed isomerides (20 g.) are dissolved in 400 g. of conc. H_2SO_4; after stirring for ½ hr. and heating at 45° 5 g. of pure S and 100 g. of oleum (35% SO_3) are added gradually. The temp. is kept at 90—95° for 2 hr. The mixture is poured on 2000 c.c. of H_2O and 2000 g. of ice while stirring thoroughly; 1 : 8-$C_{10}H_6(NO_2)_2$, m.p. 170°, is collected whilst 1 : 5-$C_{10}H_6(NO_2)_2$ is transformed into naphthazarin, which remains in the filtrate.

O. F. L.

Course of the catalytic hydrogenation of anthracene. K. Fries and K. Schilling [with G. Littmann] (Ber., 1932, 65, [*B*], 1494—1502).—The observation that the hydrogenation of anthracene (I) proceeds continuously to the octahydride raises doubts as to the general validity of the course, (I) ⟶ 9 : 10-di- ⟶ 1 : 2 : 3 : 4-tetra- ⟶ 1—8-octa-hydroanthracene (cf. Schroeter, A., 1925, i, 127). The 9 : 10-compound, as true C_6H_6 derivative, is much more slowly hydrogenated than (I) or 1 : 2 : 3 : 4-tetrahydroanthracene. A mixture of (I) and its dihydro-derivative (II) is hydrogenated initially at the same rate as (I); subsequently retardation is observed and the greater part of (II) is recovered unchanged. In the presence of different catalysts (Ni, Pt, or Pd) the absorption of $1H_2$ by (I) proceeds very rapidly, but the yield of (II) is only about 12%; more than 50% of the initial material is unchanged and the rest is transformed into more highly hydrogenated compounds. It appears that hydrogenation of (I) proceeds to a minor extent according to Schroeber's scheme, but mainly takes an immediate and direct course to 1 : 2 : 3 : 4-tetrahydro- and thence to 1—8-octahydro-anthracene. Ultimately a perhydride is produced, but evidence of a hexahydride is never obtained. In presence of PtO_2 and AcOH at room temp., (I) gives *perhydroanthracene,* $C_{14}H_{24}$, m.p. 61·5°, whereas in absence of solvent at 100° under pressure and with Ni as catalyst an isomeride, m.p. 93°, identical with that described by Ipatiev (A., 1908, i, 330), results.

H. W.

Polynuclear, aromatic hydrocarbons. XV. Constitution of phenanthrene and the polynuclear-ring systems derived therefrom. Separation of aromatic hydrocarbons. E. Clar and L. Lombardi (Ber., 1932, 65, [*B*], 1411—1420; cf. this vol., 608).—The extinction curve of phenanthrene (I) shows the presence of bands above 300 mμ corresponding with the 9 : 10-diyl condition, of one at 250 mμ due to the side nuclei, and of a group between 260 and 300 mμ due to a naphthalene complex or the condition (II). The curve of chrysene (freed from a yellow impurity by heating with maleic anhydride in $C_6H_4Me_2$) resembles that of (I), but the 9 : 10-diyl condition is more marked and the bands at 270—330 mμ are more pronounced. The extinction curve of triphenylene indicates that it is 1 : 2 : 3 : 4-dibenznaphthalene, whereas its dodecahydro-derivative behaves as an alkylbenzene. Comparison of the max. extinction coeffs. of the first *R* bands of $C_{10}H_8$, chrysene, (I), and triphenylene, and the potentials of the corresponding *o*-quinones shows that hydrocarbons not derived from anthracene and produced by angular annelation, which therefore do not contain an *o*-quinonoid linking, are built so that a double linking always exists between two rings. Their inability to react with maleic anhydride is thus explained. 2′ : 3′-Naphtho-9 : 10-phenanthrene shows bands characteristic of (I) and anthracene; addition of maleic anhydride destroys the anthracene character and the product behaves as an alkylated (I). In 2′ : 3′-naphtha-1 : 2-phenanthrene the bands due to the anthracene-9 : 10-diyl overlap those due to phenanthrene-9 : 10-diyl, whereas the phenanthrene character becomes obvious in the extinction curve after reaction with maleic anhydride. The extinction curve of 2′ : 3′-naphtho-2 : 3-phenanthrene does not indicate a derivative of (I), the relationships resembling those of 2 : 3-benzanthracene. If the anthracene character is withdrawn by action with maleic anhydride, the extinction curve of the product is of the pure (I) type.



(II.)

A method of separation of the individual 2′ : 3′-naphthophenanthrenes from the mixture obtained by pyrolysis of *o*-toluylphenanthrene is based on fractional treatment with maleic anhydride in boiling $C_6H_4Me_2$. The following substances are described: 2′ : 3′-*naphtho*-2 : 3-*phenanthrene,* m.p. 262—264°; 2′ : 3′-*naphtho*-9 : 10-*phenanthrene*-, leaflets, m.p. 251—253° (decomp.), prisms, m.p. 253—255° (decomp.); 2′ : 3′-*naphtho*-1 : 2-*phenanthrene*-, m.p. 268—269° (decomp.); 2′ : 3′-*naphtho*-2 : 3-*phenanthrene*-, m.p. 273° (decomp.), -endo-1′ : 4′-αβ-*succinic anhydride.*

H. W.

Polynuclear, aromatic hydrocarbons and their derivatives. XVIII. Synthesis of 1 : 9-5 : 10-di*peri*naphthyleneanthracene. E. Clar and A. Guzzi (Ber., 1932, 65, [*B*], 1521—1525).—9 : 10-Dihydroxy-9 : 10-di-α-naphthyl-9 : 10-dihydroanthracene is converted by $AlCl_3$ in presence of a trace of C_5H_5N at 90—110° into 1 : 9-5 : 10-*di*peri*naphthyleneanthracene,* m.p. 580° (decomp.; in sealed tube), to which the constitution (I) is assigned, since an analogous hydrocarbon could not be prepared from the corresponding 1 : 4-Me_2 derivative and with maleic anhydride it gives the colourless 1 : 9-5 : 10-*di*peri*naphthyleneanthracene*-endo-9 : 10-αβ-*succinic anhydride,* decomp. 310° when rapidly heated. The absorption spectra of (I) and *meso*-di-α-naphthylanthracene are closely similar. (I) and Br in C_6H_6 immediately afford a pale yellowish-green ppt. from which the hydrocarbon is regenerated when the suspension is heated to boiling or when the ppt. is dried. I does not decolorise the hydrocarbon, whereas Cl_2 appears to yield a more stable product. O_2 does not oxidise (I) in direct light or in the dark, but the possible formation of a very readily dissociable peroxide is not excluded. The free valencies are therefore unusually weak. (I) is considered to form a link between the aromatic hydrocarbons and graphite.

(I.)

H. W.

Reduction of Schiff bases. II. Polymeric states and structures of methylene-aniline and

-*p*-toluidine. Condensation of aniline and acetaldehyde. J. G. Miller and E. C. Wagner (J. Amer. Chem. Soc., 1932, 54, 3698—3706; cf. this vol., 378).—Cryst. methyleneaniline (I) and methylene-*p*-toluidine (II) are definitely trimeric at 5—80°, but the average mol. wts. decrease at higher temp. (176°). Reduction of (I) with Zn dust and cold conc. HCl gives 19·2% NH_2Ph, 18·6% NHPhMe, and 8·5% $NPhMe_2$; at 70°, the respective % are 21·1, 1·8, and 0·4. Reduction (cold) of (II) gives 36·3% *p*-$C_6H_4Me{\cdot}NH_2$, 39·5% *p*-$C_6H_4Me{\cdot}NHMe$, and 21% *p*-$C_6H_4Me{\cdot}NMe_2$. These results indicate that (I) and (II) possess cyclic structures. Amorphous (I) and (II) (the higher polymerides) give similar results on reduction. The primary product of the condensation of NH_2Ph and MeCHO (representing the straight-chain aliphatic aldehydes) is the di-imine; the products hitherto obtained are due to secondary reactions. There is no satisfactory evidence for the intermediate formation of the monomeric azomethine.

C. J. W. (*b*)

Rearrangement of alkylanilines. V. Trimethylethylene, the intermediate product in the rearrangement of *iso*amylaniline hydrobromide to *p*-amino-*tert.*-amylbenzene hydrobromide. W. J. Hickinbottom (J.C.S., 1932, 2396—2400).—*iso*Amylaniline, b.p. 253—254°/751 mm. (m-*nitrobenzenesulphonyl* derivative ,m.p. 104—105°), heated with $CoCl_2$, $CoBr_2$, or $CdCl_2$ at 210—280° gives mainly *p*-amino*iso*amylbenzene, b.p. 262—264°/756 mm. (Bz derivative, m.p. 151—153°; m-*nitrobenzenesulphonyl* derivative, m.p. 99—101°; *diphenyl*-p-*isoamylthiocarbamide*, m.p. 122°), with a little NH_2Ph, a primary *amine*, b.p. above 290°, unchanged amylamine, and a *substance* (? a $NHPh_2$ derivative), b.p. 325—330°. The yield of the last increased with the time of heating and depended on the nature of the promoter. No *p*-amino-*tert.*-amylbenzene was detected. NH_2Ph,HBr and $CMe_2{:}CHMe$ in presence of $CoCl_2$ or $CoBr_2$ give only *tert.*- and no *iso*amyl-*p*-aminobenzene, similar results being obtained under various conditions with *iso*amylaniline hydrobromide alone. The latter isomerisation takes place through the separation of $CMe_2{:}CHMe$, which is always detected, whilst a different mechanism is necessary to explain the action with metal salts alone.

A. A. L.

Arylamine salts of naphthalenesulphonic acids. VII. Salts of 1 : 5- and 1 : 6-naphthalenedisulphonic acids. R. B. Forster and K. Hishiyama (J.S.C.I., 1932, 51, 297—298T).—The arylamine salts of 1 : 5-$C_{10}H_6(SO_3H)_2$ are easily prepared, whereas those of the 1 : 6-acid are much more sol. and are difficult to prepare unless comparatively pure specimens of the base and acid are used. None of the salts prepared is suitable for the separation of the two isomerides, but several of them may be used for characterising the respective acids, *e.g.*, *ψ-cumidine* 1 : 5-, m.p. 216—217°, 1 : 6-, m.p. 294°, and α-naphthylamine 1 : 5-, m.p. 231°, and 1 : 6-, m.p. 272°, -naphthalenedisulphonates. The following were also prepared: *aniline* 1 : 5-, no. m.p., 1 : 6-, m.p. 298—299°, o-*toluidine* 1 : 5-, m.p. 338—339°, 1 : 6-, m.p. 323—324°, m-*toluidine* 1 : 5-, m.p. 312°, p-*toluidine* 1 : 5-, m.p. 332°, 1 : 6-, m.p. 314—315°, m-4-*xylidine* 1 : 5-, m.p. 338—340°, 1 : 6-, m.p. 324°, β-naphthylamine 1 : 5-, m.p., 204°, 1 : 6-, no m.p., *benzidine*, *tolidine*, no m.p., p-*chloroaniline* 1 : 5-, m.p. 338—339°, 1 : 6-, m.p. 313—315°, p-*nitro*-o-*toluidine* 1 : 5-, m.p. 275°, 1 : 6-, m.p. 282—283°, p-*anisidine* 1 : 5-, m.p. 322°, and 1 : 6-, m.p. 299°, -naphthalenedisulphonates. All m.p. are with decomp. except ψ-cumidine salts.

Condensation of bromal with nitroanilines. D. C. Knowles, jun., and R. P. Jacobsen (J. Amer. Chem. Soc., 1932, 54, 3730—3731).—*p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and $CBr_3{\cdot}CHO$ in C_6H_6 or Et_2O give 48% of βββ-*tribromoethylidenebis*-p-*nitroaniline*, m.p. 127—128°; the o-, m.p. 106—107°, and m-, m.p. 117—118°, *isomerides* are similarly prepared.

C. J. W. (*b*)

Reactivity of sodium azide with acid chlorides. J. Nelles.—See this vol., 1118.

Nitro-derivatives of diphenylamine. N. M. Cullinane and, in part, (Miss) O. E. Embrey and D. R. Davies (J.C.S., 1932, 2363—2364; cf. this vol., 733).—Chloro- or bromo-nitrohydrocarbons with the appropriate amines and NaOAc at 150—160° give (% yields in parentheses) 2 : 4-dinitro-5-methyl-, m.p. 148° (70), -5 : 2′-, m.p. 111° (70), and -5 : 3′-*dimethyl*-, m.p. 136·5° (80), -5 : 2′ : 4′-, m.p. 138° (70), and -5 : 2′ : 5′-*trimethyl*-, m.p. 114·5°, -2′-methoxy-5-methyl-, m.p. 146° (90), -3′-ethoxy-, m.p. 153° (75), -3′-*ethoxy*-5-*methyl*-, m.p. 115° (70), and -4′-ethoxy-5-methyl-diphenylamine, m.p. 148·5° (90), and 2 : 4-*dinitro*-5-*methylphenylbenzylamine*, m.p. 102° (70). The following are obtained similarly at 180°: 2 : 4-dinitro-2′-methoxy-, m.p. 165·5° (80), and -4′-ethoxy-diphenylamine, m.p. 121—122° (90), and 2 : 4-*dinitrophenylbenzylamine*, m.p. 116° (90). 2 : 4-Dinitro-4′-methoxy-, m.p. 141° (90), and -2′ : 5′-dimethyl-diphenylamine, m.p. 144°, require a temp. of 200°. The following are obtained in EtOH: 2 : 4-dinitro-2′-ethoxy-, m.p. 172°, 2 : 4-*dinitro*-2′-*ethoxy*-5-*methyl*-, m.p. 179·5° (75), and 2′-*bromo*-2 : 4 : 6-*trinitro*-4′-*methyl-diphenylamine*, m.p. 176° (90) (also obtained in C_6H_6), and 2 : 4 : 6-trinitrophenylbenzylamine, m.p. 141·5° (90). 2 : 4 : 6-Trinitrophenylmethylnitroamine was used to obtain the following in place of picryl chloride: 2 : 4 : 6-trinitro-4′-hydroxy-, m.p. 178°, -4′-*ethoxy*-, m.p. 138·5° (90), and -4′-amino-diphenylamine, m.p. 194° (90). NH_2Bz, picryl chloride, and NaOH in EtOH give *benzo*-2 : 4 : 6-*trinitroanilide*, m.p. 191°.

A. A. L.

Isomeric 2 : 4-dinitrophenyl derivatives of 3 : 4-tolylenediamine. K. C. Roberts (J.C.S., 1932, 2358—2360).—4-Nitro-*m*-toluidine and *p*-toluenesulphonyl chloride in C_5H_5N give p-*toluenesulphon*-4-*nitro*-m-*tolyluidide*, m.p. 135°, reduced by Sn and HCl to 3-p-*toluenesulphonamido*-p-*toluidine*, m.p. 120°, which with 4-chloro-1 : 3-dinitrobenzene and NaOAc in PrOH gives 2′ : 4′-*dinitro*-2-p-*toluenesulphonamido*-4-*methyldiphenylamine*, m.p. 217°, hydrolysed to 2′ : 4′-*dinitro*-2-*amino*-4-*methyldiphenylamine*, m.p. 162·5° and 173° (two forms), also obtained by fractionation of the condensation product of 3 : 4-tolylenediamine and 4-chloro-1 : 3-dinitrobenzene (A., 1891, 299). 2′ : 4′-*Dinitro*-2-p-*toluenesulphonamido*-, m.p. 184°, and -2-*amino*-5-*methyldiphenylamine*, m.p.

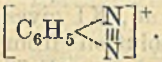
195° and 191° (two forms), are similarly obtained. 2′ : 4′-Dinitro-2-aminodiphenylamine has m.p. 147° and 152°. A. A. L.

Stereochemistry of diphenyl. F. R. SHAW and E. E. TURNER (Nature, 1932, **130**, 315).—Optical resolution of the monomethiodide of 2 : 2′-tetramethyldiaminodiphenyl has been effected. The *d*- and *l*-methiodides have $[\alpha]^{20}_{5791}$ ±48° in aq. solution. Activity is retained indefinitely in cold solutions, but at 100° half-racemisation occurs in approx. 2 hr. L. S. T.

Action of halogens on arylazoacetoacetates and related compounds. II. F. D. CHATTAWAY and R. J. LYE (Proc. Roy. Soc., 1932, A, **137**, 489—503 ; cf. this vol., 377).—Cl_2 or Br reacts with arylazoacetoacetates of the type $NHPh\cdot N{:}CAc\cdot CO_2Et$ (I), causing both substitution (max. of 2 halogen atoms introduced) in the Ph nucleus and either displacement of the Ac or CO_2Et or halogenation of the Ac group, derivatives of the types $R{:}CX\cdot CO_2Et$ (II), $R{:}C(CO\cdot CH_2X)\cdot CO_2Et$ (III), $R{:}C(CO\cdot CHX_2)\cdot CO_2Et$ (IV) or $R{:}CX\cdot CO\cdot CHX_2$ (V) ($R=2:4\text{-}Br_2C_6H_3\cdot NH\cdot N{:}$) being formed according to the experimental conditions. With Cl_2 only stages (II) and (III) are realised, the more vigorous reaction required for stages (IV) and (V) causing disruption of the mol. Thus from (I) are obtained : *Et α-bromoglyoxylate*-p-*bromo*-, m.p. 149—150°, -2 : 4-*dibromo*-, m.p. 140°, and -2 : 4-*dichloro*-, m.p. 117°, -*phenylhydrazone* : *Et α-chloroglyoxylate*-p-*chloro*-, m.p. 146—147°, -p-*bromo*-, m.p. 163°; -2 : 4-*dichloro*-, m.p. 98°, and -*dibromo*-, m.p. 108°, -*phenylhydrazone* [all of type (II)]. By coupling the appropriate diazotised base with Et halogenoacetoacetate or halogenation of the arylazoacetate are obtained : *Et γ-bromo*-p-*bromobenzeneazo*-, m.p. 113—114°, *Et benzeneazo*-, m.p. 81°, *Et* 2 : 4-*dichloro*-, m.p. 113°, and -*dibromo*-, m.p. 144—135°, -*benzeneazo-acetoacetate* : *Et γ-chloro-benzeneazo*-, m.p. 92°, -p-*chloro*-, m.p. 102—103°, and -2 : 4-*dichloro*-, m.p. 105°, -*benzeneazo-acetoacetate* [all of type (III)]. In the cold Br (3 mols.) in AcOH converts (I) into *Et γγ-dibromo*-p-*bromobenzeneazoacetoacetate*, m.p. 135—138°, but at 60—70° the corresponding *acid*, m.p. 205° (decomp.), is obtained. *Et γγ-dibromo*-2 : 4-*dibromo*-, m.p. 153—154°, and -*dichloro*-, m.p. 128°, -*benzeneazoacetoacetate* [type (IV)] are obtained similarly. With excess of Br (I) affords ββω-*tribromo-α-ketopropaldehyde-2 : 4-dibromophenylhydrazone*, m.p. 140—141°, also obtained from Br in hot AcOH and *α-ketopropaldehyde-2 : 4-dibromophenylhydrazone*, m.p. 165° (from $C_6H_3Br_2\cdot N{:}N\cdot Cl$ and $CH_2Ac\cdot CO_2H$) [type (V)]. Heated with KOAc in EtOH, derivatives of types (III) and (IV) are cyclised to 4-hydroxypyrazoles with elimination of HX, and thus are obtained : *Et* 4-*hydroxy*-1-2′ : 4′-*dibromophenyl*-, m.p. 166° (*Ac*, m.p. 103—104°, and *Bz*, m.p. 137°, derivatives), and its -5-*Br*-derivative, m.p. 189° (*Ac* derivative, m.p. 91—92°) ; *Et* 4-*hydroxy*-1-*phenyl*-, m.p. 85° [in agreement with Wolff (A., 1900, i, 691) ; the substance, m.p. 258—260°, obtained by Favrel (A., 1913, i, 898) cannot be this compound], -1-p-*bromophenyl*-, m.p. 136—137°, and its -5-*Br*-derivative, m.p. 103° (*Ac* derivative, m.p. 134°), -1-p-*chlorophenyl*-, m.p. 137—138°, -1-2′ : 4′-*dichlorophenyl*-, m.p. 154—155°, and its -5-*Cl*-, m.p. 161°, and -5-*Br*-, m.p. 176—177°, derivatives, -*pyrazole*-3-*carboxylate*. J. W. B.

Chemical changes involved in the formation of aminoazo-compounds. I. J. C. EARL and N. F. HALL (J. Proc. Roy. Soc. New South Wales, 1932, **66**, 157—166).—In MeOH at 0—3°, NH_2Ph,HCl (2 mols.) and $NaNO_2$ (1 mol.) afford some diazoaminobenzene and unchanged NH_2Ph, but at 14—16° give a good yield of aminoazobenzene. The vol. change shown by dilatometer experiments is probably due to the change of initially formed amine nitrite into a NO- or diazo-compound, this necessitating acidity, which is provided by excess of amine hydrochloride. J. L. D.

Heteropolarity. XVIII. Colour and structure of diazonium salts. W. DILTHEY, C. BLANKENBURG, W. BRANDT, and W. HUTHWELKER (J. pr. Chem., 1932, [ii], **135**, 36—48).—Conversion of $[ArNH_3]^+$ into $[Ar\cdot N_2]^+$ is accompanied by slight deepening of shade (in the examples quoted from colourless to yellow) ; this agrees best with the formulation of diazonium salts as carbonium salts, *e.g.*,



$\left[C_6H_5{<}\begin{matrix}N\\|||\\N\end{matrix}\right]^+$. The following NH_2-compounds are prepared by reduction of the known NO_2-compounds : p-*aminophenyl* p-*diphenylyl ketone*, m.p. 203—204° [*oxime*, m.p. 182—183° ; *Ac* derivative, m.p. 204° ; *hydrochloride*, m.p. 218° ; *diazonium chloride* (+1H_2O), m.p. 120° (rapid heating) (+β-*naphthol*, m.p. 210—212°)] ; 4-*amino*-4′-*phenoxybenzophenone*, m.p. 125° [*Ac* derivative, m.p. 151—152° ; *hydrochloride*, m.p. 190° ; *diazonium chloride* (+1H_2O), m.p. 114° (decomp.) (+β-*naphthol*, m.p. 188°)] ; 4-*amino*-4′-*phenylthiolbenzophenone*, m.p. 155° {*oxime*, m.p. 164° [*diazonium chloride*, m.p. 105° (+β-*naphthol*, m.p. 195—197°)] ; *Ac* derivative, m.p. 175° ; *hydrochloride*, m.p. 167—170° ; *diazonium chloride*, m.p. 108—109°}. H. A. P.

Reactions with boron fluoride. III. Condensation of propylene with phenol. F. J. SOWA, H. D. HINTON, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1932, **54**, 3694—3698 ; cf. this vol., 735).—C_3H_6 (0·5 mol.) passed (10 g. per hr.) into a mixture of 1 mol. of PhOH, 5 g. of BF_3, and 100 g. of C_6H_6 at −2° to 2° gives 54% of $PhOPr^{\beta}$ and 41% of *o*-$C_6H_4Pr^{\beta}\cdot OH$. When the reaction is carried out at 13—17°, using 2 mols. of C_3H_6, there results $PhOPr^{\beta}$, (mainly) *o*-*iso*propylphenyl Pr^{β} ether (I), b.p. 225—227°, and 2 : 4-di*iso*propylphenyl Pr^{β} ether (II), b.p. 248°. (II) results in 39% yield when C_3H_6 is passed into PhOH–BF_3 at 22° ; other products are *o*-$C_6H_4Pr^{\beta}\cdot OH$, (I), alkali-sol. products, b.p. 230—240° and 240—256°, and (III) (below). If the reaction is maintained at 30—40° and C_3H_6 passed in until absorption is complete, there results 92% of 2 : 4 : 6-tri*iso*propylphenyl Pr^{β} ether (III), b.p. 263°. The catalyst serves as a condensing and a rearranging agent. C. J. W. (*b*)

Catalytic dehydration of phenols ; influence of the nature and position of substituents. E. BRINER and A. A. BRON (Helv. Chim. Acta, 1932, **15**, 1234—1241).—Dehydration of the following phenols in N_2 by ThO_2, best at the temp. stated,

gives the following percentage yields of ethers: resorcinol and its Me ether, pyrocatechol, quinol, orcinol, and phloroglucinol, 0; guaiacol (475°), 16; *o*-, *m*-, and *p*-cresol (400°), 2, 7·5, and 28, respectively; 1 : 3 : 4-, 1 : 2 : 4-, 1 : 3 : 5-, 1 : 2 : 5-, and 1 : 2 : 6-xylenol (450°), 25, 8, 21, 0, and 0, respectively; creosol (450°), a trace; thymol (450°), 10—15% of an oil; 2-, 3-, and 4-hydroxydiphenyl (550°), 8, 10, and 10—12, respectively. β-Naphthol gives better yields than α-naphthol. The results show the steric effect of *o*-substituents and the hindering effect of OH groups. *Di*-2-, -3-, and -4-*diphenylyl ethers* melt at 75°, 71—72°, and 191°, respectively.
R. S. C.

Optical activity of aluminium pyrocatechoxide. W. D. Treadwell, G. Szabados, and E. Haimann (Helv. Chim. Acta, 1932, 15, 1049—1052).—Freshly prepared $Al(OH)_3$ and pyrocatechol in aq. NH_3 give the complex salt, $(NH_4)_3[Al(C_6H_4O_2)_3]$, changed by strychnine sulphate in H_2O into the *strychnine* salt, which, when washed with successive small portions of H_2O at 10°, gives a residue of the less sol. l-*strychnine*-l-*aluminium pyrocatechoxide*, cryst., $[\alpha]_D$ —39·2° in EtOH. This salt with aq. KI gives insol. strychnine hydriodide and a solution from which $COMe_2$ ppts. the l-K_3 salt, cryst., $[\alpha]_D$ —61·7° in H_2O. Al, therefore, has a covalency of 6 in these salts. The racemisation of *l*-$K_3[Cr(C_2O_4)_3]$ is a unimol. reaction (time of half change 34·9 min. at 16°). The Al pyrocatechoxide salts racemise at similar rates. R. S. C.

Preparation of resorcinol monobenzoate. J. Benet (Bull. Soc. chim., 1932, [iv], 963—964).—Partial hydrolysis of resorcinol dibenzoate by $Na_2HPO_4+Na_3PO_4$ in aq. EtOH gives the monobenzoate, m.p. 133°, in 60% yield. The yield is increased to 90% of theory in presence of CH_2O.
H. A. P.

Hydroxy- and dihydroxy-phenylethylmethylamines and their ethers. J. S. Buck (J. Amer. Chem. Soc., 1932, 54, 3661—3665; cf. A., 1930, 1575).—Four of the seven previously unknown hydroxy- and dihydroxy-phenylethylmethylamines have been synthesised. The following new intermediates were prepared: β-o-*methoxyphenylpropionamide*, m.p. 110°; β-2 : 4-*dimethoxyphenylpropionamide*, m.p. 113°; β-2 : 5-*dimethoxyphenylpropionic acid*, m.p. 101° (*amide*, m.p. 111°); o-*methoxy*-, b.p. 117°/9 mm., m-*methoxy*-, b.p. 118°/6 mm., 2 : 3-*dimethoxy*-, b.p. 138°/8 mm., 2 : 4-*dimethoxy*-, b.p. 140°/1 mm., and 2 : 5-*dimethoxy*-, b.p. 150°/8 mm., -β-*phenylethylamines*. The following substituted β-phenylethylmethylamines are described: o-*methoxy*-, b.p. 115°/9 mm. (*hydriodide*, m.p. 101°; *hydrochloride*, m.p. 119°); m-*methoxy*-, b.p. 118°/7 mm. (*hydriodide*, m.p. 108°; *hydrochloride*, m.p. 119°); 2 : 3-*dimethoxy*-, b.p. 136°/6 mm. (*hydriodide*, m.p. 90°; *hydrochloride*, m.p. 117°); 2 : 4-*dimethoxy*-, b.p. 136°/4 mm. (*hydriodide*; *hydrochloride*, m.p. 145°); 2 : 5-*dimethoxy*-, b.p. 155°/8 mm. (*hydriodide*, m.p. 137°; *hydrochloride*, m.p. 110°). β-o- and -m-*Hydroxyphenylethylmethylamine hydrochlorides*, m.p. 148° and 89°, and β-2 : 3-, m.p. 149°, and -2 : 5-, m.p. 128°, -*dihydroxyphenylethylmethylamine hydrochlorides* are prepared.
C. J. W. (*b*)

Synthesis of pharmacologically important amines. VI. Synthesis of mescaline. K. Kindler and W. Peschke (Arch. Pharm., 1932, 270, 410—413; cf. this vol., 843).—Two syntheses of mescaline (I), m.p. 35—36° (lit. an oil), are recorded. The $NaHSO_3$ compound of 3 : 4 : 5-trimethoxybenzaldehyde and aq. KCN give 3 : 4 : 5-trimethoxymandelonitrile, yielding with Ac_2O the *Ac* derivative, b.p. 163—165°/0·1 mm., which is hydrogenated (Pd-black) in AcOH to (I). β-Benzoyloxy-*N*-benzoyl-β-3 : 4 : 5-trimethoxyphenylethylamine with Pd-black in boiling tetralin affords *N*-benzoylmescaline, slowly hydrolysed by 20% KOH. R. S. C.

Amino-alcohols derived from methyl*cyclo*hexane. J. Matti (Bull. Soc. chim., 1932, [iv], 51, 974—979).—Interaction of *cyclo*hexene with CH_2O in AcOH–H_2SO_4 at 35—40° gives a complex mixture of acetates, of which the fraction of b.p. 120—145°/19 mm. is hydrolysed by KOH in EtOH to a mixture containing 2-hydroxymethyl*cyclo*hexanol (I) and its dimeric (?) *methylene ether*, $(C_8H_{14}O_2)_x$, m.p. 205° (sublimes 120°). This crude mixture of glycols gives with HBr in AcOH the *bromohydrin*, b.p. 185°/19 mm., and *bromoacetin*, b.p. 131—135°/21 mm., of (I), mixed with other products. Condensation of the crude bromination mixture with $NHMe_2$ and subsequent deacetylation gives 2-dimethylaminomethyl*cyclo*hexanol (A., 1920, i, 851; 1927, 659); similarly, $NHEt_2$ gives 2-*diethylaminomethyl*cyclo*hexanol* (II), b.p. 126—128°/17 mm. (*benzoate hydrochloride*, m.p. 183—183·5°; p-*nitrobenzoate hydrochloride*, m.p. 180°), also obtained by the method of Mannich (*loc. cit.*). The formation of stereoisomerides by this route was not observed. The 1-*Cl*-derivative, b.p. 123°/18 mm., corresponding with (II) is obtained by the action of $SOCl_2$ in C_6H_6, and is converted by 8-amino-6-methoxyquinoline at 145° into Δ^2-*diethylaminomethyl*cyclo*hexene*, b.p. 95—96°/19 mm.
H. A. P.

Pinacolin deamination. II. Action of nitrous acid on amino-alcohols derived from *iso*valine. A. McKenzie and W. Mitchell (Ber., 1932, 65, [*B*], 1358—1362; cf. this vol., 382).—*iso*-Valine hydrochloride is transformed into the *Et ester hydrochloride* (I), m.p. 119—120°, converted by MgPhBr into r-β-*amino*-αα-*diphenyl*-β-*methylbutanol*, m.p. 94° (*hydrochloride*, m.p. 220·5°), deaminated in AcOH to a liquid, b.p. 171—174°/15 mm., which is free from N and does not react with semicarbazide. (I) and $BrMg{\cdot}C_6H_4Me(p)$ yield r-β-*amino*-αα-*di*-p-*tolyl*-β-*methylbutanol*, m.p. 91·5—92·3° (*hydrochloride*, m.p. 220—228°), which behaves similarly to the Ph derivative when deaminated. r-β-*Amino*-αα-*dibenzyl*-β-*methyl*-n-*butanol*, m.p. 81—81·5° (*hydrochloride*, m.p. 102—105°), from (I) and $ClMg{\cdot}CH_2Ph$, is converted by HNO_2 into (?) -r-*benzyl* α-*benzyl*-α-*methyl*-n-*propyl ketone* (II), m.p. 63·5—64°, which does not react with MgPhBr or yield a semicarbazone. (+)-*iso*Valine, $[\alpha]_D^{15}$ +13° in H_2O, is transformed into the Et ester hydrochloride and thence by $ClMg{\cdot}CH_2Ph$ into (—)-β-*amino*-αα-*dibenzyl*-β-*methyl*-n-*butanol* (III), m.p. 91—92°, $[\alpha]_D^{16}$ —9·1° in EtOH, $[\alpha]_D^{14·5}$ —20·8° in C_6H_6. (III) and HNO_2 yield (II) and an oil, b.p. 130—145°/1·5 mm., $[\alpha]_D^{15}$ +14·3°, which does not yield a semicarbazone or oxime. H. W.

Manufacture of β-di(arylmethyl)aminoethyl alcohols. I. G. Farbenind. A.-G.—See B., 1932, 833.

Heteropolarity. XVII. Constitution and colour. W. Dilthey and R. Wizinger (Ber., 1932, 65, [*B*], 1329—1333).—In reply to Burawoy (this vol., 792), it is demonstrated that the freely-active NR_2 group in aromatic union generally has a more strongly bathochromic action than a similarly placed OR group. NR, O, or S atoms or groups which close a six-membered ring or are attached directly to the central atom have a hypsochromic or feebly bathochromic effect, but retain their character as auxochromes, since they stabilise the ions in cations. p-*Dimethylaminotriphenylcarbenium perchlorate*, m.p. 198—199°, after softening, is described. H. W.

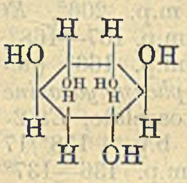
Soluble compounds of cholesterol with various soaps. L. Velluz and E. Bouchara (Compt. rend. Soc. Biol., 1931, 106, 1131—1132; Chem. Zentr., 1932, i, 1908).—Stable colloidal solutions are obtained when 2% Na oleate or ricinoleate, instead of H_2O, is added to a suspension of cholesterol in $COMe_2$. A method employing ricinoleic, linoleic, or linolenic acid is also described. A. A. E.

Water-soluble cholesteryl esters. R. Schönheimer and F. Breusch (Z. physiol. Chem., 1932, 211, 19—22).—The alkali salts of the mono-esters of butanetetracarboxylic acid are very sol. in H_2O. The following esters were obtained as mixtures of the two isomerides: *cholesteryl* H_3 n-*butane*-αβγδ-*tetracarboxylate* [separated into less sol. ester, m.p. 240° (decomp.), and more sol. ester, m.p. 186° (decomp.)]; *sitosteryl*, m.p. 168° (decomp.), *ergosteryl* [less sol., m.p. 230° (decomp.), more sol., m.p. 160—168° (decomp.)], *allocholesteryl* (as Na salt), and *vitamin*-D_2 m.p. 100° (decomp.), esters. J. H. B.

Sterol group. XVI. (*a*) Molecular formula of ergosterol. (*b*) Oxidation of ergosterol and of α-dihydroergosterol with manganese dioxide and sulphuric acid. I. M. Heilbron and J. C. E. Simpson (J.C.S., 1932, 2400—2403).—Ergostanone with Br in $CHCl_3$ gives *bromoergostanone*, m.p. 191° (decomp.). Similarly, β-ergostenone at −15° gives *bromodehydroergostenone*, m.p. 178—179° (decomp.), reduced by Zn and AcOH to *dehydroergostenone*, m.p. 147—148° (*oxime*, m.p. 212—213°), which is also obtained from dehydroergostenol when heated with Cu-bronze. Analyses of the Br-derivatives indicate that the formula of ergosterol is $C_{28}H_{44}O$ (or less probably $C_{29}H_{46}O$) (cf. this vol., 845). Ergosterol with MnO_2 in 57% H_2SO_4 gives benzenepentacarboxylic acid (isolated as the Me ester through the Ag salt), which is similarly obtained in small yield from α-dihydroergosterol. A. A. L.

Inositolphosphoric compounds. Compounds of ferric inositolphosphate with ammonia and amines. S. Otolski (Rocz. Chem., 1932, 12, 621—630).—Amines react in aq. solution with $C_6H_6O_{24}P_6Fe_4$ to yield *compounds* with: NH_3, NH_2Et, $NHEt_2$ (6 mols., $8H_2O$), NMe_3, piperidine (6 mols., $12H_2O$), $(NH_2CH_2)_2$, and piperazine (4 mols., $12H_2O$). NH_2Ph, C_5H_5N, quinoline, 2-aminopyridine, and hexamethylenetetramine do not yield compounds. R. T.

Configuration of *d*-quercitol. T. Posternak (Helv. Chim. Acta, 1932, 15, 948—955).—*d*-Quercitol (I) and aq. $KMnO_4$ (=2·8 O) at 0° give a trihydroxyadipic acid, identical with metasaccharic acid (II), m.p. 162° (decomp.) (lit. 155°), an *acid* [(?) a dihydroxyglutaric acid] (III), $C_5H_8O_6$, m.p. 162—164° (decomp.), and (in one experiment only) an *acid*, m.p. 158—160°. More (III) is formed when $KMnO_4$ equiv. to 5 O is used. (I) with HNO_3 gives $H_2C_2O_4$, *l*-trihydroxyglutaric acid, mucic acid, and (in one experiment) a little (II). Kiliani's arguments (A., 1931, 1411) concerning the configuration of (I) are unsound. The 2-deoxypentose obtained from metasaccharin is identical with *d*-2-xylodeose. The above and previously known facts and application of Hudson's rule indicate for (I) the annexed configuration. R. S. C.



Structure of glutaconic acids and esters. IV. Cyclic glutaconic derivatives. G. A. R. Kon and H. R. Nanji. **V. α-Benzyl- and α-benzyl-β-methyl-glutaconic acids.** G. A. R. Kon and E. M. Watson. **VI. Derivatives of β-phenylglutaconic acid.** B. S. Gidvani and G. A. R. Kon (J.C.S., 1932, 2426—2433, 2434—2443, 2443—2451; cf. this vol., 252, 601).—IV. Et *cyclo*pentanonecarboxylate, $CN{\cdot}CH_2{\cdot}CO_2Et$, and C_5H_5N (50% yield) or KOEt (59% yield) give *Et 2-carbethoxy*-Δ^1-cyclo*pentenylcyanoacetate* (I), b.p. 188°/16 mm., giving a K derivative (II) with KOH or KOEt, from which (I) is regenerated with BzOH in Et_2O, or with aq. acid. Ozonolysis of (I) gives *Et* α-*cyano*-βε-*diketosuberate*, b.p. 150—190°/30 mm. [*diphenylhydrazone*, m.p. 256° (decomp.)]. (II) with MeI gives *Et* α-*cyano*-α-2-*carbethoxy*-Δ^1-cyclo*pentenylpropionate* (III), b.p. 177—178°/17 mm., ozonised to *Et* α-*cyano*-βε-*diketo*-α-*methylsuberate*, b.p. 140—170°/16 mm. (*diphenylhydrazone*, m.p. 217—218°), and converted by NaOEt into α-2-α-*carbethoxy*-Δ^1-cyclo*pentenylpropionitrile*, b.p. 151°/20 mm., which with O_3 gives *Et* ξ-*cyano*-βε-*diketo-octoate* [*diphenylhydrazone*, m.p. 210—211°; *semicarbazone*, m.p. 242° (decomp.)]. Hydrolysis of (I) with (*a*) KOH gives a C_5H_5N derivative, $C_8H_9O_2N$, m.p. 258° (darkens); (*b*) HCl gives a C_5H_5N derivative (IV), $C_{11}H_{13}O_4N$, m.p. 241° (decomp.) (*Bz* derivative, m.p. 80—100°), and 2-*carbethoxy*-Δ^1-cyclo*pentenylacetic acid* (V), m.p. 187° [*Et* ester (VI), b.p. 155°/20 mm.], which gives an anomalous *hydroxyanhydride*, $C_{10}H_{10}O_4$, m.p. 150° [*anilic acid*, m.p. 300° (darkens 240°)], and a little of the normal anhydride, isolated as the *semianilide*, m.p. 172°; (*c*) H_2SO_4 gives (IV), and *Et* 2-*carbethoxy*-Δ^1-cyclo*pentenylmalonamate*, m.p. 89°, hydrolysed by HCl to (V). (VI) with O_3 gives Et βε-diketosuberate [*phenylhydrazine* derivative (? phenylhydrazidopyrazolone), m.p. 126°], and is unchanged by NaOEt. The K derivative of (VI) (formed in C_6H_6) with MeI gives *Et* 2-*carbethoxy*-Δ^1-cyclo*pentenylpropionate*, b.p. 149—150°/13 mm. [and unchanged (V)], hydrolysed to the *acid*, m.p. 151°. Acid or alkaline hydrolysis of (III) gives a C_5H_5N derivative, $C_9H_{11}O_2N$, m.p. 252°. Et 2-methyl*cyclo*pentanonecarboxylate did not react with $CN{\cdot}CH_2{\cdot}CO_2Et$. The following series of compounds is similarly obtained from Et *cyclo*hexanonecarboxylate: *Et* 2-*carbethoxy*-Δ^1-cyclo*hexenylcyanoacetate*, b.p. 190—191°/19 mm. (yields 18 and 38%), *Et* α-*cyano*-βζ-*diketoazelate*, b.p. 160—180°/16 mm. (*diphenylhydrazone*, m.p. 246°), *Et* α-*cyano*-α-2-*carbethoxy*-Δ^1-cyclo*hexenylpropionate*, b.p. 185°/17 mm., *diphenylhydrazone*, m.p. 206°, of Et α-cyano-βζ-diketo-α-methylazelate, α-2-*carbethoxy*-Δ^1-cyclo*hexenylpropionitrile* (VII), b.p. 162°/19 mm., iso*quinoline* derivative, $C_9H_{11}O_2N$, m.p. 206°, *Et* 2-*carboxy*-Δ^1-cyclo*hexenylmalonamate*, m.p. 167—168°, 2-*carboxy*-Δ^1-cyclo*hexenylacetic acid*, m.p. 166° (decomp.) (*Et* ester, b.p. 162°/20 mm.), *phenylhydrazine* derivative, m.p. 172°, of Et βξ-diketoazelate, *Et* 2-*carbethoxy*-Δ^1-cyclo*hexenylpropionate*, b.p. 158°/17 mm., and the corresponding *acid*, m.p. 136—137° (*hydroxyanhydride*, b.p. 177°/6 mm.; *semianilide*, m.p. 135—136°), iso*quinoline* derivative, $C_{10}H_{17}O_5N$, from (VII), m.p. 172°. The above glutaconic derivatives are all stable in the βγ-form.

V. The structure of the following esters was determined by ozonolysis. Interaction of the K derivatives of the stereoisomeric Et β-methylglutaconates with CH_2PhCl in C_6H_6 is accelerated by addition of MeI, giving *cis*- (II) and *trans*-βγ-methylbenzylglutaconic esters (I) (? a little αβ). On hydrolysis (I) gives the *trans*-βγ-acid (III), stable to ultra-violet light, whilst (II) gives the *cis*-αβ-acid (IV), m.p. 148° [Et ester, (V), from the Ag salt], converted by ultraviolet light into trans-α-*benzyl*-β-*methyl*-Δ^α-*propene*-αγ-*dicarboxylic acid*, m.p. 157—158° (*Et* ester, b.p. 195—196°/14 mm.). (III) gives (IV) with conc. HCl, whilst the reverse change, studied quantitatively, is effected with KOH. The K derivatives (probably αβ) of (II) and (V) with MeI give a mixture of the αβ-forms of α-benzyl-β-methyl- and α-benzyl-βγ-dimethyl-glutaconic esters, the latter being also obtained in small amount and accompanied by much βγ-isomeride from the benzylation of Et αβ-dimethylglutaconate. *trans*-α-Benzyl-Δ^β-propene-αγ-dicarboxylic acid (VI) (from the corresponding tetracarboxylic acid) with $KMnO_4$ and Na_2CO_3 gives PhCHO and $H_2C_2O_4$. The Et ester, from the Ag salt, or with EtOH–H_2SO_4, is mainly βγ (? a little αβ), whilst that regenerated from the K derivative contains a little Et α-benzylideneglutarate (VII), and gave a little of the corresponding acid on hydrolysis, together with (VI). The hydroxyanhydride (VIII) from (VI) in Et_2O by extraction with $NaHCO_3$ gives cis-α-*benzyl*-Δ^α-*propene*-αγ-*dicarboxylic acid* (IX), m.p. 149—150° [Et ester, b.p. 189—190°, mainly βγ, with some (VII)], converted by H_2O into a eutectic mixture, m.p. 139° (cf. J.C.S., 1911, 99, 2208), and by more prolonged action into the *trans*-βγ-acid. (IX) with $KMnO_4$ in Na_2CO_3 gives phenylpyruvic acid and no $H_2C_2O_4$. The eutectic mixture gives oxidation products indicating both αβ- and βγ-forms (mainly the former), and gives an Et ester similar to that from (IX). (VIII) in $NaHCO_3$ with $KMnO_4$ gives PhCHO, $H_2C_2O_4$, and a little BzOH. *Et* α-*benzyl*-γ-*methylglutaconate*, b.p. 192°/10 mm. (from Et α-benzylglutaconate), is mainly the βγ-form, and is hydrolysed to the *acid*, m.p. 184—185°, which is oxidised to PhCHO (? a little $AcCO_2H$), and gives the above ester in the pure βγ-form. The more symmetrical glutaconic derivatives appear to be the more stable.

VI. The products of hydrolysis of Et α-carbethoxy-β-phenyl-α-methylglutaconate are (*a*) the *trans*-βγ-acid, m.p. 155° (Et ester, b.p. 165°/5 mm., consisting mainly of the βγ-form, with a little αβ, and also obtained by the action of MeI in Et_2O on the K derivative of Et β-phenylglutaconate, which may be regenerated from the K derivative), (*b*) the *cis*-αβ-acid (I), m.p. 151° (Et ester, b.p. 163°/5 mm., mainly αβ, with a little βγ), (*c*) cis-β-*phenyl*-α-*methyl*-Δ^β-*propene*-αγ-*dicarboxylic acid*, m.p. 130—131° (*Et* ester, b.p. 159°/4 mm., mainly βγ, with a little αβ), and (*d*) an *acid*, $C_8H_{10}O_3$, m.p. 87° (cf. A., 1922, i, 553). Et phenylpropiolate and $CN{\cdot}CHNa{\cdot}CO_2Et$ give the *Na* derivative (II) of Et α-cyano-β-phenylglutaconate (III), which with HCl gives a mixture of αβ- and βγ-forms, whilst with BzOH in Et_2O it gives the pure βγ-form, which is similarly obtained from the K derivative (IV). The ester gives phenylhydroxypyridine on hydrolysis. (IV) in Et_2O or C_6H_6, and (II) only in EtOH, with MeI give Et α-cyano-β-phenyl-α-methyl-Δ^β-propene-αγ-dicarboxylate. (III) is also obtained in small yield from the action of C_5H_5N on Et benzoylacetate and $CN{\cdot}CH_2{\cdot}CO_2Et$. Et γ-sodio-α-carbethoxy-β-phenylglutaconate (this vol., 601) with hot EtOH gives the α-*sodio*-derivative, converted by BzOH in Et_2O into the parent ester, m.p. 38°. Similar results are obtained with the corresponding α-CN-ester. Et α-carbethoxy-β-phenyl-α-methylglutaconate (J.C.S., 1913, 103, 1569) is unaffected by NaOEt. An electronic explanation of this is suggested. The Na derivative with MeI gives a little Et_2CO_3, and an ester from which (I) was isolated. $CHNa(CO_2Et)_2$ and $CPhCl_3$ with NaOEt give a small yield of Et α-carbethoxy-β-ethoxycinnamate. A. A. L.

Peroxide of hexahydrobenzoic acid. F. Fichter and W. Siegrist (Helv. Chim. Acta, 1932, 15, 1304—1307).—Hexahydrobenzoic acid (I) and its K salt (II) form an *acid salt* (? or mixture), 3(I) : 1(II). The anhydride (modified prep.) of (I) and $BaO_2,8H_2O$ in Et_2O give the Ba salt of (I) and *hexahydrobenzoyl peroxide* (III), an oil, which decomposes at room temp. to give CO_2, a little O_2, *cyclo*hexanol, di*cyclo*hexyl, and the *cyclo*hexyl ester of (I). These products are the same as those obtained by electrolysis of (II). (III) is considered to be formed at the anode and to yield the ultimate products of the reaction by decomp. R. S. C.

Derivatives of 2-iodo-5-nitrobenzoic acid. H. Goldstein and A. V. Grampolov (Helv. Chim. Acta, 1932, 15, 1102—1105).—2-Iodo-5-nitrobenzoic acid (I) and HNO_3 (*d* 1·5) at 50° gives 2-iodoso-5-nitrobenzoic acid (II), m.p. 197° (decomp.) (cf. A., 1894, i, 32), reduced to (I) by very dil. KI and H_2SO_4, and giving with MeOH or EtOH and H_2SO_4 a small amount of the corresponding ester and (?) 2-*iodo*-5-*nitrobenzoic anhydride*, m.p. about 200—205° (decomp.). (II) with Ac_2O gives the *mixed anhydride*, m.p. 187—188° (decomp.), and with NaOCl at room temp. affords 2-*iodoxy*-5-*nitrobenzoic acid*, m.p. about 199—202° (deflagration). 2-Chloro-3 : 5-dinitrobenzoic acid and aq. NH_3 at 100° give the 2-NH_2-acid, which by diazotisation etc. affords impure 2-*iodo*-3 : 5-*dinitrobenzoic acid*, m.p. 219° (changed by NaOH to 3 : 5-dinitrosalicylic acid), and a *substance*, m.p. 286° (decomp.). R. S. C.

Friedel–Crafts reaction. Unsymmetrical acid anhydrides and their behaviour with benzene and aluminium chloride. J. M. Zeavin and A. M. Fisher (J. Amer. Chem. Soc., 1932, 54, 3738—3742).—The following *anhydrides* are prepared from the appropriate acid and BzCl or AcCl in Et_2O–C_5H_5N at 0° : *mono*-o-*benzoyloxybenzoic*, m.p. 67—67·8° (from o-$OH{\cdot}C_6H_4{\cdot}CO_2H$ and BzCl); *mono*-o-*methoxybenzoic*, m.p. 76·3—77·2°; *mono*-p-*chlorobenzoic*, m.p. 66·5—70°; *mono*-p-*bromobenzoic*, m.p. 82—83°; *mono*-o-*nitrobenzoic*, m.p. 65—65·5°; *benzoic* 3 : 5-*dinitrobenzoic*, m.p. 115·5°; α-*naphthoic benzoic*, m.p. 89·5—90·3°; β-*naphthoic benzoic*, m.p. 54—57·5°; α-*naphthoic acetic* (I), a clear brown oil, decomp. readily; β-*naphthoic acetic* (II), m.p. 50·5—51°; *dibenzoic phthalic* (III), m.p. 131—132°. All the anhydrides except the last three give $COPh_2$ with C_6H_6 and $AlCl_3$. (I) and (II) give COPhMe; (III) gives BzOH and diphenylphthalide. C. J. W. (*b*)

General synthesis of α-unsaturated acids from malonic acid. II. M. Dalal and S. Dutt (J. Indian Chem. Soc., 1932, 9, 309—314; cf. A., 1925, i, 882).—The following bases are catalysts for the prep. of cinnamic acid from PhCHO and $CH_2(CO_2H)_2$ (they are best used in the ratio 1 mol. of base : 1 mol. of PhCHO) : quinoline, *iso*quinoline, 2-methylquinoline, α- and β-naphthquinolines, phenanthroline, acridine, 9-methylacridine; C_5H_5N, 2-methylpyridine, lutidine, collidine, piperidine, $NPhMe_2$, $NPhEt_2$, and *N*-benzyl-*N*-methyl- and -ethyl-anilines. The following aldehydes condense with $CH_2(CO_2H)_2$ in presence of quinoline (1 mol. per 1 mol. of aldehyde) : *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, *o*-$C_6H_4Cl{\cdot}CHO$, *m*- and *p*-$OH{\cdot}C_6H_4{\cdot}CHO$, vanillin, *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$, *p*-$C_6H_4Me{\cdot}CHO$, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, veratraldehyde, piperonal, furfuraldehyde, citronellal, citral, cinnamaldehyde, paracetaldehyde, EtCHO, Pr^βCHO, and Bu^βCHO; the yields of unsaturated acid vary from 10·6 to 82·5%. Cinnamic acid is not produced from PhCHO and $CH_2(CO_2H)_2$ even at 130°. H. B.

Aromatic fluoro-compounds. XII. Fluorinated amino-acids and their derivatives. II. Fluorophenylalanines. G. Schiemann and W. Roselius (Ber., 1932, 65, [*B*], 1439—1442).—*o*-Fluorobenzaldehyde, hippuric acid, anhyd. NaOAc, and Ac_2O at 100° afford 4-o-*fluorobenzylidene*-2-*phenyloxazol*-5-*one*, m.p. 165·5—166·5° (yield 35%), transformed by NaOH–50% EtOH into α-*benzamido*-o-*fluorocinnamic acid*, m.p. 209·5—210° (decomp.), reduced and hydrolysed by HI (*d* 1·96), Ac_2O, and red P to α-*amino*-β-o-*fluorophenylpropionic acid*, m.p. 258·5—259° (decomp.). From *m*-$C_6H_4F{\cdot}CHO$ are obtained similarly, 4-m-*fluorobenzylidene*-2-*phenyloxazol*-5-*one*, m.p. 156·5—157° (70% yield), α-*benzamido*-m-*fluorocinnamic acid*, m.p. 203—203·5° (decomp.) (yield 63%), and dl-α-*amino*-β-m-*fluorophenylpropionic acid*, m.p. 262—263° (decomp.) (*Cu* salt). *p*-$C_6H_4F{\cdot}CHO$ yields successively 4-p-*fluorobenzylidene*-2-*phenyloxazol*-5-*one*, m.p. 181—181·5°, α-*benzamido*-p-*fluorocinnamic acid*, m.p. 225° (decomp.), and dl-α-*amino*-β-p-*fluorophenylpropionic acid*, m.p. 263·5—264° (decomp.) (*Cu* salt). H. W.

Action of sodium hydrogen sulphite on derivatives of 1-nitroso-β-naphthol. M. Battegay and E. Riesz (Bull. Soc. chim., 1932, [iv], 51, 902—916).—Interaction of 1-nitroso-2-hydroxy-3-naphthanilide (I) with $NaHSO_3$ at 40—45° for a short time gives the $NaHSO_3$ derivative, converted by HCl into the H_2SO_3 derivative (cf. A., 1924, i, 722; Lantz and Mingasson, A., 1931, 1291), but at 100° 1 : 2-*dihydroxy*-3-*naphthanilide*-4-*sulphonic acid* (II) is produced (as Na salt; cf. G.P. 70,867). (II) is identified by hydrolysis by conc. aq. HCl at its b.p. to H_2SO_4 and 1 : 2-*dihydroxy*-3-*naphthanilide*, m.p. 167°, also obtained by reduction of 1 : 2-naphthaquinone-3-carbanilide with $Na_2S_2O_4$ or SO_2 in AcOH. With oxidising agents in neutral (H_2O_2) or alkaline solution (H_2O_2, air) or with HNO_2 in AcOH (II) gives 2-*hydroxy*-1 : 4-*naphthaquinone*-3-*carboxylanilide*, m.p. 202°, with liberation of SO_2, and with NH_2Ph (and O_2) the corresponding 4-*anil*, m.p. 226°, identified by reduction by SO_2 to 1 : 2-*dihydroxy*-4-*anilino*-3-*naphthanilide*, m.p. 200° (decomp. begins at 160°), is formed.

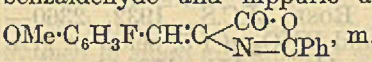
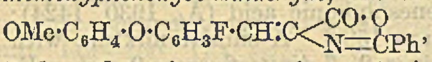
The stability of the 3-CO·NHPh group, in contrast with the 3-CO_2H group, which is eliminated by $NaHSO_3$ (cf. Lantz and Mingasson, *loc. cit.*), is in accordance with the behaviour of these compounds as derivatives of β-ketonic acids. Consequently *Me* 1-*nitroso*-2-*hydroxy*-3-*naphthoate*, m.p. 153—154° (from aq. $NaNO_2$ and Me 2-hydroxy-3-naphthoate in AcOH) gives a $NaHSO_3$ derivative, converted by cold aq. HCl into the H_2SO_3 derivative, and by NaOH at 0° into the original Me ester, m.p. 153—154°. H. A. P.

Nitration of benzilic acid and fluorenecarboxylic acid. F. L. Rose (J.C.S., 1932, 2360—2362).—Benzilic acid and HNO_3, *d* 1·5, below 0° give (*a*) 2 : 2′-*dinitrobenzilic acid*, m.p. 171—172° (decomp.) (isolated as the NH_2Ph salt), oxidised by CrO_3 in AcOH to 2 : 2′-dinitrobenzophenone, and reduced to 2 : 2′-*diaminobenzilic acid dihydrochloride*, and (*b*) a mixture of nonacidic *isomerides*, $C_{28}H_{16}O_{12}N_4$, oxidised to 2 : 3′- and 3 : 3′-dinitrobenzophenone. Fluorenecarboxylic acid in $CHCl_3$ or CCl_4 with HNO_3, *d* 1·43, gives 2-*nitrofluorene*-9-*carboxylic acid*, m.p. 186—187° (decomp. giving 2-nitrofluorene, oxidised to 2-nitro fluorenone), which with H_2SO_4 gives 2-nitro-7-sulphofluorene-9-carboxylic acid [*K* salt, decomp. 190° giving nitrofluorenesulphonic acid (A., 1930, 1424); *diacid chloride*, m.p. 159°]. A similar mixture with HNO_3, *d* 1·51, gives 2 : 7-*dinitrofluorene*-9-*carboxylic acid*, decomp. 150° giving 2 : 7-dinitrofluorene, oxidised to the fluorenone. The above nitro-acids with Sn and HCl give 2-*amino*-, m.p. 207—208° (decomp.) (*Ac* derivative, m.p. 195°), 2 : 7-*diamino*-, m.p. 209—210° (decomp.) (Ac_2 derivative, m.p. 263—264°), and 2-*amino*-7-*sulpho-fluorene*-9-*carboxylic acid*, darkens at 290°. A. A. L.

Derivatives of di-iodotyrosine and thyroxine. Action of acetic anhydride on di-iodotyrosine. C. S. Myers (J. Amer. Chem. Soc., 1932, 54, 3718—3725).—*l*-Di-iodotyrosine and Ac_2O in cold 2*N*-NaOH give the ON-Ac_2 derivative (I), m.p. 186—187°, $[\alpha]_{546}^{30}$ +21·52° in abs. EtOH; with Ac_2O in boiling

AcOH the dl-*isomeride* (II), m.p. 186°, results. Partial hydrolysis of (I) with NaOH in dil. EtOH gives the N-*Ac* derivative (III), decomp. 198—200°, $[\alpha]_{546}^{30}$ +34·54° in abs. EtOH (*Me* ester, m.p. 152—153·5°, also obtained from the Me ester and AcCl or Ac_2O). Hydrolysis of (II) gives the dl-N-*acetyldi-iodotyrosine* (IV), decomp. 205—206° (*Me* ester, m.p. 136—137°; *Et* ester, m.p. 140—141°). (III) and Me_2SO_4 in EtOH–5*N*-NaOH give the l-N-*Ac*-O-*Me* derivative, m.p. 207—208°, $[\alpha]_{546}^{28·5}$ +14·5° in EtOH, hydrolysed to l-o-*methyldi-iodotyrosine*, m.p. 204—206° (decomp.), $[\alpha]_{546}^{28·5}$ −3·2° in 5% NaOH. The compound obtained by Wheeler and Jamieson (A., 1905, i, 350) is not the simple Ac derivative; it has the empirical formula $C_{24}H_{18}O_6N_2I_4$ and is probably an anhydride of (III) with the OH groups only partly acetylated. With NaOH it yields (IV), with NaOEt the Et ester of (IV), and with aq. NH_3 the *amide*, decomp. 204—206°, of (IV); PhOH gives a mixture of Ph esters of the Ac and Ac_2 derivatives, containing approx. 65% of the latter. Di-iodotyrosine heated gently with Ac_2O until turbidity results gives the *azlactone*, m.p. 135—138°, of (IV); (II) and Ac_2O at 100° yield an *azlactone*, m.p. 87—89°. The azlactone is probably an intermediate in the formation of the anhydride. *dl-N*-Acetylthyroxine and Me_2SO_4 in NaOH–EtOH give the O-*Me* derivative, m.p. 214—217°, hydrolysed to dl-O-*methylthyroxine*, decomp. 210—213°.

C. J. W. (*b*)

Fluorinated amino-acids and their derivatives. I. Nuclear fluorinated amino-acids. G. SCHIEMANN [with W. WINKELMÜLLER and W. ROSELIUS (Ber., 1932, 65, [*B*], 1435—1438).—The following schemes are outlined: 3-fluoro-*p*-tolyl Me ether to 3-*fluorotyrosine*, decomp. 277°; 3-fluoro-4-methoxybenzaldehyde and hippuric acid to the *azlactone*  $OMe\cdot C_6H_3F\cdot CH{:}C{<}\begin{matrix}CO\cdot O\\ N{=}CPh\end{matrix}$, m.p. 206·5°, and thence through α-*benzamido-3-fluoro-4-methoxycinnamic acid*, m.p. 214°, to 3-fluorotyrosine: *m*-fluorophenylalanine to α-*amino*-β-3-*fluoro-4-nitrophenylpropionic acid*, decomp. 209·5°, thence to α-*amino*-β-3-*fluoro-4-aminophenylpropionic acid* and 3-fluorotyrosine: *p*-methoxydiphenyl ether to 3-*nitro*- and 3-*amino*-4-*methoxydiphenyl ether* (to which the BF_3 process could not be satisfactorily applied); *m*-bromofluorobenzene with quinol Me ether to 3-4′-*methoxyphenoxyfluorobenzene*, b.p. 161·5°/14 mm., whence successively 2-*fluoro*-4 : 4′-*methoxyphenoxybenzaldehyde*, the *azlactone*  $OMe\cdot C_6H_4\cdot O\cdot C_6H_3F\cdot CH{:}C{<}\begin{matrix}CO\cdot O\\ N{=}CPh\end{matrix}$, m.p. 155°, and 2-*fluorothyronine* [α-*amino*-β-4 : 4′-*hydroxyphenoxyphenylpropionic acid*], decomp. 264·5°: β-3-fluoro-4-hydroxyphenylethylamine (*picrate*, decomp. 194·5°) and β-3-fluorophenylethylamine (*picrate*, decomp. 157°) by decarboxylation of the corresponding acids; *m*-fluorobenzaldehyde successively to m-*fluorocinnamic acid*, m.p. 166·5°, β-3-*fluorophenylpropionic acid*, m.p. 46°, its *amide*, m.p. 95·5°, and β-3-*fluorophenylethylamine*, b.p. 87°/15 mm.

H. W.

***peri*-Condensation of phthalic anhydride. II. Phthalylnaphthalene.** A. RIECHE, H. SAUTHOFF, and O. MÜLLER (Ber., 1932, 65, [*B*], 1371—1381; cf. A., 1931, 1060).—Condensation of phthalic anhydride with $AlCl_3$ and the requisite hydroxynaphthalene at 190—210°, 200—220°, and 235—245°, respectively, leads to 1 : 8-*phthalyl*-2 : 6-, m.p. 302°, and -2 : 7-*dihydroxynaphthalene*, m.p. 267° (*Ac* derivative, m.p. 233—234°), and 2-*hydroxy*-1 : 8-*phthalylnaphthalene-3-carboxylic acid*, m.p. 276°. Of these, only the last-named is degraded by molten NaOH, whereby β-*naphthol*-3 : 8-*dicarboxylic acid*, m.p. 320°, is produced.

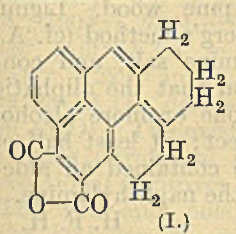
In reply to Fieser (A., 1931, 1292), the 1 : 8-phthalyl structure of 1 : 8-phthalyl-β-naphthol (I) is maintained for the following reasons. The "lactone-like" structure cannot be deduced from analysis of the Na or Ba salts. Etherification of the OH group yields *Et* 1 : 8-*phthalyl*-β-*naphthyl ether*, m.p. 163·5°, insol. in boiling alkali. The demonstration of the presence of one CO group by the action of MgPhBr does not exclude the presence of a second CO, masked by the *o*-OH group. Treatment of (I) with PCl_5 and $POCl_3$ yields 2-chlorophthalylnaphthalene (II), transformed by N_2H_4,H_2O in presence of Pd–$CaCO_3$ and KOH–MeOH into 1 : 8-*phthalylnaphthalene* (III), m.p. 178°, also derived from *o*-1-naphthoylbenzoic acid. (II) and (III) yield only *mono*(*dinitrophenyl*)-*hydrazones*, m.p. 265° and 278°, respectively, but (III) is transformed by MgEtBr in hexahydroanisole into a *substance*, $C_{22}H_{22}O_2$, both CO groups having reacted. (III) is readily sol. in MeOH–KOH, but titration shows that alkali is not neutralised even after boiling for 2 hr.; since (III) is pptd. by CO_2 or by dilution, it is assumed that the CO can add KOH. Distillation of (I), (II), or (III) with Zn dust in H_2 gives 1 : 8-*o*-*xylylenenaphthalene*, m.p. 116·5°, oxidised by a large excess of $Na_2Cr_2O_7$ in AcOH to (III). In agreement with Fieser (*loc. cit.*), oxidation of (I) with $KMnO_4$ ultimately yields benzophenone-2 : 3 : 2′-tricarboxydilactone, but the intermediate acid is probably $C_{16}H_{12}O_6$ instead of $C_{16}H_{10}O_6$. The main product is *Bz*-3-hydroxybenzanthrone. A scheme is suggested.

H. W.

Structure, chemical reactivity, and absorption in the ultra-violet. The acids $C_6H_5\cdot[CH_2]_n\cdot CH[CH_2\cdot CO_2H]\cdot CO_2H$ and their derivatives. (MME.) RAMART-LUCAS and Z. PAPADAKIS (Ann. Chim., 1932, [x], 18, 32—78; cf. this vol., 557).—The ultra-violet absorption curves of the series $Ph\cdot[CH_2]_n\cdot CH[CH_2\cdot CO_2H]\cdot CO_2H$ (n=0—4), and, where possible, of their dialkyl and alkyl H esters, anhydrides, and imides, have been examined. The mutual influence of Ph and the succinic acid (etc.) residue (R) is marked where n=0, but rapidly diminishes as the series is ascended; the curves of homologues are almost identical when n>1, and then approximate to those of an equimol. mixture of PhEt and RH. Chemical properties, *e.g.*, the formation and rehydration of acid anhydrides, show a closely parallel behaviour. Similarly, the H esters of the higher members, unlike those of phenylsuccinic acid, decompose on distillation into anhydride and neutral ester, whilst the NH_4 salts (the phenylsuccinate alone excepted) give on heating the anhydride as well as the imide. There is a slight difference in absorption between the two isomeric Et H phenylsuccinates, and a corresponding difference in chemical reactivity.

β-*Carbethoxy*-β-*phenylpropionic acid*, m.p. 88—89°, is prepared by partial hydrolysis of Et_2 phenylsuccinate, and *Et β-carboxy-β-phenylpropionate*, m.p. 95—96°, from phenylsuccinic anhydride and abs. EtOH; *phenylsuccinamide*, m.p. 209—210°, is obtained in poor yield from the acid chloride and NH_3. The acids $Ph{\cdot}[CH_2]_n{\cdot}CH[CH_2{\cdot}CO_2H]{\cdot}CO_2H$ (n=1—4) are prepared by interaction of $CHNa(CO_2Et)_2$ with $Br{\cdot}[CH_2]_n{\cdot}Ph$, further condensation of the product with $CH_2Br{\cdot}CO_2Et$, hydrolysis, and decarboxylation of the resulting tribasic acid (this procedure in some cases yields the anhydride). The products are contaminated with a little unsaturated acid which needs to be removed with H_2–PtO_2 before the absorption curves are determined. The following are described: *Et_3 α-carboxy-α-benzylsuccinate*, b.p. 200°/11 mm.; *Me_2 benzylsuccinate*, b.p. 159°/7 mm.; *benzylsuccinimide*, m.p. 97—98°, b.p. 200—205°/5 mm.; *Et_3 α-carboxy-α-(β-phenylethyl)succinate*, b.p. 213°/13 mm. [free *acid*, m.p. 165° (decomp.)]; β-phenylethylsuccinic acid (*Me_2* ester, b.p. 160°/5 mm.; *anhydride*, m.p. 58°, b.p. 188°/2 mm.; *imide*, m.p. 78°, b.p. 207—210°/5 mm.); *Et_2 γ-phenylpropylmalonate*, b.p. 178°/5 mm.; *Et_3 α-carboxy-α-(γ-phenylpropyl)succinate*, b.p. 217—218°/9 mm. [free *acid*, m.p. 140° (block, decomp.); *γ-phenylpropylsuccinic acid* [*anhydride*, m.p. 64°, b.p. 196°/3 mm.; *Me_2*, b.p. 168°/4 mm., and *Me H* esters; *imide*, m.p. 80° (together with anhydride by heating NH_4 salt)]; *Et_2 δ-phenylbutylmalonate*, b.p. 180°/5 mm.; *Et_3 α-carboxy-α-(δ-phenylbutyl)succinate*, b.p. 201—202°/1 mm. [free *acid*, m.p. 145° (block, decomp.)]; *δ-phenylbutylsuccinic acid*, m.p. 133° (*anhydride*, m.p. 76°, b.p. 195—200°/high vac.; *Me_2* ester, b.p. 183°/5 mm.; *imide*, m.p. 86°). Attempts to prepare H esters of definite structure from benzylsuccinic acid failed. H. A. P.

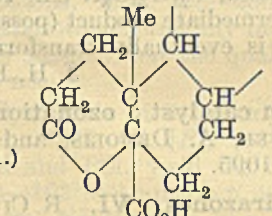
Polynuclear hydrocarbons. XVII. Preparation of a pyrene derivative from benzanthrene. E. CLAR (Ber., 1932, **65**, [*B*], 1425—1428).—Benzanthrene is converted by maleic anhydride in boiling xylene into 2 : 3-trimethylene-4 : 5-dihydropyrene-6 : 7-dicarboxylic anhydride (I), m.p. 227—230° (decomp.). The nature of its extinction curve excludes the possibility that it is an *endo*-derivative or a phenanthrene compound, but suggests a pyrene compound. Benzanthrone, phenanthrene, and chrysene do not react with maleic anhydride. The yellow colour of technical pyrene can be removed by prolonged treatment with maleic anhydride in boiling xylene. H. W.



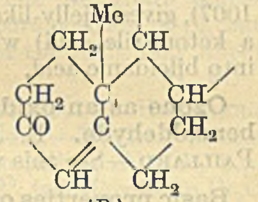
(I.)

Ring-system of sterols and bile acids. O. ROSENHEIM and H. KING (Nature, 1932, **130**, 315).—A criticism (cf. this vol., 971). L. S. T.

Proof of a methylene group in position 1 of the cholesterol ring system. R. TSCHESCHE (Annalen, 1932, **498**, 185—193).—The Me ester of the acid $C_{26}H_{46}O_2$ (I) (Diels *et al.*, A., 1928, 169) [prepared by Clemmensen reduction of the acid, $C_{26}H_{44}O_3$ (Windaus, A., 1906, i, 579; 1917, i, 265)] and MgPhBr give a carbinol which, when distilled, passes into the corresponding unsaturated hydrocarbon; oxidation (O_3) of this affords $COPh_2$ and an *acid*, $C_{25}H_{44}O_2$ (II), m.p. 153—154°, $[\alpha]_D^{19}$ +45·7° in $CHCl_3$ (*anilide*, m.p. 149—150°), convertible by the same series of reactions into an *acid*, $C_{24}H_{42}O_2$ (III), m.p. 181—182°, $[\alpha]_D^{16}$ +15·6° in $CHCl_3$ (*anilide*, m.p. 105—108°). The CO_2H group of (III) is derived from C_1 of cholesterol [the numbering is that of Wieland and Dane (following abstract)], which must, therefore, exist as CH_2. The velocity of esterification of (III) with $Bu^{\beta}OH$ at 155° is much smaller than of (I) or (II); (III) eliminates CO_2 extremely readily when treated with conc. H_2SO_4. These facts indicate that (III) contains the $>CMe{\cdot}CO_2H$ group, thus supporting Wieland and Dane's structure (*loc. cit.*; cf. Rosenheim and King, this vol., 736). The acid $C_{27}H_{44}O_4$ (*Me* ester, m.p. 148—149°, $[\alpha]_D^{18}$ +44° in $CHCl_3$), formed as a by-product in the oxidation of cholestenone with $KMnO_4$ (Windaus, *loc. cit.*), probably contains the grouping (*A*). It is suggested [by E. DANE] that cholestenone [from which (I) is derived] is (*B*). H. B.

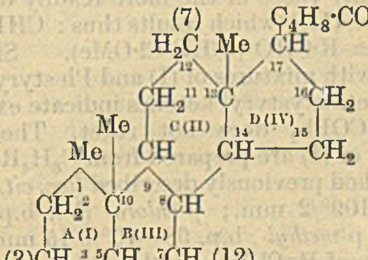


(*A.*)



(*B.*)

Constitution of bile acids. XXXIX. 12-Hydroxycholanic acid. H. WIELAND and E. DANE (Z. physiol. Chem., 1932, **210**, 268—281; cf. this vol., 614).—Hydrogenation of 7 : 12-diketocholanic acid (I) in AcOH in presence of PtO_2 gives *7-keto-12-hydroxycholanic acid* (II), m.p. 176° [semicarbazone (III)]. When heated at 170—175° with NaOEt (III) gives *12-hydroxycholanic acid* (IV), m.p. 96—102° (+H_2O), oxidised by CrO_3 in AcOH to *12-ketocholanic acid* (V), m.p. 148—150°. Oxidation of (V) with HNO_3 opens ring III and affords the tricarboxylic acid *thilobilianic acid*, m.p. 260—262° (decomp.) (*Me_3* ester, m.p. 109°), forming on vac. distillation the *anhydride*, m.p. 201°. Thermal decomp. of (IV) yields *apo*cholenic acid. Bromination of (V) gives *bromo-12-ketocholanic acid*, m.p. 178° (decomp.). Partial oxidation of 7 : 12-dihydroxycholanic acid with CrO_3 affords *12-keto-7-hydroxycholanic acid* (VI), m.p. 178° (+H_2O). Thermal decomp. of (VI) gave, not the 12-keto-acid, but the *lactone*, m.p. 217°, by linking of the OH with the CO_2H of the side-chain. An improved prep. of (I) is given.



(The typical C atoms 3, 7, and 12 are shown by parentheses.)

Since ring III of cholanic acid, although 6-membered, does not yield the 5-membered ketone, the Blanc rule does not hold and it is now unnecessary to suppose ring II is 5-membered. The most probable structure for cholanic acid now conforms to the chrysene structure (cf. Rosenheim and King, this vol., 736) with the exception of the 5-membered ring IV which is retained. J. H. B.

Bile acids. XXXVI. M. Schenck (Z. physiol. Chem., 1932, 211, 88—96; cf. this vol., 849).—In the inversion of the oximinoamino-acid (cf. A., 1931, 1293, and this vol., 742) a second *product*, m.p. 226° (decomp.), is obtained. Van Slyke determination indicates that it is a diamino-acid, but it has the same C val. as the original material. With HNO_3 at room temp. the blue NO-compound, $C_{24}H_{33}O_8N$ (A., 1928, 1007), gives a jelly-like intermediate product (possibly a ketonitrile acid) which is eventually transformed into biloidanic acid. J. H. B.

Ozone as an oxidation catalyst; ozonation of benzaldehyde. E. Briner, A. Demolis, and H. Paillard.—See this vol., 1095.

Basic properties of hydrazones. VI. R. Ciusa and G. Ottolino (Gazzetta, 1932, 62, 791—795).—Benzaldehyde- and *m*-nitrobenzaldehyde-phenylmethylhydrazones combine respectively with PhCHO in HCl to give *compounds* of m.p. 170° (I) (this vol., 51) and 169°, and respectively with *m*-nitrobenzaldehyde to give *compounds*, m.p. 177° and 181°. By-products of the prep. of (I) are the *carbinol*, $CPh(OH)(\cdot C_6H_4\cdot NMe\cdot N\colon CHPh)_2$, m.p. 111° [also obtained by treating (I) with EtOH and NH_3], and the corresponding *leuco-base*, m.p. 136°; the substance of m.p. 155° (A., 1922, i, 475), also formed, is now regarded as benzylidene-*pp'*-dimethyldihydrazinotriphenylmethane, $C_{28}H_{28}N_4$. E. W. W.

Distyryl ketone and triphenylmethane. XV. Thermal decomposition of α-alkoxyalkyl chlorides. F. Straus and H.-J. Weber (Annalen, 1932, 498, 101—128).—Thermal decomp. of α-methoxybenzyl chloride (I) (this vol., 383) into PhCHO and MeCl is best accomplished at 120°; the time of half change is 34 min. (mean val.). α-Methoxycinnamyl chloride (II) and α-chlorodiphenylmethyl Me ether (III) decompose more readily than (I); the ratio of the times of half change at 100° is (III) : (II) : (I)= 1 : 6·8 : 75. Mixtures of (I) and cinnamaldehyde and of (II) and PhCHO show times of half change which are essentially those of the more readily decomposed chloride [*i.e.*, (II)] (which results thus: $CHRCl\cdot OMe+R'\cdot CHO \rightleftharpoons R\cdot CHO+CHR'Cl\cdot OMe$). Similar experiments with mixtures of (I) and Ph styryl, distyryl, and di-*p*-methoxystyryl ketones indicate exchanges of radicals; $COPh_2$ does not react. The following derivatives of (I) are prepared from $C_6H_4R\cdot CH(OMe)_2$ by the method previously described (*loc. cit.*): p-*nitro*- (IV), b.p. 109°/2 mm.; p-*chloro*- (V), b.p. 80—82°/0·15 mm.; p-*methyl*-, b.p. 68—70°/0·15 mm. (*complex* with 4 mols. of $HgCl_2$); p-*methoxy*- (*complex*, decomp. 90°, with 2 mols. of $HgCl_2$). The ratio of the times of half change at 120° compared with (I)=1 is (in the order quoted) 10·8 (calc. from Δ10°) : 2·8 : 0·41 : 0·03 (calc. from Δ10°); decomp. is facilitated by increase in the polarity of the C·Cl linking and the positivity of the Me-C atom. These results are compared with the degrees of dissociation of *p*-$C_6H_4R\cdot CPh_2Cl$ (Ziegler and Wollschitt, A., 1930, 545) and the velocities of hydrolysis of *p*-$C_6H_4R\cdot CH_2Cl$ (Olivier). p-*Chloro*-, b.p. 114—115°/19 mm., and p-*methyl*-, b.p. 99—100°/15 mm., -*benzaldehyde dimethylacetals* are new. An equilibrium mixture of (I) and (IV) is obtained from (I) and *p*-$NO_2\cdot C_6H_4\cdot CHO$ or from (IV) and PhCHO.

The rate of decomp. of (I) is accelerated by addition of PhCHO [max. at about 2 mols. per mol. of (I)], $C_2H_4Cl_2$, PhCN, and $PhNO_2$, and decreased by PhBr, $C_6H_4Me_2$, and di*iso*amyl ether (in this case, 19% of HCl is evolved with MeCl and a Cl-containing residue is obtained); PhOMe also causes acceleration, but the residue contains 10·4% Cl. Similar results are observed with (II), (IV), and (V). The effect of the solvent is proportional to its polarisability. $CHPh(OEt)_2$ and AcCl give (cf. *loc. cit.*) *α-ethoxybenzyl chloride*, b.p. 52—54°/0·05 mm., the time of half change of which at 120° is 70 min. *α-Methoxybenzyl bromide* [from $CHPh(OMe)_2$ and AcBr at 0°] and its p-*NO_2*-derivative, m.p. 59—60°, decompose much more readily than the corresponding chlorides.

[By N. Stancovici.] The *dimethylacetal*, b.p. 112° (corr.), of PrCHO (VI) with AcCl and a trace of Cu-bronze at 65—70° gives *α-methoxy*-n-*butyl chloride*, b.p. 29°/12 mm., converted by NaOEt into the *methylethylacetal*, b.p. 134—135° (corr.), of (VI) and decomp. at 110° to MeCl (20—25%), HCl (30%), and a Cl-containing residue (=about 50% Cl). *α-Ethoxy*-n-*butyl chloride*, b.p. 47° (corr.)/12 mm., is similarly prepared from the *diethylacetal*, b.p. 142·5—143·5° (corr.), of (VI). $CMe_2(OMe)_2$ and PCl_3 below 0° give *β-chloro-β-methoxypropane*, b.p. 14—15°/88 mm., which decomposes readily at 40° to MeCl (60%) and HCl (40%). H. B.

Chemistry of pine wood. P. Klason (Svensk Kem. Tidskr., 1932, 44, 177—188).—A discussion of the chemical constituents of pine wood. Lignin prepared from this by Freudenberg's method (cf. A., 1929, 1046) gives a naphthylamine salt, and consequently the latter's assumption that the aliphatic part of lignin is composed of one or more alcohol groups linked together is incorrect; at least half of Freudenberg's lignin must have contained an aldehyde group, which reacted with the naphthylamine. H. F. H.

Reactions catalysed by aluminium chloride. IV. Experiments with poisoned catalysts. C. D. Nenitzescu and I. P. Cantuniari (Ber., 1932, 65, [*B*], 1449—1453; cf. this vol., 744).—The formation of 2-acetyl-1-methyl-Δ^1-*cyclo*pentene (I), in addition to the saturated ketones, from *cyclo*hexane, AcCl, and $AlCl_3$ (cf. Unger, this vol., 514) is due to the presence of H_2O in the $AlCl_3$. Other substances which yield mol. compounds with $AlCl_3$ ($POCl_3$, $PhNO_2$, COPhMe, $COMe_2$) behave similarly. In presence of $COMe_2$, nearly homogeneous (I) is obtained. The production of MeCHO during the interaction of *cyclo*hexane, AcCl, and poisoned $AlCl_3$ is established, whereas only traces of the hydrocarbon $C_{12}H_{22}$ are produced; H for the reduction of AcCl is derived from the saturated ketone. 2-Acetyl-1-methyl*cyclo*pentane is not affected by BzCl and $AlCl_3$

suspended in *cyclo*hexane, but behaves as a catalyst poison; the production of PhCHO is accompanied by that of an equiv. amount of $C_{12}H_{22}$. $POCl_3$, $COMe_2$, PhNO, or COPhMe diminishes the activity of $AlCl_3$ so greatly that reaction is scarcely induced between *cyclo*hexane and BzCl. *n*-Hexane reacts with AcCl and $AlCl_3$ similarly to *cyclo*hexane, yielding *Me* n-*hexyl ketone*, b.p. 154—155° (*semicarbazone*, m.p. 120°), and *Me* n-*hexenyl ketone*, b.p. 177—178° (*semicarbazone*, m.p. 220°); the production of MeCHO is established. 1-Methyl-Δ^1-*cyclo*pentene, AcCl, and $AlCl_3$ in CS_2 afford 2-acetyl-1-methyl-Δ^1-*cyclo*pentene. H. W.

Stereoisomerism of alicyclic oximes. W. Hückel and M. Sachs (Annalen, 1932, 498, 166—184).—The oxime of *trans*-2-ketodecahydronaphthalene (*trans*-β-decalone) exists in inactive stereoisomeric *forms*, m.p. 99° (I) and 91° (II). These are obtained by hydrolysis of their respective *Bz* derivatives, m.p. 108—110° (III) and 87°, which are separable by fractional crystallisation of the product (*A*) obtained by benzoylation (pyridine method) of the oxime, m.p. 76°, previously described (A., 1925, i, 258). (I) and (II) are converted into the same mixture, m.p. about 63°, by long heating above their m.p. (III) is a racemate; suitable crystallisation of (*A*) gives also a *Bz* derivative, m.p. 135°, $[\alpha]_D^{18}$ ±100° in Et_2O, hydrolysed to the *oxime*, m.p. 87—88°, $[\alpha]_D^{18}$ +62·7° in Et_2O, which exhibits mutarotation. Fenchoneoxime (from *d*-fenchone) (cf. Wallach, A., 1908, i, 809), in which the C atoms adjacent to the oxime group are not attached to H [hence tautomerism is excluded (cf. Raikowa, A., 1929, 911)], also exists in stereoisomeric *forms*, m.p. 167°, $[\alpha]_D^{20}$ +46·5° in 96% EtOH (*Bz* derivative, m.p. 81°, $[\alpha]_D^{20}$ +49° in 96% EtOH), and m.p. 123°, $[\alpha]_D^{17\cdot7}$ +148° in 96% EtOH (*Bz* derivative, m.p. 125°, $[\alpha]_D^{20}$ +128·5° in 96% EtOH); the latter rearranges into the former when heated, but the Bz derivatives are stable. Similarly, *d*-3-methyl*cyclo*hexanoneoxime (Wallach, A., 1904, i, 754) exists in stereoisomeric *forms*, m.p. 60°, $[\alpha]_D^{21\cdot5}$ +3·6° in EtOH (*Bz* derivative, m.p. 99°, $[\alpha]_D^{20\cdot4}$ +22·9° in Et_2O), and m.p. 47°, $[\alpha]_D^{21\cdot5}$ −88·5° in EtOH (*Bz* derivative, m.p. 82—83°, $[\alpha]_D^{20\cdot8}$ −86·2° in Et_2O). The existence of the above stereoisomeric oximes (structural isomerism is excluded by their reactions) disproves the theory of Raikowa (*loc. cit.*). The vol. and polarisability of substituents affect the stability of oximes; various cases are briefly discussed.

A second isomeride of the following could not be isolated: *cis*- (*Bz* derivative, m.p. 114°) and *trans*- (*Bz* derivative, m.p. 138°) -α-decaloneoximes; α-tetraloneoxime (*Bz* derivative, m.p. 125°); α-hydrindoneoxime (*Bz* derivative, m.p. 133°); 2-*cyclo*pentyl*cyclo*pentanoneoxime (*Bz* derivative, m.p. 70°); *cyclo*hexanoneoxime (*Bz* derivative, m.p. 63—64°). Contrary to the previous statement (A., 1925, i, 258), *cis*-α-decalone (*oxime*, m.p. 103°) is not converted into the *trans*-form when treated with NH_2OH,HCl and NaOAc. H. B.

Action of acetyl chloride on *m*-chlorotoluene. F. Mayer, H. Albert, and K. Schön (Ber., 1932, 65, [*B*], 1295—1299; cf. Borsche and others, A., 1917, i, 15).—Condensation of *m*-chlorotoluene with AcCl in presence of $AlCl_3$ and CS_2 gives a mixture of ketones, b.p. 118—127°/14 mm., oxidised to chloroterephthalic and 4-chlorophthalic acid. The mixture yields a *semicarbazone*, m.p. 208—210°, from which 3-chloro-6-acetyltoluene (I) is isolated. Condensation of Et sodioacetoacetate with 3-chloro-*o*-toluoyl chloride and hydrolysis of the product with H_2SO_4–EtOH gives (I), b.p. 120—122°/14 mm., nitrated to 3-*chloro*-4-*nitro*-6-*acetyltoluene*, m.p. 75—76° (*semicarbazone*, m.p. 221—223°), identical with the product obtained by nitration of the ketone mixture (see above). 3-*Chloro*-4-*acetyltoluene*, b.p. 120—126°/14 mm. (*semicarbazone*, m.p. 192°), derived from Et sodioacetoacetate and 3-chloro-*p*-toluoyl chloride, is nitrated to 3-*chloro*-6-*nitro*-4-*acetyltoluene*, m.p. 47—48° (*semicarbazone*, m.p. 228—230°). The Ac group enters *m*-chlorotoluene mainly in the *para* position to Cl, but it is possible that the quality of the $AlCl_3$ may affect the result. H. W.

Synthesis of 5-ψ-cumylacetone. B. Holmberg (Ber., 1932, 65, [*B*], 1348—1349).—5-ψ-Cumylacetic acid and PCl_5 yield the corresponding *chloride*, b.p. 100—102°/0·8 mm., m.p. 40—42°, transformed in Et_2O by aq. $NHMe_2$ into the *dimethylamide*, m.p. 79·5—80·5°, from which 5-ψ-cumylacetone, m.p. 69—70°, is obtained by aid of MgMeI. The ketone is identical with that obtained from conifer distillates (cf. A., 1923, i, 226; B., 1929, 158). H. W.

Mechanism of the pinacol synthesis by the system $Mg+MgI_2$. E. Bergmann (J. Amer. Chem. Soc., 1932, 54, 3773—3774).—A reply to Bachmann (this vol., 737). C. J. W. (*b*)

Reduction of ketones by magnesium+magnesium iodide and by sodium. W. E. Bachmann (J. Amer. Chem. Soc., 1932, 54, 3774—3775).—A reply to Bergmann (preceding abstract; cf. A., 1931, 1059). The products obtained by addition of Na to aromatic ketones are not radicals existing in the unimol. state but consist for the most part of the bimol. form, viz., Na pinacolate. C. J. W. (*b*)

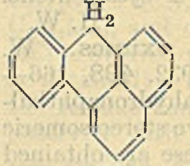
Haloform reaction. VI. α-Halogen derivatives of hindered ketones. C. H. Fisher, H. R. Snyder, and R. C. Fuson (J. Amer. Chem. Soc., 1932, 54, 3665—3674; cf. this vol., 514).—αα-Dibromoacetylmesitylene is converted by dil. NaOBr into the ααα-Br_3-derivative. α-Bromopropionyl chloride, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 give 55·5% of α-*bromopropionylmesitylene* (I), b.p. 174—176°/31 mm. [3 : 5-$(NO_2)_2$-derivative (II), m.p. 148·5—149°]. Propionylmesitylene and NaOBr give an oil, which on nitration yields αα-*dibromo*-3 : 5-*dinitropropionylmesitylene*, m.p. 99—99·5°, also obtained from (I) and NaOBr, followed by nitration, or from (II) and NaOBr. Bromination and subsequent nitration of *iso*butyrylmesitylene gives the α-bromo-3 : 5-dinitro-derivative, m.p. 124·5—125·5°, also obtained by bromination of 3 : 5-dinitro-*iso*butyrylmesitylene. 3 : 5-Dibromo*iso*butyrylmesitylene and NaOBr give the α : 3 : 5-Br_3-derivative (III), m.p. 104—106°. Di-β-*iso*duryloylmethane and Br or NaOBr give the *bromomethane* (IV), m.p. 163·5—164°, converted by NaOBr into the *dibromomethane* (V), m.p. 136—136·5°; Cl_2 in CCl_4 gives the *chloromethane* (VI), m.p. 157·5—158°, whilst NaOCl gives the *dichloromethane* (VII), m.p. 104—104·5°. Cleavage with alkali is effected only in the case of ααα-tribromomesitylene. In some cases the alkali acts as a dehalogenating agent; thus, (V) gives 41% of (IV) and (VII) affords 54% of (VI). These compounds are also dehalogenated by PhOH, *p*-halogenophenols being formed. Thus, ααα-tribromoacetylmesitylene and PhOH at 100° give the αα-Br_2-derivative (60%) and *p*-$C_6H_4Br{\cdot}OH$; (V) and PhOH give 47% of (IV). Dehalogenation is also effected by the Grignard reagent; this reaction involves an interchange of radicals. ααα-Tribromoacetylmesitylene and MgEtBr give 68·7% of αα-dibromoacetylmesitylene, m.p. 73—74°, converted by MgEtBr into α-bromoacetylmesitylene, which with MgEtBr gives acetylmesitylene. ααα-Trichloroacetylmesitylene and MgPhBr give 46% of the αα-Cl_2-derivative. α-Chloroacetylmesitylene does not react with MgEtBr. (III) and MgBuBr give the 3 : 5-Br_2-derivative; BuBr is formed in 57·6% yield. Mg amyl bromide behaves similarly, as do MgPhBr and *p*-$C_6H_4Me{\cdot}MgBr$; the corresponding alkyl or aryl bromide is obtained in 60—70% yield.

C. J. W. (*b*)

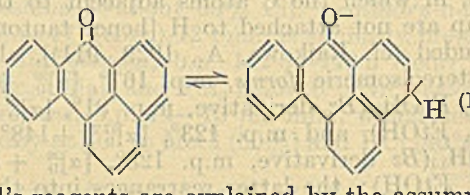
Carbon rings. XIX. 16-Membered *m*- and *p*-benzopolymethylene rings. L. Ruzicka, J. B. Buijs, and M. Stoll (Helv. Chim. Acta, 1932, 15, 1220—1226; cf. this vol., 253).—ζζ′-m-*Phenylenedihexyl ketone* (I), *m*-$C_6H_4{<}^{[CH_2]_6}_{[CH_2]_6}{>}CO$, is obtained from the appropriate dibasic acid, but εε′-*p*-phenylenediamyl ketone could not be prepared by the analogous reaction. The constitution of the ketone (A., 1931, 1290) from ω-*p*-carboxymethylphenylundecoic acid is doubtful, (*a*) because the acid (improved prep.) is not homogeneous, yielding with $KMnO_4$ terephthalic and (probably) a little phthalic acid, and (*b*) because it is not proved whether $CH_2Ph{\cdot}CO_2H$ adds on to the ι- or κ-C atom of Δι-undecenoic acid. Terephthalaldehyde (modified prep.) and malonic acid give *p*-phenylenediacrylic acid, converted by PCl_5 into the acid chloride and thence into the *Me_2* ester, m.p. 167—168°, which with Na and EtOH affords γγ′-p-*phenylenedipropyl alcohol*, m.p. 55°, b.p. 178—180°/1 mm. This with dry HBr yelds the *dibromide*, b.p. 158—162°/1 mm., which by the malonic ester synthesis gives *Et_2* δδ′-p-*phenylenedi*-n-*valerate*, b.p. about 195°/0·4 mm. This led to εε′-p-*phenylenedi*-n-*amyl alcohol*, m.p. 46—47°, b.p. 200—205°/1 mm., which by the cyanide synthesis gives εε′-p-*phenylenedi*-n-*hexoic acid*, m.p. 124—125°. *iso*Phthalaldehyde (modified prep.) led by similar reactions to *Me_2* ββ′-m-*phenylenediacrylate*, m.p. 133°, γγ′-m-*phenylenedipropyl alcohol*, b.p. 165—168°/0·2 mm., the corresponding *dibromide*, b.p. 165—168°/0·2 mm., *Et_2* εε′-m-*phenylenedi*-n-*valerate*, b.p. 185—187°/0·3 mm., εε′-m-*phenylenedi*-n-*amyl alcohol*, b.p. 192—195°/0·3 mm., and *Me_2* ζζ′-m-*phenylenedi*-n-*heptoate* (II), b.p. 207—210°/0·3 mm. The *Ce* salt of the acid from (II) at 400—450° gives an oil, whence (I), b.p. about 205°/0·8 mm. (*semicarbazone*, m.p. 153—155°), was isolated in 2% yield. *m*-Xylylene dibromide and KCN give m-*xylylene dicyanide*, m.p. 27°, b.p. 228—233°/30 mm., which led to *Et_2* m-*phenylenediacetate*, b.p. 190—195°/17 mm., and, in very poor yield, ββ′-m-*phenylenediethyl alcohol*.

R. S. C.

Polynuclear hydrocarbons. XVI. Constitution of benzanthrone and its reduction products. E. Clar and F. Furnari (Ber., 1932, 65, [*B*], 1420—1425; cf. Scholl and others, A., 1911, i, 626, 677).—Benzanthrene, m.p. 81—82°, readily prepared by distillation of 9-hydroxy-1 : 10-trimethylenephenanthrene with Zn dust, is colourless, insensitive to air in the dark, slowly discoloured by exposure to direct sunlight, and not oxidised to benzanthrone (I) by exposure to air (contrast Scholl, *loc. cit.*). The close resemblance of its extinction curve to that of 1-benzylnaphthalene suggests the constitution (II). 1 : 10-Trimethylenephenanthrene (Scholl's dihydrobenzanthrene), preparable by treating (I) with P and HI, is colourless when solid or dissolved, insensitive to air, and becomes brownish-yellow when exposed to sunlight without apparent production of (I). Its extinction curve shows marked phenanthrene characteristics. It does not react with maleic anhydride in boiling xylene. Reduction of benzanthrone with Zn dust and NaOH, alkaline $Na_2S_2O_4$, or Zn, AcOH, and HCl yields 9-hydroxy-1 : 10-trimethylenephenanthrene, which slowly darkens when exposed to light, but is not converted in alkaline solution into (I) by air. It appears identical with the 1 : 9-trimethyleneanthran-9-ol of von Braun and Bayer (A., 1926, 172). The ready reduction of (I) and its behaviour towards Grignard's reagents are explained by the assumption of an equilibrium (III).



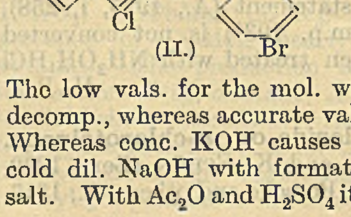
(II.)



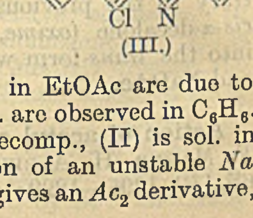
(III.)

H. W.

So-called 2 : 3-quinone of 1-methylnaphthalene. K. Fries and K. Schimmelschmidt (Ber., 1932, 65, [*B*], 1502—1507; cf. A., 1909, i, 809).—6-Bromo-3-nitro-1-methyl-1 : 2-naphthaquinol in AcOH is reduced by Cu–Zn dust and HCl and the product is transformed by Cl_2 in AcOH into 1 : 4 : 4-trichloro-6-bromo-2 : 3-diketo-1-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, reduced by Zn dust and AcOH to 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene (I), m.p. 184°. Treatment of the Pb salt of (I) with I in $CHCl_3$ yields "4-chloro-6-bromo-1-methyl-2 : 3-naphthaquinone" (*loc. cit.*), to which the structure (II) is assigned for the following reasons.



(II.)



(III.)

The low vals. for the mol. wt. in EtOAc are due to decomp., whereas accurate vals. are observed in C_6H_6. Whereas conc. KOH causes decomp., (II) is sol. in cold dil. NaOH with formation of an unstable *Na* salt. With Ac_2O and H_2SO_4 it gives an *Ac_2* derivative, m.p. 237°. It affords the naphthophenazine (III). (II) is smoothly reduced by Zn dust in boiling AcOH to the initial material. With NHPh·NH$_2$ (II) suffers fission with production of the *monohydrazone* $C_{11}H_7OClBr:N_2Ph$, from one portion of the mol.

Repeated failure to obtain naphtha-2 : 3-quinone or its derivatives leads to the conclusion that only Erlenmeyer's formulation of $C_{10}H_8$ is satisfactory.

H. W.

Anthracene derivatives. VIII. E. de B. Barnett (Ber., 1932, 65, [*B*], 1301—1304).—Condensation of 3 : 6-dichlorophthalic acid with *p*-xylene in presence of AlCl$_3$ and tetrachloroethane leads through the corresponding phthaloyl acid to 5 : 8-*dichloro*-1 : 4-*dimethylanthraquinone* (I), not molten below 310°, which scarcely becomes coloured when treated with NaOH, NH$_3$, and Zn or Na$_2$S$_2$O$_4$, but is reduced by Al and conc. H$_2$SO$_4$ to 5 : 8-*dichloro*-1 : 4-*dimethylanthrone* (II), m.p. 221° after softening, from which 5 : 8-*dichloro*-1 : 4-*dimethylanthranyl acetate*, m.p. 220°, is obtained by means of Ac$_2$O and C$_5$H$_5$N at 100°. (II) is reduced by Zn dust and KOH to 5 : 8-*dichloro*-1 : 4-*dimethylanthracene*, m.p. 230°, which yields 5 : 8-*dichloro*-9 : 10-*dibromo*-1 : 4-*dimethyl*-9 : 10-*dihydroanthracene*, decomp. 170°, with Br in CS$_2$. (II) and Br in CS$_2$ slowly afford 5 : 8-*dichloro*-10-*bromo*-1 : 4-*dimethylanthrone*, decomp. 210—220°, whence the corresponding -10-*anilino*-, m.p. 195°, -10-*piperidino*-, m.p. 225°, -10-*methoxy*- m.p. 181°, -10-*phenyl*-, m.p. 224°, and -10-benzyl-, m.p. 179° after softening, compounds. 1 : 4-*Dichloro*-10-*methoxyanthrone*, m.p. 114°, is obtained from 1 : 4-dichloro-10-bromoanthrone, MeOH, and CaCO$_3$. H. W.

Specific oxidising agents in the preparation of aminoanthraquinones. K. Lauer (J. pr. Chem., 1932, [ii], 135, 7—14).—A study of the effect of addition of various oxidising agents on the yield and purity (using technical methods of isolation) of aminoanthraquinones prepared by the reaction :

$C_{14}H_7O_2 \cdot SO_3H + NH_2R = C_{14}H_7O_2 \cdot NHR + H_2SO_3$.

The purity of the product is evaluated in terms of the yield and purity (shade) of a derived dye. The three oxidising agents in order of val. which give the best results in individual cases are as follow : 1-NH$_2$ [*m*-nitrobenzenesulphonic acid (I), MnO$_2$, KBrO$_3$]; 2-NH$_2$ [K$_2$Cr$_2$O$_7$+NH$_4$Cl (II), Na$_2$HAsO$_4$, MnO$_2$, (I)]; 1 : 5-(NH$_2$)$_2$ [MnO$_2$, (I), Na$_2$HAsO$_4$]; 2 : 6-(NH$_2$)$_2$ [Na$_2$HAsO$_4$, MnO$_2$, (II)]: 1-NHMe [KBrO$_3$, (I), MnO$_2$]; 1 : 5-(NHMe)$_2$ [(I), KBrO$_3$, MnO$_2$]. K$_2$Cr$_2$O$_7$ alone, KClO$_3$, and KNO$_3$ are not beneficial, and are often harmful. H. A. P.

1 : 4-Dihydroxy-compounds of 2-acetylanthraquinone from 4-acetylphthalic acid. F. Mayer, O. Stark, and K. Schön (Ber., 1932, 65, [*B*], 1333—1337).—PhCl is transformed by AcCl in presence of AlCl$_3$ and CS$_2$ into *p*-chloroacetophenone, b.p. 108—111°/13 mm., converted by HNO$_3$–H$_2$SO$_4$ at −12° into 4-*chloro*-3-*nitroacetophenone* (I), m.p. 104° (*semicarbazone*, m.p. 256—257°) and a little 4-chloro-3-nitrobenzoic acid, m.p. 181°. (I) is converted by NH$_3$ in presence of C$_6$H$_6$ and H$_2$O at 150° into 3-*nitro*-4-*aminoacetophenone*, m.p. 153—154° (*Ac* derivative, m.p. 140—141°), transformed by diazotisation and treatment with CuSO$_4$ and NaCN into 3-*nitro*-4-*cyanoacetophenone* (II), m.p. 115°, which with dil. AcOH and Fe filings yields 2-*amino*-4-*acetylbenzamide*, m.p. 203—204°, hydrolysed by KOH–H$_2$O to 2-*amino*-4-*acetylbenzoic acid*, m.p. 236°. The *Me* ester, m.p. 121°, is obtained in unusually poor yield by means of MeOH–HCl. 2-*Hydroxy*-4-*acetylbenzoic acid*, m.p. 197° (*Ac* derivative, m.p. 118°), is described. (II) is hydrolysed by boiling 55% H$_2$SO$_4$ to 2-*nitro*-4-*acetylbenzoic acid*, m.p. 178—179°, the *Me* ester, b.p. 211—214°/22 mm., m.p. 58°, of which is reduced to *Me* 2-*amino*-4-*acetylbenzoate* (III). Diazotisation of (III) followed by treatment with NH$_3$, CuSO$_4$, and NaCN leads to *Me* 2-*cyano*-4-*acetylbenzoate*, m.p. 109—110°, hydrolysed by boiling conc. HCl to 4-*acetylphthalic acid* (II), m.p. 210—211° (*anhydride*, m.p. 107—110°; *imide*, m.p. 220—223°); the yield is 13% (calc. on PhCl). Quinol, (IV), NaCl, and AlCl$_3$ at 160—190° afford 5 : 8-*dihydroxy*-2-*acetylanthraquinone*, m.p. 202—203° (*Ac* derivative, m.p. 180—181°). Similarly, 5 : 8-*dihydroxy*-2-*acetyl*-6(or 7)-*methylanthraquinone*, m.p. 188—200° (Ac$_2$ derivative), and 5 : 8-*dihydroxy*-2-*acetyl*-6 : 7-*benzanthraquinone*, m.p. 230—250°, are derived from toluquinol and naphthaquinol, respectively. H. W.

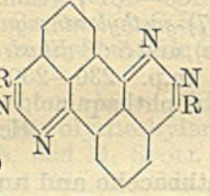
Ketonic derivatives of anthracene and anthraquinone. H. de Diesbach, H. Lempen, and H. Benz (Helv. Chim. Acta, 1932, 15, 1241—1250).—The preps. of anthraquinone-2-carboxylic (I), 1- and 3-chloroanthraquinone-2-carboxylic acid (II) and (III) are modified. The acid chloride of (I), anthracene, and AlCl$_3$ in C$_6$H$_3$Cl$_3$ at 100° give 9-*anthracyl* 2-*anthraquinonyl ketone* (IV), m.p. 242—244° (decomp.), 2-*anthracyl* 2-*anthraquinonyl ketone* (V), m.p. 297°, and *substances* (VI) and (VII), $C_{29}H_{16}O_4$, m.p. about 323° (decomp.) (giving in H$_2$SO$_4$ violet and pale green colours, respectively). The constitution of (IV) is proved by oxidation by CrO$_3$ to anthraquinone and (I), and that of (V) by synthesis. (VI) slowly changes into (VII) when kept, and more of (VI) and (VII) is formed at the expense of (IV) if the Friedel–Crafts reaction be prolonged. (VII) is probably ?-*hydroxy*-9-*anthracyl* 2-*anthraquinonyl ketone*, since when oxidised it yields (I) only. (VI) possibly contains a OH group in the anthraquinone nucleus, since in one experiment oxidation afforded a hydroxyanthraquinonecarboxylic acid. (II) gives similarly 9-*anthracyl* 1-*chloro*-2-*anthraquinonyl ketone*, m.p. 263—264° [oxidised to anthraquinone and (II)], 2-*anthracyl* 1-*chloro*-2-*anthraquinonyl ketone*, m.p. 277°, and a *substance* (possibly containing a OH group), which is oxidised to (II) only. (III) yields similarly 9-*anthracyl* 3-*chloro*-2-*anthraquinonyl ketone*, m.p. 232°, 2-*anthracyl* 3-*chloro*-2-*anthraquinonyl ketone*, m.p. 263°, and another substance. 3 : 3′-Diamino-4 : 4′-dimethylbenzophenone (modified prep.) affords (Sandmeyer) 3 : 3′-*dicyano*-4 : 4′-*dimethylbenzophenone*, m.p. 172°, hydrolysed to the corresponding *dicarboxylic acid*, m.p. 308°, the chloride of which with AlCl$_3$ and C$_6$H$_6$ at 100° gives 3 : 3′-*dibenzoyl*-4 : 4′-*dimethylbenzophenone*, m.p. 127—128°. This with Cl$_2$ in C$_6$H$_3$Cl$_3$ at 180° gives *di*-9 : 9-*dichloro*-2-*anthranyl ketone*, m.p. 212—215°, rapidly changed to (V) by H$_2$SO$_4$ at 100°.

R. S. C.

2 : 2′-Dianthraquinonyl ketone. F. Mayer and O. Hoffmann (Ber., 1932, 65, [*B*], 1338).—3 : 3′-Dinitro-4 : 4′-diaminobenzophenone is transformed into benzophenone-3 : 3′ : 4 : 4′-tetracarboxylic anhydride (I), which is condensed with $2C_6H_6$; the product is transformed by H_2SO_4 into 2 : 2′-*dianthraquinonyl ketone*, m.p. 300—301°. (I) and quinol in presence of $AlCl_3$–NaCl afford 5 : 8 : 5′ : 8′-*tetrahydroxy*-2 : 2′-*dianthraquinonyl ketone*, m.p. 350°.

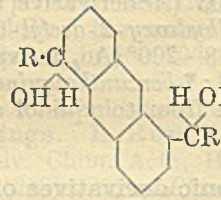
H. W.

Syntheses in the field of *trans-bisang*-diphthalylanthraquinone. R. Scholl and K. Meyer [with H. von Hoessle and F. Renner] (Ber., 1932, 65, [*B*], 1396—1406; cf. A., 1929, 190).—1 : 5-Di-*m*-xyloylanthraquinone is oxidised by dil. HNO_3 at 180—190° to 1 : 5-*dibenzoylanthraquinone*-2′ : 4′ : 2″ : 4″-*tetracarboxylic acid* (I) (corresponding *quinol* derivative), converted by N_2H_4,H_2O into the *di*-o-*diazinetetracarboxylic acid* (II). (I) is reduced by Zn, NaOH, and $CuSO_4$–NH_3 at 120° or by Zn and NaOH at 200° to a mixture of the *carbinoltetracarboxylic acids* (III) and (IV). (III) and boiling $POCl_3$ yield the corresponding *dilactone*. (IV) is converted by boiling Ac_2O containing HI through 1 : 5-*dibenzyl*-9 : 10-*dihydroanthracene*-2′ : 4′ : 2″ : 4″-*tetracarboxylic acid* into the mixed *anhydride* (V), transformed by moist C_5H_5N or boiling conc. HCl into the *diacetyldicarboxylic acid* (VI), by hot dil. NaOH into the *anthranolcarboxylic acid* (VII), and by moderately conc. HCl at 220° into the *anthronecarboxylic acid* (VIII), not attacked by P and HI at 240—250°. Oxidation of (V), (VI), (VII), or (VIII) with CrO_3 in boiling AcOH followed by CrO_3 in dil. H_2SO_4 or HNO_3 at 210° leads to 1 : 2 : 5 : 6-*diphthalylanthraquinone*-4 : 4′-*dicarboxylic acid* (corresponding *bis*-o-*diazine*, $C_{32}H_{12}O_6N_4$, and its *sulphate*). 2′ : 3′ : 2″ : 3″-*Dinaphtho*-1 : 2 : 5 : 6-*anthracene* (IX) is prepared by reduction of *trans-bisang*-diphthalylanthraquinone with P and HI at 220° and dehydrogenation of the hexahydro-compound thus obtained by sublimation with Cu powder in CO_2 at 460°/vac. or by reduction and decarboxylation of (VIII) by distillation with Zn dust in CO_2 at 500°/20 mm.



(II.)

[$R=C_6H_3(CO_2H)_2$]



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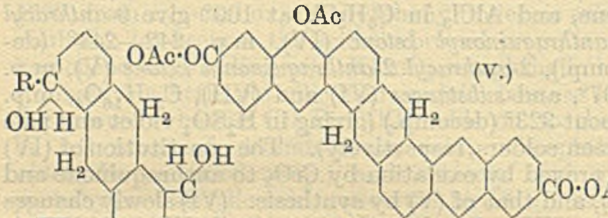
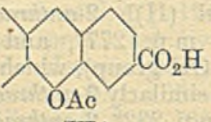


(IV.)

(V.)



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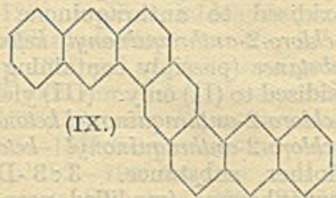

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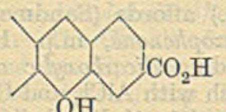
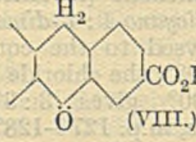


(VII.)



(VIII.)

Anthracene-1 : 5-dicarboxylic acid is converted by successive treatments with PCl_5 and $FeCl_3$ in *m*-xylene into *di*-m-*xyloylanthracene*, m.p. 214°, oxidised by CrO_3 in AcOH to di-*m*-xyloylanthraquinone and passing when distilled into 6′ : 6″-*dimethyl*-2′ : 3′ : 2″ : 3″-*dinaphtho*-1 : 2 : 5 : 6-*anthracene*, readily oxidised to the corresponding quinone.

The following compounds are incidentally described: 2 : 6-*di*-m-*xyloylanthraquinone*, m.p. 256°, from the 2 : 6-dicarboxylic acid, *m*-xylene, and $AlCl_3$; 1 : 5-*dichloro*-2 : 6-*dimethylanthraquinone*, m.p. 295°, from 2 : 6-dimethylanthraquinone, I, and SO_2Cl_2 in $PhNO_2$; oxidised by HNO_3 (*d* 1·1) at 200—220° to 1 : 5-*dichloroanthraquinone*-2 : 6-*dicarboxylic acid*, m.p. 320—330° (decomp.); 2 : 6-*dimethylanthraquinone*-1-*carboxylic acid*, m.p. 234°, from dimethylbenzanthrone.

H. W.

Rearrangements in the condensation of methylated derivatives of *o*-α-naphthoylbenzoic acid. L. F. Fieser and M. A. Peters (J. Amer. Chem. Soc., 1932, 54, 3742—3751).—*o*-2-Methyl-α-naphthoylbenzoic acid (I) heated with NaCl–$AlCl_3$ gives a mixture of 2′- and 3′-methyl-1 : 2-benzanthraquinones, necessitating the migration of the phthalic acid residue to a β-position of the originally unsubstituted ring. The following alkyl derivatives of *o*-α-naphthoylbenzoic acid are prepared: 2′ : 6′-Me_2, m.p. 238° (*Me* ester, m.p. 162°); 2′ : 7′-Me_2, m.p. 210° (*Me* ester, m.p. 131°); 2′ : 3′-Me_2, m.p. 205° (*Me* ester, m.p. 170°; *Et* ester, m.p. 165°). Oxidation of (I) gives diphthalylic acid, m.p. 277°, whilst reduction affords o-2-*methyl-α-naphthylmethylbenzoic acid*, m.p. 187°. The above *o*-dimethyl-α-naphthoylbenzoic acids are converted into 2′ : 4-, 3′ : 4-, and 2′ : 3′-*dimethyl*-1 : 2-*benzanthraquinones*, m.p. 190°, 195°, and 236°, respectively. 1 : 2′ : 3′-*Trimethyl*-2 : 3-*benzanthraquinone* has m.p. 275°. 1-*Benzoyl*-2 : 3-*dimethylnaphthalene*, m.p. 126°; 4-*methyl*-1 : 2-*benz*-9-*anthrone*, m.p. 150°; 4-*methyl*-1 : 2-*benzanthracene*, m.p. 107° (*picrate*, m.p. 119—120°), and 4-*methyl*-1 : 2-*benzanthraquinone*, m.p. 167° (*quinol diacetate*, m.p. 220°), are also described.

C. J. W. (*b*)

Dibenzanthraquinones. H. Waldmann (J. pr. Chem., 1932, [ii], 135, 1—6).—Condensation of naphthalene-1 : 2-dicarboxylic anhydride with $C_{10}H_8$ under the influence of $AlCl_3$, and cyclisation of the product with P_2O_5 in $PhNO_2$ gives 1 : 2 : 5 : 6- (cf. A., 1918, i, 494) and 1 : 2 : 7 : 8-*dibenzanthraquinone* (I), m.p. 226°. The identity of (I) is proved as follows: *bis*-o-*nitrobenzylidene*-m-*phenylenediacetic acid*, m.p. 240° (from K *m*-phenylenediacetate and *o*-$NO_2·C_6H_4·CHO$ in Ac_2O), is reduced to the $(NH_2)_2$-compound, decomp. 140—150°, which is diazotised and treated with Cu; the dicarboxylic acid thus formed gives on decarboxylation 1 : 2 : 7 : 8-*dibenzanthracene*, m.p. 195—196°, which is oxidised to (I) by CrO_3–AcOH. Reduction of 5 : 8-dihydroxy-1 : 2 : 6 : 7-dibenzanthraquinone with HI at 160°, and oxidation of the resulting crude hydrocarbon with CrO_3–AcOH, gives, not the expected 1 : 2 : 6 : 7-dibenzanthraquinone, but 2 : 3-*phthaloylphenanthraquinone*, m.p. 318°.

H. A. P.

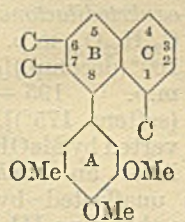
Manufacture of ketones [and vat dyes] of the anthraquinone series [from 5- and 8-nitroanthraquinone-2-carboxylic halides]. A. Carpmael. From I. G. Farbenind. A.-G.—See B., 1932, 879.

Yellow dyes of ergot. I. Ergoflavin. II. Ergochrysin. W. Bergmann (Ber., 1932, 65, [*B*], 1486—1488, 1489—1494).—I. The yellow dyes present in ergot vary in nature with different samples of material. Extraction of the residues from the technical prep. of the alkaloids with C_6H_6 causes dissolution of the greater part, but addition of light petroleum to the extract ppts. only amorphous, yellow material similar to that obtained by acidifying alkaline solutions of ergochrysin (cf. II). The undissolved portion when treated with Et_2O gives ergoflavin, $C_{15}H_{14}O_7$, m.p. 344° (cf. Freeborn, Proc. C.S., 1912, 71). It is converted by Ac_2O and C_5H_5N or boiling Ac_2O into the Ac_5 derivative, m.p. 244°. Contrary to Freeborn, it is converted by short boiling with dil. aq. KOH or KOH–EtOH into *ergoflavic acid*, $C_{15}H_{16}O_8$, m.p. above 340° after becoming yellow at 200°, which passes into ergoflavin when its aq. solution is boiled. The dye therefore contains 5 OH and one lactone group.

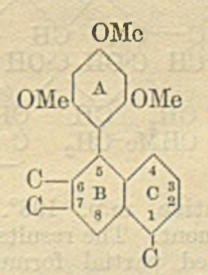
II. A second sample of technical residues (see above) was extracted with Et_2O, which dissolved ergosterol, and the residue was treated with $CHCl_3$ yielding ergochrysin (I), $C_{28}H_{28}O_{12}$, m.p. 266°, identical with Jacobi's product and sclerocrystallin of Dragendorff and Podwyssotzki. The secalonic acid of Kraft (A., 1906, i, 979) appears to be $C_{28}H_{28}O_{12},0{\cdot}5H_2O$ and is derived from ergochrysin by dissolution in warm C_5H_5N and addition of EtOH. (I) and boiling Ac_2O containing a little C_5H_5N yield the Ac_{10} derivative, m.p. 240°, in very small yield. Methylation of (I) does not give cryst. material. Distillation of (I) with Zn dust or, preferably, sand affords a *phenol*, $C_9H_{10}O_3$, m.p. 92° (Ac_1 derivative, m.p. 65°), in very poor yield. Aq. or alcoholic alkali converts (I) into amorphous, yellow, ill-defined substances, whereas molten KOH at 250—260° gives AcOH, $H_2C_2O_4$, 5-hydroxy-*m*-toluic acid, m.p. 208°, resorcinol, and 2 : 4 : 2′ : 4′-tetrahydroxydiphenyl (II), m.p. 224° (*Ac* derivative, m.p. 118°). It is improbable that (II) is formed from resorcinol during the fusion. Treatment of (I) with conc. HNO_3 at room temp. yields the *compound* $C_{16}H_{15}O_9N$, m.p. 260°.

H. W.

Constitution of podophyllotoxin and picropodophyllin. E. Späth, F. Wessely, and L. Kornfeld (Ber., 1932, 65, [*B*], 1536—1549).—The residue obtained from the $CHCl_3$ extract of *Podophyllinum indicum* is dissolved in EtOH and pptd. with C_6H_6. After crystallisation from dil. EtOH, podophyllotoxin (I), m.p. 117° (decomp.), is obtained, identical with the products of Dunstan and Henry (J.C.S., 1898, 73, 209) and Borsche (this vol., 618) and containing C_6H_6, H_2O, and, apparently, small and varying amounts of EtOH. When dried at 110°/high vac. and crystallised from aq. EtOH or $CHCl_3$–light petroleum it gives a *modification* (II), m.p. 158°, containing only H_2O and converted into (I) by dissolving in EtOH and adding C_6H_6 and H_2O. Occasionally, a third form, m.p. 106—107° (decomp.) (cf. Borsche, *loc. cit.*), is obtained. (I) contains 3 OMe groups and 1 OH (Zerevitinov). (I) or (II) is transformed by NH_3 in hot EtOH–H_2O into picropodophyllin (III), which when air-dried contains only H_2O (cf. Borsche) and after desiccation has m.p. 228°, $[\alpha]^{20}_{D}$ +9·38° in $CHCl_3$, $[\alpha]^{20}_{D}$ +9·58° in $COMe_2$; in agreement with Borsche, it is $C_{22}H_{22}O_8$, and contains a lactone and 3 OMe groups, but only 1 OH. (I) and boiling Ac_2O or C_5H_5N and Ac_2O gives *monoacetylpodophyllotoxin*, m.p. 204° after softening at 200° (not identical with Borsche's product), whereas boiling Ac_2O and NaOAc afford monoacetylpicropodophyllin, m.p. 214°, also obtained from (III) and Ac_2O with C_5H_5N or NaOAc. Boiling Ac_2O transforms (III) into a substance (IV), $C_{22}H_{20}O_7$, m.p. 216°, $[\alpha]^{24}_{D}$ +75·72° in $COMe_2$, apparently identical with Borsche's *apo*picropodophyllin. (I) and (III) appear to give identical salts as judged from the $[\alpha]_D$ of alkaline solutions. Oxidation of (I) and (III) with $KMnO_4$ affords 3 : 4 : 5-trimethoxybenzoic acid, whilst distillation with Zn dust yields 1 : 6-dimethylnaphthalene (V) in small amount. Since derivatives of *o*-phthalic acid are never obtained by oxidation, it follows that the C_6H_6 nuclei obtained in (V) are so substituted as to be readily oxidised. If the mol. is opened to attack by demethylating (I) or (III) with fuming HCl at 110° and the crude product is treated with $KMnO_4$, 1 : 2 : 4 : 5-$C_6H_2(CO_2H)_4$ (identified as the Me_4 ester) is obtained. Dehydrogenation of (I) or (III) with spongy Pd gives an optically inactive *substance*, $C_{22}H_{18}O_7$ (VI), m.p. 266° after softening at 264°, which contains 3 OMe and one lactone group but no OH; it is also obtained from (IV). Oxidation of (IV) or (VI) by successive treatment with HNO_3 and alkaline $KMnO_4$ yields $C_6H(CO_2H)_5$. The presence of the skeletons A or B is therefore established.



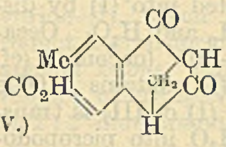
(A.)



(B.)

The action of the HI and AcOH on (I) or (III) gives podophyllomeronic acid, $C_{13}H_{10}O_4$ (VII), m.p. 240°, best purified through the *Me* ester, m.p. 130·5°, on account of the simultaneous formation of a *by-product*, m.p. 284°, in very small amount. (VII) is readily acetylated by Ac_2O and C_5H_5N, but the ready hydrolysis of the Ac derivative indicates that it is probably an enolic Ac compound; the Me ester does not contain an OH group (Zerevitinov). Energetic oxidation of (VII) leads to pyromellitic acid, whereas milder treatment gives Borsche's acid,

$C_7H_5(CO_2H)_3$, oxidised further to (III) and thus characterised as *toluene*-2 : 4 : 5-*tricarboxylic acid.* Distillation of (VII) with Zn dust yields 1 : 6-$C_{10}H_6Me_2$, whilst it is stable towards alkali, resistant to catalytic hydrogenation under mild conditions, but apparently attacked by Na–Hg and HI. The annexed constitution is tentatively suggested. For (I) and (III) the subjoined formulæ are advanced, in which the details of nucleus C of the naphthalene ring are speculative.



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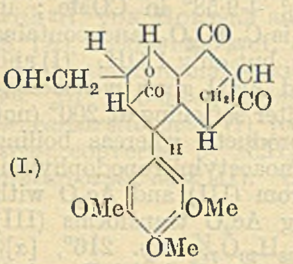
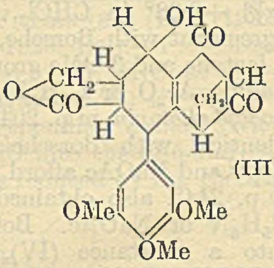


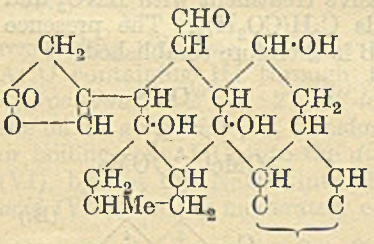
(I.)



(III.)

H. W.

Strophanthin. XXVII. Ring III of strophanthidin and related aglucones. W. A. Jacobs and R. C. Elderfield (J. Biol. Chem., 1932, 97, 727—737; cf. this vol., 948).—Monoanhydrodihydrostrophanthidin with $KMnO_4$ gives in $COMe_2$ or C_5H_5N (less good) *anhydrodihydrostrophanthidinic acid,* m.p. 185—186° (decomp.), and in NaOH a *tetrahydroxylactone acid,* $C_{23}H_{34}O_8$, m.p. 215—218° (decomp., softens 160°). The *Me* ester, m.p. 207—208° (*di*-p-*bromobenzoate,* m.p. 297—298°), of the latter with Kiliani's CrO_3 solution gives a *Me H diketohydroxylactonedicarboxylate,* $C_{24}H_{32}O_9$, m.p. 220—221° (decomp.) [*Me_2* ester, m.p. 180° (softens 116—118°)], reduced with Adams and Shriner's catalyst to a *dihydroxydilactone* ester, $C_{24}H_{34}O_8$, (I), m.p. 280—281° [*Ac* derivative, m.p. 216—217° ; *sulphite,* m.p. 229° decomp.)], and a little *isomeride,* decomp. 243—244°, and then m.p. 281—282°. (I) with CrO_3 in AcOH gives a *hydroxyketodilactone* ester, $C_{24}H_{32}O_8$, m.p. 159—160° (decomp.) [*oxime,* m.p. 195 — 200° (softens 175°)], converted by MeOH–HCl into an *anhydro*-derivative, m.p. 198°. (I) is unaffected by this treatment. The results indicate that ring III in the annexed partial formula for strophanthidin is a methyl*cyclo*pentane ring attached to ring I by C atoms (5) and (6). A. A. L.



Constituents of the leaves of *Ginkgo biloba,* L. I, II. S. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 27—38, 39—42).—I. The EtOH-extract of the air-dried leaves contains sitosterol and its *d*-glucoside, a *substance A* (I), $C_{11}H_{14}O_5,H_2O$, m.p. 325° (decomp.), $[\alpha]_D^{13}$ −54·8° in EtOH (*diacetate,* m.p. 290—292°, $[\alpha]_D^{22}$ −103° in EtOH; amorphous *Me ether,* m.p. about 215°), a *substance B* (II), $C_{16}H_{12}O_5,H_2O$, m.p. 238—240° (*diacetate,* m.p. 226—228° ; *Me_2* derivative, m.p. 225—227° ; *demethyl* derivative, $C_{15}H_{10}O_5$, not melted at 300°), and *ginnol* (III), $C_{29}H_{60}O$ (cf. Kawamura, Jap. J. Chem., 1928, 3, 2, 89), m.p. 82·5—83° (*acetate,* m.p. 43·5—44°). (I) is converted by 33% KOH into a OH-acid (*Ag* salt), whilst KOH fusion of (II) gives *p*-$OH·C_6H_4·CO_2H$. Oxidation of (III) with CrO_3 in AcOH affords *ginnone,* $C_{29}H_{58}O$, m.p. 74—74·5° (*oxime,* m.p. 50—51°).

II. Beckmann rearrangement (H_2SO_4–AcOH) of ginnoneoxime gives *eicos*-n-*nonylamide,* m.p. 83·5—84°, hydrolysed by EtOH–KOH to eicosoic acid and *n*-nonylamine, indicating that ginnone is nonocosan-κ-one. This is proved by synthesis of the latter from eicosoic and decoic acids and P_2O_5 at 200—250°. (III) is, therefore, nonacosan-κ-ol. H. B.

Betulin. III. R. Vesterberg (Ber., 1932, 65, [*B*], 1305—1307).—Gentle oxidation of betulin monoacetate gives acetoxybetulin ketone, $C_{30}H_{47}(\colon CO)·OAc$, m.p. 182—183°, $[\alpha]_D^{20}$ +30·26°, apparently identical with a product obtained by Traubenberg (A., 1912, i, 261, 972) by the oxidation of betulin by CrO_3 in AcOH. The hydroxy-ketone, m.p. 207°, $[\alpha]_D^{19}$ +19·97°, derived therefrom appears identical with heterobutelone of Dischendorfer and the hydroxybetulin of Postovski and Traubenberg. *allo*Betulone is also obtained by this oxidation. Gentle oxidation of dihydrobetulin with CrO_3 gives a *ketone,* $C_{30}H_{50}O_2$, m.p. 180—182°, $[\alpha]_D^{20}$ +10·43°, whereas more drastic treatment yields the ketone $C_{30}H_{48}O_3$, m.p. 252—253°, $[\alpha]_D^{18}$ +12·79°, apparently identical with Ruzicka's dihydrobetulonic acid (this vol., 750). Oxidation of dihydrobetulin with HNO_3 in AcOH at −5° affords *dihydrobetulindicarboxylic acid,* $C_{30}H_{48}O_8$, m.p. 170°, (*anhydride*; *Me_2* ester), which absorbs $4H_2$ when hydrogenated, and *dihydrobetulonedicarboxylic acid,* $C_{30}H_{44}O_6$, m.p. 285°, $[\alpha]_D^{19}$ −22·80° (*Me_2* ester), which contains the CO group and yields a ketone when heated in CO_2 or in a high vac. The last-named acid is also obtained by oxidising dihydrobetulonic acid with HNO_3 in AcOH. Betulin monoacetate is transformed by PCl_5 into apo*betulin acetate,* $C_{30}H_{47}O(OAc)$, m.p. 203—204°, $[\alpha]_D^{20}$ −44·38°, hydrolysed to the monohydric alcohol, $C_{30}H_{48}O$, m.p. 186—187°, $[\alpha]_D^{20}$ −28·69°, identical with Ruzicka's β-*apoallo*-betulin (*loc. cit.*). When heated with fuller's earth, dihydrobetulin affords the liquid hydrocarbon $C_{30}H_{48}$, obtained by Ruzicka (*loc. cit.*) by the action of 2-$C_{10}H_7·SO_3H$. Dihydrobetulin has $[\alpha]_D^{22}$ −22·0°, whereas betulin has $[\alpha]_D^{15}$ +19·96° in C_5H_5N. It is not possible to prepare a monoacetate by partial hydrolysis of dihydrobetulin diacetate. H. W.

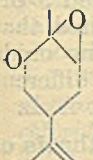
Reversible hydrogenation and dehydrogenation of polyenes. R. Kuhn and P. J. Drumm (Ber., 1932, 65, [*B*], 1458—1460).—Dehydrogenation of methyldihydrobixin to β-methylbixin (yield 70—80%) and of dihydrocrocetin Me_2 ester to crocetin Me_2 ester occurs when the substances in C_5H_5N are shaken with air. The quality of the base is very important. More than 1 O is rapidly absorbed, so that the double linkings are partly attacked. Reaction is not measurably impeded by HCN. Similar change is observed in α-pipecoline, $NHEt_2$, tropine, and piperazine, but not in coniine, nicotine, C_5H_5N, αpicoline, 2-methylquinoline, or NH_2Ph. Me_2 dihydromuconate and αθ-diphenyl-$\Delta^{\beta\delta\zeta}$-octatriene in piperidine are not affected by O. H. W.

Caoutchouc and thioglycollic acid. B. Holmberg (Ber., 1932, **65**, [*B*], 1349—1354).—Crêpe rubber is converted by very prolonged contact with thioglycollic acid at room temp. into a *substance* of the approx. composition $(C_5H_9\cdot S\cdot CH_2\cdot CO_2H)_n$, from which cryst. salts could not be prepared. Successive treatments with the acid brings caoutchouc almost completely into solution: AcOH is unsuitable as diluent, but C_6H_6 can be used if only incomplete action is desired. Rise in temp. expedites the change, which becomes irregular. The behaviour of balata closely resembles that of caoutchouc, whereas guttapercha scarcely reacts with thioglycollic acid. H. W.

Production of synthetic *l*-menthol and *d*-menthol. J. Read and W. J. Grubb (J.S.C.I., 1932, **51**, 329—332T).—Details are given for the resolution of *dl*-menthol by crystallisation of the *l*-menthoxyacetate from MeOH. The m.p. of the stereoisomeric menthyl menthoxyacetates and their binary mixtures are discussed, as is also the m.p. of *dl*-menthol.

Solvent influence. V. Dipole moments of solvents and rotatory power of dissolved menthyl dialkylmalonates. H. G. Rule and J. T. R. Ritchie.—See this vol., 1083.

Autoxidation of αβ-unsaturated ketones. V. Course of the change and products of the autoxidation of carvone. W. Treibs (Ber., 1932, **65**, [*B*], 1314—1324; cf. A., 1931, 1299, 1421; this vol., 398).—*Carvone oxide* [cf. (I)], b.p. 120—122°/15 mm., d^{20} 1·033, α_D −86·4°, is prepared by the action of 30% H_2O_2 on a well-cooled solution of carvone in MeOH in presence of a little KOH. It is transformed by boiling KOH–anhyd. MeOH mainly into the compound $C_{11}H_{18}O_3$ [cf. (II)] with a little hydroxycarvone; the relative proportions of the compounds are reversed if H_2O is present in the alkaline solution. Carvone and its oxide in hot KOH–MeOH afford the compound $C_{20}H_{28}O_3$ [cf. (III)]. Autoxidation of carvone in presence of KOH–MeOH without (A) or with addition of H_2O (B) gives $C_{20}H_{28}O_3$ (yield A, 10—15%, B, 3—5%), hydroxycarvone (yield A, very small; B, 6—8%), $C_{10}H_{16}O_3$, m.p. 132° (yield 1—2%), and much brown resin. The compound $C_{11}H_{18}O_3$ gives an *acetate*, $C_{13}H_{20}O_4$, b.p. 152—155°/15 mm., α_D −34°, and a *benzoate*. It absorbs 2H, yielding $C_{11}H_{18}O_3$, b.p. 150—156°/18 mm., α_D −46° (l=1). When hydrolysed by KOH–MeOH it affords the *OH-acid* $C_{11}H_{20}O_4$, readily transformed into the *lactone* $C_{11}H_{18}O_3$, b.p. 162—166°/15 mm., α_D +7·6° (l=1), reduced to the *dehydrolactone*, $C_{11}H_{20}O_3$, b.p. 159—162°/15 mm. The constitution (II) is therefore assigned to $C_{11}H_{18}O_3$ (contrast A., 1931, 1299). Hydroxycarvone [cf. (IV)] is hydrolysed by aq. $Ba(OH)_2$ to the *keto-acid*, $C_{10}H_{16}O_3$, b.p. 189—190°/20 mm. (*semicarbazone*, m.p. 158°). Reduction with Na and Pr^aOH yields the *menthenediol*, $C_{10}H_{18}O_3$ [cf. (V)], m.p. 105—106°, whereas H in presence of Pd–MeOH transforms acetoxycarvone into its *dihydro-compound*, $C_{12}H_{18}O_3$, b.p. 150—154°/15 mm., from which *hydroxydihydrocarvone*, m.p. 180°, is derived. The *tert.* nature of the OH in $C_{20}H_{28}O_3$ is established by the ready evolution of H_2O at 250°. Prolonged treatment of $C_{20}H_{28}O_3$ with KOH–anhyd. MeOH affords the isomeric *compounds* $C_{20}H_{28}O_3$, m.p. 136° and 176°, respectively, which behave as monobasic acids and develop the characteristic odour of dihydroresorcinols when exposed to air. Prolonged action of KOH leads to non-cryst. acids. The *compound* $C_{20}H_{16}O_3$, m.p. 132°, most readily prepared by the rapid oxidation of carvone with H_2O_2, behaves as a monobasic acid. With $MeOH–H_2SO_4$ it gives a *Me* derivative, b.p. 150—155°/15 mm., slowly hydrolysed by $KOH–H_2O$ to the initial material.



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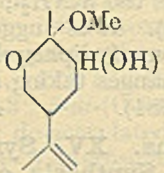

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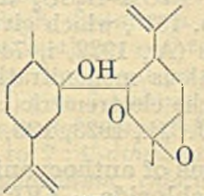

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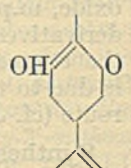

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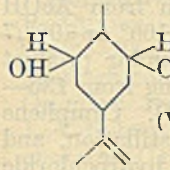
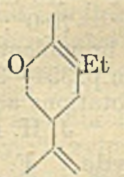


(V.)

The residue obtained by the prolonged action of KOH–MeOH on carvone at room temp. in absence of air is a *polycarvone*, $(C_{10}H_{14}O)_n$ (n=about 3). In AcOH it adds 1 HBr per $C_{10}H_{14}O$ unit. It is depolymerised by heat to the monomeric carvone with the initial $[\alpha]_D$. The action therefore consists of an aldol condensation between several carvone mols. which is reversed by heat. Cryst. dimeric *carvone* is obtained by the action of KOH–MeOH. H. W.

Action of Grignard's reagent on hydroxycarvone and transformation of the products of the reaction into aromatic compounds. W. Treibs (Ber., 1932, **65**, [*B*], 1324—1329).—Hydroxycarvone (cf. preceding abstract) is converted by a large excess of MgEtBr into an unstable adduct which readily loses H_2O when decomposed, giving *ethylcarvone* (I), b.p. 142°/15 mm. (*semicarbazone*, m.p. 160—161°). (I) with $CMeEt_2\cdot OH$ is more readily prepared from acetoxycarvone and MgEtBr, (I) absorbs 2Br without loss of HBr in $CHCl_3$ and 2H when hydrogenated (Skita). With KOH–MeOH and 30% H_2O_2 it affords the keto-oxido-*compound*, $C_{12}H_{18}O_2$, b.p. 137—139°/13 mm. (I) is transformed by MgEtBr into a *tert.*-alcohol which immediately loses H_2O to form the *hydrocarbon* $C_{14}H_{22}$ [(II or (III)], b.p. 124—125°/15 mm., unstable to air and readily absorbing 4Br in $CHCl_3$. (I) at its b.p. is transformed by a trace of I into *ethylcarvacrol*, b.p. 265° (*phenylurethane*, m.p. 157°; *benzoate*, m.p. 53—54°); under similar conditions, the hydrocarbon $C_{14}H_{22}$ (see above) yields *diethylcymene*, b.p. 243—245°. H. W.



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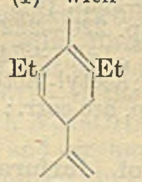

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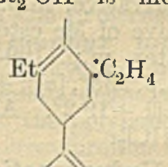


(III.)

Attempts at fractionation of solid pinene hydrochloride. R. Bousset (Bull. Soc. chim., 1932, [iv], 51, 947—952).—The fractionation of *d*-, *l*-, and *dl*-pinene hydrochlorides has been carried out by distillation at 150 mm. (*d*-), crystallisation from AcOH and $CHCl_3$ (*l*-), and by sublimation at 160° or 100°/7 mm. (*d*-, *l*-, *dl*-). In every case a similar product was obtained, the recorded m.p. varying from 136—138° to 139—140° (initial m.p. about 126°). Camphene was isolated from the products of distillation, and could also be removed from the crude hydrochloride by partial acetylation with AcOH and $PhSO_3H$.
H. A. P.

Optically active diazo-compounds. VI. Diazocamphor. W. A. Noyes and E. Meitzner (J. Amer. Chem. Soc., 1932, 54, 3768—3773; cf. A., 1931, 358).—Amino-*d*-camphor is resolved by $H_2C_2O_4$ into two amines, $[\alpha]_D$ +17·5° in EtOH, and +55·5° in EtOH (corresponding oxalates, m.p. 212° and 203°, $[\alpha]_D$ +8·49° and +43·3° in H_2O, respectively), both of which give the same diazocamphor. The theoretical aspect is discussed. C. J. W. (*b*)

Saponin group. XI. Hydroxytriterpene acid glucosides of the *Araliaceæ*. A. Winterstein and G. Stein (Z. physiol. Chem., 1932, 211, 5—18; cf. this vol., 856).—The aglucone of the saponin of *Aralia japonica* is a mixture of oleanolic acid (I) and hederagenin. The sapogenins araligenin, taraligenin, taragenin, and panaxsapogenin are either identical with (I) or are mixtures of it with sapogenins containing more oxygen. The formula for hederagenin now accepted is $C_{30}H_{48}O_4$, *i.e.*, a dihydroxytriterpene acid, thus emphasising the relationship to (I). Glucosides of (I) of different origin differ in their hæmolytic action. The physical properties of hederagenin and derivatives of (I) differ somewhat from those previously given; hederagenin: Ac_2 derivative, m.p. 160—180°, $[\alpha]_D^{19}$ +77·2°; Me ester, m.p. 236—238°, $[\alpha]_D^{20}$ +71·7°; Ac_2 derivative of Me ester, m.p. 190°, $[\alpha]_D^{20}$ +75·3°; lactone, m.p. 354°, $[\alpha]_D^{20}$ +16·2°; diacetyl-lactone, m.p. 244°, $[\alpha]_D^{19}$ +33·8°; bromolactone, $[\alpha]_D^{19}$ +72·5°; (I), m.p. 305—308°, $[\alpha]_D^{20}$ +75·2°: Ac derivative, m.p. 263—266°, $[\alpha]_D^{19}$ +70·9°; Ac derivative of Me ester, m.p. 220—222°, $[\alpha]_D^{19}$ +70·0°; Me ester, m.p. 199—201°, $[\alpha]_D^{19}$ +74·3°; bromolactone, m.p. 238°, $[\alpha]_D^{21}$ +588°; acetyl-lactone, m.p. 354—355°, $[\alpha]_D^{19}$ +19·2°. All m.p. are corr.; all rotations are in $CHCl_3$. J. H. B.

Hydrogenation of furfuraldehyde. F. E. Brown, H. Gilman, and R. L. Van Peursem (Iowa State Coll. J. Sci., 1932, 6, 133—136).—Hydrogenation at 175—275° at atm. pressure, with Cu–asbestos as catalyst, afforded only furfuryl alcohol (max., 4·0—4·3% of theoretical at 215—225°; with Ni at 200°, 5%). *Furfuryl H phthalate* has m.p. 85° (decomp. 135°). Ch. Abs.

Condensations of furan derivatives. I. Mutual relationships of furfurylideneacetone with other [aldehyde–]acetone condensation products. V. V. Tschelincev and E. K. Nikitin (Bull. Soc. chim., 1932, [iv], 51, 875—883).—Interaction of furfuraldehyde in slight excess with benzylidene-, vanillylidene-, or piperonylidene-acetone in aq. H_2SO_4 results in displacement of the aldehyde concerned and formation of furfurylideneacetone. Furfuraldehyde is displaced from furfurylideneacetone by CH_2O, MeCHO, citral, heptaldehyde, and cinnamaldehyde.
H. A. P.

Condensation of α-formylphenylacetonitriles with phenols. II. I. C. Badhwar and K. Venkataraman (J.C.S., 1932, 2420—2423; cf. A., 1931, 963).—Hydroxyquinol triacetate (I) and α-formylphenylacetonitrile by the Hoesch reaction give 6 : 7-*dihydroxy*-3-*phenylcoumarin*, m.p. 242° (*Ac_2* derivative, m.p. 190—191°), also obtained by condensing (I) with Et hydroxymethylenephenylacetate in 80% H_2SO_4. Benzoyloxymethylenephenylacetonitrile (II) did not react by the Hoesch method with (I), the latter giving 2 : 4 : 5-trihydroxyacetophenone. Condensation of (II) with β-naphthol gives 2-phenyl-3 : 4-β-naphthapyrone (III) and a *substance*, m.p. 242°, converted into (III) by the action of NaOEt. β-*Naphthoxyacetophenone*, m.p. 108° (from Na β-naphthoxide and CH_2BzBr) in Et_2O with KCN and 30% H_2SO_4 gives α-2-*naphthoxymethylmandelonitrile*, m.p. 115—116°, converted by HCl and $ZnCl_2$ in Et_2O into (III) and 2-*hydroxy*-2-*phenyl*-1 : 4-β-*naphthapyranone*, m.p. 124° (*Ac* derivative, m.p. 125—126°), which with conc. H_2SO_4 gives 2-*phenyl*-1 : 4-β-*naphthapyrone*, m.p. 129—130°. A. A. L.

Diphenylene oxide series. III. N. M. Cullinane (J.C.S., 1932, 2365—2367).—Nitration of diphenylene oxide gives 2 : 6-dinitrodiphenylene oxide (I), m.p. 245° (A., 1923, i, 534), reduced with Sn or Fe in HCl to the 2 : 6-*diamine*, m.p. 152° (yield 80%) (*Ac_2* derivative, decomp. 290°), not identical with 2 : 7-diaminodiphenylene oxide (*Ac_2* derivative, m.p. 322°). (I) with NH_4HS in EtOH gives 6-*nitro*-2-*aminodiphenylene oxide*, m.p. 268°, converted by $NaNO_2$ in EtOH–H_2SO_4 to 6(=3)-nitrodiphenylene oxide, m.p. 151°, which gives the 3-NH_2-, and 3-Br-derivatives (A., 1922, i, 746). It is suggested that the anomalous mononitration of diphenylene oxide is due to the electromeric changes taking a different route (cf. J.C.S., 1923, 123, 684). A. A. L.

Synthesis of anthocyanins. XV. Synthesis of hirsutin chloride. XVI. Synthesis of malvin chloride. XVII. Syntheses of pelargonin, peonin, and cyanin chlorides. R. Robinson and A. R. Todd (J.C.S., 1932, 2293—2299, 2299—2305, 2488—2496).—XV. 2-*O*-Tetra-acetyl-β-glucosidyl-4-*O*-methylphloroglucinaldehyde, 4-acetoxy-3 : 5-dimethoxy-ω-*O*-tetra-acetyl-β-glucosidoxyacetophenone (I), and dry HCl in EtOAc give hydrated (?) 4′-*hydroxy*-7 : 3′ : 5′-*trimethoxy*-3 : 5-*di*-(O-*tetra-acetyl*-β-*glucosidoxy*)*flavylium chloride* (?), decomp. 125—128° (sinters at 75°), which when treated with cold 10% NaOH in H_2 and then with warm 2% HCl affords 4′-*hydroxy*-7 : 3′ : 5′-*trimethoxy*-3 : 5-*di*-β-*glucosidoxyflavylium chloride* (+4H_2O) (II). This is identical with natural hirsutin chloride (Karrer and Widmer, A., 1927, 1197); both chlorides show identical colour reactions (in buffered and other solutions), distribution ratios (BuOH), and absorption spectra. The effects of co-pigments on solutions of (II) are discussed. 3-β-*Glucosidylhirsutidin chloride* (+1·5H_2O) (an *œnin chloride Me ether*), prepared (as above) from (I) and 2-*O*-benzoyl-4-*O*-methylphloroglucinaldehyde with subsequent hydrolysis, resembles œnin chloride in many of its properties.

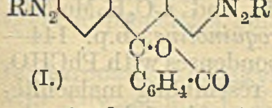
XVI. Phloroglucinaldehyde, tetra-acetylglucosidyl bromide, and 10% KOH in cold MeCN give 2-O-*tetra-acetyl-β-glucosidylphloroglucinaldehyde* (+0·5H_2O) (III), m.p. 77—80°, $[\alpha]^{19}_{5461}$ —47·84° in $CHCl_3$, 2 : 4-*di-*(O-*tetra-acetyl-β-glucosidyl*)*phloroglucinaldehyde*, m.p. 194—195°, $[\alpha]^{19}_{5461}$ —52·5° in $CHCl_3$, and a little of a *substance*, m.p. 109—110° (see below). ω : 4-Dihydroxyacetophenone, (III), and dry HCl in $CHCl_3$–EtOAc afford 3 : 7 : 4′-*trihydroxy*-5-O-*tetra-acetyl*-β-*glucosidoxyflavylium chloride* (+H_2O), hydrolysed (dil. NaOH followed by dil. HCl) to pelargonenin chloride (A., 1931, 1423). (I) and (III) similarly give 7 : 4′-*dihydroxy*-3′ : 5′-*dimethoxy*-3 : 5-*di*-β-*glucosidoxyflavylium chloride* (+2H_2O), decomp. 165°, identical with natural malvin chloride.

2 : 4-*Dicarbethoxyphloroglucinaldehyde*, m.p. 76°, from the aldehyde, $ClCO_2Et$, and 5% NaOH in $COMe_2$, condenses with ω-hydroxyacetophenones to give flavylium salts.

XVII. A somewhat better yield of (III) is obtained when MeCN is replaced by $COMe_2$ in the above method; the substance, m.p. 109—110°, is probably 2-O-*monoacetyl*-β-*glucosidylphloroglucinaldehyde* (IV), $[\alpha]^{21}_{5461}$ —49·32° in $CHCl_3$. ω : 4-Dihydroxyacetophenone and (IV) condense to give pelargonenin chloride, whilst 4-acetoxy-ω-*O*-tetra-acetyl-β-glucosidoxyacetophenone and (IV) condense (HCl–EtOAc) to 7-*hydroxy*-4′-*acetoxy*-5-O-*monoacetyl*-β-*glucosidoxy*-3-O-*tetra-acetyl*-β-*glucosidoxyflavylium chloride* (+2H_2O), deacetylated to 7 : 4′-*dihydroxy*-3 : 5-*di*-β-*glucosidoxyflavylium chloride* (+4H_2O) [pelargonin chloride], m.p. about 187° (sinters at 178°). The absorption spectra curves of pelargonin (synthetic), monardin, and salvinin chlorides agree very closely, but differ slightly from that of natural pelargonin chloride (which contains a little malvin chloride). 4-Acetoxy-3-methoxy-ω-*O*-tetra-acetyl-β-glucosidoxyacetophenone (improved prep. given; cf. A., 1931, 1423) and (III) give 7-*hydroxy*-4′-*acetoxy*-3′-*methoxy*-3 : 5-*di*-(O-*tetra-acetyl*-β-*glucosidoxy*)*flavylium chloride*, de-acetylated to 7 : 4′-*dihydroxy*-3′-*methoxy*-3 : 5-*di*-β-*glucosidoxyflavylium chloride* (+5H_2O) [peonin chloride], decomp. 165—167°. 3 : 4-Diacetoxy-ω-*O*-tetra-acetyl-β-glucosidoxyacetophenone and (III) give 7-*hydroxy*-3′ : 4′-*diacetoxy*-3 : 5-*di*-(O-*tetra-acetyl*-β-*glucosidoxy*)*flavylium chloride* (+2H_2O), deacetylated to 7 : 3′ : 4′-*trihydroxy*-3 : 5-*di*-β-*glucosidoxyflavylium chloride* (+3H_2O) [cyanin chloride], m.p. 205° (decomp.). Various tests are given showing the identity of the synthetic and natural products.

H. B.

Some lactonic fluorescein compounds. F. Ingraffia (Gazzetta, 1932, 62, 781—790).—Fluorescein yields a *bisbenzeneazo*-compound (I), m.p. 187°, which gives an Ac_2 derivative, m.p. 170°, and must therefore be lactonic (I). The following are also described. *Benzeneazo-*, m.p. 170°, *bis*-p-*nitrobenzeneazo-*, m.p. 190°, p-*nitrobenzeneazo-*, *bis*-o-*tolueneazo-*, m.p. 190°, and o-*tolueneazo-*, m.p. 210°, *-fluorescein*; these all form Ac_2 derivatives, m.p. 142°, 230°, 244°, 160°, and 190°, respectively. (I) is reduced by NHPh·NH_2 to diaminofluorescein (*dihydrochloride*), identical with that prepared from dinitrofluorescein (cf. A., 1905, i, 897). E. W. W.



(I.)

Derivatives of dioxan. R. K. Summerbell and R. Christ (J. Amer. Chem. Soc., 1932, 54, 3777—3778).—The results of Butler and Cretcher (this vol., 949) are confirmed. Dichlorodioxan (I) reacts with Grignard reagents to give disubstituted dioxans; 1 : 2-diphenyldioxan, m.p. 49°, is prepared. Pyrocatechol and (I) give a compound similar to 1 : 4 : 5 : 8-naphthodioxan. C. J. W. (*b*)

Electrolytic reduction of pyrrolones and Δ²-pyrrolines. R. Lukeš (Coll. Czech. Chem. Comm., 1932, 4, 351—363).—Electrolytic reduction of 1-methyl-5-ethyl-2-pyrrolone in 50% H_2SO_4 gives 1-methyl-5-ethylpyrrolidine (I), b.p. 123°, and 1-*methyl-5-ethyl-2-pyrrolidone*, b.p. 229—230° (corr.) (hydrolysed by HCl at 180° to γ-methylaminohexoic acid). 1-Methyl-2-ethyl-Δ²-pyrroline gives (I). 5-Hydroxy-5-phenyl-1-methyl-2-pyrrolone gives 2-*phenyl*-1-*methylpyrrolidine*, b.p. 96°/11 mm. (*chloroplatinate*, +H_2O, m.p. 118—120°; *picrate*, m.p. 145°; *chloroaurate*, m.p. 114—115°) (also formed from 2-phenyl-1-methyl-Δ²-pyrroline), and 5-*phenyl*-1-*methyl*-2-*pyrrolidone*, b.p. 175°/10 mm. 5-Benzyl-1-methyl-2-pyrrolone gives 2-*benzyl*-1-*methylpyrrolidine*, b.p. 113·0° (corr.)/12 mm. (*chloroplatinate*, m.p. 183—184°; *picrate*, m.p. 144°) [also obtained from 2-*benzyl*-1-*methyl*-Δ²-*pyrroline*, b.p. 155°/10 mm. (*perchlorate*, m.p. 109—110°), prepared from 1-methyl-2-pyrrolidone and CH_2Ph·MgBr], and 5-*benzyl*-1-*methyl*-2-*pyrrolidone*, b.p. 191°/11 mm. The duration of the reduction of the pyrrolones does not affect the relative yields of pyrrolidine and pyrrolidone derivatives, and the latter cannot be further reduced electrolytically; it is, therefore, presumed that the pyrrolone, or the hydroxypyrrolidone which is (sometimes) in equilibrium with it, is reduced in either of two independent ways, and that reduction does not proceed by way of the pyrrolidone or the open-chain NH_2-acid.

R. S. C.

Isolation of glycylserylprolyltyrosylproline and serylprolyltyrosylproline in the progressive degradation of silk fibroin (*Bombyx mori*). E. Abderhalden and A. Bahn (Z. physiol. Chem., 1932, 210, 246—267).—In the progressive degradation of silk fibroin with *N*-NaOH at 37° the polypeptides glycylserylprolyl- and serylprolyl-tyrosylproline were isolated and identified by partial hydrolysis. In determining structure use was made of the observation that the *N*-Bz group of serine, in contrast to those of aliphatic NH_2-acids having no OH group, is very easily hydrolysed by dil. acid. Dibenzoylglycylserine, when warmed with 25 vol.-% H_2SO_4, yields BzOH, hippuric acid, and glycine. J. H. B.

Oxidation of pyrrole [by hydrogen peroxide; catalysis by iron]. A. Quilico (Gazzetta, 1932, 62, 478—487).—Oxidation of pyrrole to hydroxypyrrole-black is strongly catalysed by salts of Fe, and to a smaller degree by those of Cu (which gives a brown product) and V; Mn, Ni, Co, and U are inactive. Variations in the yield according to the amount of Fe or H_2O_2 used are studied. E. W. W.

Action of ozone on heterocyclic compounds. I. Pyrrole. M. Freri (Gazzetta, 1932, 62, 600—605).—Passage of O_2+O_3 through pyrrole, alone or suspended in H_2O, or dissolved in AcOH or dil. H_2SO_4, gives oxidation products of high mol. wt., similar to pyrrole-blacks. The product in Et_2O is unstable, and may be an ozonide. E. W. W.

Indoles. II. Preparation of some derivatives of 5 : 6-dimethoxyindole. F. Lions and (Miss) M. J. Spruson (J. Proc. Roy. Soc. New South Wales, 1932, 66, 171—180).—Interaction of 3 : 4-dimethoxybenzenediazonium chloride with esters of the type $CHRAc·CO_2Et$ in NaOH–EtOH gives hydrazones (oils, except the *monoveratrylhydrazone* of βγ-diketo-α-phenylbutane, m.p. 173°) which with HCl in EtOH yield indoles. The following are described : 3-*methyl*-, m.p. 208° (decomp.) (*Et* ester, m.p. 182°), and 5 : 6-*dimethoxy*-3-*phenylindole*-2-*carboxylic acid*, m.p. 203° (decomp.) (*Et* ester, m.p. 167°); *Et* (5 : 6-*dimethoxy*-2-*carbethoxy*-3-*indolyl*)*butyrate*, m.p. 163°; 5 : 6-*dimethoxy*-2-*aceiyl*-3-*phenylindole*, m.p. 181°. J. L. D.

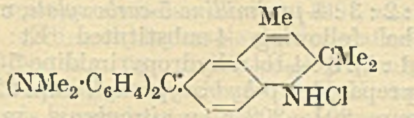
5-Ethoxyindolinones. K. Brunner and H. Moser (Monatsh., 1932, 61, 15—28).—n-*Valer*-p-*ethoxyphenylhydrazide*, m.p. 125·5°, heated with CaO gives 21·6% of 5-*ethoxy*-3-*propyl*-2-*indolinone*, m.p. 119°; 5-*ethoxy*-3-iso*propyl*-, m.p. 132°, and 5-*ethoxy*-3-*methyl*-3-*ethyl*-, m.p. 158°, -2-*indolinones* are similarly prepared from *iso*valer-, m.p. about 120°, and α-*methylbutyr*-, m.p. 146°, -p-*ethoxyphenylhydrazides*, respectively. iso*Valer*-, m.p. 80·5°, and α-*methylbutyr*-, m.p. 78°, -as-p-*ethoxyphenylmethylhydrazides* are similarly converted into 5-*ethoxy*-1-*methyl*-3-iso*propyl*-2-*indolinone*, m.p. 40°, and 5-ethoxy-1 : 3-dimethyl-3-ethyl-2-indolinone (I), m.p. 41° (cf. Stedman and Barger, A., 1925, i, 292) [*Br*-, m.p. 115—116°, and $(NO_2)_2$-, m.p. 195°, derivatives], respectively. (I) is reduced by Na and EtOH to the corresponding indolinol (indolinium *picrate*, m.p. 146—147° with darkening). The indolinone from *valer*-as-p-*ethoxyphenylmethylhydrazide*, m.p. 63°, could not be obtained cryst. *as*-*p*-Ethoxyphenylmethylhydrazine, b.p. 137—140°/10 mm., is prepared by reduction (Zn dust, aq. AcOH) of the *NO*-derivative, m.p. 49°, of p-$OEt·C_6H_4·NHMe$ (*hydrochloride*; *picrate*, m.p. 168°). H. B.

Toad poisons. V. Basic components of toad secretion. H. Jensen and K. K. Chen (Ber., 1932, 65, [*B*], 1310—1314).—The secretion, after being dried at room temp., is extracted with 95% EtOH. The extract is evaporated nearly to dryness in vac. and the residue extracted with H_2O. The aq. solution is shaken repeatedly with amyl alcohol and then with $CHCl_3$. The bufotenins are isolated as the flavianates. The same *bufotenin flavianate*, $C_{13}H_{20}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 200·5°, 199°, and 198—199°, respectively, is isolated from *Ch' an Su*, *Bufo bufo gargarizans*, and *B. Fowleri*. The *flavianates* $C_{12}H_{18}O_2N_2,C_{10}H_6O_8N_2S$, m.p. 186—187°, 180—181°, and 170°, respectively, from *B. formusus*, *B. bufo bufo*, and *B. viridis viridis* form a closely related group nearly resembling the first group. The bufotenin from *B. valliceps* (flavianate, m.p. 261—262°) appears identical with tryptophan; those from *B. marinus* (*flavianate*, m.p. 270—271°) and *B. alvarius* (*flavianate*, m.p. 224—225°) are probably methyltryptophan and methyltetrahydrotryptophan, respectively. The bufotenins from *B. arenarum* and *B. viridis viridis* (*flavianate*, $C_{12}H_{20}O_3N_2,C_{10}H_6O_8N_2S$, m.p. 130—131°) appear identical. The probable relationship of the bufotenins to β-3-indolylethylamine is indicated. Cinobufotenin flavianate evolves NMe_3 when heated with 10% KOH. H. W.

Preparation of iodinated derivatives of phenolisatin. W. C. Sumpter (J. Amer. Chem. Soc., 1932, 54, 3766—3768).—Conc. H_2SO_4 and 5-iodoisatin in molten PhOH give 70% of 5-*iodophenolisatin* (5-*iodo*-3 : 3-*di*-p-*hydroxyphenyloxindole*), m.p. 220°, re-solidifying with m.p. 264—265° (*Ac_3* derivative, m.p. 169—170°); 5 : 7-*di*-*iodo*-3 : 3-*di*-p-*hydroxyphenyloxindole*, m.p. 239—240° (*Ac_2* derivative, m.p. 256—257°), is prepared similarly. Phenolisatin and *N*-I (in KI) in conc. aq. NH_3 give about 80% of impure 3 : 3-*bis*-(3′ : 5′-*di*-*iodo*-4′-*hydroxyphenyl*)*oxindole*, not melted at 265° (*Ac_3* derivative, m.p. 267—268°); 5-*iodo*- (*Ac_3* derivative, m.p. 272—273°) and 5 : 7-*di*-*iodo*- (*Ac_2* derivative, m.p. 255—256°) -3 : 3-*bis*-(3′ : 5′-*di*-*iodo*-4′-*hydroxyphenyl*)*oxindoles* are prepared similarly. C. J. W. (*b*)

Supposed acetoneanil. G. Reddelien and A. Thurm (Ber., 1932, 65, [*B*], 1511—1521).—Re-examination of the acetoneanil of Knoevenagel (A., 1921, i, 785) shows it to be 2 : 2 : 4-*trimethyl*-1 : 2-*dihydroquinoline* (I), b.p. 134°/13—14 mm., m.p. 25—26°. It is obtained in 32% yield by the action of I on a boiling mixture of $COMe_2$ and NH_2Ph (*loc. cit.*), whereby much NH_2Ph remains unchanged and the true acetoneanil is produced in very small amount; evidence of the formation of *mesityl oxide anil*, $CMe_2{:}CH·CMe{:}NPh$, b.p. 125°/16 mm. (obtained from mesityl oxide and NH_2Ph without catalyst), is not afforded. Greatly improved yields are secured by the gradual addition of an excess of $COMe_2$ to NH_2Ph and I at 155—160°. (I) is unchanged by boiling dil. HCl, but with conc. HCl affords the *hydrochloride*, m.p. 209°; the *sulphate* and *perchlorate*, m.p. 146—147°, are described. (I) combines readily with MeI to the *methiodide*, m.p. 148°, transformed by KOH into 1 : 2 : 2 : 4-*tetramethyldihydroquinoline*, b.p. 142°/13 mm. ("methylacetoneanil," *loc. cit.*). (I) is indifferent towards HCN and $NaHSO_3$. The presence of the NH group in (I) is established by the isolation of 1-*acetyl*-, m.p. 53°, readily hydrolysed by boiling dil. HCl, and 1-*benzoyl*-, m.p. 83°, -2 : 2 : 4-*trimethyldihydroquinoline*. 2 : 2 : 4-*Trimethyldihydroquinolinophenylcarbamide*, m.p. 125°, and the corresponding *compound*, m.p. 135°, from "acetone-*p*-tolil" are described. (I) with H at 100°/10 atm. in presence of Ni–SiO_2 yields 2 : 2 : 4-*trimethyltetrahydroquinoline* (II), b.p. 119—122°/10 mm., m.p. 41°, identical with 2 : 2 : 3 : 3-tetramethylindoline obtained by reduction of "acetoneanil" with Na and boiling EtOH (A., 1922, i, 1060); the formation of NH_2Ph during the process is not observed. The product of the action of $COMe_2$ and p-$C_6H_4Me·NH_2$ is 2 : 2 : 4 : 6-*tetramethyldihydroquinoline*, b.p. 144—145°/15 mm., m.p. 40·5°. (I) condenses with PhCHO, yielding when oxidised a *dye* resembling malachite-green, whilst with Michler's ketone it yields the *dye*

(III), bluer than crystal-violet and exhibiting a much more marked affinity for mordanted cotton. With diazotised sulphanilic acid (I) couples with marked evolution of gas, giving a dye of the helianthin class, whereas (II) couples normally.


(III.)

iso*Propylaniline*, b.p. 203—204°, from NH_2Ph and $Pr^{\beta}Cl$ at 120°, gives an *Ac* derivative, m.p. 38°.

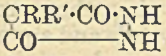
H. W.

Iodo-derivatives of quinoline. L. Musajo (Gazzetta, 1932, 62, 566—570).—2-Phenylquinoline-4-carboxylic acid with ICl in AcOH forms a *compound*, $C_{16}H_{12}O_2NClI_2,5EtOH$, m.p. 155—156° (decomp. from 200°). 5-Iodoisatin (cf. A., 1924, i, 1342; prep. modified) condenses with *p*-iodoacetophenone to 6 : 4′-*di-iodo-2-phenylquinoline*-4-*carboxylic acid*, m.p. 285—286°, from which the *base*, m.p. 228°, is obtained on heating.

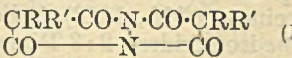
E. W. W.

Manufacture of therapeutically valuable compounds. A. Carpmael. From I. G. Farbenind. A.-G.—See B., 1932, 912.

Alkylated diketopyrazolidines and tetraketopyrazopyrazoles from alkylmalonic esters and hydrazine. A. W. Dox (J. Amer. Chem. Soc., 1932, 54, 3674—3678).—The N_2H_4 condensation with homologous alkylmalonic esters (cf. Conrad and Zart, A., 1906, i, 608) invariably gives pyrazolones of type (I) with the dialkylated esters, whereas monosubstituted esters afford the double condensation product of type (II). In neither case could the type be interchanged by varying the proportions of the reacting substances. The following are prepared from the appropriate malonic esters and N_2H_4,HCl or $NHPh{\cdot}NH_2$ in EtOH–NaOEt: 4 : 4-*diethyl-*, m.p. 267°, 4 : 4-*dipropyl-*, m.p. 254°, 4 : 4-*dibutyl-*, m.p. 220°, 4 : 4-*di*iso*amyl-*, m.p. 289—290°, 4-*ethyl*-4-iso*amyl-*, m.p. 228°, 4-*ethyl-4-hexyl-*, m.p. 182°, 4-sec.-*butyl-4-allyl-*, m.p. 186—187°, 4-*phenyl*-4-*ethyl-*, m.p. 196—197°; 1-*phenyl-4-ethyl-*, m.p. 108°, 1-*phenyl*-4-sec.-*butyl-*, m.p. 94°, and 1-*phenyl*-4 : 4-*diethyl-*, m.p. 114°, -3 : 5-*diketopyrazolidines*; 2 : 6-*diethyl-*, m.p. 246—247°, 2 : 6-*dipropyl-*, m.p. 278°, and 2 : 6-*di*-sec.-*butyl-*, m.p. 207°, -1 : 3 : 5 : 7-*tetraketopyrazo*-(1 : 2-α)-*pyrazoles*. The last three compounds with Br in AcOH give the 2 : 6-Br_2-derivatives, m.p. 171—173°, 138°, and 111°, respectively. Diketodiethylpyrazolidine does not condense with $CHEt(CO_2Et)_2$. A tentative explanation of the difference in behaviour between the mono- and di-alkylmalonic esters is a possible enolisation of the intermediate diketomonoalkylpyrazolidine which renders it capable of further reaction to form the pyrazopyrazole. Compounds of type (I) show some antipyretic properties but no hypnotic action.

(I.)


$$\begin{array}{l} CRR'{\cdot}CO{\cdot}NH \\ CO\text{———}NH \end{array}$$


(II.)

$$\begin{array}{l} CRR'{\cdot}CO{\cdot}N{\cdot}CO{\cdot}CRR' \\ CO\text{———}N\text{——}CO \end{array}$$

C. J. W. (*b*)

Decomposition of alkyl pyrazolinecarboxylates. K. von Auwers and F. König (Annalen, 1932, 496, 252—282).—Thermal decomp. of the simpler alkyl pyrazolinecarboxylates usually gives alkyl alkenecarboxylates (I) as the main product, whilst the more complex esters generally afford a preponderance of alkyl *cyclo*propanecarboxylates (II). Mixtures of (I) and (II) are often formed; the amount of (I) is determined by Br titration (when possible). Carbalkoxy-groups have a marked influence on the decomp.; (I) generally predominates with pyrazolinemonocarboxylates, whilst (II) is usually the main product with pyrazolinedicarboxylates. Δ^2-Pyrazolines give a preponderance of (I), whilst Δ^1-pyrazolines afford mainly (II); in the last case, no H is eliminated during the decomp. *cis*- and *trans*-Pyrazolinedicarboxylates give almost entirely *cis*- and *trans-cyclo*propanedicarboxylates, respectively. Resinous material is formed in all cases. Me pyrazoline-3-carboxylate gives Me Δ^{β}-butenoate; Me 5-methylpyrazoline-3-carboxylate affords (mainly) Me Δ^{β}-pentenoate (impure *dibromide*, b.p. 104—106°/13 mm.); Me 4-methylpyrazoline-3-carboxylate (N-*Ac*, b.p. 140—142°/10 mm., 208—210°, m.p. 60—61°, and N-*Me*, b.p. 120—126°/1 mm., derivatives) yields Me β-methyl-Δ^{α}-butenoate (*dibromide*, b.p. 90—94°/12 mm.) and a trace of Me 4-methylpyrazole-3(5)-carboxylate; Me 4 : 5-dimethylpyrazoline-3-carboxylate furnishes Me β-methyl-Δ^{β}-pentenoate {free acid, b.p. 200—204° (lit. 199°) [chloride, b.p. 48—50°/12 mm.; amide, m.p. 126—127° (lit. 124°)]}; *Et* 4-*methylpyrazoline*-3 : 5-*dicarboxylate*, m.p. 69° (from Et crotonate and $CHN_2{\cdot}CO_2Et$), gives Et β-methylglutaconate (probably admixed with some Et methyl*cyclo*propanedicarboxylate); Et 5-methyl-Δ^1-pyrazoline-5-carboxylate affords Et 1-methyl*cyclo*propane-1-carboxylate and Et tiglate in the ratio 37 : 63; Me 4 : 5-dimethyl-Δ^1-pyrazoline-5-carboxylate yields Me αβ-dimethyl-Δ^{α}-butenoate (*dibromide*, b.p. 104—105°/13 mm.) and Me 1 : 2-dimethyl*cyclo*propane-1-carboxylate in the ratio 77 : 23; Me 3 : 4 : 5-trimethyl-Δ^1-pyrazoline-5-carboxylate furnishes *Me* 1 : 2 : 3-*trimethyl*cyclo*propane*-1-*carboxylate*, b.p. 68—70°/39 mm. (free *acid*, b.p. 210—211°), and Me αβ-dimethyl-Δ^{α}-pentenoate in the ratio 86 : 14; Et 4-methyl-Δ^1-pyrazoline-5 : 5-dicarboxylate gives *Et* iso*propylidenemalonate*, b.p. 112°/12 mm.; Me pyrazoline-3 : 4-dicarboxylate affords (cf. von Pechmann, A., 1894, i, 438) Me mesaconate and Me *cis*- and *trans-cyclo*propane-1 : 2-dicarboxylates in the ratio 65 : 2 : 23; Me *cis*-5-methyl-Δ^1-pyrazoline-4 : 5-dicarboxylate yields mainly Me *cis*-1-methyl*cyclo*propane-1 : 2-dicarboxylate, a little of the *trans*-ester, and some Me dimethylmaleate; Me 4-methylpyrazoline-3 : 4-dicarboxylate furnishes Me *trans*-1-methyl*cyclo*propane-1 : 2-dicarboxylate; Me *trans*-5-methyl-Δ^1-pyrazoline-4 : 5-dicarboxylate gives mainly Me *trans*-1-methyl*cyclo*propane-1 : 2-dicarboxylate and a trace of Me α-methylitaconate; Me *cis*-4 : 5-dimethyl-Δ^1-pyrazoline-4 : 5-dicarboxylate gives *Me* cis-1 : 2-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylate*, b.p. 215—216° (free *acid*, m.p. 115—117°), and the *trans*-isomeride in the ratio 95 : 5; Me *trans*- 4 : 5-dimethyl-Δ^1-pyrazoline-4 : 5-dicarboxylate affords *Me* trans-1 : 2-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylate*, b.p. 210° (free *acid*, m.p. 230—231°), and a trace of the *cis*-isomeride; Me Δ^1-pyrazoline-4 : 5-dicarboxylate-5-acetate (from Me aconitate and diazomethane) yields *Me* cyclo*propane*-1 : 2-*dicarboxylate*-2-*acetate*, b.p. 146—148°/14 mm., and Me pyrazole-3 : 4(4 : 5)-dicarboxylate in the ratio of about 2 : 1. Et 3 : 5-dimethylpyrazoline-5-carboxylate decomposes readily, giving some Et 3 : 4(or 5)-dimethylpyrazole-5(or 4)-carboxylate [*hydrobromide*, m.p. 150—152° (decomp.)], the formation of which involves migration of Me or CO_2Et. Numerous spectrochemical data are recorded. H. B.

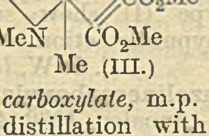
Chromoisomerism of nitrosoantipyrine. G. Rossi and A. Benzi (Gazzetta, 1932, 62, 411—414).—Green nitrosoantipyrine is depolymerised by prolonged boiling with EtOH into a more sol. yellow *isomeride*, decomp. 175°. E. W. W.

Formation of 4(5)-aminoglyoxalines. II. Non-reactivity of the halogen atom in 4(5)-bromoglyoxaline-5(4)-carboxylic acid. I. E. Balaban (J.C.S., 1932, 2423—2425).—Et 2 : 5-dibromoglyoxaline-4-carboxylate is converted (partly) by boiling with aq. Na_2SO_3 into the Et ester of 4(5)-bromoglyoxaline-5(4)-carboxylic acid (I) (King and Murch, J.C.S., 1923, 123, 621) [NH_4 *salt*, m.p. 259°, formed from (I) and conc. aq. NH_3 or EtOH–NH_3 at 150°]. (I) is recovered (partly) or completely destroyed when treated with KCN, Na_2SO_3, Na_3AsO_3, or $CH_2(CO_2Et)_2$ in EtOH; with Cu-bronze, no satisfactory product is obtained. Et glyoxaline-4(5)-carboxylate and aq. NH_3 (*d* 0·88) at 150° give *glyoxaline*-4(5)-*carboxylamide* (+H_2O), m.p. 215° (*picrate*, m.p. 228°), which could not be converted (Hofmann reaction) into 4(5)-aminoglyoxaline, is reduced (Na–Hg, dil. H_2SO_4) to a little 4(5)-hydroxymethylglyoxaline, and with Br (1 mol.) in $CHCl_3$ gives (mainly) 2 : 5-*dibromoglyoxaline*-4-*carboxylamide*, m.p. 256°. An NH_2 group could not be introduced into glyoxaline or 5-chloro-1-methylglyoxaline by $NaNH_2$ in xylene. H. B.

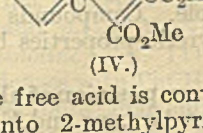
Amino-acids. III. Piperonylalanine. V. Deulofeu and J. Mendive (Z. physiol. Chem., 1932, 211, 1—4; cf. this vol., 949).—*Piperonylalanine* (I), m.p. 262—264° (*phenylcarbimido*-derivative, m.p. 192—193°), was obtained from piperonal (II) in good yield by various methods. (1) Erlenmeyer synthesis: (II) +hippuric acid ⟶ azlactone ⟶ piperonyl-*N*-benzamidoacrylic acid ⟶ N-*benzoylpiperonylalanine* (III), m.p. 181—182°. Hydrolysis of (III) with aq. $Ba(OH)_2$ yields (I). (2) Condensation with hydantoin: (II) +hydantoin ⟶ piperonylidenehydantoin ⟶ *piperonylhydantoin*, m.p. 182—183° ⟶ [with aq. $Ba(OH)_2$] (I). Similarly, thiohydantoin ⟶ *piperonylidene-2-thiohydantoin*, m.p. 288—290° (decomp.) ⟶ piperonylidenehydantoin. (3) (II) condenses with diketopiperazine, giving *bis*(*piperonylidene*)*diketopiperazine*, m.p. not below 300°, which on reduction with Zn forms *bis*(*piperonyl*)*diketopiperazine*, m.p. 251—252°. Hydrolysis of the last with aq. $Ba(OH)_2$ at 115° affords (I). J. H. B.

Pyrimidines. CXXX. Synthesis of 2-keto-1 : 2 : 3 : 4-tetrahydropyrimidines. K. Folkers, H. J. Harwood, and T. B. Johnson (J. Amer. Chem. Soc., 1932, 54, 3751—3768).—Condensation of $CO(NH_2)_2$, a β-ketonic ester, and an aldehyde (cf. Biginelli, A., 1893, i, 645) is accelerated by HCl and occurs in abs. EtOH or glacial AcOH. PhCHO, $CO(NH_2)_2$, and $CH_2Ac·CO_2Et$ in EtOH containing a little conc. HCl give 78·5% of *Et* 2-*keto*-4-*phenyl*-6-*methyl*-1 : 2 : 3 : 4-*pyrimidine*-5-*carboxylate*, m.p. 202—204°. The following 4-substituted Et 2-keto-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylates are prepared: p-*hydroxyphenyl*, m.p. 227—229°; *anisyl*, m.p. 201—202°; p-*nitrophenyl*, m.p. 207—208·5°; m-*nitrophenyl*, m.p. 226—227·5°; *styryl*, m.p. 238—239·5°; β-*phenylethyl*, m.p. 179·2—180·2°; *hexyl*, m.p. 151—152°; *methyl*, m.p. 189—190°; p-*aminophenyl*, m.p. 220—221°, and m-*aminophenyl*, m.p. 208·2—209·5°, prepared by catalytic reduction of the NO_2-derivatives; 4′-*hydroxy*-3′-*methoxyphenyl*, m.p. 232—233°; 3′ : 4′-*dimethoxyphenyl*, m.p. 178—178·5°; 3′ : 5′-*di-iodo*-4′-*hydroxyphenyl*, m.p. 216°; 2′ : 4′ : 6′-*trimethoxyphenyl*, m.p. 185—185·5°; o-*hydroxyphenyl*, m.p. 201—202°; 2′ : 4′-*dihydroxyphenyl*, m.p. 225·5—226·5°; *furyl*, m.p. 204·5—205°; 3′ : 4′-*methylenedioxyphenyl*, m.p. 187—188°; βζ-*dimethyl*-$\Delta^{\alpha\epsilon}$-*heptadienyl*, m.p. 150·5—151·5° (accompanied by a *substance*, m.p. 110—111·5°). *Et* 2-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylate* has m.p. 253·8—256°. C. J. W. (*b*)

Synthesis in the hydroaromatic series. O. Diels and K. Alder. **XVI, XVII. "Dien"-syntheses of heterocyclic nitrogen compounds. 4. Syntheses with pyrroles, glyoxalines, and pyrazoles.** [With H. Winckler and E. Petersen.] **5. Syntheses with pyridine, quinoline, 2-methylquinoline, and *iso*quinoline.** [With T. Kashimoto, Friedrichsen, W. Eckardt, and H. Klare] (Annalen, 1932, 498, 1—15, 16—49).—XVI. 2-Methylpyrrole and Me acetylenedicarboxylate (I) give an *adduct*, m.p. 52°, in addition to that (m.p. 111°) previously described (A., 1931, 849); both are reduced (H_2, colloidal Pd, MeOH) to Me α-2-methyl-5-pyrrylsuccinate (*ibid.*, 1428), indicating that they are *cis-trans*-isomerides. 2 : 3-Dimethylpyrrole and aq. maleic anhydride give α-2 : 3-*dimethyl*-5-*pyrrylsuccinic acid*, m.p. 113° (decomp.) [*Me* ester (II), m.p. 82°]; with (I), isomeric (maleate and fumarate) *adducts*, m.p. 98° and 132° [both reduced (Pd) to (II)], are produced. 2 : 3 : 4-Trimethylpyrrole and maleic anhydride in C_6H_6 afford an *adduct*, $C_{11}H_{13}O_3N$, m.p. 148° (decomp.); with (I), an *adduct*, $C_{13}H_{17}O_4N$, m.p. 137—138° (*H_2* derivative, m.p. 95°), results. Prolonged interaction of 1-methylindole and (I) gives *Me* αα′-*di*-(1-*methyl*-2-*indolyl*)*succinate*, m.p. 157—158°. 4(5)-Methylglyoxaline and (I) in Et_2O afford *Me* α-4-*methyl*-2(or 5)-*glyoxalinylmaleate*, m.p. 103—104°, whilst 1 : 2-dimethylglyoxaline similarly gives *Me* 1 : 8-*dimethyl*-1 : 8-*dihydropyriminazole*-4 : 5 : 6 : 7-*tetracarboxylate* (III), m.p. 163° (decomp.), formed by addition of 2 mols. of (I) to the ·N:CMe· group. (III) and Br in MeOH give *Me* 2-*methylpyridine*-3 : 4 : 5 : 6-*tetracarboxylate*, m.p. 73° (the free acid is converted by distillation with CaO into 2-methylpyridine). Treatment of (III) with AcOH affords NH_2Me and



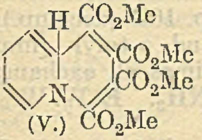
(III.)

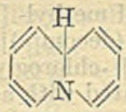


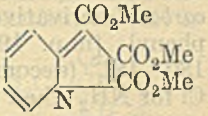
(IV.)

the *indolizine ester* (IV), m.p. 138—139°. Pyrazole and (I) in Et_2O give an *adduct*, $C_{12}H_{14}O_4N_4$, m.p. 158° (in one case an *isomeride*, m.p. 139°, was obtained), whilst 3 : 5-dimethylpyrazole similarly affords *adducts*, $C_{11}H_{14}O_4N_2$, m.p. 58°, and $C_{16}H_{22}O_4N_4$, m.p. 188°.

XVII. Addition of (I) to C_5H_5N and related compounds occurs in a manner analogous to that with 1 : 2-dimethylglyoxaline. C_5H_5N and (I) in AcOH give [by polymerisation of (I)] Me mellitate; in Et_2O, *Me quinolizine*-1 : 2 : 3 : 4-*tetracarboxylate* (V), yellow, m.p. 187—188° (becoming red) [*chloroplatinate*, m.p. 197—198° (decomp.); *dinitrate*, decomp. 103—105°], and an *isomeride*, red, m.p. 124—125° (slight decomp.) [converted into (V) by crystallisation from hot MeOH, MeCN, or 50% AcOH], are produced. Reduction (H_2, PtO_2, AcOH) of (V) gives a *H*$_4$ derivative, m.p. 144°, whilst oxidation with H_2O_2 in AcOH affords an *acid*, $C_9H_7O_5N$, m.p. 161° (decomp.), which when heated to about 180° passes into pyridine-*N*-oxide and on reduction (H_2, PtO_2, AcOH) gives piperidine-2-carboxylic acid. (V) is converted by boiling dil. HCl into an *acid hydrochloride*, $C_{10}H_{10}O_2NCl$ (*octahydro*-derivative, m.p. 249—250°), and by boiling anhyd. HCO_2H into *Me*$_3$, m.p. 75°, and *Me*$_2$ *H*, m.p. 200°, *quinolizinetricarboxylates* [the *Me H*$_2$ ester ($+H_2O$), m.p. 245° (decomp.), is obtained by hydrolysis of the Me_2 and Me_3 esters with dil. HCl or moist HCO_2H]. Hydrolysis of (V) with aq. KOH gives first a *salt*, $C_{15}H_{11}O_8NK_2,H_2O$, and then the K salt of *quinolizinedicarboxylic acid*, m.p. 229° (decomp.). Distillation of this acid with CaO affords *quinolizine* (VI), b.p. 210—220° (*picrate*, m.p. 96°), reduced (H_2, PtO_2, AcOH) to *octahydroquinolizine*, b.p. 166—167° (*picrate*, m.p. 203°), which is converted by CNBr into 2-*n*-butylpiperidine (*hydrochloride*, m.p. 191°). Oxidation of (V) with dil. HNO_3 or $Na_2Cr_2O_7$–AcOH gives *Me indolizinetricarboxylate* (VII), m.p. 151—152°, hydrolysed by aq. KOH to a *salt*, $C_{11}H_6O_6NK$, which when heated with dil. HCl affords (by loss of CO_2) *indolizinemonocarboxylic acid*, m.p. 240—242° (darkens from about 220°). Distillation of this with CaO gives *indolizine*, m.p. 75° (*picrate*, m.p. 101°), the H_8 derivative (*picrate*, m.p. 225°) of which is converted by CNBr into *dl*-coniine. A small amount of a *Me*$_3$ ester (VIII), $C_{16}H_{13}O_8N$, m.p. 186—187°, is formed in addition to (V) and its isomeride from C_5H_5N and (I); (VIII) is also obtained [as *nitrate*, m.p. 92—93° (decomp.)] from (V) and cold fuming HNO_3. (VIII) is reduced (H_2, PtO_2, AcOH) to a *H*$_6$ derivative, m.p. 153—154°, is oxidised by H_2O_2 in AcOH to the acid, $C_9H_7O_5N$ (above), and is hydrolysed by dil. HCl to a *Me H*$_2$ ester, m.p. 190—191° (decomp.) [converted by diazomethane into (VIII)].


(V.)


(VI.)


(VII.)

The *adduct*, $C_{21}H_{19}O_8N$, m.p. 165—167° (becoming red), from *iso*quinoline and (I) is oxidised by dil. HNO_3 to a *compound*, $C_{18}H_{15}O_6N$, m.p. 154—155°. Quinoline and (I) in Et_2O give an *adduct*, $C_{21}H_{19}O_8N$, m.p. 181—182° (becoming red), whilst 2-methylquinoline affords two isomeric *adducts*, $C_{22}H_{21}O_8N$, yellow, m.p. 174—175° (becoming red), and red, m.p. 204°.

H. B.

Products of condensation of *o*-homophthalimide with aromatic aldehydes. A. Meyer (Bull. Soc. chim., 1932, [iv], 51, 953—963; cf. A., 1928, 773).—The m.p. of *o*-vanillylidenehomophthalimide is now given as 311°. Interaction of *o*-aminobenzaldehyde with homophthalimide under the standard conditions gives 7-keto-7 : 8-dihydro-2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine, m.p. 246° (cf. A., 1927, 1089).

H. A. P.

Attempted synthesis of pentazole. Action of diazomethane on azoimide. E. Oliveri-Mandalà (Gazzetta, 1932, 62, 716—720).—This reaction, in Et_2O, gives only methylazoimide.

E. W. W.

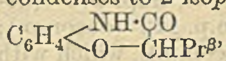
Acetylene and its *iso*oxazolic derivatives. IX. Some *iso*oxazole derivatives. A. Quilico and M. Freri (Gazzetta, 1932, 62, 436—444).—P_2O_5 converts *iso*oxazole-5-carboxylamide (A., 1930, 622) into 5-*cyano*iso*oxazole* (I), b.p. 168°, easily hydrolysed by dil. H_2SO_4, and very easily degraded by alkalis to cyanoacetic acid and HCN. Attempts to reduce (I) to the amine did not succeed; with MeMgI in Et_2O, (I) gives 5-*acetyl*iso*oxazole* (II), m.p. between 20° and 35° [$NaHSO_3$ *compound*; *phenylhydrazone*; p-*nitrophenylhydrazone*, m.p. 220—221°; *semicarbazone*, m.p. 207° (decomp.)]. (II) is converted by warm HNO_3 (*d* 1·41) into 5 : 5′-di*iso*oxazoloylfuroxan [*phenylhydrazone*, m.p. 145° (decomp.)], obtainable from C_2H_2 (cf. A., 1931, 968) and *iso*oxazole-5-carboxylic acid. NaOEt opens the ring of (II), giving $CN{\cdot}CH_2{\cdot}CHO$.

E. W. W.

Curtius degradation applied to *iso*oxazole-5-carboxylic acid and 5-methyl*iso*oxazole-3-carboxylic acid. M. Freri (Gazzetta, 1932, 62, 457—463).—*iso*Oxazole-5-carboxylamide (A., 1930, 622) yields iso*oxazole-5-carboxylhydrazide*, m.p. 141—142° (decomp.), oxidised by $NaNO_3$ and HCl at 0° to the -5-*carboxylazide*, m.p. 37° (decomp.), explosive, from which the -5-*urethane*, m.p. 74—75°, is obtained (EtOH), but in insufficient amount for the prep. of the amine (cf. A., 1931, 1170). Me 5-methyl*iso*oxazole-3-carboxylate yields successively the -3-*carboxylhydrazide*, m.p. 131—132°, the -3-*carboxylazide*, m.p. 112° (decomp.), explosive, and the -5-*urethane*, m.p. 82°. The last, decomp. on heating with conc. HCl in a sealed tube, gives with dil. HCl a product (I) which forms a *Bz* derivative (II), m.p. 160—161°, not of an amine, but of a OH-compound. Since (I) gives no colour with $FeCl_3$, (II) is considered to be 2-*benzoyl*-5-*methyl*iso*oxazol*-3-*one*, an isomerisation having taken place after the hydrolysis.

E. W. W.

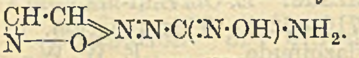
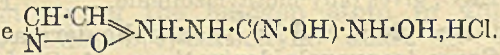
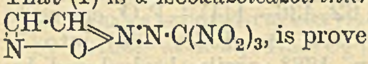
New ketomorpholine derivatives. G. Sanna (Gazzetta, 1932, 62, 555—557; cf. A., 1931, 747).—o-α-*Bromo*iso*valeramidophenol*, m.p. 114°, obtained from α-bromo*iso*valeroyl chloride, in presence of KOH condenses to 2-iso*propylphenmorpholone*,



$C_6H_4{<}\begin{matrix}NH{\cdot}CO\\ O{-}CHPr^{\beta}\end{matrix}$, m.p. 125°. o-α-*Bromo*iso*hexamidophenol*, m.p. 115°, similarly yields 2-iso*butylphenmorpholone*, m.p. 128°.

E. W. W.

Acetylene and its *iso*oxazolic derivatives. XI. Structure of reaction products of nitric acid and

acetylene. A. QUILICO (Gazzetta, 1932, 62, 503—518).—The explosive compound $C_4H_2O_7N_6$ (I), the hydrochloride $C_4H_8O_3N_5Cl$ (II), the yellow compound $C_4H_5O_2N_5$ (III), and the compound $C_4H_2O_3N_4$ (IV) (A., 1931, 194) were re-investigated. With conc. HCl, (III) [*Ag*, *Cu* salts; *Ac* derivative, m.p. 195° (decomp.); *Bz* derivative, m.p. 218°] forms in the cold a *hydrochloride*, m.p. 100—105° (decomp.), but in the hot it is decomposed to CO_2, NH_2OH,HCl, and NH_4Cl. By the action of $SnCl_2$ and HCl (III) takes up the elements of H_2O to form (II), which is reconverted into (III) by KOH. With KOBr, (III) yields α-*iso*-oxazolediazoimide (this vol., 171); it is therefore identified as α-iso*oxazoleazoformamidoxime*,  $\begin{array}{l}CH\cdot CH\\N—O\end{array}\!\!>N\!:\!N\cdot C(\!:\!N\cdot OH)\cdot NH_2$. From this, (II) would probably be  $\begin{array}{l}CH\cdot CH\\N—O\end{array}\!\!>NH\cdot NH\cdot C(N\cdot OH)\cdot NH\cdot OH,HCl$. That (I) is α-iso*oxazoleazotrinitromethane*,  $\begin{array}{l}CH\cdot CH\\N—O\end{array}\!\!>N\!:\!N\cdot C(NO_2)_3$, is proved by synthesis. *Benzeneazotrinitromethane* is prepared from PhN_2Cl and the NH_4 salt of $CH(NO_2)_3$; it explodes violently on percussion or at 70—75°, but when heated slowly in AcOH it forms a *compound*, $C_7H_5O_2N_3$, m.p. 83°, very similar to (IV). p-*Nitrobenzeneazotrinitromethane* is also prepared, and when heated forms a *compound*, m.p. 160°. The product from α-*iso*oxazolylamine and the NH_4 salt of nitroform is identical with (I).

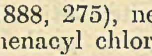
E. W. W.

Dioximes. LXXXVII, LXXXVIII. G. PONZIO. **LXXXIX.** G. CARBONE. **XC.** M. MILONE. **XCI.** G. PONZIO. **XCII.** G. LONGO (Gazzetta, 1932, 62, 415—423, 424—427, 428—431, 432—435, 633—639, 640—644).—LXXXVII. The substance considered by Böeseken (A., 1912, i, 723) to be 5-hydroxy-3-benzoyl-1 : 2 : 4-oxadiazole (A., 1926, 1159) is 5-*phenyl*-1 : 2 : 4-*oxadiazole*-3-*carboxylic acid* (*Ag* salt), since on boiling with H_2O it loses CO_2 and isomerises to benzoylcyanamide, and since its *K* salt reacts with $POCl_3$ followed by aq. NH_3 to form 5-phenyl-1 : 2 : 4-oxadiazole-3-carboxylamide (A., 1930, 1410), which is hydrolysed again to the acid, and is the first product from KOEt and 4-amino-3-benzoyl-1 : 2 : 5-oxadiazole. 4-Amino-3-*p*-toluoyl-1 : 2 : 5-oxadiazole (A., 1928, 414) with KOEt gives 5-p-*tolyl*-1 : 2 : 4-*oxadiazole*-3-*carboxylic acid* (*Ag* salt), which ($+0{\cdot}5H_2O$) loses CO_2 at 130°, or in boiling H_2O, forming p-*tolylcyanamide*, m.p. 155—156° [*Ag* salt, m.p. 260° (decomp.)], also prepared from cyanamide.

LXXXVIII. α-Chloro-β-methyl- and α-chloro-β-phenyl-glyoximes with $AgNO_2$ in Et_2O form, not the NO_2-derivatives, but βγδε-tetraoximinohexane diperoxide (A., 1925, i, 79) and αβγδ-*tetraoximino*-αδ-*diphenylbutane diperoxide*, m.p. 162° (decomp.), respectively. The mechanism of the reaction is discussed.

LXXXIX. α-Chloro-β-methylglyoxime with NaI in $COMe_2$ yields α-*iodo*-β-*methylglyoxime*, m.p. 173° (decomp.) [*Ni* salt; *Ac*$_2$ derivative, m.p. 122° (decomp.); *Bz*$_2$ derivative, m.p. 190° (after decomp.)], which with Na_2CO_3 gives diacetylglyoxime dioxime peroxide, with KCN the α-CN-compound, and with $AgNO_2$ in Et_2O gives βγδε-tetraoximinohexane diperoxide. α-Chloro-β-phenylglyoxime similarly yields α-*iodo*-β-*phenylglyoxime*, m.p. 179° (after decomp.) (*Bz*$_2$ derivative, m.p. 187°), which has similar properties, and with NaOAc and AcOH gives hydroxyphenylglyoxime. α-*Iodo*-β-p-*tolylglyoxime* has m.p. 170° (decomp.).

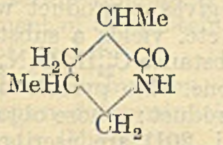
XC. The absorption spectra (cf. this vol., 558) of phenyl-, *p*-bromophenyl-, *p*-methoxyphenyl-, 3 : 4-methylenedioxyphenyl-, and 3 : 4-dimethoxyphenylmethylglyoxime peroxide confirm the structures which have been assigned to them (A., 1928—1931). p-*Bromophenylmethyloxadiazole*, m.p. 64°, is prepared by reducing *p*-bromophenylmethylfuroxan (A., 1928, 888) with $SnCl_2$.

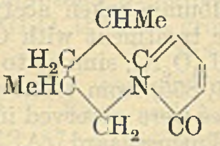
XCI. The isomeric form of dibenzoylglyoxime peroxide (cf. A., 1888, 275), new m.p. 188°, new prep. from oximinophenacyl chloride in an acetate buffer of p_H 4·6, is regarded as 4 : 5-*dibenzoyl*-1 : 2 : 3 : 6-*dioxadiazine*,  $CBz\!\!<\!\!\begin{array}{l}CBz\!:\!N\\N\cdot O\cdot O\end{array}$. It is converted by 5% NaOH into cyanoformhydroxamic acid, $CN\cdot C(OH)\!:\!NOH$ ($+0{\cdot}5H_2O$), m.p. 114—115° (decomp.), which is hydrolysed by 20% H_2SO_4 to CO_2, HCN, and NH_2OH.

XCII. α-Chloroglyoxime (I) (A., 1930, 1409) forms with PhNCO a *dicarbanil* derivative (cf. this vol., 513), m.p. 156—157° (decomp.), converted by aq. NH_3 into (I), and by aq. HCl into β-chloroglyoxime (*loc. cit.*), of which the *dicarbanil* derivative, m.p. 163—164° (decomp.), is converted by aq. NH_3 into aminoglyoxime. Since substitution in the oximino-groups of (I) and (II) thus does not affect the reactivity of the Cl atoms, the isomerism of (I) and (II) is not thought to be due to *syn–anti* configurations of OH and Cl (*loc. cit.*), and remains unexplained. *Dicarbanil* derivatives of methyl- [m.p. 166° (decomp.)], phenyl- [m.p. 190° (decomp.)], and *p*-tolyl- [m.p. 180—181° (decomp.)] -chloroglyoximes all exchange Cl for NH_2 when treated with aq. NH_3. E. W. W.

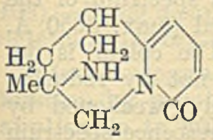
Constitution of cytisine. E. SPÄTH and F. GALINOVSKY (Ber., 1932, 65, [*B*], 1526—1535).—The Hofmann degradation of cytisine gives bimol. products in its first stage when performed according to Partheil (A., 1893, i, 119; 1894, ii, 558; 1895, ii, 119, 254) or Ing (A., 1931, 1171). Elimination of H_2O from the quaternary base from methylcytisine methiodide occurs readily at 90°/vac. and the product is readily hydrogenated to *de*-N-*dimethyldihydrocytisine* (I), b.p. 150—160° (bath)/0·001 mm. (*picrate*, m.p. 174—175°, $[\alpha]_D^{21}$ −46·94° in MeOH); at a higher temp., bimol. products result which are not readily hydrogenated. (I) and MeI in MeOH afford the *methiodide*, converted by successive treatment with Ag_2O and heating at 100—120°/10 mm. into NMe_3 and *dihydrohemicytisylene*, $C_{11}H_{13}ON$, b.p. 140° (bath)/0·01 mm., $[\alpha]_D$ −1·1° in C_6H_6 (*chloroplatinate*), hydrogenated in aq. MeOH in presence of Pd–C to *tetrahydrohemicytisylene* (II), b.p. 130—140° (bath)/0·001 mm., $[\alpha]_D$ −0·26° (*chloroplatinate*), which does not contain a NMe group. Since attempts to show the presence of a 1-methyl-2-quinolone complex in (II) were unsuccessful and the presence of a 2-pyridone ring is established (Späth, A., 1919, i, 451, 453), it follows that the N atom of (II) belongs to two rings and that the quinoline ring of the degradation products of Freund (A., 1904, i, 263) and of Späth (*loc. cit.*) is not initially present in cytisine. Further evidence is deduced from the degradation of tetrahydrodeoxycytisine, transformed through the methiodide and the corresponding hydroxide and subsequent hydrogenation (Pd–C in AcOH) into *dihydrode*-N-*dimethyltetrahydrodeoxycytisine* (III), b.p. 132°/11 mm. (*chloroplatinate*). (III) affords two (?) stereoisomeric *dimethiodides*, $C_{15}H_{32}N_2I_2$, cryst., decomp. 325—327° (vac.), and amorphous. The base from the cryst. compound at 90—100°/vac. affords NMe_3 and a base which contains 1 NMe group and absorbs $2H_2$ (Pd–C in AcOH) with production of the *compound* $C_{12}H_{25}N$ (IV), b.p. 90—110° (bath)/10 mm. The final stage of the degradation leads through the non-cryst. *methiodide* to a base containing 2 Me groups attached to N and hydrogenated to the *compound* $C_{13}H_{29}N$. Further evidence of the existence of the pyridone complex is obtained by hydrogenating cytisine to *tetrahydrocytisine*, m.p. 113—114° (vac.), oxidised by 1% $KMnO_4$ at room temp. to $H_2C_2O_4$ and glutaric acid (similar treatment of cytisine gives solely $H_2C_2O_4$); analogously (II) is converted into *octahydrohemicytisylene*, b.p. 120—130° (bath)/0·05 mm., oxidised to glutaric acid identified as the dianilide, m.p. 225°. Ozonolysis of (II) affords the *lactam* (A), m.p. 70—75° after softening at 65°, transformed by conc. HCl at 100° into an NH_2-acid, oxidised by $KMnO_4$ in hot, feebly alkaline solution to a mixture of the inactive forms of αα′-dimethylglutaric acid. To (II) the constitution (II) is assigned. For cytisine the structure (III), (IV), or (V) is suggested. H. W.

(A)

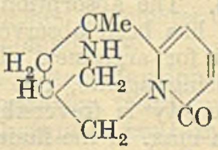




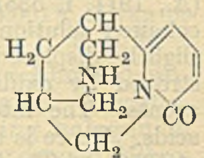
(II.)



(III.)



(IV.)



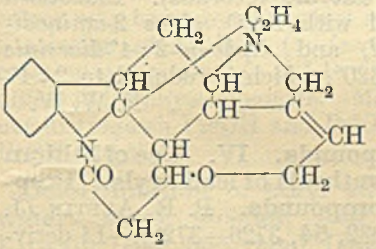
(V.)

Ergot alkaloids. I. Oxidation of ergotinine. W. A. Jacobs (J. Biol. Chem., 1932, 97, 739—743).—Oxidation of ergotinine with HNO_3 gives, besides BzOH and p-$NO_2\cdot C_6H_4\cdot CO_2H$, a tribasic *acid*, $C_{14}H_9O_8N$, m.p. >350° (darkens 265°, sinters 290°) [*Me* ester, m.p. >350° (darkens 260°, sinters 285°)]. A. A. L.

Detection of solanine. B. Alberti (Z. Unters. Lebensm., 1932, 64, 260—262).—Solanine or solanidine give a yellow colour with conc. H_2SO_4, and reddish-purple, intensifying on keeping, when conc. H_2SO_4 and 1 drop of either 1% CH_2O or 0·5% H_2O_2 are added in succession to a solution of the alkaloid residue in conc. AcOH. The sensitiveness of the latter reaction is 0·0025 mg. (Autenrieth's H_2SeO_4 reagent, 0·025 mg.) and it is inert towards saponins and most alkaloids; morphine reacts with CH_2O, but not with H_2O_2. J. G.

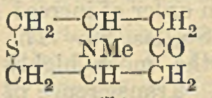
Strychnine and brucine. XX. Derivatives of ψ-strychnine. Comments on a recent memoir of H. Leuchs, "Über Strychnos-alkaloide." LXVIII. B. K. Blount and R. Robinson (J.C.S., 1932, 2305—2310).—ψ-Strychnine (Warnat, A., 1931, 1312) [*perchlorate*, not melted at 300° (blackens above 240°); *ferrichloride*, m.p. 234—235° (decomp.) after darkening] is reduced (Zn dust, 2*N*-HCl) to strychnine and is relatively stable to alkaline $K_3Fe(CN)_6$. The *methiodide*, m.p. 213° (decomp.) (depends on rate of heating), of *O*-methyl-ψ-strychnine (*loc. cit.*) is converted by aq. KOH in MeOH into *de*-N : O-*dimethyl*-*ψ-strychnininium hydroxide*, m.p. 174—175° (decomp.), which with PhCHO and a little KOH in MeOH gives *substances*, m.p. 153° and 189—193° (sinters at 180°), and is hydrolysed by dil. HCl at 100° to N-*methylchano*-*ψ-strychnine*, m.p. 270—271° (decomp.) [*perchlorate*, blackens at 250° and explodes at 295°; *dibenzylidene* derivative, m.p. 284—285° (decomp.) (previous darkening)]. ψ-Strychnine is most probably hydroxystrychnine, which contains the group ⁚N(*b*)·C(OH)⁚ and probably the group ⁚N(*b*)·$\dot{C}$(OH)·CH_2·.

Contrary to the opinion of Leuchs (this vol., 953), strychnine does not behave like a dihydroindole (or even hexahydrocarbazole); hence, one (α or β) of the C atoms of the indole group must be attached by a C chain to N (*b*). The β-C atom is probably attached to H, since dioxonucidine is readily monobrominated (Leuchs, *loc. cit.*). The annexed constitution best expresses the known chemical behaviour of strychnine (and its derivatives). H. B.



Hydroferro- and hydroferri-cyanides of the alkaloids. W. M. Cumming and J. A. Stewart (J.S.C.I., 1932, 51, 273—276T).—An extension (cf. J.S.C.I., 1925, 44, 110T; 1928, 47, 84T). The *hydroferro*- and *hydroferri-cyanides* of the following have been prepared in acid, neutral, and EtOH solutions: papaverine, benzamine, quinidine, quinaldine, berberine, thebaine, atropine, hyoscyamine (*l*-atropine), arecoline, cotarnine, percaine, stovaine, tropacocaine, triacetoneamine, diamorphine. Their constitutions have been determined, and photomicrographs of some of the most characteristic cryst. formations are given. No salts were obtainable from benzocaine, orthocaine, borocaine, ephedrine, and diacetoneamine. The only stable hydroferricyanides in neutral solution so far isolated are those of berberine and cotarnine, both bases of the NH_4OH type.

Analogues of ψ-pelletierine, namely, thiotropinone, selenotropinone, and *N*-methylaztropinone. B. K. Blount and R. Robinson (J.C.S., 1932, 2485—2487).—Thiobisacetaldehyde, Ca acetonedicarboxylate, and aq. NH_2Me condensed essentially by the method previously described (A., 1917, i, 581; 1924, i, 1335) give *thiotropinone* (I), m.p. 126—127° (*dipiperonylidene* derivative, m.p. 241°; *picrate*, darkens at 230° and explodes at 255°). Chloroacetal, Na_2Se, and KI in aq. EtOH in absence of air give



(I.)

impure *selenobisdiethylacetal*, b.p. 145—155°/0·1 mm., hydrolysed by warm 0·5% HCl to selenobisacetaldehyde [*di-*p*-nitrophenylhydrazone*, m.p. 205—210° (decomp.)], convertible (as above) into *selenotropinone* (I, S=Se), m.p. 142° (*dipiperonylidene* derivative, m.p. 240°). *N*-Methylaztropinone (I, S=NMe) [*dipicrate*, m.p. 198° (decomp.); *dipiperonylidene* derivative, m.p. 214—216°] is prepared similarly from methyliminobisacetaldehyde (by hydrolysis of its dimethylacetal). H. B.

Arsenical derivatives of diphenyl: molecular size of some arseno-derivatives. C. Finzi and E. Bartelli (Gazzetta, 1932, 62, 545—555).—3 : 3′-Dimethyldiphenyl-4 : 4′-diarsinic acid (A., 1924, i, 1247) with HNO_3 (*d* 1·52) forms a $(NO_2)_2$-derivative, $C_{14}H_{14}O_{10}N_2As_2$, reduced ($Na_xHg_y$) to the $(NH_2)_2$-derivative, stable to 290°. 3 : 3′-Dicarboxydiphenyl-4 : 4′-diarsinic acid (*loc. cit.*) [$(NO_2)_2$- and $(NH_2)_2$-derivatives] is reduced by H_3PO_2 to 4 : 4′-*arsenodiphenyl*-3 : 3′-*dicarboxylic acid* (?) (mol. wt. determinations with the *Na* salt are recorded). Diazotised 2 : 4′-diaminodiphenyl with As_2O_3 gives 2-*aminodiphenyl*-4′-*arsinic acid*, and *diphenyl*-2 : 4′-*diarsinic acid*, no m.p. below 320°, which is reduced to 2 : 4′-*arsenodiphenyl* (?). E. W. W.

Organic lead compounds. IV. Use of lithium derivatives in the synthesis of lead aryls. Preparation of amino-compounds. P. R. Austin (J. Amer. Chem. Soc., 1932, 54, 3726—3729).—Li derivatives are generally applicable to the prep. of org. compounds of Hg, Sn, and Pb. Li *p*-tolyl and $HgCl_2$ give 89% of Hg di-*p*-tolyl; *p*-$NMe_2\cdot C_6H_4\cdot Li$ affords 12% of $Hg(C_6H_4\cdot NMe_2\text{-}p)_2$; LiPh and $PbCl_2$ give 48% of $PbPh_4$ (the initial product, $PbPh_2$, is transformed into $PbPh_4$ by heat; if the heating is interrupted, a mixture of $PbPh_3$ and $PbPh_4$ is formed). $PbPh_3Cl$ and Li *p*-tolyl give 41% of Pb triphenyl *p*-tolyl, m.p. 124—125°; $PbPh_2Cl_2$ similarly gives 38% of *Pb diphenyl ditolyl*, m.p. 121—122°. $PbCl_2$ heated with *p*-$NMe_2\cdot C_6H_4\cdot Li$ gives 17% of *Pb tetra*-p-*dimethylaminophenyl*, m.p. 197—198°; $PbPh_3Cl$ similarly affords 77% of *Pb triphenyl* p-*dimethylaminophenyl* (I), m.p. 124—125°, whilst $PbPh_2Cl_2$ gives 16% of *Pb diphenyl di*-(p-*dimethylaminophenyl*), m.p. 134—135°. $SnCl_4$ and Li *p*-tolyl give 91% of Sn tetra-*p*-tolyl; *Sn tetra*-(p-*dimethylaminophenyl*), m.p. 198—199°, is prepared in 58% yield. (I) and AcOH give some Ph_3PbOAc, m.p. 206—207°. $PbEt_4$ and Li *p*-tolyl in C_6H_6–Et_2O give some di-*p*-tolyl. C. J. W. (*b*)

Transference of a phenyl radical from an organometallic derivative to another metal. A. E. Shurov and G. A. Razuvaiev (Ber., 1932, 65, [*B*], 1507—1511).—The appropriate metallic phenyl is heated with the requisite metal, prepared by pptn. from the metallic salt by Zn, at 150—300°, or, less advantageously, in presence of $C_6H_4Me_2$, whereby the following sequence is observed in order of increasing affinity to Pb: Hg, Bi, [Pb], Sb, As, Sn. The product consisted invariably of the most highly phenylated derivative of the metal. Transference of Ph occurs at temp. markedly lower than those of decomp. of the Ph derivative even when, as in the case of Pb, the second metal does not participate in the change. H. W.

[Metallic derivatives of thiophen.] G. Renwanz (Ber., 1932, 65, [*B*], 1556; cf. this vol., 762).—A reply to Steinkopf (*ibid.*, 950). H. W.

Relation of structure to rate of hydrolysis of peptides. VII. Hydrolysis of dipeptides by alkali. P. A. Levene, R. E. Steiger, and A. Rothen (J. Biol. Chem., 1932, 97, 717—726).—The following dipeptides were prepared and their rates of hydrolysis by 0·5*N*-NaOH at 25° determined: *dl*-valylglycine, *dl*-leucylglycine, glycyl-*dl*-valine, glycyl-*dl*-leucine, *d*-alanyl-*d*-alanine, *d*-leucyl-*d*-leucine. Comparison with the corresponding ketopiperazines indicated that any two radicals (attached to the same C) have the same relative effect on the stability of the peptide linking as on that of the ring structure. F. O. H.

Structure of proteins. II. A. Bernardi and M. A. Schwarz (Gazzetta, 1932, 62, 464—468).—Ovalbumin when acetylated gives a product which after treatment with C_2HCl_3 etc. yields a substance $C_{18}H_{24}O_5N_2$, similar to the substance $C_{24}H_{30}O_5N_2$ (A., 1931, 855) from Witte's peptone. No pyrrole derivatives were observed in the product; those obtained by Troensegaard (A., 1921, i, 201) are ascribed to secondary reactions. E. W. W.

Colour reaction and fluorescence of proteins and their derivatives in presence of diacetyl. (Mme.) A. Roche (Bull. Soc. Chim. biol., 1932, 14, 1026—1031).—The colour reaction and fluorescence are independent, being sp. for different groupings. The former depends on the grouping $NH{:}C(NH_2)\cdot NH\cdot R$ (A., 1911, i, 588). The absorption spectrum of the coloured solution has been observed (max. 5250 Å. slightly displaced for arginine). The colour is destroyed by oxidising agents, but not by reducing agents. The intensity is (reversibly) weakened by acids. There is a max. in the fluorescence spectrum at 5950 Å. The fluorescence is shown by degradation products of proteins down to dipeptides, but not by NH_2-acids, and the intensity increases during proteolysis. It is more slowly destroyed by oxidising agents than the coloration, and is unaffected by acids. A. A. L.

Constitution of the keratin molecule. C. Rimington (Nature, 1932, 130, 401).—A reply (cf. this vol., 867). L. S. T.

Constitution of the keratin molecule. J. B. Speakman (Nature, 1932, 130, 401; cf. preceding abstract). L. S. T.

Basic amino-acids of crystalline ovalbumin. H. B. Vickery and A. Shore (Biochem. J., 1932, 26, 1101—1106).—Cryst. ovalbumin yields after acid hydrolysis histidine 1·42%, arginine 5·39%, and lysine 4·97%. S. S. Z.

Preparation of methionine from caseinogen. N. W. Pirie (Biochem. J., 1932, 26, 1270—1274).—The acid hydrolysate, previously cleared by $Pb(OAc)_2$, is extracted with BuOH from which methionine is removed by extraction with NaOH. The yield is 1·4%. S. S. Z.

Determination of methionine in proteins. H. D. Baernstein (J. Biol. Chem., 1932, 97, 663—668).—Zeisel (OMe) procedure gave vals. from 0·54 (arachin) to 5·29% (albumin). The negative results given by the method on 11 NH_2-acids show that true methionine vals. are obtained. F. O. H.

Sulphur distribution in proteins. H. D. Baernstein (J. Biol. Chem., 1932, 97, 669—674).—Determinations of the (thiol+disulphide)-S and of the methionine-S of 32 proteins give vals. accounting for 101·5±6·6% of the total S, of which the first fraction forms 17·7—84·3% and the second 26·0—90·0%. F. O. H.

Point of attachment of heavy metals to proteins. F. Lieben and L. Löwe (Biochem. Z., 1932, 252, 64—69; cf. Ettisch, this vol., 465).—At reactions near to neutral the K in K–caseinogen compound is almost quantitatively replaced by Cu or Ag on addition of $CuSO_4$ or $AgNO_3$. Since the amount of the compound produced by addition of KOH to caseinogen or to serum-albumin is not diminished by previous treatment of the protein with CH_2O, the NH_2 groups do not bind K. W. McC.

Micro-combustion method for carbon and hydrogen determination. P. L. Kirk and A. G. McCalla (Mikrochem., 1932, 12, 87—97).—Apparatus and procedure are described for combustion of 2—2·5 mg. of substance in O_2 using Mn_2O_3 (prepared by reducing NH_4MnO_4 with MeOH) as catalyst. E. S. H.

Micro-analytical methods in the industrial laboratory. IV. Application of micro-Dumas [method] to substances with small nitrogen content. F. Vetter (Mikrochem., 1932, 12, 102—108).—Using a capillary nitrometer 0·001% N can be determined in org. compounds. E. S. H.

Micro-halogen determination without combustion by precipitation from organic solvents, applicable to substances containing halogen in an easily ionisable form. A. Schloemer (Mikrochem., 1932, 12, 114—116).—Interaction with $AgNO_3$–HNO_3 is effected in EtOAc, AcOH, $COMe_2$, EtOH, or MeOH. E. S. H.

Determination of chlorine and bromine in organic substances by combustion in the calorimetric bomb. F. Garelli and B. Saladini (Atti R. Accad. Sci. Torino, 1931, 66, 406—409; Chem. Zentr., 1932, i, 2870—2871).—In a modification of Valeur's method, the substance (0·1—0·3 g.) is treated with decalin (0·5—0·8 c.c.) and burned in a calorimetric bomb containing 10 c.c. of aq. NH_3 (*d* 0·93), the halogen being titrated by Volhard's method. A. A. E.

Determination of sulphur in organic compounds. R. J. Rosser and F. N. Woodward (J.C.S., 1932, 2357—2358).—A modification of Asbóth's method (A., 1896, ii, 448), in which a Ni test-tube replaces the crucible, gives trustworthy results with all org. S compounds. J. W. B.

Microanalytical determination of sulphur in organic substances by a volumetric method. A. Friedrich and O. Watzlaweck (Z. anal. Chem., 1932, 89, 401—411).—The low vals. for S sometimes given by the method previously described (A., 1929, 1328) are due to incomplete oxidation of SO_2 to H_2SO_4, even after passing through aq. H_2O_2. By neutralising before evaporation loss of SO_2 is avoided, and, on subsequent evaporation, the Na_2SO_3 is oxidised to Na_2SO_4. When adding H_2SO_4 and evaporating, as a preliminary to the $NaHSO_4$ back-titration, care must be taken that salts of volatile acids do not separate around the edge while unused H_2SO_4 remains at the bottom of the dish. The method is applicable in the presence of Cl and Br, but not in the presence of I. M. S. B.

Determination of propyl alcohol in mixtures of ethyl alcohol and water. O. Noetzel (Z. Unters. Lebensm., 1932, 64, 288—293).—The sample is adjusted to contain 40 vol.-% of total alcohols and distilled with CrO_3 and H_2SO_4, the distillate being collected at 0°, and 0·6 c.c. heated for 6 min. at 65° with 3 drops of a 2% solution of vanillin in EtOH and 4 c.c. of fuming HCl. The cool solution is orange if 3% of $Pr^{\alpha}OH$ is present (the limit of the test), reddish-brown for 10%, and deep purple for 20%, and the colour may be matched against a standard mixture or a solution of colloidal Cu ferrocyanide. A similar reaction is given by $CH_2Pr^{\alpha}OH$, which, however, differs in its physical consts. Measurements of *n* will not distinguish $Pr^{\alpha}OH$ and $Pr^{\beta}OH$ in the presence of EtOH and H_2O. J. G.

Determination of ethyl ether in presence of water, ethyl alcohol, and acetaldehyde. A. Lalande (Bull. Soc. chim., 1932, [iv], 51, 916—921).—An apparatus is described in which the Et_2O is entrained by a current of air or O_2, freed from EtOH and MeCHO by conc., strongly alkaline K_2MnO_4 (or $KMnO_4$?), and absorbed in acidified aq. $K_2Cr_2O_7$ (the excess of which is determined iodometrically), or, alternatively, determined by combustion with CuO. H. A. P.

Action of ultra-violet light on pyridine. I. New test for some primary amines and pyridine. H. Freytag and W. Neudert (J. pr. Chem., 1932, [ii], 135, 15—35; cf. A., 1911, ii, 242).—Irradiation of C_5H_5N with light of $\lambda < 300$ μμ gives rise to *photopyridine*, a yellowish-brown microcryst. solid, which may be isolated by irradiation in EtOH and removal of excess of C_5H_5N with $ZnCl_2$. The reaction is accelerated by acids or by solvents that give rise to them on irradiation ($COMe_2$, EtOH), and by many inorg. salts, and is retarded or completely inhibited by strong bases, alkali-metal salts, $HgCl_2$, $CoCO_3$, and $NiCl_2$. Photopyridine is decomposed by heat and by cold H_2O into C_5H_5N and unidentified cryst. products. It reacts with primary arylamines to form highly coloured substances, which are in general sensitive to acids and alkalis; this reaction is a sensitive test for C_5H_5N or the amine in question. The red product obtained with β-$C_{10}H_7\cdot NH_2$ is isolated in a cryst. state; it melts with decomp. and formation of a white cryst. sublimate. H. A. P.

Determination of aniline by means of picryl chloride. I. Determination of aromatic amines by means of picryl chloride. II. B. Linke, H. Preissecker, and J. Stadler (Ber., 1932, 65, [B], 1280—1282, 1282—1284).—An approx. 0·1*M* solution of NH_2Ph in EtOAc is treated with an equally conc. solution of picryl chloride in the ratio 1 : 1·5 and about 0·1 g. of $NaHCO_3$ for 15 min. at room temp. After addition of H_2O, the mixture is heated for 15 min. on the water-bath, kept for 3 hr., and filtered. Cl′ is determined in the filtrate gravimetrically or volumetrically (Mohr). The reaction is $NH_2Ph+C_6H_2Cl(NO_2)_3+NaHCO_3=NaCl+CO_2+H_2O+NHPh{\cdot}C_6H_2(NO_2)_3$.

II. In EtOAc aromatic amines with negative substituents react incompletely or not at all with picryl chloride. *o*- and *p*-Toluidine react quantitatively, whereas *m*-toluidine gives irregular results. *p*-Aminophenol gives low vals., but its Me ether can be determined. *o*- and *p*-Anisidine react quantitatively. *sec.*-Amines are almost without action. Both NH_2 groups of benzidine undergo nearly quant. change, but the base is not readily determined by this method owing to the difficultly filterable ppt. α-$C_{10}H_7{\cdot}NH_2$ condenses uniformly to the extent of about 97%, whereas the β-compound behaves irregularly. H. W.

Analysis of hydrazines. Y. G. Vendelshtein (Anilinokras. Prom., 1932, 2, No. 1, 37—39).—Richter's method for determining arylhydrazinesulphonic acids by oxidation with 2 mols. of $CuSO_4$ gives 68—89% of the total N; quant. vals. are obtained by the use of a 10-fold excess of $CuSO_4,5H_2O$ in HCl. Ch. Abs.

Detection and determination of phenylalanine. R. Kapeller-Adler (Biochem. Z., 1932, 252, 185—200).—The violet colour of the NH_4 salt of the *diaci*dinitro*cyclo*hexadienecarboxylic acid (cf. Meisenheimer, A., 1919, i, 389) produced when phenylalanine (or *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, which is an intermediate product; BzOH is not produced) is nitrated with $KNO_3+H_2SO_4$ and the product reduced with NH_2OH in aq. NH_3 is used as a basis for the detection and colorimetric micro-determination of these two substances (0·1 mg. of the former in 15 c.c. of H_2O can be determined). The method can be applied to protein hydrolysates, provided that histidine is removed with phosphotungstic acid and tyrosine by oxidation with acid $KMnO_4$. W. McC.

Micro- and histo-chemical identification of putrescine, cadaverine, phenylethylamine, tyramine, and histamine. G. Klein and S. D. Boser (Arch. Pharm., 1932, 270, 374—385).—The following new m.p. for, first, the hydrochlorides, and, secondly, the Bz derivatives, are recorded: putrescine (I), decomp. 315°, m.p. 175—177°; cadaverine (II), m.p. 275°, 130—135°; histamine (III), m.p. 233—240° (decomp.), 188—190°; β-phenylethylamine (IV), m.p. 205—206°, 108—112°; and tyramine (V), m.p. 260—270°, 169—171°. These derivatives cannot be separated by micro-sublimation. The dihydrochloride of (II) can be separated from mixtures by its solubility in Et_2O. The following reagents give characteristic ppts. with the bases stated, even when all five are present in the mixture: $AuBr_3$ (V); AuI_3, none; PtI_4 (III); picric acid (III), (IV), and (V); picrolonic acid (I), (II), and (V); trinitroresorcinol (II) and (III) [mixtures of (I) and (II) give mixed crystals]; trinitrobenzoic acid (II); phosphotungstic acid (V). Alcoholic extracts of ergot give with these reagents only the picrate and trinitroresorcinol test for (III). Ergot, freed from fat by $CHCl_3$, and then extracted with EtOH etc., gives positive tests for (I), (II), (III), and (V). When treated for 3 hr. with 5% H_2SO_4 at 1·3 atm., ergot gives positive tests for all five bases. R. S. C.

Adenylic acid and adenine nucleotide. R. Klimek and J. K. Parnas (Biochem. Z., 1932, 252, 392—396).—The pentose residue of adenylic acid is, and of adenine nucleotide of yeast nucleic acid is not, able to form a complex Cu compound such as is obtained with polyhydric alcohols. When the H_3PO_4 of adenine nucleotide is removed, the resulting adenosine (m.p. 229°) readily forms such a complex. The bearing of this reaction on the structure of these substances is discussed. P. W. C.

Extremely sensitive reaction of caffeine and its application to the local detection of this purine derivative in vegetable tissue. A. Martini (Mikrochem., 1932, 12, 109—110).—A characteristic ppt., probably $C_8H_{11}O_2N_4,AuBr_4,2H_2O$, is formed when 0·1% aq. caffeine hydrochloride is added to 10% $HAuCl_4$, followed by saturated aq. NaBr. The test can be made in the vegetable tissue. E. S. H.

Sensitive micro-chemical reaction of cocaine. A. Martini (Mikrochem., 1932, 12, 111).—Characteristic micro-crystals are formed by adding aq. $KPbI_3$ to aq. cocaine hydrochloride, preferably in presence of $COMe_2$. The reaction with $KPbBr_3$ is less sensitive. E. S. H.

Reduction indicator. L. Michaelis.—See this vol., 1102.

Iodometric determination of purines and their derivatives. M. Z. Grynberg (Biochem. Z., 1932, 253, 143—145).—Xanthine, guanine, and uric acid, whether free or after liberation from combination by hydrolysis (but not hypoxanthine, adenine, caffeine, theophylline, or theobromine), can be determined by titration with I. W. McC.

Biochemistry.

Importance of the time element in determining respiratory metabolism of fishes. N. A. Wells (Proc. Nat. Acad. Sci., 1932, 18, 580—585).

Respirometry. I. Combined gas burette–interferometer respirometer. W. R. Thompson. **II. Influence of infra-red radiation on carbon dioxide respiration of *Drosophila* imagos in dry air. III. Application of refractovolumetric respirometry to the observation of continuous respiratory changes in wet or dry systems.** W. R. Thompson and R. Tennant (J. Gen. Physiol., 1932, 16, 5—22, 23—26, 27—31).—I. A respirometer is described by means of which the concn. of O_2 and

CO_2 in a vol. of gas may be determined by interferometric measurements of refractive indices.

II. The R.Q. of *Drosophila* imagos is increased when they are exposed to light from an electric lamp. The effects of visible and of infra-red irradiation have been examined.

III. The O_2 uptake and CO_2 output of *Drosphila* imagos have been followed in dry and moist conditions. The mean R.Q. is approx. the same in both states. W. O. K.

Sulphur content of human hæmoglobin. Z. Aszódi (Biochem. Z., 1932, 252, 387—391).—A table summarises the S contents of the hæmoglobins of 32 hospital cases. The vals. vary from 0·60 to 0·69%, mean val. 0·65%. P. W. C.

Hæmoglobin-building properties of soya-bean products. W. H. Adolph and H. C. Kao (Chinese J. Physiol., 1932, 6, 257—263).—Soya-bean products had a curative action on rats rendered anæmic by an exclusive diet of cows' milk. Analyses of these products indicated an appreciable Fe and Cu content. The rate of recovery appeared to be approx. proportional to the Fe and Cu content of the ingested food, but it could not be said that the soya-bean products owed their curative activity to the presence of these metals. R. N. C.

Effect of chlorophyll on formation of hæmoglobin. S. Aoki (Sei-i-kwai Med. J., 1931, 50, No. 5, 1—11).—Injection of chlorophyll into the normal rabbit does not affect the blood-hæmoglobin, but in experimental (particularly $NHPh\cdot NH_2$) anæmia rapid recovery of hæmoglobin occurs. Ch. Abs.

Influence of pyrrole nucleus in the formation of hæmoglobin. L. Villa (Annali Chim. Appl., 1932, 22, 515—517).—2-Acetopyrrole was dissolved in a solution of known Fe content. Once a day 2-c.c. doses (corresponding with 0·05 g. of ferropyrrole compound) were injected intramuscularly into 25 patients suffering from different forms of anæmia. Except in 4 cases, after 20—30 days' treatment the hæmoglobin content of the blood increased 30—100%. O. F. L.

Factors influencing the blood–benzidine reaction as applied to the micro-determination of hæmoglobin. W. D. McFarlane and R. C. M. Hamilton (Biochem. J., 1935, 26, 1050—1060).—Conditions under which hæmoglobin can be determined in small amounts of blood are described. S. S. Z.

Improved benzidine test for blood in urine and other clinical material. J. Ingham (Biochem. J., 1932, 26, 1124—1126).—"Hyperol," a dry stable powder containing 35% H_2O_2, can be used for blood tests in clinical laboratory practice. S. S. Z.

Oxygen affinity of chlorocruorin. H. M. Fox (Proc. Roy. Soc., 1932, B, 111, 356—363).—The O_2 dissociation curves of chlorocruorin in the diluted blood of the worm *Spirographis spallanzanii* determined spectrophotometrically over a p_H range from 7·35 to 8·2 and at 10—26° are sigmoid in type and similar to those of hæmoglobin. At p_H 7·35 and 26° half saturation is obtained at an O_2 pressure of 29 mm. in presence of 40 mm. CO_2. In equilibrium with air at atm. pressure approx. 96% saturation is reached. W. O. K.

Mol. wts. of the blood-pigments of *Arenicola* and of *Lumbricus*. T. Svedberg and I. B. Eriksson (Nature, 1932, 130, 434—435).—The mol. wt. of the blood-pigment of *Arenicola*, determined by the sedimentation velocity method, is of the order $n\times10^6$. The sedimentation const. is of the same order as that of *Octopus* and *Helix* hæmocyanins, but is different from that of vertebrate hæmoglobin. There is a small difference between the consts. of the blood-pigments of *Arenicola* and *Lumbricus*. Hæmoglobin with its relatively low mol. wt. may be strictly confined to the blood of vertebrates, and the respiratory pigments of high mol. wt. to that of invertebrates. L. S. T.

Physico-chemical properties of hæmocyanins. II. J. Roche (Bull. Soc. Chim. biol., 1932, 14, 1032—1043).—The hæmocyanin from *Helix pomatia* has an isoelectric point at p_H 5·2, acts as a monacid base of p_K 3·2, and as a tribasic acid of p_K 10·5, 8·6, and 7·6, the last changing to 7·0 in oxyhæmocyanin. The hæmocyanins from different sources are different, but respiratory chromoproteins all appear to have an acid function at about p_K 7 which varies with the state of oxidation. A. A. L.

Influence of hydrochloric acid on the combination of oxygen with the hæmocyanin of *Limulus polyphemus*. A. C. Redfield, E. D. Mason, and E. N. Ingalls (J. Cell. Comp. Physiol., 1932, 1, 93—112).—The hæmocyanin reacts with HCl to produce a colourless compound which does not combine with dissociable O_2. Its formation is not the result of the removal of Cu from the hæmocyanin mol. Equilibrium between HCl and hæmocyanin depends on the formation of a salt in which only a proportion of the total basic groups (possibly those of the radical associated with O_2 transport) is involved. A. G. P.

Spectrochemical analysis of serum-pigments. P. Müller (Klin. Woch., 1932, 11, 189—192; Chem. Zentr., 1932, i, 2198).—All normal sera show the violet hæmoglobin bands. Spectra of hæmoglobin, lipochrome, and bilirubin are distinguished, and results are given for sera of static icterus, hæmolytic icterus, pernicious anæmia, and Biermer's anæmia. The yellow colour of blood-serum is due to hæmoglobin. A. A. E.

Composition of membrane of red blood-corpuscles. T. P. Chou (Chinese J. Physiol., 1932, 6, 277—280).—Analysis of the membrane, free from sol. material, showed a composition of 50% protein and 46% lipins. Phosphatide calc. as lecithin amounted to 27%, and total cholesterol to 14%. R. N. C.

Catalase content of white blood-corpuscles. K. Iglauer (Magyar Orvosi Arch., 1932, 33, 135—145; Chem. Zentr., 1932, i, 2961).—The greatest catalase activity (3—4 times that of erythrocytes) is shown by polynuclear neutrophile leucocytes; myelocytes show less, and lymphocytes and myeloblasts only slight, activity. A. A. E.

Chemical changes in blood during preservation. I. S. Balachovski, F. Ginsburg, R. Farberova, T. Palitzina, and S. Rzhina (Biochem. Z., 1932, **252**, 370—377).—During preservation of blood the sugar content, the osmotic resistance of the erythrocytes, and the power to unite with O_2 tend to decrease, the inorg. P content to increase, whilst the catalase and residual N contents are unaffected. Blood may, however, be kept without change for a long time by addition of citrate or physiological saline. P. W. C.

Constitution of the fractions of human serum-protein. K. Lang and A. Braun (Arch. exp. Path. Pharm., 1932, **167**, 708—716).—The proteins of normal and pathological sera were fractionated and the contents of arginine (I), tyrosine (II), tryptophan (III), and cystine (IV) determined. With (II), (III), and (IV), but not with (I), the proportions are related to the distribution of the protein fractions. The abs. content of any one acid varies in different persons with the same disease by as much as 50%; hence the accuracy of the refractometric determination of serum-proteins appears doubtful. Pathological sera show characteristic abnormalities in composition. F. O. H.

Colorimetric determination of glutathione in blood and tissues. B. Braier and A. D. Marenzi (Compt. rend. Soc. Biol., 1932, **109**, 319—321; Chem. Zentr., 1932, i, 2872).—Deproteinised ($CCl_3{\cdot}CO_2H$) blood, plasma, or tissue-extract filtrate (2 c.c.) (glutathione 0·7—2·8 mg.) is shaken with 20% Na_2SO_3 (0·2 c.c.) and then treated with 20% Li_2SO_4 (0·2 c.c.), 20% Na_2CO_3 (2 c.c.), and Folin–Marenzi phosphotungstic acid reagent (2 c.c.). After 4 min. the solution is diluted to 25 c.c. with 2% Na_2SO_3 and compared within 10 min. with a similarly treated solution of cystine (0·4 mg. in 2 c.c.). A. A. E.

Determination of residual nitrogen in blood by means of the step photometer. C. Urbach (Biochem. Z., 1932, **252**, 406—413).—The N content of deproteinised blood is determined by direct Nesslerisation using the step photometer. P. W. C.

Total nitrogen of the blood-plasma of normal albino rats at different ages. P. P. Swanson and A. H. Smith (J. Biol. Chem., 1932, **97**, 745—750).—The total plasma-N increases from 0·81 (21—28 days) to 1·22 g. per 100 c.c. (360 days), the greatest increase being during the first 50 days. A slight but definite temporary decrease occurs at an age of approx. 100 days, and is probably correlated with the onset of sexual maturity. F. O. H.

Colorimetric micro-determination of labile blood-iron. G. Barkan (Klin. Woch., 1932, **11**, 598—599; Chem. Zentr., 1932, i, 2871—2872).—$Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ are determined with the aid of Et_2O free from, or containing, peroxide. A. A. E.

Volumetric determination of sodium in blood-serum. S. Rusznyák and E. Hatz (Biochem. Z., 1932, **252**, 414—419).—The serum is deproteinised by $CCl_3{\cdot}CO_2H$ or by heating with H_2SO_4–HNO_3, the PO_4''' removed by treatment with alcoholic $Zn(OAc)_2$, and the Na pptd. as $(UO_2)_3ZnNa(OAc)_9,6H_2O$. This is finally determined by boiling with 0·05M-Na_2HPO_4 and titrating the excess with uranyl acetate using cochineal as indicator. P. W. C.

Obtaining representative samples of blood for inorganic phosphorus in dairy heifers. H. O. Henderson and A. H. van Landingham (J. Dairy Sci., 1932, **15**, 313—319).—Considerable daily variation in the inorg. P content of the blood of heifers is recorded. Representative samples are obtained by alternate-day sampling over a period of 12 days. No appreciable changes in the inorg. P content occurred during the storage of blood at 2° for 2 weeks. A. G. P.

Calcium and phosphorus contents of the blood of pigs. E. H. Hughes and H. Hart (Proc. Amer. Soc. Animal Produc., 1932, **24**, 274—277).—The normal pig's serum-Ca is slightly >12 mg. per 100 c.c. of blood; the inorg. P is 8—9 mg. The serum-Ca of brood sows was materially reduced by feeding with a ration low in Ca and vitamin-*A* and relatively high in P. Ch. Abs.

(*a*) Calcium content of the blood of dogs during twenty-four hours. (*b*) Calcium content of the blood of dogs kept in cages. (*c*) Variation in the calcium content of dogs in a state of inanition. (*d*) Calcium content of the arterial blood of dogs according to age, sex, and weight. J. Cheymol and A. Quinquaud (Bull. Soc. Chim. biol., 1932, **14**, 1044—1045, 1046—1047, 1048—1050, 1051—1066).—(*a*) The variation is small.

(*b*) The variations were slightly greater than the daily variations, and were independent of changes in wt., which first decreased and then increased.

(*c*) The Ca content falls considerably with time, after passing through a min.

(*d*) The content falls with age, is usually slightly higher in females, and is the higher the heavier is the animal. A. A. L.

Effect of intravenous injection of glycine on the serum-calcium. N. Morris, J. B. Rennie, and S. Morris (Brit. J. Exp. Path., 1932, **13**, 132—134).—With rabbits and goats the serum-Ca is diminished. Comparatively little of the NH_2-N remains in the blood. Return to normal serum-Ca vals. is probably due to deamination of the glycine and release of Ca from the tissues. Excessive NH_2-acid production after parathyroidectomy may play a part in lowering serum-Ca. Ch. Abs.

Determination of lactic acid and ketonic substances in the same small amount of blood. R. Sturm (Arch. exp. Path. Pharm., 1932, **167**, 654—659).—The blood (2—4 c.c.) is deproteinised and the lactic acid determined by a modified method of Brehme and Brahdy (A., 1926, 1282). Following the iodometric titration for MeCHO, the distillate is oxidised by Na_2O_2 and the unchanged $COMe_2$ distilled over into aq. $NaHSO_3$, which is finally titrated iodometrically. F. O. H.

Distribution of glucose in human blood. E. M. MacKay (J. Biol. Chem., 1932, **97**, 685—689).—Glucose occurs in the same concn. in the H_2O contained in the plasma and erythrocytes of freshly-drawn blood. Addition of glucose after withdrawal is followed by a simple diffusion leading again to equality of concn. F. O. H.

Lipins and immunity. F. M. MIRANDA (Los prog. clin., 1930, 38, No. 8).—Organs have a sp. serological val. Antibodies produced by pancreas extract are related to the lipins of the organ; similar results were obtained with the thyroid, liver and brain (ox), and kidney (man). The testicle is not sp.; proteins of the ovary are only slightly sp. and the lipins not at all. The adrenal cortex is sp. with regard to the lipins applied in the rat, but of insignificant proteinic sp. action in the rabbit. Brain, liver, and thyroid show related lipins. CH. ABS.

Immunological properties of alkali-treated proteins. L. R. JOHNSON and A. WORMALL (Biochem. J., 1932, 26, 1202—1213).—Alkalis have a more marked destructive effect than acids on the power of horse-serum proteins to react with antibodies to the untreated serum-proteins. Up to about p_H 11 there is, however, very little loss of antigenic properties in 24 hr. at 19°. Iodination is not as effective in regenerating antigenic properties in alkali-treated proteins as is nitration. S. S. Z.

Animal tissue-proteases. X. Appearance of defence enzymes in blood-serum of rabbits. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, 252, 343—361).—The cathepsin and trypsin contents of normal rabbits' serum is very const., varying by not more than $\pm 5\%$ for cathepsin and $\pm 7\%$ for trypsin. The vals. are the same when taken either immediately after or 14 hr. after food, and are uninfluenced by intravenous or subcutaneous injection of solutions at blood-p_H of foreign proteins, *e.g.*, caseinogen, edestin, and horse serum. P. W. C.

Fraction- and species-specificity of serum-proteins. I. GYÖRFFY (Magyar Orvosi Arch., 1932, 33, 147—158; Chem. Zentr., 1932, i, 2969).—Relative species-specificity of horse serum-protein fractions is indicated. A. A. E.

Analysis of mixtures of antigens by adsorption. H. RUDY (Biochem. Z., 1932, 253, 204—214).—The components of two-component mixtures of antigens can be completely or almost completely separated by treatment with an appropriate adsorbent [$Al(OH)_3$, $CaCO_3$, kaolin, etc.] which removes one component. The latter can then be separated from the adsorbent by elution (elution of *S. pallida* antigen has not yet succeeded). The method has been applied with one natural and four artificial mixtures (brain, Wassermann, Forssmann heterogenetic, and *S. pallida* antigens used). W. McC.

Specific substance of [blood-]group. A. K. FREUDENBERG, H. EICHERL, and W. DIRSCHERL (Naturwiss., 1932, 20, 657—658).—From the urine of blood-group A a highly conc. prep. of the sp. substance has been obtained, $0{\cdot}02 \times 10^{-6}$ g. of which can be detected serologically; it retains 80% of the original activity of the urine, is lævorotatory, contains 4—5% N, reduces Fehling's solution after boiling with acid, and is probably a polysaccharide. A. C.

Serological differentiation between the anterior and posterior pituitary lobes. E. WITEBSKY and H. O. BEHRENS (Z. Immunität., 1932, 73, 415—428; Chem. Zentr., 1932, i, 2058).—In rabbits suspensions of the anterior pituitary lobe produce only species-sp. antibodies. The posterior lobe produces antisera which react only with their homologous antigen, with brain extract (slightly), and with spinal cord extract (very slightly). A. A. E.

Osmotic relationships in the hen's egg, as determined by colligative properties of yolk and white. E. HOWARD (J. Gen. Physiol., 1932, 16, 107—123).—The osmotic pressures of the white and yolk of a hen's egg determined by the direct f.-p. method, by dialysis, or by v.-p. measurements are equal. The yolk and white are in osmotic equilibrium, and no vital activity in the membrane to maintain the osmotic pressure need be postulated. Certain experimental difficulties may account for the abnormally high vals. for the osmotic pressure of the yolk previously recorded. W. O. K.

Alkaline hydrolysis of lecitho-vitellin with particular reference to the separation of an organic fraction containing iron and copper. W. D. MCFARLANE (Biochem. J., 1932, 26, 1061—1071).—During hydrolysis there is a gradual evolution of NH_3 and a steady increase in the amount of non-protein-N, but no increase in free NH_2 groups. $CCl_3{\cdot}CO_2H$, or neutralisation with AcOH, ppts. a protein which contains about 50% of the lecitho-vitellin-N, but does not contain Fe or P. Part of the non-protein-N is contained in a fraction pptd. from acid solution by $Pb(OAc)_2$. Two different samples of lecitho-vitellin contained practically the same amount of Cu (0·0033%) and Fe (0·046%). S. S. Z.

Intra-uterine development in cattle. W. W. YAPP (Proc. Amer. Soc. Animal Produc., 1932, 24, 133—136).—The liver and spleen of bovine fœti contained 0·0065—0·201% Fe and 0·00171—0·00315% Cu; very little Ca was deposited before the sixtieth day, the oldest fœti containing most (1·43%). The P content was about half the Ca content. CH. ABS.

Presence of potassium, sulphur, magnesium, manganese, arsenic, and phosphorus in the fœtal liver of vertebrates. G. ROUSSEL and DUFOUR-DEFLANDRE (Compt. rend. Soc. Biol., 1931, 106, 1118—1119; Chem. Zentr., 1932, i, 1917).—In oxen and sheep the above elements (little Mn, much P) were found. A. A. E.

Combined creatine in frog muscle. S. OCHOA, F. GRANDE, and M. PERAITA (Biochem. Z., 1932, 253, 112—118).—In oxygenated frog muscle (especially during rest) the amount of combined creatine is sometimes greater than that corresponding with the phosphagen-phosphate content. On the average 140 mols. of the total creatine of the muscle are found for each 100 mols. of directly determinable phosphate. W. McC.

Denaturation of proteins in muscle juice by freezing. D. B. FINN (Proc. Roy. Soc., 1932, B, 111, 396—411).—Denaturation of protein occurs when fresh ox-muscle juice, expressed after the onset of rigor, is stored at temp. below its f.p., the max. attained after a period of 25—40 days at −2° to −3° reaching about 20% of the total coagulable N.

When the muscle juice is adjusted to various p_H vals., the denaturation which occurs on freezing is low at p_H 6·0—7·0 and increases rapidly on the acid side of p_H 6·0. On the acid side of p_H 6·0 there exists a certain salt concn. at which max. denaturation occurs, which at p_H 5·2 is 0·8*M*. At —2° to —3° the salt concn. in muscle-juice is 0·8*M* and the [H$^{\cdot}$] is on the acid side of p_H 6·0, whilst at temp. below —3° the p_H tends to exceed 6·0 and the salt concn. is $>$0·8*M*. The protein fraction denatured by freezing is probably part of the myogen fraction of von Fürth (Ergebn. Physiol., 1919, 17, 382). W. O. K.

Glycogen distribution in *Urodela* and seasonal variation. I. Chung (J. Chosen Med. Assoc., 1931, 21, 569—603).—The glycogen contents of all the organs of *Diemictylus pyrrhogaster* are generally low and scarcely change during different seasons, although the central nervous system, testicles, and ovaries show slight increases in the winter. Ch. Abs.

Reducing substances in brain. I. Distinguishing the reducing power of the sugar from that of the creatinine. Determination of true blood-sugar. II. Carbohydrate metabolism in brain. Sugar content of the blood of rabbits treated in various ways. H. Maruyama (Biochem. Z., 1932, 253, 161—171, 172—184).—I. Since glucose (also galactose, fructose, arabinose), creatine, and creatinine exhibit different degrees of stability towards boiling dil. solutions of alkali hydroxides and carbonates, it is possible by methods described to determine sugar and creatinine in brain, spinal cord, blood, and other biological material. Human blood contains 64·7 mg. of true sugar per 100 c.c.

II. Rabbit brain immediately after death contains free sugar, which rapidly disappears, and glycogen. The post-mortal increase in the amount of lactic acid in the brain results from the disappearance of the sugar and the reduction in the glycogen content. The lactic acid, creatine, and creatinine contents of EtOH extracts of the brain, its content of glycogen, the sugar content of rabbits' blood, and the effect on these vals. of fasting, of administration to the rabbits of luminal, strychnine, or insulin, and of anæsthesia with Et_2O have been determined. W. McC.

Mechanism of oxidation in sympathetic [nervous] tissue. S. Huszák (Biochem. Z., 1932, 252, 397—400).—Sympathetic ganglia and the suprarenal medulla (different from all the other tissues investigated, *e.g.*, muscle, liver, kidney, suprarenal cortex, sensory ganglia, grey matter of brain) do not contain any cytochrome-respiration enzyme (indophenol-oxidase system). P. W. C.

Existence of paracrystals and their distribution in cerebrosides and phosphatides as plasmatic components. F. Rinne (Kolloid-Z., 1930, 60, 288—296).—A description of the forms of growth of kerasin, nervon, lecithin, and sphingomyelin. E. S. H.

Determination of thymonucleic acid by means of fuchsin-sulphurous acid. T. Caspersson (Biochem. Z., 1932, 253, 97—111).—The acid, after hydrolysis, is determined by a modification of the method of Widström (A., 1928, 1393). Two concurrent reactions take place between the reagent and the hydrolysate. W. McC.

Occurrence of melanogen, particularly *o*-dihydroxybenzene-substances, in the organism. II. H. Schmalfuss and H. Barthmeyer [with W. Hinsch] (Z. indukt. Abstamm. Vererbungslehre, 1931, 58, 332—371; Chem. Zentr., 1932, i, 2191).—There is no direct relationship between the colour of the case of beetles and the content of *o*-$C_6H_4(OH)_2$-substances (I), although in Tenebrionids the white portions are free from such substances. In all insects the more is present, the harder is the case. The substance is formed together with chitin, but their origins are unconnected. Non-insects cannot form excess of (I), but form excess of melanogen as do insects. A. A. E.

Detection of small amounts of formic acid in blood and tissues, especially in skin. H. Droller (Z. physiol. Chem., 1932, 211, 57—64).—A method is described for the colorimetric determination of HCO_2H in biological material. It detects 0·04 mg. in 5—10 c.c. aq. solution. It depends on reduction of the protein- and sugar-free tissue filtrates with Mg ribbon and 25% HCl in presence of fuchsin-SO_2, with which the CH_2O formed gives a bluish-violet colour. J. H. B.

Isolation of chemically unstable substances from animal tissues. M. G. Eggleton and P. Eggleton (Nature, 1932, 130, 275).—A method using Na_2SO_4 is described for obtaining a protein-free solution of the H_2O-sol. constituents of muscle in a conc. form. Anserine has been obtained from the muscles of sheep, goats, and rabbits, and carnosine from ox and frog. L. S. T.

Mallory's connective tissue stain following hæmatoxylin. S. Weiss (Stain Tech., 1932, 7, 131—133).—The combination of these stains is useful in bringing out nuclei, as well as in differentiating tissue. H. W. D.

Determination of milk-proteins by formaldehyde titration. G. H. Pyne (Biochem. J., 1932, 26, 1006—1014).—The vals. obtained by the method as hitherto used are composite, determined mainly by the protein of the milk, but affected in various directions by both colloidal and sol. phosphates, to an extent which depends on the type of alkali used in the titration. The disturbing effects of both classes of phosphate can be avoided by treating milk with an oxalate prior to titration. S. S. Z.

Absorption of milk precursors by the mammary gland. V. Physico-chemical aspects of milk secretion. J. H. Blackwood and J. D. Stirling (Biochem. J., 1932, 26, 1127—1137).—Analytical data for the composition and yield of milk from six cows do not support the view that milk consists of a conc. and transformed blood-plasma minus colloids; they are more in consonance with the hypothesis of selective absorption of milk precursors at the membranes separating the secreting cells from the blood supply. According to this theory, milk secretion does not require the expenditure of any energy by the gland cells other than that necessary for the synthesis of milk constituents. S. S. Z.

Effect of maize oil on milk and butter-fat production and on the composition of butter-fat in the dairy cow. T. S. Sutton, J. B. Brown, and E. W. Johnson (J. Dairy Sci., 1932, **15**, 209—211).—Ingestion of 1 lb. of maize oil per day did not affect the milk yield or the % of fat in milk, but markedly changed the composition of the butter-fat. The fatty acids were more unsaturated and of higher mean mol. wt. The sol. volatile acids decreased. A. G. P.

Effect of cod-liver oil in the ration on the quantity and quality of cows' milk. W. E. Peterson (J. Dairy Sci., 1932, **15**, 283—286).—Addition of cod-liver oil (5 oz. daily) to the ration reduced the fat content of the milk without affecting the quantity of milk produced. A. G. P.

Effect of thyroidectomy alone and in conjunction with treatment with extract of the anterior lobe of the pituitary gland or with placenta extract and corpus luteum on milk secretion in goats. T. von Fellenberg and F. Grüter (Biochem. Z., 1932, **253**, 42—63).—In the milk of normal cows and goats the ratio P_2O_5 : CaO varies but slightly and is independent of the abs. content of the substances concerned. The ratio, which depends on the function of the thyroid gland, is reduced by administration of cod-liver oil, but increased by that of white cabbage. Extirpation of the thyroid gland results in moderate decrease in P content of the milk, very great increase in the Ca, and increase in the Cl contents. It also results in reduction in the alkalinity of the ash of the milk and alters the fat content. Administration of extracts of the anterior lobe of the pituitary gland after extirpation of the thyroid results in increase in the mineral content of the milk, but does not alter the P_2O_5 : CaO ratio, whilst it increases the Cl content and reduces the alkalinity of the ash. Administration of fœtal placenta extract or of this extract together with corpus luteum before the extirpation does not alter the effects of the latter. W. McC.

Milk of cows in heat. A. Meyer (Z. Unters. Lebensm., 1932, **64**, 235—250).—Analytical data of samples taken twice daily for several consecutive days before and after the beginning of heat are tabulated for 14 cows. A fall and rise in quantity followed by a fall to normal was observed in 9 cases, and in the course of 3 days the fat content decreased and then returned to normal. Acidity, caseinogen/(albumin+globulin), and coagulation capacity in the fermentation test decreased, conductivity, f.p., and catalase val. increased (cf. B., 1931, 315), n ($CaCl_2$-serum) showed slight fluctuations, and solids, lactose, ash, and total protein did not change. Except for the fluctuations (0·4—1·2%) in fat content, these variations are masked on admixture with 80% of normal milk. J. G.

Isolation from bile of a pigment having a direct Van den Bergh reaction. W. J. Griffiths (Biochem. J., 1932, **26**, 1155—1163).—The pigment, cholebilirubin, $C_{32}H_{50}O_{11}N_2$, was prepared by pptg. from alkaline solution of the Et_2O- and $CHCl_3$-extracted dried bile with $COMe_2$, extracting the ppt. with 80% $COMe_2$, and pptg. the $COMe_2$ product by acid from its aq. solution. S. S. Z.

Gall-bladder function. VIII. Fate of bile pigment in hepatic bile subjected to gall-bladder activity. C. Riegel, C. G. Johnston, and I. S. Ravidin (J. Exp. Med., 1932, **56**, 1—11).—In dogs bile pigment is not absorbed from the gall-bladder bile. Cholesterol is probably not normally secreted in the gall-bladder. Ch. Abs.

Anavenoms. VII. Paravenoms. M. Arthus (J. physiol. path. gén., 1932, **30**, 75—86).—Cobra venom (1%) in $CaCl_2$ (1%) immunises rabbits against the venom. Venoms treated with $CaCl_2$ are " paravenoms " in the class of anavenoms. Ch. Abs.

Secretion of urine in man. C. Brunner (Biochem. Z., 1932, **253**, 119—136; cf. Descombes, this vol., 535).—In human urine the excretion of creatinine is parallel with that of sulphate. Confirmation is thus provided for the theory of Brandt-Rehberg. When the sulphate content of the blood is calc. from that of the urine in accordance with the theory, vals. in agreement with those in the literature are obtained. W. McC.

Luminescence analysis of urine. Y. Yoneyama (Z. ges. exp. Med., 1931, **76**, 680—688; Chem. Zentr., 1932, i, 2872).—Urea, uric acid, NH_3, NaCl, and phosphate exhibit no luminescence in ultraviolet light, whether alone or in admixture. Urobilin in EtOH (acid) gives a deep reddish-brown, or (ammoniacal) yellowish-green; in NH_3–EtOH–$ZnCl_2$ it is light green. Uroerythrin in EtOH (acid) is yellowish-red, or (alkaline) green; after oxidation with $KMnO_4$ it is greyish-white. Hæmatoporphyrin in EtOH (acid) is dark pinkish-red; urochrome in H_2O (acid or alkaline) is yellowish-white, bilirubin in EtOH (neutral) is deep yellow, biliverdin in AcOH is greenish-black, indirubin in Et_2O is bluish-white. Indigotin suspension is dark olive-green; after reduction with $Na_2S_2O_4$ it is opaque greenish-blue. A. A. E.

Determination of total nitrogen in urine by the step photometer. C. Urbach (Biochem. Z., 1932, **252**, 292—304).—The method uses 1 c.c. of urine, distillation and titration are avoided, and the accuracy is of the same order as with the macro-Kjeldahl process. P. W. C.

Direct colorimetric determination of urea in urine. J. F. Barrett and E. B. Jones (Biochem. J., 1932, **26**, 1246—1250).—Interfering substances are removed from the urine by $FeCl_3$ and $NaHCO_3$ and the urea is pptd. from the filtrate by xanthhydrol. The ppt. is centrifuged in presence of $BaSO_4$ and its N content determined colorimetrically after micro-Kjeldahl digestion. S. S. Z.

Distribution of organic acids in human urine. M. Lafargue (Bull. Soc. Chim. biol., 1932, **14**, 1017—1025).—Fatty acids up to C_5 are determined after acidifying with tartaric acid by distillation in vac. at 40—45°, and titration of the distillate. CO_2 is first removed from urine of $p_H > 5{\cdot}8$ by application of a vac. at room temp. after acidifying. Hippuric and lactic acids are determined in the remainder of the org. acids extracted as previously described (A., 1931, 1082). The composition of the acids in normal urine is discussed. A. A. L.

Determination of small quantities of oxalic acid [in urine]. E. C. Dodds and E. J. Gallimore (Biochem. J., 1932, 26, 1242—1245).—By preliminary esterification and distillation the $H_2C_2O_4$ in urine is freed from interfering substances. It can then be pptd. as CaC_2O_4. S. S. Z.

Equol, a new inactive phenol isolated from the ketohydroxyœstrin fraction of mare's urine. G. F. Marrian and G. A. D. Haslewood (Biochem. J., 1932, 26, 1227—1232).—*Equol*, $C_{15}H_{12}O(OH)_2$, m.p. 189—190·5°, $[\alpha]_{5461}$ −21·5° [*Me_2 ether*, m.p. 89°; *diacetate*, m.p. 122·5°; *dibenzoate*, m.p. 187—189° and 223·5—225° (liquid crystal formation)], was prepared by distillation of the ketohydroxyœstrin fraction at 160—180°/0·01—0·03 mm. subsequent to distilling at 100—110°. S. S. Z.

Determination of uric acid in poultry excrement. K. Suzuki and A. Nishizaki (J. Agric. Chem. Soc. Japan, 1931, 7, 507—514).—The dry material (1 g.) is boiled with H_2O (20 c.c.) for 1 min.; conc. HCl (5 c.c.) is added, boiling and stirring being continued for a few sec. After 12 hr. (cold) the mixture is filtered; the residue is washed with cold H_2O, 90% EtOH, and Et_2O, and then boiled for several min. with H_2O (20 c.c.). Aq. NH_3 (5 c.c.) is added, and after 1 hr. at room temp. the solution is evaporated and the residue heated at 100° for several hr. Boiling with 5% HCl (20 c.c.) for 1 min. again liberates uric acid, which is collected from the cold liquid and washed with cold H_2O. The filtrate and washings are evaporated to about 10 c.c. and then diluted with abs. EtOH to 100 c.c., 50 c.c. being treated with a slight excess of dil. alcoholic KOH and the NH_3 distilled with steam into standard H_2SO_4. The quantity of uric acid is calc. from that of NH_3. The error is 0·5%. Ch. Abs.

Content of reduced glutathione in tissues of rabbits in acidosis and alkalosis. S. Tatsuzawa (Sei-i-kwai Med. J., 1931, 56, No. 11, 70—86).—When neutral phosphate is given orally, only the heart (slight increase) shows a change in glutathione content. In alkalosis produced by $NaHCO_3$, Na_2HPO_4 orally, or subcutaneous injection of O_2 or N_2 the adrenal-glutathione is markedly increased; acidosis produced by NaH_4PO_4 (orally) is accompanied by a similar increase. Vals. for alkali reserve, urinary p_H, NH_3-N, and total N are recorded. Ch. Abs.

Catalase and glutathione content of red blood-corpuscles in experimental anæmia. E. Bach and B. Korpássy (Klin. Woch., 1931, 10, 2312; Chem. Zentr., 1932, i, 1677).—In rabbits with experimental anæmia the red blood-corpuscles contained a relatively increased amount of catalase and glutathione, possibly connected with increased respiration. A. A. E.

Tissue factor (glutathione) which affects the oxygen tension of venous blood in normal and (venesected) anæmic rabbits. G. Litarczek, H. Aubert, I. Cosmulesco, and B. Nestoresco (Compt. rend. Soc. Biol., 1931, 106, 110—112; Chem. Zentr., 1932, i. 2341).—It is assumed that in the erythrocytes there is between the glutathione and hæmoglobin an equilibrium such that the O_2 affinity of the latter or its dissociation curve represents a resultant of the activities of the oxido-reduction system hæmoglobin-glutathione. A. A. E.

Extrinsic (deficiency) factor in pernicious and related anæmias. M. B. Strauss and W. B. Castle (Lancet, 1932, 223, 111—115).—The extrinsic factor essential for the sp. reaction with the intrinsic factor of normal human gastric juice in the production of hæmopoiesis in pernicious anæmia is a substance closely related to, if not identical with, vitamin-B_2. L. S. T.

Autolysed liver therapy in pernicious anæmia. W. F. Herron and W. S. McEllroy (Science, 1932, 76, 127). L. S. T.

Is there a relation between ergosterol and calcification of the aorta in human atherosclerosis ? R. Schönheimer (Z. physiol. Chem., 1932, 211, 65—68).—In the fat from atherosclerotic aortæ vitamin-*D* could not be detected. A substance with absorption band at 238 mμ was present. J. H. B.

Glycæmia in cachexia of nurslings. E. Jaso (Amer. J. Dis. Children, 1932, 43, 1051—1061).—The blood-sugar of under-nourished infants is up to 43% lower than the normal val. Ch. Abs.

Production of cancer by pure hydrocarbons. I. J. W. Cook, I. Hieger, E. L. Kennaway, and W. V. Mayneord. **II.** J. W. Cook (Proc. Roy. Soc., 1932, B, 111, 455—484, 485—496).—I. Of all the polycyclic hydrocarbons, composed only of C_6 rings, tested, only 1 : 2 : 5 : 6-dibenzanthracene and some closely related compounds have produced cancers. In a very pure state (method of purification given) this substance shows undiminished carcinogenic power. Other impure hydrocarbons have produced tumours, but the active substances have not been isolated.

II. 6-*iso*Propyl-1 : 2-benzanthracene, m.p. 131—132°, is carcinogenic together with other compounds containing the 1 : 2 : 5 : 6-dibenzanthracene ring. Mol. structure consisting of new rings attached to the 1 : 2- and 5 : 6-anthracene positions is particularly efficacious in promoting carcinogenic activity. H. G. R.

Inhibition of enzymes by carcinogenic compounds. E. Boyland (Nature, 1932, 130, 274—275).—The oxidation of lactate by lactic dihydrogenase of yeast or muscle is inhibited by dil. C_6H_6 or PhMe solutions of certain hydrocarbons exposed to air and light. Carcinogenic hydrocarbons, *e.g.*, 1 : 2 : 5 : 6-dibenzanthracene and 5 : 6-*cyclo*penteno-1 : 2-benzanthracene, have a greater effect than anthracene, 1 : 2-benzanthracene, or chrysene. The inhibiting factor may be an *o*-$(OH)_2$-derivative. L. S. T.

Growth(-promoting) substance of malignant tumours. E. Maschmann (Naturwiss., 1932, 20, 721—722).—Mouse and fowl sarcoma and mouse carcinoma contain a substance which promotes growth in *Avena* coleoptiles, and the amount is greater in rapidly growing than in necrotic tumour tissue. It is a thermostable weak acid with aliphatic ethylenic linkings, sol. in H_2O, MeOH, EtOH, $COMe_2$, and Et_2O, insol. in light petroleum and C_6H_6. It also occurs in the livers of cancerous and healthy mice, fowls, and fowl embryos, and is closely related to, if not identical with, rhizopin (A., 1931, 1091) and auxin (this vol., 661). A. C.

Comparison of the reducing power of some typical transplantable tumours and of tumours produced by filterable viruses. E. S. G. Barron (J. Exp. Med., 1932, 55, 829—835).—The tissues of Rous chicken sarcoma and of infectious myxoma of the rabbit do not contain succinodehydrogenase. Filterable-virus diseases produce in the affected tissues a partial inhibition of succinodehydrogenase. Ch. Abs.

Cataphoresis experiments on the filterable agent of Rous chicken sarcoma. H. Nakajima and W. Nakahara (Gann, 1932, 26, 181—189).—The causative agent has a negative charge and is constantly associated with the tissue proteins. Ch. Abs.

Properties of the causative agent of a chicken tumour. III. Attempts at isolation of the active principle. J. B. Murphy, E. Sturm, A. Claude, and O. M. Helmer. **IV. Association of an inhibitor with the active principle.** J. B. Murphy and E. Sturm. **V. Antigenic properties of the chicken tumour. I.** J. B. Murphy, E. Sturm, G. Favilli, D. C. Hoffman, and A. Claude (J. Exp. Med., 1932, 56, 91—106, 107—116, 117—129).—III. There can be separated a protein fraction carrying all the tumour-producing agent, which can be largely separated from the protein by absorption of the latter with $Al(OH)_3$.

IV. Desiccated tumour is more active after washing with H_2O, and a tumour extract is more potent after removal of some factor by adsorption on $Al(OH)_3$. When the tumour-producing factor in an extract of a slow-growing tumour has been destroyed by heating at 55°, it has the property of neutralising a highly active tumour extract. The inhibiting property is destroyed by heating above 65°.

V. Tumour extract largely free from protein induces in rabbits the formation of neutralising antibodies, but not of precipitins. Highly purified tumour agent did not induce precipitins, and only 2 out of 15 sera gave evidence of neutralising bodies. Ch. Abs.

Chemical and morphological phases of the blood of normal and cholera-infected swine. I. E. A. Hewitt (Iowa State Coll. J. Sci., 1932, 6, 143—226).—Non-protein-N, creatinine, and creatine are high, whilst urea-N, sugar, P, and Ca are low with cholera-infected swine. Ch. Abs.

Blood-glutathione in dermatoses. Y. Matsumoto (Japan J. Dermat. Urol., 1931, 31, 1136—1152).—Conditions associated with high, low, and normal vals. are recorded. Ch. Abs.

Relative proportion of fermentable and non-fermentable reducing substances of hyperglycæmic bloods of diabetics without glycosuria. I. M. Rabinowitch (Biochem. J., 1932, 26, 963—969).—Hyperglycæmia in diabetes is due chiefly to fermentable sugar and not to other reducing substances which are ordinarily present in blood. S. S. Z.

Afternoon glycosuria. V. J. Harding, D. L. Selby, and A. R. Armstrong (Biochem. J., 1932, 26, 957—962).—"Afternoon glycosuria" (I) has been found in 14 out of 28 subjects who showed "sugar" (Benedict test) on routine examination. Renal glycosuriacs can show (I). More than 60% of the total subjects show a blood-sugar peak after 50 g. of glucose higher at 4 p.m. than at 9 a.m. One subject showing almost identical a.m. and p.m. glucose tolerance curves gave marked (I). S. S. Z.

Influence of diet or treatment with insulin on the sugar dose test. R. Boller and K. Ueberrack (Klin. Woch., 1932, 11, 511; Chem. Zentr., 1932, i, 2481).—Administration of glucose to normal persons who have been kept on a diabetic diet causes an abnormally high rise in blood-sugar. A similar result follows pre-treatment with insulin. A. A. E.

Galactose, a substitute carbohydrate. H. Kosterlitz and H. W. Wedler (Klin. Woch., 1932, 11, 553; Chem. Zentr., 1932, i, 2862).—Addition of galactose to the diet in diabetes causes the appearance of much less urinary glucose than administration of an equal amount of glucose. A. A. E.

Urinary excretion of the anterior pituitary hormone in endocrine disease. H. U. Hirsch-Hoffmann (Klin. Woch., 1932, 11, 94—97; Chem. Zentr., 1932, i, 1546).—A clinical report. A. A. E.

Water and mineral balances in epileptic children. I. I. McQuarrie, R. C. Manchester, and C. Husted (Amer. J. Dis. Children, 1932, 43, 1519—1543).—The urinary K : Na ratio is markedly increased during positive H_2O balance. Ch. Abs.

Basal oxygen consumption of goitrous and non-goitrous rats. A. W. Spence (Brit. J. Exp. Path., 1932, 13, 149—157).—The basal O_2 consumption was not definitely disturbed in goitrous rats, although some animals showed subnormal vals. after 9 months. Ch. Abs.

Pathogenesis of exophthalmic goitre. Diminished excretion or decomposition of thyroxine? P. Vogt-Möller (Acta med. Scand., 1931, 76, 437—452; Chem. Zentr., 1932, i, 1679—1680).—Tyrosine and tyramine do not give the Reid Hunt reaction (resistance of mice towards nitriles after administration of thyroid); sera of persons with "hyperthyroid const.," exophthalmic goitre, or progressive nephritis, or of normal persons immediately after intravenous administration of thyroxine, give a positive reaction. The reaction was negative after administration of KI. It is supposed that in certain disabilities over-production of thyroxine takes place, excretion and metabolic decomp. also being diminished. A. A. E.

Influence of insulin on sulphur metabolism in exophthalmic goitre. S. Tasaka and S. Nisikori (Folia endocrinol. Japon., 1931, 7, 1).—Increased N and S metabolism (particularly $RHSO_4$ and neutral S) is arrested. Ch. Abs.

Fluorides in the treatment of exophthalmic goitre and hyperthyroidism. L. Goldemberg

(Semana méd., 1932, I, 1659—1665).—The action of NaF is explained by its paralysing effect on the lipases and oxidases of the thyroid; it ppts. thyroxine. CH. ABS.

Supposed presence of fluorine in the blood in hæmophilia. W. BRANDES (Z. klin. Med., 1932, 119, 504—507; Chem. Zentr., 1932, i, 1680).—Both normal and hæmophilic blood contain similar min. traces of F. A. A. E.

Plasma-proteins in hookworm disease. G. G. VILLELA and J. C. TEIXEIRA (Mem. Inst. Oswaldo Cruz, 1930, 23, 50—58).—As in lipin nephrosis, fibrinogen was generally increased, serum-albumin greatly decreased, globulins normal or slightly increased, and non-protein-N normal. CH. ABS.

Skin pigmentation and urinary bile pigments in icterus. I. Determination of bilirubin and more highly oxidised bile pigments in urine. K. FRANKE (Z. ges. exp. Med., 1931, 79, 107—124; Chem. Zentr., 1932, i, 2873).—Solutions of bilirubin (Homburg) and icteric urine (or its amyl-alcoholic extract) exhibit very similar extinction curves. On slow oxidation (0·1% $KMnO_4$) they show a similar increase in reddish-yellow adsorption (max. 610—590 mμ). On oxidation beyond the biliverdin–cholecyanin stage the red absorption decreases. By means of the spectrocolorimeter biliverdin can be determined by comparison with standard bilicyanin solutions. Determination of biliverdin before and after oxidation gives the bilirubin content. A. A. E.

Blood-serum-calcium in leprosy. G. G. VILLELA (Sciencia Med., 1928, 6, No. 3, 19 pp.).—Vals. were low: nervous 8·06, mixed 8·42, nodular 9·26, tubercular 9·34 (average of all types 8·82) mg. per 100 c.c. CH. ABS.

Liver function. IV. Glycuronic acid. V. Urobilin. S. BOKU and T. KIN (J. Chosen Med. Assoc., 1931, 21, 67—78, 190—200).—IV. The urine of non-hepatic patients contained (average) 0·013% of glycuronic acid, or 0·057% after oral administration of camphor (0·5 g.); that of hepatic cases contains practically no glycuronic acid in either event. Rabbits poisoned with P or CCl_4 show a marked decrease in the production of camphorglycuronic acid.

V. Urine of non-hepatic patients contained (average) 0·63 mg. of urobilin per 100 c.c. (10·46 mg. per day); in hepatic cases vals. were 10·09 and 122·11 mg., and in cancer of the liver 3·73 and 32·07. In severe salvarsan jaundice the urine often contained no urobilin; in rabbits poisoned with P or CCl_4 urinary urobilin was increased. CH. ABS.

Cause of existence of two types of the van den Bergh bilirubin reaction. N. SOFUE (Japan. J. Med. Sci., IV, Pharmacol., 1929, 3, 137—172).—The velocity of the reaction depends on the amount of urobilin and the inhibiting effect of the cell stromata; if the former is larger the reaction occurs quickly. If the inhibition is accompanied by the oxidising action of the stromata, the urobilin is partly changed and gives a permanent yellow colour, *i.e.*, a retarded reaction. CH. ABS.

Respiratory quotient in obese subjects. D. M. LYON, D. M. DUNLOP, and C. P. STEWART (Biochem. J., 1932, 26, 1107—1117).—In a series of 34 observations on subjects on a diet of 2000 g.-cal. or more there was a loss of wt., the average R.Q. being 0·755. Of these, 3 were below 0·70. When the diet was reduced to 1000—1200 g.-cal., the average R.Q. in 117 observations was 0·721, with 51 below 0·70. When the carbohydrate content of the latter diets was reduced without altering the calorific val., the average R.Q. fell to 0·678, 12 out of 15 being below 0·70. Administration of thyroid to the subjects on this diet produced a slight increase in the R.Q., the average of 70 determinations being 0·727, with only 14 below 0·70. Ketonuria was usually absent and when present only slight. S. S. Z.

Experimental œdema produced by plasma-protein depletion. M. J. LEPORE (Arch. Int. Med., 1932, 50, 488—505).—In dogs, the plasma-protein content of which had been lowered by removing daily a quantity of blood and returning the erythrocytes suspended in Ca-free Locke's solution, general œdema developed. This development is hastened by the administration of large quantities of 0·9% NaCl solution by mouth. Storage of NaCl runs parallel to the storage of H_2O, but the percentage of Cl′ to H_2O stored in different organs is not const., being higher in the muscles than in the skin. During recovery increase of plasma-protein occurs, H_2O is removed by diuresis, excess of NaCl is also excreted, whilst there is decreased absorption of H_2O from the intestine. W. O. K.

Action of tartaric acid in chronic opisthorchiasis. A. ERHARDT and W. KEIL (Arch. exp. Path. Pharm., 1932, 167, 334—337).—Of the four optical isomerides of tartaric acid only the *d*-acid is efficient in the treatment of opisthorchiasis in cats as indicated by the excretion of eggs. This is probably due to its partial conversion into dihydroxymaleic acid, which is more effective than *d*-tartaric acid. Dihydroxytartaric acid is ineffective. F. O. H.

Metabolic studies in a case of osteitis deformans. I. M. RABINOWITCH (J. Nutrition, 1932, 5, 346).—Metabolic balances of inorg. materials are recorded and discussed. A definite loss of S is associated with the diseased condition. A. G. P.

Iron-deficiency hypothesis in pellagra. G. A. WHEELER (Science, 1932, 76, 101).—A criticism (cf. this vol., 419). L. S. T.

Diets in pregnancy in relation to low blood-serum-calcium at lactation. H. T. FRENCH and C. E. BOLSER (New Engl. J. Med., 1932, 206, 14—16).—The serum-Ca decreases at the beginning of lactation and is normal after 3—4 days. The serum-Ca of women who normally have low vals. increases at the beginning of lactation and tends to remain high. CH. ABS.

Blood-inorganic sulphate in eclampsia. D. F. ANDERSON and S. L. THOMPSETT (Brit. J. Exp. Path., 1932, 13, 130—132).—High vals. not found so markedly in normal gestation or in toxæmias of pregnancy other than eclampsia, were observed. Inorg. SO_4 may be less readily excreted than N. CH. ABS.

Serum-calcium content in eclampsia. D. F. Anderson (Brit. J. Exp. Path., 1932, **13**, 182—188).—In eclampsia (36 of 44 cases) the vals. were subnormal ($\nless$9 mg. per 100 c.c.); in nephritic and pre-eclamptic toxæmia (10 of 17 cases), and in normal pregnancy (6 of 17 cases) the vals. were also subnormal. Ch. Abs.

[Clinical] action of potassium. I. On pruritus. II. Experimental. J. Sauer (Deut. Arch. klin. Med., 1931, **172**, 219—222, 223—227; Chem. Zentr., 1932, i, 1263).—II. Large oral doses of KOAc lead to a rise in blood-serum- and cerebrospinal fluid-K and (serum-)Ca; the -Na falls. There is no parallelism between the effect of K in pruritus and the serum-K. A. A. E.

Urea clearance test as an index of renal function. I. Studies of normal subjects. II. Effect of ingestion of glucose. M. Bruger and H. O. Mosenthal (Arch. Int. Med., 1932, **50**, 351—357, 358—361).—I. Determinations of urea clearance (standard and max.; cf. McIntosh and Van Slyke, J. Clin. Invest., 1928, **6**, 427) on 8 normal subjects showed marked variations in the vals. obtained with a tendency towards vals. above the average during moderate exercise. Clinical importance is to be attached to low vals. only when these are given by a subject consistently.

II. Ingestion of 100 g. of glucose by 6 subjects who were normal except that some showed glycosuria did not significantly affect urea clearance. W. O. K.

Uric acid content of duodenal bile of patients subjected to mud treatment. A. Bich (Minerva Med., 1932, I, 600—605).—Vals. for rheumatic patients were 0·5—3·3 mg. per 100 c.c. The ratio blood- : duodenal bile-uric acid was 2·05—3·08. No direct relation was observed between the increase in blood- and bile-uric acid. Ch. Abs.

Experimental rickets. III. Influence of ammonium chloride on mineral metabolism of the rachitic rat. F. Rogozinski (Bull. Acad. Polonaise, 1931, B, 555—566).—Addition of 4% of NH_4Cl to Steenbock and Black's rachitic diet causes a large increase in the inorg. P of the urine of rats receiving it, but fails to affect the general P balance or to alleviate the rachitic condition. P. G. M.

Effect of rachitogenic diets on the thyroid gland of the albino rat. J. Thompson (J. Nutrition, 1932, **5**, 359—377).—Development of hyperplasia in rats is associated with I deficiency and excess of $CaCO_3$ in the diet. A. G. P.

Effect of ammonium chloride administration on metabolism in infantile tetany and rickets. N. Morris and O. MacCrae (Arch. Dis. Childhood, 1932, **7**, 47—58).—Increased retention of Ca, P, and excess Cl, and increased excretion of titratable acid (but not acidosis), are caused. Ch. Abs.

Metabolism in tetany. I. Greenwald (Biochem. J., 1932, **26**, 954—956).—Criticism of Morris, Watson, and Morris (A., 1931, 979). S. S. Z.

New error of tyrosine metabolism: tyrosinosis. Intermediary metabolism of tyrosine and phenylalanine. G. Medes (Biochem. J., 1932, **26**, 917—940).—The condition which was studied in one patient consists in a slowing of the first steps in the intermediary metabolism of tyrosine and a complete stop at the stage of *p*-hydroxyphenylpyruvic acid (I), which in the case of exogenous tyrosine metabolism is at first excreted with tyrosine and then with *l*-*p*-hydroxyphenyl-lactic acid (II), and when the tyrosine metabolism is raised also with *l*-3 : 4-dihydroxyphenylalanine. 1·6 g. of (I) is excreted daily as a result of endogenous tyrosine metabolism. Phenylalanine when fed causes elimination of tyrosine, increased elimination of (I), and excretion of traces of (II) which is not metabolised when consumed directly. In the case of hydroxyphenylalanine it is excreted partly unchanged, and causes elimination of tyrosine and increased elimination of (I). (I) when ingested reappears unchanged, and also causes elimination of (II), but does not give rise to tyrosinuria. Homogentisic acid is oxidised without influencing the above compounds. Melanin was not detected in the urine. In the case of a normal patient, N-free melanin prepared from (I) was recovered quantitatively from the urine. S. S. Z.

Application of the chain reaction theory to biochemical processes. D. Richter (Diss., Oxford, 1932, 8 pp.).—Evidence is discussed concerning the view that biochemical processes are propagated by chain reactions, the energy transfer from an activated mol. being sp. and occurring most readily to another similar mol. J. W. S.

Relation of ultra-violet light to nutrition. H. Chick (Lancet, 1932, **223**, 325—329, 377—383).—Two lectures. L. S. T.

Metabolic rate and habitat. H. M. Fox and B. G. Simmonds (Nature, 1932, **130**, 277—278).—The metabolic rate of the fresh-water species *Gammarus pulex* is 1½ times that of the marine *G. locusta* and *G. marinus*; that of the fresh-water *Asellus aquaticus* is 3 times that of the marine *Idotea neglecta*. The metabolic rates of fresh-water animals living in rapid streams are greater than those of animals inhabiting still water. L. S. T.

Effect of atmospheric humidity on the metabolism of the fasting mealworm (*Tenebrio molitor*). K. Mellanby (Proc. Roy. Soc., 1932, B, **111**, 376—390).—Analyses of fasting mealworms show that they live chiefly on fat, and to some extent on carbohydrate (chiefly glycogen) and protein. The loss of H_2O is approx. proportional to the saturation deficiency of the air at 8°, 23°, 30°, and 37° and at most humidities, but in hot dry air the worms conserve their H_2O, whilst in moist air of 90% R.H. they take up H_2O from the atm. at 8°, 23°, or 30°. At 23° metabolism is so regulated that the % of H_2O to dry matter in the worms remains const., and therefore necessarily is a function of the humidity. At higher temp. the metabolism and rate of formation of H_2O are greater, and in moist warm air accumulation of H_2O results. W. O. K.

Combination of water in muscle. E. Ernst [with K. Czimber] (Pflüger's Archiv, 1931, **228**, 683—689; Chem. Zentr., 1932, i, 2604).—Dried muscle takes up H_2O partly by swelling. The crystalloids present in fresh muscle cannot be freely diffusible. The lowering of v.p. of fatigued muscle is due to increased swelling caused by lactic acid. A. A. E.

Rôle of potassium, phosphate, and lactic acid in muscle contraction. E. Ernst and I. Takács (Pflüger's Archiv, 1931, **228**, 690—699; Chem. Zentr., 1932, i, 2604).—Indiffusible K and PO_4 compounds are present in muscle; stimulation leads to renewed ionisation. The phenomenon is not observed under physiological conditions. A. A. E.

Specific function and metabolism of muscle. E. Ernst [with I. Fricker] (Pflüger's Archiv, 1931, **228**, 700—709; Chem. Zentr., 1932, i, 2604—2605).—Extended muscle contains more lactic acid than non-extended. The production of lactic acid is a truly metabolic phenomenon. The osmotic theory of muscular contraction is discussed. A. A. E.

Metabolism of carbohydrate after starvation. M. W. Goldblatt and R. W. B. Ellis (Biochem. J., 1932, **26**, 991—1005).—Intolerance for carbohydrate manifested after starvation for about 40 hr. is not due to either ketosis or acidosis. Insulin does not completely re-establish normal carbohydrate oxidation in human subjects after 40 hr. starvation. S. S. Z.

Non-fermentable residue in the blood in galactose metabolism. N. Fiessinger and A. Schrumpf (Compt. rend. Soc. Biol., 1932, **109**, 289—290; Chem. Zentr., 1932, i, 2059).—Galactose is practically non-fermentable by yeast, but when glucose is added the reducing val. diminishes rapidly and becomes const. at the val. attained in the fermentation of glucose alone. *In vivo* the non-fermentable residue of the reducing val. of the blood rises after administration of galactose, and falls rapidly if glucose is simultaneously administered. A. A. E.

Influence of succinic, fumaric, malic, and acetic acids on the deposition of liver-glycogen. A. P. Ponsford and I. S. MacLean (Biochem. J., 1932, **26**, 1340—1344).—In the normal rat addition of succinic, malic, or fumaric acid to a diet poor in carbohydrate leads to an increase of liver-glycogen. AcOH does not produce this effect. H. W. D.

Metabolism of normal and tumour tissue. VI. Conversion of fructose and glucose into lactic acid by embryonic tissue. F. Dickens and G. D. Greville (Biochem. J., 1932, **26**, 1251—1269).—In the anaërobic conversion of the sugars by fœtal membranes at p_H 7·5, the whole embryo and its tissues have been studied. Whilst glucose is readily converted into lactic acid by most embryonic tissues, the conversion of fructose depends on both the tissue and the species, varying from zero to a val. equal to that observed with the same tissue in glucose. For a given tissue the degree of conversion of fructose or glucose may show a considerable variation. S. S. Z.

Effect of sulphur on carbohydrate metabolism. I, II. T. Koyasako (Folia endocrinol. Japon., 1931, **7**, 9).—Daily application of S (15%) ointment to the skin of rabbits for 1 month had no effect on blood-sugar, but raised the sugar tolerance. It increased hypoglycæmia after insulin and changed hyperglycæmia after adrenaline. Ch. Abs.

Metabolism of pectin. K. Imhäuser (Arch. exp. Path. Pharm., 1932, **167**, 702—707).—Oral administration of pectin to dogs is followed by neither an appreciable increase in the blood-sugar nor, in phloridzinised dogs, a prevention of fat deposition in the liver. In the latter case, however, there is a marked decrease in the excretion of ketonic substances, indicating a definite utilisation of at least part of the pectin carbohydrate. F. O. H.

Value of vegetarian diet for maintenance. S. Wan and H. Wu (Chinese J. Physiol., 1932, **6**, 251—256).—The body-wts. of rats on a vegetarian diet increased at a lower rate than those of rats on a normal diet. There was also some suggestion that the mortality rate was higher on the vegetarian diets. R. N. C.

Rôle of the spleen in carbohydrate and fat metabolism. M. Rubinstein (Biochem. Z., 1932, **253**, 193—201).—In rabbits and dogs to which adrenaline and insulin are administered splenectomy has inconst. effects on the sugar and cholesterol contents of the blood. W. McC.

Fat metabolism in the lactating goat. R. C. Bender and L. A. Maynard (J. Dairy Sci., 1932, **15**, 242—253; cf. A., 1930, 636).—A low-fat ration equicaloric with a normal ration caused considerably reduced yields of milk and total butter-fat. Marked changes in blood-lipins follow variations in fat intake. Curves for total lipins, phospholipins, and cholesterol show a general parallelism. A low-fat diet and also a coconut-oil diet produced fat of higher saturation and lower mean mol. wt. than a linseed-oil diet. Variations in I and sap. vals. of milk-fat resulting from diet changes showed an inverse relationship throughout. A. G. P.

Influence of the lungs on the blood-volatile fatty acids. L. Binet, E. Aubel, and M. Marquis (Compt. rend. Soc. Biol., 1932, **109**, 2—4; Chem. Zentr., 1932, i, 2197).—On perfusion of the isolated lung with citrated blood the quantity of added HCO_2H, AcOH, $EtCO_2H$, or $PrCO_2H$ diminishes. A. A. E.

[Non-]relation between blood-cholesterol and basal metabolic rate. G. P. Grabfield and A. G. Campbell (New England J. Med., 1931, **205**, 1148—1149). Ch. Abs.

Cholesterol metabolism of various tissues. IV. Effect of extirpation of thyroid and adrenal. O. Yoshimura (J. Chosen Med. Assoc., 1931, **21**, 1079—1092).—The course of hypercholesterolæmia following removal of one adrenal gland or the thyroid gland from the rabbit or dog is described. Ch. Abs.

Fate of intravenously injected phosphatides. L. Pasternak and I. H. Page (Biochem. Z., 1932, **252**, 254—277).—When moderate or small doses of cephalin emulsions are intravenously injected into rabbits, the plasma-lipin content is considerably increased, but returns to normal val. in 30 min. With large doses. 30 min. after injection, the liver-phosphatide content is greatly increased, but the fat content remains normal. The latter then begins to increase, and remains high for several days after the phosphatide val. has returned to normal (12 hr.). The phosphatide val. of brain does not increase. Increased urinary excretion of PO_4''' is often, and changes in the cholesterol content of the organs, especially in brain, may be occasionally, observed. The effect also of injection of oleic, ricinoleic, and linolenic acids, mixed liver-oil fatty acids and their esters, lanolin, human fat, and mixed cerebrosides and phosphatides is also examined. P. W. C.

Relations of intermediary protein metabolism to carbohydrate economy. Intermediary amino-acid metabolism. K. Paschkis (Z. ges. exp. Med., 1932, **81**, 156—168; Chem. Zentr., 1932, i, 2603).—After oral administration of NH_2-acid, human blood-NH_2-N increases; sugar causes a decrease. In fasting or after insulin the blood-NH_2-N slowly falls. After simultaneous administration of sugar and NH_2-acid the blood-NH_2-N usually rises less than after ingestion of NH_2-acid alone. A. A. E.

Influence of insulin and glucose on purine metabolism. T. Ogawa (Folia endocrinol. Japon., 1931, **7**, 7—9).—Injection of insulin or administration of glucose lowers the total excretion of N, particularly of allantoin-N. Intravenous injection of hypertonic glucose solution decreases the total N and increases the urinary purine substances. Ch. Abs.

Influence of adrenaline on purine metabolism. T. Ogawa (Folia endocrinol. Japon., 1931, **7**, 6—7).—Subcutaneous injection of adrenaline (0·35 c.c. of 0·1% solution per kg.) into dogs increases the urinary N; the allantoin- and uric acid–purine base-N was increased both absolutely and relatively. Ch. Abs.

Effect of the amount of feed consumed by cattle on the utilisation of its energy content. H. H. Mitchell and T. S. Hamilton (J. Agric. Res., 1932, **45**, 163—191).—With a steer receiving the same feed in varying amounts the most complete digestibility of all nutrients occurred with the lowest level of feeding. With increasing amounts fed, there was a steady decline in the digestibility of the N-free extract, Et_2O extract, and total dry matter. The metabolisable energy per kg. of dry matter and the % metabolisability of the gross energy increased from the highest to the lowest levels of feeding. The net energy of a ration may be defined, not by a const., but by a linear equation relating it to the intake of dry matter. A. G. P.

Nutritive value of muscle in growth and reproduction. A. Scheunert and C. Venus (Biochem. Z., 1932, **252**, 231—253).—In feeding experiments with young growing rats on a synthetic diet, the best growth was obtained when 10% muscle-protein of ox or sheep was used as the source of protein. Differences in nutritive val. were not obtained when the muscle was given raw, boiled, or roasted, and there was no difference between fresh and frozen flesh. For the best results as to reproduction 2% muscle-protein should be used, although a partial replacement with caseinogen does not seriously interfere with its val. Again no difference was observed between fresh and frozen flesh. P. W. C.

Addition of raw beef or meat scraps to a whole-milk diet. W. C. Russell (J. Nutrition, 1932, **5**, 347—357).—In feeding experiments with rats the addition of meat to a wheat and milk diet improved reproduction and increased the growth rate and vigour of the young. The effect cannot be attributed to the increased Ca or P. Use of dried yeast with the wheat and milk ration slightly improved reproduction, but was without effect on the young. A. G. P.

Growth and reproduction of rats on an improved stock diet. H. Wu, S. Wan, and T. T. Chen (Chinese J. Physiol., 1932, **6**, 295—306).—A new diet on which growth and reproduction are better than on the best diets now in use is described. R. N. C.

Comparison between ground soya beans and linseed-oil meal as protein supplements for growing dairy calves. J. H. Hilton, J. W. Wilbur, and S. M. Hague (J. Dairy Sci., 1932, **15**, 277—281).—For heifer calves on a lucerne diet ground raw soya beans and linseed meal were equally effective protein supplements. A. G. P.

Rabbits maintained on barley or lucerne. F. Bischoff, W. D. Sansum, M. L. Long, and R. D. Evans (J. Nutrition, 1932, **5**, 403—411).—No significant differences occurred in the CO_2 content of the blood or the p_H of the plasma of rabbits fed for nearly 2 years on a barley diet (p_H of urine 5·2—6·2) or of those on lucerne (p_H of urine 8·2—9·5). A. G. P.

Cottonseed meal [as food]. C. H. Hunt (Ohio Agric. Exp. Sta. Bimonth. Bull., 1932, No. 158, 178—182).—When fed to rats, cottonseed meal proved deficient in certain NH_2-acid constituents of the protein and in minerals, but may be satisfactorily supplemented by caseinogen and yeast. The meal retains some of the toxic principle (gossypol), the effects of which may be minimised by suitably arranged rations, but not by additions of Fe_2O_3. A. G. P.

Mineral requirements of pregnant sows. R. E. Evans (J. Min. Agric., 1932, **39**, 544—548).—For pregnant sows (not having good grazing) a daily ration of 1 oz. of a mixture of ground chalk and common salt (4 : 1) is satisfactory. During lactation the quantity is increased to 2½ oz. A. G. P.

Mineral metabolism of the lactating cow. E. B. Hart, G. C. Humphrey, and J. A. Keenan (Proc. Amer. Soc. Animal Produc., 1932, **24**, 120—126).—The ration need not be supplemented by Ca and P unless the daily intake is much lower than 25—28 g. of Ca. Ch. Abs.

Calcium and phosphorus metabolism in dairy cows. V. Relative assimilation of calcium from grades 1 and 3 of timothy hay. W. A. Turner, E. A. Kane, and W. S. Hale (J. Dairy Sci., 1932, **15**, 267—276; cf. A., 1931, 869).—Ingestion of Na citrate had little effect on the Ca and P metabolism. For heavily milking cows good quality timothy hay was more favourable to Ca assimilation than were inferior grades. A. G. P.

Utilisation of calcium in soya-bean diets. W. H. Adolph and S. Chen (J. Nutrition, 1932, **5**, 379—385).—Cows' milk and soya bean were equally effective sources of Ca for Chinese adults. The attainment of a Ca equilibrium was facilitated by increasing the protein intake. A. G. P.

Microscopically detected metabolism of iron. G. WALLBACH (Klin. Woch., 1932, 11, 353—356; Chem. Zentr., 1932, i, 1683).—Deposition of Fe in the cells does not indicate the degree of blood decomp., but only that the cell has reached a particular functional condition associated with deposition of Fe pigment. Endogenous Fe metabolism can be followed microscopically. A. A. E.

Excretion of sulphur and nitrogen by fasting dogs during short periods. B. M. JACOBSON (Arch. exp. Path. Pharm., 1932, 167, 358—364).—The distribution of N and S in the urine of dogs at various stages of starvation indicates that the renal excretion during 24 hr. or shorter periods is not const. Hence control experiments with the same animals are essential in the investigation of hormonal or nervous influence on renal excretion of these elements.
F. O. H.

Value of iodine for livestock in central Pennsylvania. E. B. FORBES, G. M. KARNS, S. I. BECHDEL, P. S. WILLIAMS, T. B. KEITH, E. W. CALLENBACH, and R. R. MURPHY (J. Agric. Res., 1932, 45, 111—128).—Administration of I to cows infected with *B. abortus* did not affect the course of the disease. Heavy I feeding during the last 6 months of pregnancy was not harmful to cows, but milk and cream produced had an objectionable odour and contained much I. Calves, sheep, pigs, or chickens were not appreciably affected by I feeding. A. G. P.

Control of luminescence in the male lampyrid firefly (*Photurus pennsylvanica*) with special reference to the effect of oxygen tension on flashing. P. A. SNELL (J. Cell. Comp. Physiol., 1932, 1, 37—51).—Reduced O_2 tension (to 20 mm. Hg) decreased the intensity of the flash, but not its duration. With O_2 tension of 20—4 mm. the duration of the flash lengthened and at <4 mm. no flash occurred. A. G. P.

Quantitative measurement of cell permeability. M. H. JACOBS and D. R. STEWART (J. Cell. Comp. Physiol., 1932, 1, 71—83).—Permeability consts. for ethylene glycol, NH_2Ac, propion- and butyr-amide, and glycerol are recorded. Vals. for the three amides increase with their mol. wt. A. G. P.

Effect of fertilisation on the permeability of eggs of *Arbacia* and *Asterias* to ethylene glycol. D. R. STEWART and M. H. JACOBS (J. Cell. Comp. Physiol., 1932, 1, 83—92).—Fertilisation and, to a smaller extent, exposure to distilled H_2O increase the permeability of the eggs to ethylene glycol.
A. G. P.

Osmotic passage of water and gases through the human skin. A. R. G. WHITEHOUSE, W. HANCOCK, and J. S. HALDANE (Proc. Roy. Soc., 1932, B, 111, 412—429).—Moisture passes through the skin under normal conditions mainly by osmosis, increasing very rapidly as the skin-temp. rises, until completely interrupted by the presence of a covering of liquid sweat. In the intermediate stage this has a considerable influence on the regulation of body-temp. Passage of gas through the skin runs a parallel course.
H. G. R.

Influence of amputation on blood-sugar, -calcium, -inorganic phosphorus, and -non-protein-nitrogen. S. HONGO (Sei-i-kwai Med. J., 1931, 50, No. 8, 39—44).—Amputation of the femur of male rabbits causes a fall in blood-Ca and a rise in -inorg. P and -sugar. Blood-non-protein-N is unaffected. Rabbits similarly treated, but without injury to the bone, showed a similar rise in -inorg. P.
CH. ABS.

Biological action of parenterally injected ethyl alcohol. W. MILBRADT (Z. ges. exp. Med., 1932, 80, 782—802; Chem. Zentr., 1932, i, 2485).—Intravenous or intramuscular injection of 0·05—0·5 c.c. EtOH in 1 c.c. H_2O leads in man to accelerated clotting, retarded deposition of corpuscles, and diminution of surface tension and plasma-stability of the blood, apparently owing to alteration of the plasma-colloids. Blood-NH_2-acid increases and -sugar diminishes.
A. A. E.

Passage of ethyl alcohol into human parotid saliva. P. LINDE (Arch. exp. Path. Pharm., 1932, 167, 285—291).—The EtOH content of the parotid saliva of normal fasting humans increases after ingestion of aq. EtOH, whilst the content in plasma or whole blood follows a parallel course, although the concn. is higher in the saliva than in the blood. The passage of EtOH into the saliva is due to a simple diffusion process. F. O. H.

Influence of cortical and subcortical narcotics on blood-catalase. N. HIKARU (J. Chosen Med. Assoc., 1931, 21, 129—141).—$CHCl_3$, Et_2O, EtCl, and morphine cause in rabbits a decrease in blood-catalase in the first 10—15 min. (min. val. 30 min. after sleep); luminal, veronal, and urethane decrease the catalase 10—15 min. after injection (min. 60—100 min. after injection). The narcotic power is parallel with the power of decreasing blood-catalase. CH. ABS.

Detoxication of various doses of avertin. L. LENDLE (Arch. exp. Path. Pharm., 1932, 167, 590—598).—Continuous intravenous injection of avertin into rabbits is followed by a rate of detoxication which bears a linear relationship to the dosage. F. O. H.

Pharmacological influence on the detoxication of avertin. A. BECK and L. LENDLE (Arch. exp. Path. Pharm., 1932, 167, 599—608).—The action of various analeptics, thyroxine, and insulin on the detoxication of avertin in rabbits was investigated.
F. O. H.

Effect of drugs on purine economy. H. SEEL and G. CREUZBERG (Z. ges. exp. Med., 1932, 80, 806—818; Chem. Zentr., 1932, i, 2607).—Normally, and in gout, administration of atophan, santonin, or uricedin diminishes the blood- and increases the urinary uric acid. Excretion of allantoin is increased by atophan, arrested by uricedin, and unaffected by santonin. In rabbits atophan causes a diminution of the allantoin excretion without affecting the uric acid excretion. Santonin causes a small increase in uric acid, allantoin, and quantity of urine. Uricedin increases the excretion of uric acid and diminishes that of allantoin. In all three cases the blood-uric acid is slightly and transiently increased. A. A. E.

Physiological properties of some furan derivatives. H. Gilman, A. P. Hewlett, and J. B. Dickey (Iowa State Coll. J. Sci., 1932, 6, 137—141).—Skin reactions are described. Ch. Abs.

Effect on blood-sugar of some organic compounds with labile sulphur. A. C. de Degiorgi (Anal. Asoc. Quím. Argentina, 1932, 20, 78—86).—Piperidine and Na *N*-piperidyldithiocarbamates cause intense hyperglycæmia of long duration in rabbits. Intravenous injection of 2 mg. per kg. produces a marked effect. Oral administration has no action. R. K. C.

Influence of Chosen ginseng on excretion of glycuronic acid in urine. Y. Oshima (J. Chosen Med. Assoc., 1931, 21, 562—565).—Urinary glycuronic acid increased proportionally to the dose. Ch. Abs.

Influence of Chosen ginseng on glutathione contents of animal tissue. Y. Oshima (J. Chosen Med. Assoc., 1931, 21, 566—570).—In rats the tissue-glutathione was decreased. Ch. Abs.

Detoxification of certain poisons by Congo-red. I. P. Petrov (Arch. sci. biol., Russia, 1931, 31, 59—66).—Congo-red forms ppts. with strychnine, curare, and cobra-venom; this explains the (non-uniform) diminution of the toxic effect of these substances on frogs and mice. The toxicity of cobra-venom was not reduced by pptn. with Congo-red, but previous injection renders animals more resistant to the venom. Ch. Abs.

Pharmacological action of papaverine derivatives. H. Langecker and E. Starkenstein (Klin. Woch., 1931, 10, 2257—2261; Chem. Zentr., 1932, i, 1926).—A comparison of the behaviour of papaverine with that of 6 : 7-diethoxy-1-3 : 4-dimethoxy-, 6 : 7-dimethoxy-1-3 : 4-diethoxy-, and 6 : 7-diethoxy-1-3 : 4-diethoxy-benzyl*iso*quinoline. A. A. E.

Effect of taxin on blood-sugar. H. Toratani (Sei-i-kwai Med. J., 1931, 50, No. 7, 1—19).—Neither subcutaneous nor intravenous injection of small amounts of taxin HCl ($<$ 1 mg. per kg.) affects the blood-sugar of normal rabbits; larger amounts produce slight decreases. In hyperglycæmia subcutaneous (1—5 mg. per kg.) or intravenous (0·5—2 mg.) injection produced normal vals. Ch. Abs.

Pharmacology of thebaine and its derivatives. III. Influence on blood-cells and hæmoglobin. IV. Effects on blood-calcium, -chlorine, and -magnesium. V. Influence on fatty acids and lipins contained in the blood and central nervous system. Y. Takeuchi (Sei-i-kwai Med. J., 1931, 50, No. 5, 58—76; No. 6, 56—64; No. 8, 45—61).—III. Subcutaneous injection into rabbits of 1 c.c. of 1% thebaine hydrochloride per kg. decreases the blood-hæmoglobin by 18%; larger, but non-convulsive, doses increase the hæmoglobin.

IV. On injection of thebaine, dihydrothebaine, hydroxycodeinone, or dihydrohydroxycodeinone hydrochloride into rabbits the blood-Mg is unchanged, but the -Cl and -Ca decrease.

V. Subcutaneous injection of the alkaloids respectively caused the following decreases in blood-lipin-P: (*a*) 0·008 g. per kg., 33·2% within 1 hr.; (*b*) 0·012, 39% within 2 hr.; (*c*) 0·012, 35·3% within 2 hr.; (*d*) 0·016, 18% within 7 hr. All caused a decrease in blood-cholesterol of 34·3—36·7% and in -fatty acids of 34·9—36·7% within 2—3 hr. With mice, lethal doses of the first 3 drugs caused a decrease in the fatty acid, lipin-P, and cholesterol content of the spinal cord, whilst only the fourth caused a decrease of these lipins in the cerebellum. Ch. Abs.

Effect of ephedrine on the blood-lactic acid. I. I. Nitzescu and N. Munteanu (Compt. rend. Soc. Biol., 1931, 106, 1173—1175; Chem. Zentr., 1932, i, 2197).—Injection of ephedrine into the dog (or, less markedly, the rabbit) increases the blood-lactic acid and -sugar. The increase in lactic acid arises from increased formation in the muscle. Ephetonine has a similar, but less regular and less intense, effect. A. A. E.

Quinine and spleen blood. L. Binet and R. Fabre (Compt. rend. Soc. Biol., 1931, 106, 1116—1118; Chem. Zentr., 1932, i, 2197).—The blood of the spleen of dogs, after treatment with quinine HCl, contains twice the amount of quinine as is present in arterial blood, corresponding with the quantity of red corpuscles. The plasma was free from quinine. A. A. E.

Pharmacological action of "mussel poison." M. Prinzmetal, H. Sommer, and C. D. Leake (J. Pharm. Exp. Ther., 1932, 46, 63—73).—The poisonous principle separated from *Mytilus californianus*, sol. in H_2O and EtOH, insol. in Et_2O and $CHCl_3$, paralysed respiration and had a definite but complex effect on blood-pressure and heart-rate and was without action on smooth muscle in perfusion experiments. It is slowly absorbed from the gastro-intestinal tract and rapidly excreted by the kidneys. W. O. K.

Pharmacology of salamander alkaloids. O. Gessner and P. Möllenhoff (Arch. exp. Path. Pharm., 1932, 167, 638—653).—The principal alkaloid (cf. A., 1930, 1204) is samandarine, m.p. 190° [hydrochloride (I), m.p. 325°]. The min. lethal dose of (I) for *Rana esculenta* is 0·019 mg. per g. body-wt. Concns. as low as 1 : 10^5 have a paralysing action on salamander larvæ. It induces convulsions in the snake, rabbit, and mouse, has no hæmolytic action, and does not stimulate isolated skeletal muscle. For the rabbit's cornea a concn. of 1 : 500 causes an anæsthesia lasting about 1 hr. A second alkaloid has properties identical with, but less pronounced than, those of (I). F. O. H.

Diuretic effects and changes in blood- and urinary metabolites after digitalis in normal and in œdematous persons. A. B. Stockton (Arch. Int. Med., 1932, 50, 480—487).—The diuresis which sometimes follows administration of digitalis is accompanied by a decrease in the blood-Cl and -uric acid, and thus differs from the diuresis produced by metallic compounds and purine derivatives, where a rise in blood-Cl is found. W. O. K.

Diuretic action of *Digitalis* glucosides on the isolated frog's kidney. B. C. Costopanagiotis

(Arch. exp. Path. Pharm., 1932, 167, 660—680).—All the glucosides investigated, except gitoxin, produced irreversible vaso-constriction, especially in the arterial system. The diuresis persisted despite subsequent perfusion with normal fluids. The diuresis was accompanied by an increased urine-NaCl which persisted after the cessation of diuresis. The mechanism of the action of the glucosides on the glomeruli is discussed. F. O. H.

Assay of commercial and pharmaceutical *Digitalis* preparations. B. Behrens, Gros, and Hildebrandt (Arch. exp. Path. Pharm., 1932, 167, 365—380).—A statistical application of the frog method failed to yield an exact evaluation of the preps. Various preps. kept at room temp. for a year exhibited no loss of activity greater than the limits of error of the method of assay. F. O. H.

Action of saponins. M. Bing (Z. ges. exp. Med., 1932, 80, 511—522; Chem. Zentr., 1932, i, 2734).—The surface tension of saponin solutions falls with increasing concn. to a min., and then rises. With quillaia saponin the min. is 34·03 dynes per cm. at 0·01—0·025%; with guaiacum saponin it is 47·18 at 0·01%. C suspensions and a C–H_2O–xylene system are stabilised by saponin. Saponin solutions of concn. considerably below the contraction threshold sensitise the frog's heart for digitalis. A. A. E.

Saline and alkaline drinking waters. V. G. Heller (J. Nutrition, 1932, 5, 421—429).—Deleterious effects of drinking H_2O containing high proportions of dissolved salts are related more nearly to osmotic effects than to the action of any sp. ion. The safe max. of sol. salts is 1·5—1·7%. Animals are less susceptible to sol. salts than are plants. Cl′ is less injurious than SO_4'', org. salts less than inorg. salts, and alkalis are more harmful than salts. A. G. P.

Sulphur content of the liver after administration of a sulphate- or alkali-water. W. Arnoldi, G. Liss, and L. Rosam (Z. ges. exp. Med., 1932, 80, 633—636; Chem. Zentr., 1932, i, 2484).—Both natural waters increased the total and neutral S in rats; only the former increased the SO_4-S. A. A. E.

Absorption of lead and its distribution in the organism in experimental poisoning. II. F. Weyrauch (Z. Hyg., 1931, 112, 559—568; Chem. Zentr., 1932, i, 2351).—Ingestion and inspiration of "white Pb" are compared. A. A. E.

Modifications in methods of chemico-toxicological tests for mercury. D. Ganassini (Arch. Ist. Biochim. Ital., 1932, 4, 239—244).—The success of the test for Hg by the formation of "whiskers" on Al foil depends on the purity of the Al. If the "whiskers" are treated with starch–iodide solution and $CuSO_4$ solution containing a trace of $FeSO_4$, a blue colour is formed, dependent on the simultaneous presence of Hg and H_2O_2.

After subliming Hg from a deposit on Cu it may be converted into iodide by subliming a fragment of I in the same tube. A very sensitive test is the red colour given by Cu_2I paper in Hg vapour (*e.g.*, from heated Cu on which Hg is deposited). R. K. C.

Thallium. II. Thallium acetate and hæmatoporphyrin. P. Testoni (Arch. Int. Pharmacodyn. Thér., 1931, 40, 45—53; Chem. Zentr., 1932, i, 2733).—Tl acetate did not cause hæmatoporphyrinuria in rabbits or dogs. A. A. E.

Feeding potassium iodide to pregnant ewes. J. A. Schulz, C. C. Culbertson, B. H. Thomas, and J. M. Evvard (Proc. Amer. Soc. Animal Produc., 1932, 24, 215—219).—Daily ingestion of KI (0·05 grain) increased the thyroid-I of the lambs, but not the I content of the thyroid-free carcases; the latter was increased by 0·8—3·5 grains. Ch. Abs.

Influence of potassium cyanide poisoning on the glycogen content of the liver and muscles, especially the relation of potassium cyanide poisoning to insulin action. T. Koyasako (Folia endocrinol. Japon., 1931, 6, 117—118).—Injection of KCN (1%) into rabbits decreases the liver- and slightly decreases the muscle-glycogen; the decrease is checked by simultaneous injection of insulin. Ch. Abs.

Fate of reduced glutathione content in tissues of rabbits in which the temperature is raised by puncture of the corpus striatum and by peptone injection. S. Hongo (Sei-i-kwai Med. J., 1931, 50, No. 8, 20—31).—Average glutathione contents for rabbits are: heart 0·0341, lung 0·0739, liver 0·2166, adrenal 0·0357, kidney 0·0714, testicles 0·0730, muscle 0·0230%. After heat puncture the heart, spleen, testicles, muscle, adrenals (markedly), and lung (later) gave increased vals. With rabbits injected with peptone increases also occur, but only after 24 hr. Ch. Abs.

Influence of the temperature of *Rana nigromaculata* on the reduced glutathione content in tissues. T. Yazawa (Sei-i-kwai Med. J., 1931, 50, No. 8, 32—38).—The glandular tissue of frogs is richest in glutathione; the effect of a low temp. (4—7°) is to decrease the glutathione content of all the tissues except testicle, kidney, and adrenals. Ch. Abs.

Blood-calcium of the dog during ultra-violet irradiation and after parathyroidectomy. J. Cheymol and A. Quinquaud (J. Pharm. Chim., 1932, [viii], 16, 233—235).—The serum-Ca of two dogs exposed to ultra-violet light decreased 4·6 and 8·2%, respectively, and after parathyroidectomy further decreases occurred, death of the animals taking place after 4 and 2½ days, respectively, when Ca had decreased by 54% in both cases. A. L.

Mechanism of the action of *X*-rays on living tissues. V. E. Kinsey (Nature, 1932, 130, 436).—Living tissues, normal or pathological, evolve H_2 when irradiated with *X*-rays. L. S. T.

Second oxygen-carrying enzyme and its absorption spectrum. O. Warburg and W. Christian (Naturwiss., 1932, 20, 688).—The prep. of the enzyme from bottom yeast is described. Its concn. appears to be greater in anaërobic cells. It is orange in colour, with an absorption band extending over the range 410—560 mμ. The colour is lost on reduction. It is destroyed by warming the solution containing it at 60° for 10 min., is reduced by shaking with active hexosemonophosphoric acid, but is again oxygenated by shaking with O_2. A method of determining the concn. and O-carrying power of the enzyme is described. A. J. M.

Formation of pigment in the skin, with special reference to the optical specificity of dopa-oxidase. B. Bloch and F. Schaaf (Klin. Woch., 1932, **11**, 10—14; Chem. Zentr., 1932, i, 1913).—Dopa-oxidase is not identical with tyrosinase; it reacts only with *l*- and not with *d*-3 : 4-dihydroxyphenylalanine. A. A. E.

Optical specificity of dopa-oxidase. S. M. Peck, H. Sobotka, and J. Kahn (Klin. Woch., 1932, **11**, 14; Chem. Zentr., 1932, i, 1912—1913).—Dopa-oxidase reacts with *l*- and *r*-, but not with *d*-3 : 4-dihydroxyphenylalanine. The formation of melanin probably depends on the dopa-reaction. A. A. E.

Oxidations catalysed by horse-radish- and milk-peroxidases. K. A. C. Elliott (Biochem. J., 1932, **26**, 1281—1290).—Horseradish-peroxidase (I), which is not identical with milk-peroxidase (II), does not oxidise, in the presence of H_2O_2, nitrile, tryptophan, formate, acetate, lactate, oleate, glucose, fructose, glycerol, EtOH, MeCHO, glycine, glutamic acid, phenylalanine, histidine, or brucine. Phenolic substances, with the exception of resorcinol which is oxidised by (I) but not by (II), are oxidised by both enzymes in the presence of H_2O_2. Resorcinol, pyrrole, and C_5H_5N have an inhibitory influence on both enzymes. S. S. Z.

Product of the oxidation of glucose by glucose-dehydrogenase. D. C. Harrison (Biochem. J., 1932, **26**, 1295—1299).—More than 60% of the theoretical amount of *d*-gluconic acid has been isolated (A., 1931, 1189). It is probably the sole product of the oxidation. S. S. Z.

Co-enzyme of lactic acid oxidation. I. Banga, A. Szent-Györgyi, and L. Vargha (Z. physiol. Chem., 1932, **210**, 228—235).—The prep. of the co-enzyme is described. *d*-Lactic acid is oxidised with great rapidity by washed heart-muscle in presence of the co-enzyme. The *l*-acid, although not oxidised, does not hinder the oxidation of the *d*-form. The $OH \cdot CHMe \cdot CO_2H$ utilises 3 mols. of O_2, indicating complete oxidation to CO_2 and H_2O. PO_4''' produces practically no increase in the rate of oxidation. J. H. B.

Quinones as enzyme models. VI. Catalysis of the oxidative deamination of glycyl-*l*-tyrosine. B. Kisch (Biochem. Z., 1932, **252**, 380—386).—With most of the catalysts used, glycyl-*l*-tyrosine (I) is oxidatively deaminised to the same extent and at the same optimal p_H as glycylglycine (II) and glycylleucine (III). Hydroxyquinol, however, occupies a special position in that the yield of NH_3 from (I) is twice as high as from (II) or (III) and four times as high as from glycine. (I) is not first split into tyrosine and glycine. Tyrosine itself is not perceptibly deaminised over the p_H range 7—12. P. W. C.

Determination of the action of amylase. E. A. Sym (Biochem. Z., 1932, **253**, 1—10; cf. this vol., 1063).—A method and apparatus are described. W. McC.

Ultra-violet inactivation of invertase in its dependence on hydrogen-ion concentration and ozone. G. Gorbach and H. Pick (Monatsh., 1932, **61**, 29—38).—Yeast autolysates are inactivated by ultra-violet irradiation much less readily than purified preps. (by dialysis, adsorption, elution); inactivation of the latter proceeds initially at a uniform rate and then diminishes gradually. Somewhat more inactivation occurs at p_H 3·2 and 8·2—9·2 than at p_H 7; the differences are, however, relatively small. Inactivation is accomplished very readily with O_3 alone. More inactivation occurs when irradiation is carried out in N_2 than in O_2, showing that O_3 is not the inactivator in the latter case; in presence of O_2 an activation of the invertase occurs after 10 min. probably owing to the decomp. (by activated O_2) of some substance which retards enzyme action. H. B.

Re-inactivation of irradiated invertase solutions and influence of added tryptophan and yeast-gum. G. Gorbach and D. Kimovec (Monatsh., 1932, **61**, 39—46).—Invertase solutions irradiated for 10 min. or longer lose their residual activity when kept; the loss is accelerated by addition of tryptophan or (more readily) yeast-gum both at p_H 7 and 9·6. Solutions irradiated for $<$ 10 min. remain stable. H. B.

Action of emulsin. I. Hydrolysis of 3-methylpentanol-β-*d*-glucoside by means of emulsin. S. Veibel and E. Bach (Biochem. Z., 1932, **252**, 401—405).—The prep. of 3-*methylpentanol*-β-d-*glucoside*, $[\alpha]_D^{17}$ −34·7°, and its hydrolysis by emulsin are described. The rotation of the alcohol isolated after 62% of the material had been hydrolysed was +0·20° and after complete hydrolysis −0·57°. It appears that partial separation of the optically active forms of the hexyl alcohol occurs during hydrolysis. P. W. C.

Enzymic hydrolysis of malto- and lactobionic acids. C. Neuberg and E. Hofmann (Biochem. Z., 1932, **252**, 434—439).—Enzyme solutions prepared from fresh or dried bottom yeast hydrolyse maltobionic acid (50% of the substrate being hydrolysed). Lactobionic acid is hydrolysed by emulsin at p_H 4·3 (17% hydrolysed) and much more readily by enzyme solutions prepared from three species of lactose-fermenting yeasts (*Saccharomyces fragilis*, Jörgensen, *S. Kefir*, and a third species—69% hydrolysed). P. W. C.

Optimum p_H for the hydrolysis of vegetable oils by castor-seed lipase. R. Guillemet (Compt. rend. Soc. Biol., 1931, **108**, 781; Chem. Zentr., 1932, i, 2857).—No definite optimum can be determined, since vals. depend on the method of prep. and on the buffer solution used. A. A. E.

Yeast lipase. G. Gorbach and H. Günter (Monatsh., 1932, **61**, 47—60).—Yeast lipase, best obtained by extraction of yeast with a phosphate buffer during 1 hr., shows optimum activity at p_H 6·6—6·8 and at 30°; the velocity coeff. decreases more rapidly on the acid side of the optimum, and is increased (not proportionally) by the use of larger amounts of yeast. Compressed yeast contains more lipase than brewer's yeast. The lipase content of cultured yeast is higher than that of commercial; in both cases it is increased by artificial fattening (max. after 6—7 days). The activity of lipase is decreased (to varying extents) by $CHCl_3$, Et_2O, PhMe, and $CH_2Ac·CO_2Et$; removal of these substances after autolysis increases the lipase vals. Active lipase preps. are obtained by addition of glycerol to yeast autolysates. H. B.

Relationships between the activation of pancreatic lipase and the surface effects of the compounds involved. Mechanism of inhibition and activation. D. Glick and C. G. King (J. Biol. Chem., 1932, **97**, 675—684).—The isoelectric points of the proteins related to pancreatic lipase and esterase are markedly different. The action of the lipase on tributyrin is accelerated by the following compounds in decreasing order of activity: hexylresorcinol, octyl alcohol, amyl iodide, hexyl alcohol, amyl alcohol, PhOH, hexoic acid, *cyclo*hexanol, resorcinol. Bile salts show a slight inhibition. The ability to lower the surface tension of H_2O is approx. in the same order. The activation is therefore due to a concn. of the activator on the substrate resulting in a decrease of interfacial tension between enzyme and substrate. F. O. H.

Characteristic properties of enzymes in the fission of optically-active substances. M. Werner (Klin. Woch., 1931, **10**, 2314—2317; Chem. Zentr., 1932, i, 1675).—The esterases show stereochemical specificity in the fission and synthesis of optically-active substances. The total specificity of an enzyme is a combination of the affinity- and degradative specificity, and depends on the concn. of substrate, the optically-active substance added, and the mode of prep. of the enzyme. A. A. E.

Relationship between chemical constitution and physiological action. IV. Inhibitory action of certain synthetic urethanes on the activity of esterases. E. Stedman and (Mrs.) E. Stedman (Biochem. J., 1932, **26**, 1214—1222).—Urethanes, which behave as parasympathetic stimulants (A., 1931, 1190), inhibit the activity of liver-esterases in general. This inhibitory property also extends to the esterase of the blood-serum of the guinea-pig and of certain other species. Miotine is without action on kidney-phosphatase. S. S. Z.

Histaminase. I. Histamine–histaminase reaction. II. Purification. III. Species distribution. E. W. McHenry and G. Gavin (Biochem. J., 1932, **26**, 1365—1376).—Previous to the actual inactivation of histamine by histaminase there is a lag period which varies with the enzyme concn. The rate of inactivation proceeds as a unimol. reaction. The inactivation is accelerated by O_2 and is inhibited in an atm. deficient in O_2. KCN inhibits, $Na_4P_2O_7$ has no effect on, and PO_4''' augments the reaction. At p_H 7·2 and 8·8 the enzyme liberates one atom of N as NH_3. At p_H 5·9 less NH_3 is liberated. Histaminase is absent from the kidney of the rat, guinea-pig, and chicken and is present in that of a no. of mammals. Pig kidney is the best source. A stable active powder can be prepared from pig kidney by extraction of the fats with $COMe_2$, removal of $COMe_2$ with Et_2O, and subsequent drying. The enzyme can be removed from the powder by extraction at 38° with phosphate buffer of p_H 7·0—7·2. S. S. Z.

Influence of narcotics on the autolytic degradation of histamine. Å. Bergwall and F. Techner (Arch. exp. Path. Pharm., 1932, **167**, 609—620).—The inhibitory effect of $CHCl_3$, EtOH, or Et_2O on the disappearance of depressor substances and of added histamine from autolysing ox lung is greater than that on the proteolysis. Hypnotics (avertin and somnifen) have no action, whilst 0·0025M-KCN strongly inhibits the degradation. The presence of a histaminase is therefore indicated. F. O. H.

Crystalline pepsin. IV. Hydrolysis and inactivation by acid. J. H. Northrop (J. Gen. Physiol., 1932, **16**, 33—40).—When cryst. pepsin is hydrolysed by various concns. of HCl, the peptic activity of the hydrolysate is proportional to the amount of protein which remains. When various protein substrates are used, the relative rates of action of the partly hydrolysed pepsin remain const. None of the fission products of the protein mol. therefore appears to possess activity comparable with that of the original protein. W. O. K.

Pepsin activity units and method for determining peptic activity. J. H. Northrop (J. Gen. Physiol., 1932, **16**, 41—58).—Methods are described for determining the activity of pepsin by measuring the rate of change of viscosity of solutions of gelatin, caseinogen, edestin, and milk-powder, the rate of formation of non-protein-N from caseinogen and edestin solutions, and the increase of the formol titration of solutions of the protein. Units of pepsin activity are defined. W. O. K.

Determination of pepsin with hæmoglobin. M. L. Anson and A. E. Mirsky (J. Gen. Physiol., 1932, **16**, 59—63).—Pepsin is added to a solution of dialysed ox CO-hæmoglobin, acidified with HCl, and after 5 min. at a const. temp. $CCl_3·CO_2H$ is added to ppt. the pigment and undigested hæmoglobin. The digested hæmoglobin in the filtrate is determined by means of the blue colour developed when it is treated with a phenol reagent. W. O. K.

Spectral analysis of the mitogenetic radiation in peptic digestion and in the fission of glycylglycine by erepsin. E. Billig, N. Kannegiesser, and L. Soloviev (Z. physiol. Chem., 1932, **210**, 220—227).—The mitogenetic spectra of the two processes show a general agreement and must be due to the fission of the CO·NH group, since glycylglycine contains no other hydrolysable group. The action of pepsin is apparently limited to the fission of peptide linkings. J. H. B.

Antitrypsin. III. Nature. IV. Hormonal and pharmacological effect on the albumin : globulin quotient and the antitryptic titre in human serum. V. Antitryptic titre in human serum. VI. Is the antitrypsin reaction a cachexia reaction? F. Chrometzka (Z. ges. exp. Med., 1932, **80**, 395—407, 408—419, 420—438, 439—443; Chem. Zentr., 1932, i, 2193—2194).—III. The anti-enzyme theory is rejected and the physicochemical theory is supported; a certain physico-chemical condition of protein confers on the blood and tissues protection against tryptic action. In widely different pathological conditions an increase in the serum-globulin (possibly also the appearance of sp. globulins) increases the antitryptic titre. Formation of albuminate by chemical or thermal treatment diminishes the antitryptic titre.

IV. Parenteral administration of thyroxine, "präphyson," pituitrin, insulin, adrenaline, atropine, or pilocarpine affects the antitryptic titre, which is thus subject to neuro-hormonal regulation, apparently by way of the albumin–globulin equilibrium.

V. Of 216 malign tumours 85·6% gave an increased, 9·2% a normal, and 5·2% a decreased titre; 7 benign tumours gave normal vals.

VI. A discussion. A. A. E.

Morphine and enzymes. I. E. Keeser (Arch. exp. Path. Pharm., 1932, **167**, 267—284).—The *in vitro* actions of pepsin, trypsin, cathepsin, phenolase, and pig's liver-esterase are affected by the presence of morphine only to a slight extent, but those of reductase, urease, lecithase, phosphatase, lipase, and tyrosinase are either inhibited or accelerated, according to the concn. of the alkaloid. With the latter group the formation of an intermediate oxidation product which influences the degree of toxicity of morphine does not occur. Simultaneous injection of urea or of glutathione increases the toxicity of morphine. F. O. H.

Nuclein metabolism. XXX. Enzymic fission of yeast-nucleic acid with nucleotidase from intestinal mucosa. F. Bielschovsky and F. Klemperer (Z. physiol. Chem., 1932, **211**, 69—74; cf. this vol., 776).—Guanosine, inosine, uridine, cytidine, and guanylic acid were isolated from the products of enzymic fission of yeast-nucleic acid. At the p_H employed (8·8), guanylic acid is produced even in absence of the enzyme, but there is no liberation of H_3PO_4. J. H. B.

Tumour-arginase. I. Activatability of liver-arginase by cysteine and glutathione. G. Klein and W. Ziese (Z. physiol. Chem., 1932, **211**, 23—37).—Passage of O_2 and particularly of CO_2 through suspensions of calf- and ox-liver inhibited arginase action. Cysteine and glutathione showed strong inhibition both in the acid and in the alkaline region at concns. of 0·045—0·45 mg. per c.c. There was no evidence of activation in EtOH-extracted liver or rat sarcoma extract. HCN inhibited, but H_2S was inactive. J. H. B.

Preparation and enzymic hydrolysis of amyl phosphates. F. F. von Falkenhausen (Biochem. Z., 1932, **253**, 152—160; cf. this vol., 142).—*dl*-Mono- and -tri-amyl phosphates are obtained by Limpricht's method (Annalen, 1865, **134**, 347). Takaphosphatase hydrolyses the mono-compound (the *l*-component being slightly more rapidly attacked than the *d*), but not the tri-compound. W. McC.

Preparation and enzymic hydrolysis of *l*- and *dl*-fenchyl pyrophosphates. E. Ochiai (Biochem. Z., 1932, **253**, 185—192).—l- and dl-*Difenchyl pyrophosphates*, $(C_{10}H_{17})_2H_2P_2O_7$, m.p. 176° (decomp.) (*l*-compound, $[\alpha]_D^{22}$ −13·92°), prepared by the action of $POCl_3$ on the corresponding alcohols, are hydrolysed (in the form of their Na_2 salts) by takaphosphatase. The hydrolyses are about 57% complete after 268 hr. and, in the case of the *dl*-compound, the process is asymmetric, about 50% of the alcohol liberated being lævorotatory. The H phthalate of the *dl*-alcohol was prepared from the hydrolysate. The NH_4 and Ag salts of $C_{10}H_{17}H_2PO_4$ and a *substance*, m.p. 181—182° (decomp.), $[\alpha]_D^{22}$ −14·17°, are obtained as by-products. The substance contains $C_{10}H_{17}H_2PO_4$. W. McC.

Chemistry of alcoholic fermentation. K. Myrbäck (Svensk Kem. Tidskr., 1932, **44**, 207—222).—A discussion. H. F. H.

Indene and indones in alcoholic fermentation. F. Pirrone (Annali Chim. Appl., 1932, **22**, 501—508).—Indene, β-phenyl-α-methyl- and -ethyl-indone produce max. acceleration in the fermentation of glucose by yeast when the concn. is, respectively, 5·71, 0·98, 0·95, and 0·96 mg. per 100 c.c. of solution. The accelerative power in indones containing an aromatic group is less than in those containing an aliphatic group. In the latter the accelerative power increases with the no. of C atoms. O. F. L.

Inhibition of fermentation by halogen compounds. E. Simon (Biochem. Z., 1932, **253**, 218—221).—$CH_2I{\cdot}COMe$ (concn. 1 : 5000), $CH_2I{\cdot}CHO$, and $CH_2Br{\cdot}CHBr{\cdot}CHO$ (concn. 1 : 1000) inhibit alcoholic fermentation, but $CBr_3{\cdot}CH_2{\cdot}OH$, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, $CH_2I{\cdot}CH(OEt)_2$, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH$, $CH_2I{\cdot}CH_2{\cdot}OH$, and $CH_2I{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ in concn. of 1 : 1000—1 : 5000 do not. W. McC.

Trehalose content of, and the power to form trehalose of, bottom yeast. S. Veibel (Biochem. Z., 1932, **252**, 305—308).—Quant. evidence is brought in support of the view of Robison and Morgan (A., 1928, 1285) that trehalosephosphate is actually synthesised during fermentation and not merely the result of phosphorylation of trehalose preformed in the yeast, as suggested by Kluyver (this vol., 428). P. W. C.

Classification of cultivated yeasts by means of the cytochrome spectrum. H. Fink (Z. physiol. Chem., 1932, **210**, 197—219).—The cytochrome spectra of a no. of strains of cultivated yeast may be divided into two types: (*a*) the four-banded spectra typical of reduced cytochrome, belonging to the baker's yeast or respiration type of organism, (*b*) the two-banded spectra characteristic of brewer's, distiller's, and, in general, fermentation yeasts. The wild yeasts belong to type (*a*). The cytochrome factor in type (*a*) is about double that of (*b*). A change of one type into the other does not occur spontaneously, but may be induced by suitable cultivation. It is particularly easy to convert baker's yeast into the fermentation type. The method may be used for detecting adulteration of baker's yeast with the cheaper brewer's variety. J. H. B.

Respiration of moulds. I. Respiratory quotient and the influence of oxidation–reduction processes on the gaseous metabolism of the cell. II. Energetics of growth. H. Tamiya (Acta Phytochim., 1932, **6**, 227—263, 265—304).—I. The gaseous exchanges of *Aspergillus oryzæ* and of other moulds during rest and in presence of various C-providing substrates were investigated. The R.Q. is proportionately $>$ or $<$ the combustion quotient (C.Q.) of the substrate, according to whether the val. for the C.Q. is $>$ or $<$ approx. 0·875, a val. equal to the C.Q. of the mould constituents taken as a whole. Thus the differences recorded depend on the increased or decreased provision of CO_2 and O_2 together with the effect due to growth and variations in metabolism.

II. Various theoretical concepts of the energy exchange are applied to moulds utilising different substrates as a supply of C. The energy resulting from respiration during vital synthesis appears to be mainly utilised for (*a*) the maintenance of enzymic and structural energy, (*b*) replacement of heat loss during certain stages of synthesis, and (*c*) the activation of the substrate necessary for acceleration of the velocity of the reactions during synthesis.

F. O. H.

Alcoholic fermentation by *Aspergillus oryzæ*. K. SAKAGUCHI and M. NAKANO (J. Agric. Chem. Soc. Japan, 1932, 8, 115—122).—Conditions for fermentation lead to classification of varieties of *A. oryzæ*.

CH. ABS.

Production of acids by *Aspergillus niger*. VI. Production of glycollic and glyoxylic acids from acetates. K. BERNHAUER and Z. SCHEUER. **VII. Conversion of alcohol into citric acid. VIII. Conversion of aconitic into citric acid. Degradation of acetic acid.** K. BERNHAUER and N. BÖCKL. **IX. Fixing of acetaldehyde in mould cultures.** K. BERNHAUER and H. THELEN (Biochem. Z., 1932, **253**, 11—15, 16—24, 25—29, 30—36; cf. A., 1929, 218; 1931, 1333).—VI. The $OH\cdot CH_2\cdot CO_2H$ (I), which is produced by many strains of *A. niger* from $Ca(OAc)_2$ and NaOAc, rapidly disappears from the cultures and is replaced by $CHO\cdot CO_2H$, which is also produced concurrently. Since NaOAc yields more $H_2C_2O_4$ than does $OH\cdot CH_2\cdot CO_2Na$ and sometimes more than does Na succinate, it is concluded that AcOH is converted into $H_2C_2O_4$ by way of succinic acid rather than by way of (I). The last two acids may be converted not only into $H_2C_2O_4$, but also into citric acid.

VII. Certain strains of *A. niger* convert EtOH (2% solution) in presence of $KHCO_3$ into citric acid (best yield 36%). $H_2C_2O_4$, malic acid (especially), tartaric acid, and reducing substances (probably sugars) are also produced. The yield of citric acid from EtOH is greater than that from acetates, but the yield of $H_2C_2O_4$ from the latter is greater than that from EtOH.

VIII. Although most strains of *A. niger* produce only small amounts or traces of citric acid from K aconitate, a yield of $>$ 20% was obtained with one strain, which also converted citric into aconitic acid. Usually $H_2C_2O_4$ and sometimes also reducing substances were simultaneously produced.

IX. Under suitable conditions and in presence of Na_2SO_3, MeCHO is sometimes obtained in 60% yield from sucrose by the action of *A. niger*. If Na_2SO_3 is absent, considerable amounts of $H_2C_2O_4$ and citric acid are produced, but when MeCHO is produced these acids are not. W. McC.

Production of acids from sugar by *Aspergillus niger*. V. Production of malic acid along with citric acid. K. BERNHAUER, N. BÖCKL, and H. SIEBENÄUGER (Biochem. Z., 1932, **253**, 37—41).—Together with almost theoretical yields of citric acid small amounts (2 g. from 975 g. of sucrose) of malic acid are obtained by the action of *A. niger* on sucrose. W. McC.

Acid formation and mycelium production by *Aspergillus niger*. A. FREY and H. POSCHENRIEDER (Arch. Mikrobiol., 1932, 3, 409—421).—The effect of K on the wt. of mycelium, and especially on the amount of acid produced by *A. niger*, varies with the age of the culture. In the determination of the available K content of soil by means of *A. niger*, dissolution of soil-K by org. acids produced by the organism is negligible. A. G. P.

Biological synthesis of *m*-digallic acid. M. NIERENSTEIN (Biochem. J., 1932, **26**, 1093—1094).—The acid was isolated as Me pentamethyl-*m*-digallate from solutions of gallic acid which had been acted on by *Aspergillus niger* or tannase. S. S. Z.

Inhibiting influence of colloidal starch, inulin, and agar on the stimulation of *Aspergillus niger* by zinc sulphate. K. B. STEHLE (Bull. Torrey Bot. Club, 1932, 59, 191—217).—Stimulation by $ZnSO_4$ did not occur when the concn. of sugar was below a certain level, when starch or inulin was used instead of sugar, or when agar-agar was added to the sugar. The presence of a colloid also protects the fungus from the effects of otherwise lethal concns. of $ZnSO_4$. Adsorption of Zn is partly responsible. CH. ABS.

Effect of organic stimulants on the production of kojic acid by *Aspergillus flavus*. O. E. MAY, G. E. WARD, and H. T. HERRIC (Zentr. Bakt. Par., 1932, 86, II, 129—134).—Among numerous org. compounds examined ethylene chlorohydrin alone (100 mg. per litre) stimulated kojic acid production. Thiourea, thioglycollic acid, NaCNS, chloroacetone, and *o*- and *p*-chlorophenol were inhibitory.

A. G. P.

Effect of olive oil on the metabolism of certain fungi. I. R. S. KATZNELSON (Arch. sci. biol., Russia, 1931, 31, 385—398).—*Aspergillus flavus* (I), *Penicillium sylvaticum* (II), and a white fungus (III) utilised (15—70%) olive oil as a source of C. The mycelium-N and -H_2O were diminished. Addition of olive oil to a medium containing glucose diminishes the consumption of glucose by (I) and (III). Addition of glucose to a medium containing olive oil increases the consumption of the oil by (I) and diminishes it by (II) and (III). On the basis of dry wt. the addition of glucose diminishes oil utilisation by all forms. Glycerol gives similar results when used with olive oil in the media. The acidity of the residual oil does not depend on the composition of the medium. Sap. and I vals. were relatively unchanged. The Reichert–Meissl val. was raised by (I) and (II) and lowered by (III). CH. ABS.

Iron, zinc, and *Aspergillus*. R. A. STEINBERG (Zentr. Bakt. Par., 1932, II, 86, 139—142).—A reply to Bortels (Angew. Bot., 1929, **11**, 285). The rôle of

Zn as an essential nutrient rather than a stimulant is emphasised. A. G. P.

Action of certain moulds on solutions of aldoses. IV. Formation of oxalic acid from *d*-gluconic acid. A. Angeletti (Annali Chim. Appl., 1932, **22**, 404—407; cf. A., 1930, 1620; this vol., 145).—Cultures of *Penicillium luteum purpurogenum* (strain 2A) convert a 3% solution of Ca *d*-gluconate, at 22—25°, almost quantitatively in 3 months into CaC_2O_4; no traces of other acids are found. E. W. W.

Effect of fat-soluble vitamin on the growth of some parasitic fungi. Y. Tochinai and M. Terui (J. Fac. Agric. Hokkaido, 1932, **32**, 71—107).—Retardation of the growth of pathogenic fungi from rice is reported. Ch. Abs.

Growth requirement of *Staphylococci*. T. P. Hughes (J. Bact., 1932, **23**, 437—447).—The constituent of meat extract capable of stimulating the growth of *Staphylococci* belongs to the class of "natural bases." Its chemical properties are recorded and its possible relationship to vitamin-*B* is discussed. A. G. P.

Application of the autocatalytic growth curve to microbial metabolism. H. C. Pulley and J. D. Greaves (J. Bact., 1932, **24**, 145—168).—The rates of nitrate accumulation by mixed cultures of soil organisms and of CO_2 by *Saccharomyces cerevisiæ* may be represented by equations derived from that expressing the rate of a unimol. autocatalysed reaction. A. G. P.

Isolated occurrence of carboxylase. Enzymic actions of the acetic bacterium *Bordeaux*. C. Neuberg and E. Simon (Biochem. Z., 1932, **253**, 225—230; cf. Simon, A., 1930, 1477; Quéré, A., 1931, 1334).—Under the conditions formerly chosen *B. Bordeaux* does not attack sugar. It contains carboxylase and mutase, but no zymase, and it produces methylglyoxal from hexosediphosphate, converts methylglyoxal into lactic acid, and attacks pyruvic acid. It is doubtful whether it is similar to *B. acetigenum*, Henneberg. W. McC.

Fermentation citric acid. J. H. Frydlender (Mon. Prod. chim., 1932, **14**, No. 155, 3—13; Chem. Zentr., 1932, i, 1961).—A discussion. A. A. E.

Nitrogen requirements of the lactic acid bacteria. B. A. Eagles and W. Sadler (Nature, 1932, **130**, 278).—In the fermentation of carbohydrates by lactic acid streptococci, both the source (proteose, peptone, and sub-peptone) and the amount of N employed are crit. L. S. T.

***Lactobacillus* genus with special reference to xylose fermentation by *L. pentoaceticus*.** L. Weinstein and L. F. Rettger (J. Bact., 1932, **24**, 1—28).—Fermentation of xylose by *L. pentoaceticus* yields AcOH and *r*-lactic acid in the approx. ratio 42 : 58. Excess of base, *e.g.*, $CaCO_3$, must be present to ensure complete reaction. The total acid yield corresponds with 88·90% of the xylose destroyed and is not influenced by the O_2 tension. A. G. P.

Transformation of acetylene by *Mycobacterium lacticola*. L. Birch-Hirschfeld (Zentr. Bakt. Par., 1932, II, **86**, 113—129).—C_2H_2 is oxidised by *M. lacticola* with the production of CO_2. MeCHO is an intermediate product. The activity of the organism is favoured by the presence of soil extracts. Growth is retarded in an atm. containing $> 40\%$ O_2 or $> 80\%$ C_2H_2. A. G. P.

Lipins of tubercle bacilli. XXVII. Composition of the phosphatide fraction of *Bacillus lepræ*. R. J. Anderson and N. Uyei (J. Biol. Chem., 1932, **97**, 617—637).—The phosphatides from the EtOH–Et_2O extract of *B. lepræ* (this vol., 307) are more stable than those from other acid-fast bacteria. Hydrolysis by EtOH–KOH liberates fatty acids and glycerophosphoric acid, whilst a polysaccharide complex is left intact. The latter, on hydrolysis with dil. acids, yields mannose, inositol, and a reducing hexose (invert-sugar or fructose). The fatty acids include palmitic acid, a saturated acid of high mol. wt., two unsaturated acids which yield palmitic and stearic acid, respectively, on reduction, and a saturated, optically active, liquid acid. The Et_2O extract contains an unsaturated, optically active, wax-like substance of high mol. wt. F. O. H.

Nitrogen changes produced in certain nitrogenous compounds by *Azotobacter* and the nitrogen fixed in presence of these compounds. L. G. Thompson, jun. (J. Agric. Res., 1932, **45**, 149—161).—Four species of *Azotobacter* decomposed $NaNO_3$, KNO_3, KNO_2, urea, and asparagine (amide-N only) with the production of NH_3, which was then utilised by the organisms. All compounds inhibited the fixation of free N_2 and in some cases there was a loss of NH_3. NH_2-acids were utilised to only a small extent. In general, the simpler compounds were utilised more easily, and had a greater depressive action on the fixation of free N_2, than the more complex materials. With all species except *A. vinelandii*, high N fixation in N-free media and high NO_3' consumption in NO_3' media were coincident. A. G. P.

Influence of molybdenum and of soil extract constituents on nitrogen fixation by *Azotobacter chroococcum*. L. Birch-Hirschfeld (Arch. Mikrobiol., 1932, **3**, 341—361).—The ratio of N fixed to sugar consumed by *A. chroococcum* is markedly increased by addition to media of soil extract or Na_2MoO_4. The rate of growth of the organism is accelerated by soil extracts, but not by Na_2MoO_4, the effect of the former being apparent during the assimilation of either free N_2 or of NO_3-N. The NO_3-N assimilated per unit sugar consumption is not influenced by either stimulant. Soil extracts contain both org. and inorg. activators, the former being associated with accelerated growth rates. The ash of soil extracts increases the N_2 fixed per unit of sugar consumed to approx. the same extent as does Na_2MoO_4, but does not affect growth rates. A. G. P.

Identification of *Brucella*, isolated in France, by means of the bacteriostatic action of dyes and the production of hydrogen sulphide. R. M. Taylor, M. Lisbonne, and G. Roman (Ann. Inst. Pasteur, 1932, **49**, 284—302).—Strains of *Brucella* may be classified into the types *Br. melitensis*, *Br. abortus bovis*, and *Br. abortus suis* by means of (1) the bacteriostatic action of dyes (thionine and basic fuchsin), (2) production of H_2S, and (3) the necessity of a CO_2 atm. for the growing culture. W. O. K.

Biological oxidations. I. Oxidations produced by gonococci. E. S. G. Barron and C. P. Miller, jun. (J. Biol. Chem., 1932, 97, 691—715).—Glucose, but not fructose, galactose, mannose, arabinose, or xylose, is fermented by the organism to AcOH and CO_2. Intermediate products are $AcCO_2H$ and lactic acid, which are formed by the action of two distinct enzymes. α-OH- and -keto-acids are oxidised by gonococci. The stability and $p_{\rm H}$ optima of the enzymes concerned are investigated. F. O. H.

Biochemistry of bacteriospores. A. I. Virtanen and L. Pulkki (Suomen Kem., 1932, 5, B, 46).—In *B. mycoides* the spores and corresponding vegetative cells are similar in composition with regard to H_2O, ash, N, and fat. The thermostability of the spores is therefore not due to their characteristic composition. The vegetative cells contain catalase, and four times as much polypeptidase as the spores, and ferment 80% of glucose to lactic acid. The spores contain no catalase, and do not ferment glucose. A. C.

Directive influences in biological systems. II. Lipase actions of types I and II pneumococci. K. G. Falk and G. McGuire (J. Biol. Chem., 1932, 97, 651—655).—The hydrolysing properties of various batches of broth media in which the pneumococci had been grown show marked differences when tested on four different esters. Hence the resulting enzyme action of such a culture medium is partly determined by the broth itself. F. O. H.

Antipneumococcic immunity reactions of individuals of different ages. W. D. Sutliff and M. Finland (J. Exp. Med., 1932, 55, 837—852).

Ch. Abs.

Specific antibody response of human subjects to intracutaneous injection of pneumococcus products. M. Finland and W. D. Sutliff (J. Exp. Med., 1932, 55, 853—865).—Simultaneous injection of the sp. polysaccharides of all three types of pneumococcus and of proteins and autolysates derived from types I and II produced or increased pneumococcidal power in the whole defibrinated blood and generally caused the appearance of mouse-protective antibodies and agglutinins for one or more types. Injection of the protein-free type-sp. polysaccharide of I, II, or III usually produced antibodies against the homologous, but not against the heterologous, type. Injection of the protein did not appreciably produce sp. antibodies. Autolysates from virulent strains of I, II, or III caused a rise in the pneumococcidal power with (in 33% of cases) the appearance of homologous type agglutinins and protective antibodies. Ch. Abs.

Adsorption of diphtheria antitoxin with aluminium hydroxide. A. Hansen (Compt. rend. Soc. Biol., 1931, 108, 570—572; Chem. Zentr., 1932, i, 2727).—The active constituent is not specifically adsorbed by $Al(OH)_3$, but from dil. serum protein is adsorbed together with the antibody. A. A. E.

Diphtheria toxoid precipitated with alum. D. M. Wells, A. H. Graham, and L. C. Havens (Amer. J. Pub. Health, 1932, 22, 648—650).—Complete pptn. of toxoid with alum effects concn.; $>50\%$ of the original protein remains in the filtrate.

Ch. Abs.

Effect of aliphatic amines and amides on diphtheria toxin. S. Schmidt (Compt. rend. Soc. Biol., 1931, 108, 536—537; Chem. Zentr., 1932, i, 2727).—At $p_{\rm H}$ 7·5, hexamethylenetetramine, valine, and glutamic acid have a slight detoxicating action; NH_2OH, choline, neurine, putrescine, and cadaverine are inactive. Urea has a very slight detoxicating effect. A. A. E.

Effect of benzene derivatives on diphtheria toxin. S. Schmidt (Compt. rend. Soc. Biol., 1931, 108, 537—539; Chem. Zentr., 1932, i, 2727).—PhOH, resorcinol, and cresols (particularly *m*- and *p*-) are strong detoxicants; of the aminobenzoic acids the *p*-compound is least active. Vanillin, eugenol, anisaldehyde, cinnamaldehyde, PhCHO, BzOH, COPhMe, and $NMe_2{\cdot}C_6H_4{\cdot}CHO$ are active; camphor, nicotine, and salicin are inactive. A. A. E.

Properties of cryptotoxins. H. Vincent (Compt. rend. Soc. Biol., 1932, 109, 15—17; Chem. Zentr., 1932, i, 2338).—Chemically detoxicated bacterial toxins are not decomposed by the detoxication. The complex toxin–detoxicant can regenerate the toxin, *e.g.*, at $p_{\rm H}$ 7, or in the animal body by overdosage. A. A. E.

Agglutinogens of the vibrion septique. Comparative value of anti-*O* and antitoxic serum. M. Weinberg, J. Davesne, and P. Haber (Ann. Inst. Pasteur, 1932, 49, 303—318).—The existence of the two agglutinogens, *O* and *H*, of Felix and Robertson, (Brit. J. Exp. Path., 1930, 19, 14) in the vibrion is confirmed. Anti-*O* serum has no advantage over the usual antitoxic serum prepared by immunisation with the living bacterium. W. O. K.

Comparison of results [of bacteriological examination of water] with standard-lactose, brilliant-green bile, and Dominick–Lauter broths. N. J. Howard (J. Amer. Water Works Assoc., 1932, 24, 1305—1310).—In raw H_2O samples brilliant-green bile produced 1·4% and Dominick–Lauter broth 0·7% more confirmed results than lactose broth. In filtered H_2O lactose broth gave 2·4% more than either of the others, but in chlorinated H_2O out of 29 fermented lactose tubes only one or 3·4% was confirmed, whereas the other broths had each two fermented tubes of which one was confirmed. It is suggested that extended use might be made of brilliant-green bile broth as a confirmatory medium.

C. J.

Intake of soluble matter by bacteria. II. Theory of Gram staining. H. Habs (Z. Hyg., 1932, 114, 1—10).—Gram-positive bacteria fix more I from I solutions than do negative organisms. Pretreatment with gentian-violet does not affect this action. Differences in I-fixation are probably related with variations in the lipin content. A. G. P.

Action at a distance of metals on *Bacillus coli*. E. Lagrange (Compt. rend. Soc. Biol., 1932, 109, 4—5; Chem. Zentr., 1932, i, 2339).—A thin Pb foil placed over an endo-fuchsin–agar plate inoculated with *B. coli* causes the reddening of the nutrient to disappear. Ag, Fe, and Zn behave similarly; Ni has a less marked action, whilst brass, Cu, and mica are inactive. The foil becomes oxidised. The phenomenon is probably allied to the oligodynamic effect. A. A. E.

Relationship between hydrogen-ion concentration and bactericidal action of various dyes. M. Tagami (Tôhoku J. Exp. Med., 1932, **18**, 482—511).—Fuchsin is most bactericidal in alkaline solution, Me-green at p_H 6·97—6·58, and auramine at approx. neutrality. The germicidal action of crystal-violet, methylene-blue, and trypaflavine on streptococci and *B. coli* increases with alkalinity; safranine is most active at neutral or alkaline reaction, pyocyanine in neutral or slightly acid solution, and gentian-violet (0·01%) in alkaline solution. Cyanine and gentian-violet (0·2%) are independent of p_H. Brilliant-green and malachite-green are most active in acid, and rivanol in alkaline, solution. Ch. Abs.

Relationship between hormones and the effect of non-specific cell activity on the blood-cholesterol. T. Miwa (J. Chosen Med. Assoc., 1931, **21**, 21—36).—Cholesterolæmia was produced in rabbits by intravenous injection of caseinogen, but not if parathyroid, thyroid, thymus, or testicles were previously removed. Ch. Abs.

Action of certain secretions on the intestinal dehydrogenation of fat. N. Berend (Biochem. Z., 1932, **252**, 366—369).—Ovarian and thyroid extracts increase the formation *in vitro* of triarachidonate from tristearin, whilst insulin and synthalin are inactive. P. W. C.

Effect of internally secreting organs and nutrition on the calcium content of serum. A. Beznák (Magyar Orvosi Arch., 1931, **32**, 438—450; Chem. Zentr., 1932, i, 1546).—Extirpation of spleen and pancreas is followed by a temporary fall in serum-Ca. A diet of potato or pickled cabbage raises it. No substance which increased serum-Ca could be obtained from these organs or foods. Insulin has no effect. L. S. T.

Influence of liver extract on liver metabolism. W. Milbradt (Z. ges. exp. Med., 1932, **81**, 256—267; Chem. Zentr., 1932, i, 2603—2604).—" Hepatrat " (I) produces increased ability to maintain high blood-sugar after insulin. Excretion of NH_2-acid is less than under treatment with gelatin alone. In the mouse the glutathione content of the liver increases after injection of (I). A. A. E.

Spleen as hormonal organ. E. Schliephake (Deut. Arch. klin. Med., 1932, **172**, 523—538; Chem. Zentr., 1932, i, 2859—2860).—Injection of prosplen (I) into rabbits normalises the acid val. in hyper- and sub-acid conditions. The serum-protein falls, then rises above normal, and again falls. (I) is considered hormonal in nature. A. A. E.

Spleen hormone. P. Tremonti (La Riforma Med., 1930, **46**, No. 35).—The hormone is probably acetylcholine. Ch. Abs.

Action of adrenaline and its destruction in bodies of normal, starved, and phosphorus-poisoned rabbits with special regard to adrenaline poisoning by disturbance of liver function. E. Marui and H. Machi (Fol. Pharmacol. Japon., 1932, **13**, No. 3, 338—355).—Starved or P-poisoned animals are more sensitive, and there is less destruction of adrenaline with these animals. Ch. Abs.

Effect of lactic acid on adrenaline glycogenolysis in the liver. S. Kitahara (J. Chosen Med. Assoc., 1931, **21**, 1031—1039).—Addition of lactic acid to Ringer solution used to perfuse the liver of bull-frogs *in situ* caused greater glycogenolysis than Ringer solution alone. The increased glycogenolysis persisted after removal of the reagents. Ch. Abs.

Effects of thymocrescin and of extracts of lymph glands on growth. P. Röthlisberger (Biochem. Z., 1932, **253**, 137—142).—Extracts from lymph glands, prepared in the same way as those containing thymocrescin, have no growth-promoting effect on rats. W. McC.

Physiology of glands. CXXVIII. Thymocrescin. L. Asher and A. Zenklusen (Biochem. Z., 1932, **252**, 309—324).—Further attempts to purify the active principle of thymocrescin solutions have been made (cf. A., 1930, 1615; 1931, 878). Thymocrescin is peptide-like, does not cause changes of blood-Ca and -P, but accelerates growth, especially of the sexual organs. P. W. C.

Thymus and glycæmic curve. P. Nuzzi (Morgagni, 1931, **78**, No. 8).—Thymus extract causes very slight hyperglycæmia. Ch. Abs.

Glycogen test for thyroxine in the blood of the hyperthyroidised dog. A. Wittgenstein (Pflüger's Archiv, 1932, **229**, 299—310; Chem. Zentr., 1932, i, 2599).—The liver extract of male mice contains no glycogen when the mouse has been injected with thyroxine or with the blood of pregnant, exophthalmic goitrous, or hyperthyroidised dogs. A. A. E.

Relationship between the effect of coccus toxin and hormone. Y. Muro (J. Chosen Med. Assoc., 1931, **21**, 173—189).—Experiments on guinea-pigs indicate that thyroid hormone is specially necessary for resisting *Staphylococcus* toxin. Ch. Abs.

Secretin. J. Mellanby (Proc. Roy. Soc., 1932, B, **111**, 429—436; cf. A., 1928, 1403).—The prep. from duodenal mucosa and properties are described. Analysis and physical properties suggest a polypeptide structure. It is rapidly destroyed by proteolytic enzymes and will not dialyse through collodion membranes. Physiological actions are discussed. H. G. R.

Chemical nature of secretin. R. N. Cunningham (Biochem. J., 1932, **26**, 1081—1092).—A secretin concentrate is prepared as follows: extraction of dog's intestine with H_2O acidified with HCl, pptn. by saturation with NaCl, removal of protein by boiling on acid side of neutrality, pptn. with $CCl_3{\cdot}CO_2H$, extraction with 85% EtOH, pptn. with $COMe_2$ and Et_2O, pptn. as picrate, and pptn. with $COMe_2$ from an aq. EtOH–HCl solution of the picrate. The concentrate is free from depressor substance, insol. protein, NaCl, and picric acid. The threshold dose is about 0·5 mg. for a cat of 2·5 kg. body-wt. Secretin is a secondary proteose. It is adsorbed by pptd.

protein from acid and neutral solution and by BzOH. The adsorbing power of the proteins is destroyed by denaturation with org. solvents. It passes through cellophane, but is retained by collodion membranes permeable to peptones. S. S. Z.

Hypoglycæmic action of callicrein. H. Herbig (Arch. exp. Path. Pharm., 1932, **167**, 555—572).—Injection of callicrein does not affect the blood-sugar level of starving or fed rabbits and dogs, whilst a marked decrease of the hypernormal level occurs with depancreatised dogs. The hyperglycæmia due to adrenaline is reduced to a variable extent by callicrein, the relationship of which to insulin is discussed. F. O. H.

Fundamental nature of parathormone action. J. P. McGowan (Biochem. J., 1932, **26**, 1138—1143).—The injection of large doses of parathormone intramuscularly into laying hens produces a deposition of $Ca_3(PO_4)_2$ inside the blood-vessels. S. S. Z.

Articular changes produced by various neurochemical agents. Denervation, administration of parathormone and vitamin-*D*. E. Preto (Arch. Ist. Biochem. Ital., 1932, **4**, 245—258).—Denervation of the limb causes but slight histological changes in the knee-joints of rats. Marked decalcification and other changes are observed after high doses of parathormone or of vitamin-*D*, aggravated in the first case by denervation. R. K. C.

Insulin and hyperglycæmia. Wichels and Lauber (Deut. Arch. klin. Med., 1932, **172**, 613—621; Chem. Zentr., 1932, i, 2860).—Cryst. insulin gives no initial hyperglycæmia. The anti-insulin present in ordinary preps. is inactivated at definite p_H [Novo insulin and Wellcome insulin, 5·8 (immediately), 6·6, 7 (gradually)]. A. A. E.

Effect on insulin of red and ultra-violet radiation. H. Küstner and W. Eissner (Klin. Woch., 1932, **11**, 499—501; Chem. Zentr., 1932, i, 2481).—Red irradiation does not affect the activity of insulin, but ultra-violet light causes a marked transient loss. A. A. E.

Insulin and pitutocin. K. Freudenberg, E. Weiss, and H. Eyer (Naturwiss., 1932, **20**, 658).—Quant. study of the inactivation of insulin by BzO_2H indicates a mol. wt. of 10,000—30,000 for insulin, affording further evidence that the active grouping is linked in a protein chain. The pituitary hormone is not affected by pepsin or erepsin, but is inactivated by trypsin or papain. It is of high mol. wt. or is associated with a substance of protein nature. A. C.

Pituitary and metabolism. B. A. Houssay (Rev. Circulo méd. Arg. y centro estud. méd., 1931, 356).—Pituitary gland activity stimulates protein metabolism. Deficiency of the gland has no influence on blood-sugar in normal conditions, but intensifies hypoglycæmic conditions. Ch. Abs.

Composition of the tissues of albino rats treated with alkaline anterior pituitary extracts. E. Bierring and E. Nielsen (Biochem. J., 1932, **26**, 1015—1021).—Only a small part of the increase in the wt. of rats induced by bovine anterior pituitary extracts is due to retention of H_2O. S. S. Z.

Effect of castration on the occurrence in guinea-pigs of the anterior pituitary hormone having an excito-secretory action on the thyroid gland. M. Aron and J. Benoit (Compt. rend. Soc. Biol., 1931, **108**, 784—786; Chem. Zentr., 1932, i, 1546—1547).—A few days after castration young guinea-pigs show marked thyroid activity; the serum and urine of these animals have the same effect on the thyroid of normal animals as the implantation of 0·001 g. of the anterior lobe of the ox. A. A. E.

Effect of castration on the occurrence in the fowl and the duck of the anterior pituitary hormone having an excito-secretory action on the thyroid gland. J. Benoit and M. Aron (Compt. rend. Soc. Biol., 1931, **108**, 786—788; Chem. Zentr., 1932, i, 1547).—The serum of the castrated fowl is most active towards the thyroid of guinea-pigs in spring; that of the normal fowl is of const. low activity. A. A. E.

Anterior pituitary gland, thyroid gland, and carbohydrate metabolism of the liver. H. Eitel and A. Loeser (Arch. exp. Path. Pharm., 1932, **167**, 381—403).—Intraperitoneal injection of a thyreotropic extract of the anterior pituitary lobe into guinea-pigs is followed in 2 hr. by functional and morphological changes in the thyroid gland together with a decrease in the liver-glycogen, which returns to normal levels within 24 hr. Further stimulation of the thyroid gland results in a decrease in liver-glycogen only after a latent period of approx. 4 days. Continued effective stimulation renders the liver nearly glycogen-free. The increased activity of the thyroid gland and the decrease in liver-glycogen are both reversible. No marked change occurs in the muscle-glycogen. Thyroidectomy inhibits this decrease in liver-glycogen. F. O. H.

Anterior pituitary gland and thyroid gland. (*a*) Effect of anterior pituitary on the activity of the thyroid gland. (*b*) Iodine contents of blood and thyroid gland following administration of anterior pituitary extracts. W. Grab (Arch. exp. Path. Pharm., 1932, **167**, 313—333, 413—441).—(*a*) The thyreotropic influence of the anterior pituitary lobe was investigated in dogs by means of the MeCN toxicity method. Intraperitoneal injection of anterior lobe suspensions resulted in an increased secretion of the thyroid hormone into the blood-stream followed by a compensatory increase in the activity of the thyroid gland.

(*b*) Intraperitoneal injection of $COMe_2$-dried anterior pituitary lobe is followed in normal but not in thyroidectomised dogs by a marked and prolonged decrease of the I and colloid matter of the thyroid gland, together with a more transient increase in the blood-I, especially in the EtOH-insol., protein-bound fraction. Between the injection and the excretion of I in the urine intervenes a latent period of approx. 3 days, the total urinary I forming only a fraction of that liberated into the blood. Hypophysectomy results in a decrease in blood-I. F. O. H.

Hormonal–nervous regulation of the function of the anterior pituitary lobe. W. Hohlweg and K. Junkmann (Klin. Woch., 1932, **11**, 321—323; Chem. Zentr., 1932, i, 1548). A. A. E.

Prolongation of pregnancy. A. M. Hain (Nature, 1932, 130, 402).—Experiments on rats indicate the existence of a substance, possibly in the anterior pituitary, and probably neither gonadotropic nor growth hormone, which exerts an inhibiting effect on uterine motility. L. S. T.

Hormonal action of the placenta. E. Philipp (Deut. med. Woch., 1932, 58, 217—219; Chem. Zentr., 1932, i, 1546).—In pregnancy the placenta is the source of the anterior pituitary sexual hormone. L. S. T.

Gonadotropic hormones (ρ-factors). III. Purification and properties. P. G. Marshall (Biochem. J., 1932, 26, 1358—1364).—The hormones can be purified by ultrafiltration. The purified product contains a polypeptide containing tyrosine. The presence of a sugar complex or of tryptophan is doubtful. 0·1 mg. of the product will induce rupture of the follicles with probable ovulation in the rabbit within 24 hr. S. S. Z.

Surface films of œstrin derivatives. N. K. Adam, J. F. Danielli, G. A. D. Haslewood, and G. F. Marrian (Biochem. J., 1932, 26, 1233—1241).—Surface pressure and surface potential measurements of diacetyltrihydroxyœstrin Me ether and triacetyltrihydroxyœstrin indicate that the mols. probably have an anthracene or phenanthrene skeleton or a system of four condensed rings with two alcoholic OH groups near one end of the mol., and one phenolic group near the other end. The alcoholic groups are probably in the *cis*-position relative to each other on adjacent C atoms and are inclined at a steep angle to the plane of the ring in which they are situated. *cyclo*Hexanols with long chains in the *para*-position to the OH group give condensed films of area about 30 sq. Å. per mol., slightly smaller than the cross-section of the œstrin mols. S. S. Z.

Rat and mouse units of folliculin. A. Lipschütz (Compt. rend. Soc. Biol., 1931, 108, 754—756; Chem. Zentr., 1932, i, 1546).—Six injections during 60 hr. show that the rat unit is three times as strong as the mouse unit. L. S. T.

New isomeric follicular hormone from mare's urine. E. Schwenk and F. Hildebrandt (Naturwiss., 1932, 20, 658—659).—In addition to the isomeric hormones of Butenandt and Störmer (this vol., 781), a further *isomeride*, termed "*δ-hormone*," $C_{18}H_{22}O_2$, m.p. 209°, $[\alpha]_D$ +46·33° in $CHCl_3$ (*benzoate*, m.p. 177°, $[\alpha]_D$ +36·48°), has been isolated, with much higher activity. It also differs from other isomerides in the deeper colour of conc. H_2SO_4 solution. A. C.

Concomitance of male and female sexual hormones. B. Frattini and M. Maino (Biochem. Z., 1932, 253, 202—203).—The male sexual hormone occurs in the glands and fluids of the male only, the female sexual hormone in those of the female only, but both hormones have a common action on the genital tract of both sexes. The hormones differ in their action on the secondary sex characters (cock's-comb test). Loewe and others (A., 1931, 1097) omitted to take the authors' units and doses into account. Injections of cholesterol and ergosterol (5—10 mg.) produce œstrus, and hence the effects produced by bile and fæces may be due to these substances rather than to a hormone. W. McC.

Castrated rats for the assay of testicular hormone. V. Korenchevsky (Biochem. J., 1932, 26, 1300—1305).—The average variations in the wt. of retroperineal fat, sexual and endocrine organs, as calc. per unit of body-wt., are not great in the castrated male rat of the same degree of sexual maturity. S. S. Z.

Response of castrated male rats to the injection of testicular hormone. V. Korenchevsky, M. Dennison, and R. Schalit (Biochem. J., 1932, 26, 1306—1314).—In castrated rats the most sensitive organs suitable for the assay of testicular hormone are the atrophied prostate with seminal vesicles; the penis and thymus are less sensitive. The increase in wt. of the prostate with seminal vesicles is much greater in rats castrated before than after puberty, does not vary much in rats belonging to different litters, and is proportional to the increase of the dose of the injected hormone. S. S. Z.

Growth and cell-reserves in vitamin investigations. I. Essential considerations. II. Normal growth in the rat's rib. III. Histological distinction between scurvy and Moeller–Barlow disease and their causes. IV. Aplastic-consumptive deficiency disease. (*a*) Osseous changes with diets free from vitamins or from fat-soluble vitamins. V. Aplastic-consumptive deficiency disease. (*b*) Highly unsaturated fatty acids and their salts and the occurrence of the hæmophilia of scurvy. W. Kollath (Arch. exp. Path. Pharm., 1932, 167, 469—477, 478—506, 507—520, 521—537, 538—554).—I. Preliminary considerations in the study of diseases due to dietary deficiencies are discussed.

II. A detailed histology of the ossification in the rat's rib is given.

III. With true scurvy all formation of new bone or cartilage ceases, whereas in Moeller–Barlow disease such formation may occur.

IV. In order to obtain complete efficacy of fat-sol. vitamins it is necessary to fulfil certain, and as yet mainly unknown, conditions which may be studied histologically in the developing bone in the case of *A* and *D*, and in the testes and ovaries in the case of *E*.

V. The addition of linolenic acid (or its K salt) to a diet free from vitamins and unsaturated fatty acids initiates bleeding from the intestine and bone-marrow and accelerates the loss in wt. and the incidence of death. This effect, which is probably due to an action on membrane permeability, is inhibited by the presence of cotton-seed oil. F. O. H.

Vitamin content of dried figs and dates. M. Ali (Arch. Hyg., 1932, 107, 219—233; Chem. Zentr., 1932, i, 2199).—Dried dates contain little vitamin-*B*, and no -*A*, -*C*, or -*D*. Dried figs are relatively rich in vitamin-*A*, contain a moderate amount of -*B*, very little -*C*, and possibly a trace of -*D*. A. A. E.

Action of radioactive substances on vitamins. A. G. Hogan, C. H. Shrewsbury, G. F. Breckenridge, and W. S. Ritchie (J. Nutrition, 1932, 5, 413—420).—Exposure to β-rays leads to the destruction of the vitamin-*A* of milk. Vitamins-B_1, -*C*, -*D*, and -B_2 are not affected by β- or γ-rays. A. G. P.

Evidence of the existence of a dietary principle stimulating general growth and lactation. L. W. Mapson (Biochem. J., 1932, 26, 970—986).—The principle, "physin," which is present in ox-liver is not identical with any of the hitherto known accessory food factors and has a more marked effect on the growth rate of the male than the female rat. The stimulating effect on the growth rate after weaning is transmitted from a parent which has received the active substance in its diet to the first but not second generation fed solely on the synthetic diet. In these animals the growth acceleration is more prolonged than in those which received the liver directly. The average no. born to parents fed on liver is higher than in the case of control animals. "Physin" is present in autolysed liver, in acid aq. extracts of liver, especially when the liver is previously autolysed, and in 90% EtOH extracts. The ash of liver does not stimulate growth. S. S. Z.

Vitamin-*A* content of the liver of various animals. H. Simonnet, A. Busson, and L. Asselin (Compt. rend. Soc. Biol., 1932, 109, 358—359; Chem. Zentr., 1932, i, 1921).—High vals. were obtained with the ox, and low with the guinea-pig. Other differences (*e.g.*, dog) could be attributed to conditions of nutrition. A. A. E.

Carotene and vitamin-*A*. B. Woolf and T. Moore (Lancet, 1932, 223, 13—15).—A discussion. L. S. T.

Structure of vitamin-*A*. I. M. Heilbron, R. A. Morton, and E. T. Webster (Biochem. J., 1932, 26, 1194—1196).—Treatment of the product obtained from a concentrate by the action of EtOH–HCl with Se at 300—330° gives a good yield of 1 : 6-$C_{10}H_6Me_2$. The latter compound is also obtained by dehydrogenating a vitamin-*A* concentrate with Se at 300—330°. Vitamin-*A* must therefore be a compound of a terpenoid nature and the richest concentrates must contain a substance possessing a constitution which as far as the 14th C atom must be identical with the constitution advanced by Karrer *et al.* (this vol., 200). S. S. Z.

Characteristics of highly active vitamin-*A* preparations. I. M. Heilbron, R. N. Heslop, R. A. Morton, E. T. Webster, J. L. Rea, and J. C. Drummond (Biochem. J., 1932, 26, 1178—1193).—After freeing the unsaponifiable matter of very active liver oils from sterols by cooling to $-50°$, it was distilled fractionally at a pressure below 0·0001 mm. The vitamin passed over without decomp. in a main fraction, b.p. 137—138°. Redistillation did not effect further purification. Distillation of concentrates from halibut, sturgeon, or mammalian liver oils yielded a main fraction which gave substantially the same vals. for the 328, 617, and 580 mμ bands. In spite of the const. very high potency of the fractions obtained from various sources, there are indications that they are not absolutely homogeneous. Karrer's chromatographic method of concn. (A., 1931, 1463; this vol., 200) has no advantage over the distillation procedure. A distilled concentrate from sturgeon-liver oil brought about an improvement in the general condition of and a slow resumption of growth in rats on a vitamin-*A*-free diet in daily doses of $0{\cdot}025\times10^{-6}$ g. A dose of $0{\cdot}05\times10^{-6}$ g. effects a rapid cure of the eye disease. The distilled concentrate, $C_{20}H_{30}O$ (non-cryst. monobenzoate, b.p. 188—198°), is hydrogenated fairly readily and has I val. 306—324. On treatment with O_3 it yields geronic acid. S. S. Z.

Reaction of fish-liver oils with antimony trichloride. F. Ender (Biochem. J., 1932, 26, 1118—1123).—The blue colour obtained by treating a vitamin-*A* concentrate from halibut oil with $SbCl_3$ and $CHCl_3$ at $-30°$ to $-50°$ was decomposed with excess of cooled aq. KOH. By extracting this mixture with C_6H_6, a highly saturated reddish-yellow oil, "the chromogenic fraction" (I), was obtained which still reacted with $SbCl_3$, but was biologically inactive in daily doses of 0·01—1 mg., as was also (in daily doses of 0·002—0·02 mg.) the amorphous dry powder obtained by treating (I) with EtOH. The "non-chromogenic fraction" obtained from the reaction of the oil concentrate with $SbCl_3$ was biologically inactive in daily doses of 0·05 and 0·4 mg. The absorption bands of the original concentrate and (I) together with spectra of their reaction products with $SbCl_3$ are given. (I) did not give the selective absorption in the region of 328 mμ characteristic of vitamin-*A*. S. S. Z.

Isomerisation of carotene by means of antimony trichloride. A. E. Gillam, I. M. Heilbron, R. A. Morton, and J. C. Drummond (Biochem. J., 1932, 26, 1174—1177).—When the blue solution obtained by mixing $SbCl_3$ and carotene in $CHCl_3$ is poured into H_2O red crystals can be isolated from the $CHCl_3$ layer. The absorption spectrum of the recovered product both in the visible and ultra-violet regions is quite different from that of carotene. The properties of the substance agree with those of *iso*carotene. It is biologically inactive. S. S. Z.

Absorption spectra of substances derived from vitamin-*A*. J. R. Edisbury, A. E. Gillam, I. M. Heilbron, and R. A. Morton (Biochem. J., 1932, 26, 1164—1173).—By pouring the mixture of potent liver oils or their concentrates with $SbCl_3$ into much H_2O a product is recovered which still gives a blue or purple colour with $SbCl_3$; vitamin-*A* has, however, been partly decomposed with the appearance of narrow absorption bands. The wave-lengths at the max. of these bands are const. irrespective of whether rich or poor oils or whether concentrates are used, but the intensities vary approx. with the potency of the material. Absorption bands with similar max. can be obtained with greatly enhanced definition by the action of EtOH–HCl on rich concentrates, the intensity, persistence, rate of development, and permanence depending on the concn. of HCl. They are therefore probably due in both cases to products of decomp. Similar narrow bands together with a broad continuous band with its max. at 290 mμ are obtained in certain fractions in the slow high-vac. distillation of concentrates at about 180°. Prolonged heating at 120—125° in N_2 produces the narrow bands to only a very small extent, the main product exhibiting a max. at 290 mμ. At the b.p. in EtOH vitamin-*A* is stable to prolonged exposure to a stream of O_2. O_3 rapidly destroys vitamin-*A* with the formation of products with max. at 290 and 272 mμ in the very early stages. S. S. Z.

Use of 7-methylindole in the antimony trichloride colour test for vitamin-*A*. R. A. Morton (Biochem. J., 1932, 26, 1197—1201).—7-Methylindole, which is practically transparent in the region 290—350 mμ and does not interact with vitamin-*A* before the addition of $SbCl_3$, inhibits the capacity of vitamin-*A*-containing substances to give a blue colour with $SbCl_3$. S. S. Z.

Comparison of colorimetric, spectrographic, and biological methods for the determination of vitamin-*A*. R. J. Norris (Bull. Basic Sci. Res., 1931, 3, 249—256).—The physical tests of cod-liver oil showed fairly good correlation, but the results deviated from those of the biological tests, sometimes by amounts considerably greater than the probable biological error. Only biological tests are trustworthy. Ch. Abs.

Transmission of vitamin-*A* from parents to young in mammals. W. J. Dann (Biochem. J., 1932, 26, 1072—1080).—Only a small amount of vitamin-*A*, which is not influenced by the amount of carotene in the mother's diet during gestation, is present in the liver of the rat or rabbit at birth. This amount increases two- or three-fold in the suckling or even more if the nursing mother receives extra carotene. There is a limit to this increase and to the amount of vitamin-*A* that passes into the milk. S. S. Z.

Influence of vitamin-*A* deficiency on male rats. M. M. Sampson and V. Korenchevsky (Biochem. J., 1932, 26, 1322—1339).—The organs and their functions are affected in male rats on a vitamin-*A*-deficient diet both by the decrease in the food intake and by some other influence of the deficiency. At the stage of vitamin-*A* depletion at which the rats were killed, about 2/5 of the deficiency in body-wt. seemed to be due to the decreased food intake, whilst the loss of the remaining 3/5 was caused by some other direct influence of the deficiency. These proportions are reversed for the fat deposition. Wt. for wt. a vitamin-*A*-deficient diet produces a much smaller increase in body-wt. than a complete diet. S. S. Z.

Absorption of nitrogen and of fat from the alimentary canal of rats kept on a vitamin-*A*-deficient diet. M. M. Sampson, M. Dennison, and V. Korenchevsky (Biochem. J., 1932, 26, 1315—1321).—The intake of food in proportion to body-wt. of rats on the deficient diet during the period of checking or cessation of growth was even larger than that consumed by the rats on a complete diet. During the same period the absorption of N and of fat was not appreciably altered. In the last period there was a decrease in the intake and absorption of the food. During the whole period of observation the nitrogenous metabolism increased. S. S. Z.

New technique for the preparation of vitamin-*A*-free caseinogen. M. T. Potter (Science, 1932, 76, 195—196).—Vitamin-*A*-free caseinogen can be prepared by heating powdered commercial caseinogen spread in thin layers at 110° for 7 days. L. S. T.

International standard for vitamin-*B*. H. Chick and H. M. Jackson (Biochem. J., 1932, 26, 1223—1226).—This adsorption product on fuller's earth from an acid aq. extract of rice polishings is active in a daily rat dose of about 10 mg. and is stable for one year when stored either at room temp., at 37°, or in a refrigerator. Its vitamin-B_2 content is negligible. S. S. Z.

Ultra-violet absorption spectra of certain preparations containing vitamin-*B*. F. F. Heyroth and J. R. Loofbourow (Bull. Basic Sci. Res., 1931, 3, 237—248).—The spectra resemble those of purines and pyrimidines previously examined, particularly those irradiated with ultra-violet light from which short waves are excluded (cf. A., 1931, 1308). Ch. Abs.

Independence of vitamin-B_1 deficiency and inanition. A. P. Meiklejohn, R. Passmore, and R. A. Peters (Proc. Roy. Soc., 1932, B, 111, 391—395).—The brains of pigeons suffering from vitamin-B_1 deficiency and before death treated with small quantities of B_1 extracts show a greater O_2 uptake in presence of lactate than do the brains of untreated animals. The results are independent of the general state of nutrition, but depend on the nervous symptoms exhibited by the animals at death. W. O. K.

Oxidations in avitaminosis-*B* and in fasting. P. E. Galvão and D. M. Cardosa (Pflüger's Archiv, 1932, 229, 422—438; Chem. Zentr., 1932, i, 2602).—In pigeons, all oxidations (total gaseous metabolism; respiration and glutathione content of muscle and liver) are diminished in fasting, but not in avitaminosis with food intake. Tissue and total oxidations vary in the same sense. Glutathione is markedly diminished in both fasting and avitaminosis. Diminution of oxidation processes is attributed to lack of oxidisable substances. The oxidising power of the liver is in all cases unchanged. Its glutathione content is normal in avitaminosis, but considerably diminished in fasting. A. A. E.

Comparative action of 2 : 4-dinitrophenol on the thermogenesis of pigeons in a state of inanition, normal pigeons, pigeons deprived of vitamin-*B*, and those receiving an excess of carbohydrates. (Mme.) L. Randoin and H. Simonnet (Bull. Soc. Chim. biol., 1932, 14, 993—1010).—The above four groups of pigeons resist the hyperthermal effect of 2 : 4-dinitrophenol in the (decreasing) order given. Pigeons in a state of avitaminosis-*B* react hyperthermally to sudden intense cold. The results are considered to support the theory that avitaminosis is due to a disturbance of the metabolism of energy-producing substances. A. A. L.

Chemical identification of vitamin-*C*. L. J. Harris and J. R. M. Innes (Lancet, 1932, 223, 235—237).—The antiscorbutic action of a sample of Szent-Györgyi's hexuronic acid has been confirmed. 1 mg. of acid had an activity slightly >that of 1 c.c. of orange juice. Raw suprarenal cortex has a high antiscorbutic activity approx. proportional to its hexuronic acid content. L. S. T.

Vitamin formation in plants. A. I. VIRTANEN and S. VON HAUSÉN (Suomen Kem., 1932, 5, B, 45).—The vitamin-*C* content of blossoming pea plants is max. when the quartz-sand in which they grow has p_H 6—6·5, and, with KNO_3 as source of N, is twice as great as with $(NH_4)_2SO_4$. Oats harvested just prior to blossoming are much poorer in vitamin-*C*, the content of which is not affected by the p_H of the quartz-sand or the nature of the N supply. A. C.

Vitamin-*C* content of various fodder plants. A. I. VIRTANEN, E. LUNDMARK, and E. PELTOLA (Suomen Kem., 1932, 5, B, 45—46).—The vitamin-*C* content of grasses has been determined by titrating the reducing substance with 2 : 6-dichlorophenolindophenol. Significant variations are not observed in weekly cuttings, and the following figures represent the no. of c.c. of 0·001*M* reagent equiv. to 10 g. of fodder. Purple clover 22—35, hybrid clover 49—65, cocks'-foot 20—23, meadow fescue 26—38, red fescue 43, meadow grass 20—24, timothy 36. After 6—8 months' acid preservation "A.I.V." fodder has a val. of 10—20 (50—100 on dry wt.), and the val. for dry hay determined in spring is only 0—1. Guinea-pigs are fully protected from scurvy by daily doses of 3 g. of fresh purple clover or 3 g. of "A.I.V." prepared from a clover-rich grass. A. C.

Determination of vitamin-*D* in the line test by measurement. R. S. MORGAN (Biochem. J., 1932, 26, 1144—1154).—The area of new calcification, as shown on magnified camera-lucida drawings of the bone sections, is measured. The healing is proportional to the log. of the dose of vitamin-*D*. The chief source of error is the variable response of litter mates to a given dose of vitamin. S. S. Z.

Mode of action of irradiated ergosterol on the normal organism. J. WARKANY (Wien. klin. Woch., 1932, 45, 206—208; Chem. Zentr., 1932, i, 1922).—In rats a dose of 30—50 mg. produced marked phosphaturia, which apparently causes renal injury. A. A. E.

Production of non-fatal vascular sclerosis in rabbits by means of viosterol (irradiated ergosterol). T. D. SPIES (Arch. Int. Med., 1932, 50, 443—449).—Viosterol administered in toxic but non-fatal doses to rabbits produced extensive damage, associated with Ca deposition, in the aorta, lungs, and kidneys. W. O. K.

Effects on dogs of large doses of calciferol (vitamin-*D*). H. H. DALE, A. MARBLE, and H. P. MARKS (Proc. Roy. Soc., 1932, B, 111, 522—537; cf. this vol. 434).—Calciferol in excessive doses has the same toxic action as the crude product from the irradiation of ergosterol both by the intravenous and oral routes. Complete parathyroidectomy has no effect on the fatal intoxication. There is no evidence that vitamin-*D* in excessive doses acts by promoting secretion of the parathyroid hormone or by rendering the organism more responsive to its action. H. G. R.

Rise of blood-calcium of the dog after treatment with irradiated ergosterol. Variability of commercial preparations. J. CHEYMOL and A. QUINQUAUD (J. Pharm. Chim., 1932, [viii], 16, 161—165).—Of three commercial preps. of irradiated ergosterol, one was inactive. The other two were active, but not equally so. W. O. K.

Milk, blood, and excreta of cows given moderate and excessive amounts of irradiated yeast or ergosterol. A. F. HESS, R. F. LIGHT, C. N. FREY, and J. GROSS (J. Biol. Chem., 1932, 97, 369—377).—Cows fed daily with irradiated yeast (60,000 units of vitamin-*D* and a high content of vitamin-B_1) yield a milk rich in vitamin-*D*, but only normal in -B_1. The P, Ca, and ash of the milk and the inorg. P and Ca of the serum remain normal, but all these were increased by excessive doses of irradiated ergosterol, and vitamin-*D* is also detectable in the blood (1 unit per 1·5 g.). With cows receiving 300 g. of irradiated yeast daily, about 25% of the vitamin-*D* ingested is excreted with the fæces, whilst none appears in the urine. Excessive dosage of irradiated ergosterol for long periods does not cause any lesion of cellular structure and the bone-ash remains normal. The greater is the production of milk the greater is the abs. content of the vitamin. F. O. H.

Rôle of vitamin-*D* in the nutrition of the dairy calf. I. W. RUPEL, G. BOHSTEDT, and E. B. HART (Proc. Amer. Soc. Animal Produc., 1932, 24, 137—141).—Rickets, with low blood-serum-Ca and -P, follows withholding of vitamin-*D*. CH. ABS.

Parathyroid and vitamin-*D*; influence on bones and growth. M. A. RANSON (Semana méd., 1932, I, 1424—1425).—Simultaneous treatment causes more rapid development without hypercalcification of other organs. CH. ABS.

Effect of deprivation of vitamin-*E* on the lactating rat. J. MORELLE (Compt. rend. Soc. Biol., 1931, 108, 804—805; Chem. Zentr., 1932, i, 1681).—Paralysis is induced in the suckling young. A. A. E.

Respiratory quotients of succulent plants. T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1932, 20, 293—299).—Variations in the O_2 intake and CO_2 output of darkened leaves of *Sedum prœaltum* are recorded. High vals. for the R.Q. indicate that the disappearance of malic acid is not due to its oxidation, but the acid forms a definite link in the C cycle of succulent plants. A. G. P.

Automatically recording the oxygen intake of living tissues. T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1932, 20, 281—291).—Apparatus is described in which the time taken for plant-tissue to absorb a definite vol. of O_2 is recorded automatically. The effective unit measured is 0·36 c.c. of O_2. An atm. of const. composition is maintained around the tissue. A. G. P.

Plant respiration. I. Course of respiration of *Lathyrus odoratus* during germination of the seed and the early development of the seedling. W. STILES and W. LEACH (Proc. Roy. Soc., 1932, B, 111, 338—355).—The output of CO_2 from a single germinating seed of the sweet pea measured by the katharometer exhibits 5 distinct phases: (1) a fairly rapid increase in respiration rate as the seed absorbs H_2O, (2) a period characterised by const. respiration

rate of very variable duration which continues until the seed-coat is ruptured, (3) a very rapid rise in respiration rate following the rupture of the testas, (4) a period of approx. const. respiration rate, and (5) a phase of slowly diminishing respiration rate. Removal of the testas largely eliminates phase 2. The decline of respiration in phase 5 is probably due to the particular experimental conditions tending to decrease the transpiration rate in the older seedlings and so to reduce the rate of conveyance of respirable material from the cotyledons to the growing parts.
W. O. K.

Temperature characteristic for the anaërobic production of carbon dioxide by germinating seeds of *Lupinus albus*. P. S. FANG (J. Gen. Physiol., 1932, **16**, 65—73).—The mean temp. characteristic between 7·5° and 18° is 21,500 g.-cal., which is slightly but probably not significantly lower than the val. 23,500 for aërobic CO_2 production.
W. O. K.

Metabolism of algæ. I. Influence of potassium cyanide and methylene-blue on the respiration of green algæ. A. WATANABE (Acta Phytochim., 1932, **6**, 315—335).—Although both KCN and methylene-blue increase the respiration of *Chlorella ellipsoidea*, their combined action is not additive. Glucose increases the respiration fourfold (with certain other algæ this accelerating action is, however, much less), but this increase is strongly inhibited by KCN. The accelerating action of thionine is less than that of methylene-blue on *Chlorella*, but with *Ulva lactuca* that of the former is double that of the latter. F. O. H.

Gas content of algæ. Gas contained in *Enteromorpha compressa*, i Ag. Z. DANIN (Atti R. Accad. Lincei, 1932, [vi], **15**, 831—834).—The young algæ behave like all the other species examined (A., 1930, 1072; 1931, 1198) but the % of O_2 produced is greater, owing either to greater activity of the chloroplast or to greater permeability to the other gases.
T. H. P.

Carbohydrates in the bulb of *Allium scorodoprasum*, L. II. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1931, **7**, 1067—1069).—The bulb contains scorodose. The leaves did not give Selivanov's reaction. Starch was not present in either. There is more reducing sugar in the leaves than in the bulb.
CH. ABS.

Carbohydrates in the bulb of *Narcissus tazetta*, L., var. *chinensis*, Roem. I. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1931, **7**, 1061—1066).—The rapidly dried (100°) bulb contained: H_2O 6·12, Et_2O-sol. 0·62, total sol. carbohydrates 82·16, total N 0·82, pentose 2·38, ash 2·29, crude fibre 2·88%; galactan and inulin were absent. The carbohydrate in the cold H_2O extract was a glucomannan ("suisenglucomannan"), decomp. 212°, $[\alpha]_D$ +320°, which does not reduce Fehling's solution. Hydrolysis by dil. acid affords glucose and mannose (1 : 2); it was partly hydrolysed by snail (*Eulota*) extract, but not by diastase, emulsin, or malt extract. CH. ABS.

Properties of starch from tropical and temperate climates. J. B. McNAIR (Science, 1932, **76**, 83).—Corrections of previous statements (this vol., 663) are made. Starches and glycerides from plants grown in temperate climates have higher I vals. than those from tropical plants. The low m.p. of temperate glycerides correspond with the low gelatinisation temp. of the starches. L. S. T.

A polysaccharide from the pollen of timothy grass (*Phleum pratense*). G. A. C. GOUGH (Biochem. J., 1932, **26**, 1291—1294).—The polysaccharide, which on hydrolysis with acids yielded *l*-arabinose, galactose, and a non-reducing acid, was prepared by pptn. with basic Pb acetate at alkaline reaction from the digested pollen, after clearing with $Pb(OAc)_2$, and by fractional pptn. with EtOH and MeOH of the decomposed basic Pb fraction.
S. S. Z.

Pentosan content of *Kleinia articulata*. H. EVANS (Biochem. J., 1932, **26**, 1095—1100).—*K. articulata* contains pentosan, which is present to only a small extent in solution in the cell-sap, similar to that found in other succulents. S. S. Z.

Quince-seed mucilage. A. G. RENFREW and L. H. CRETCHER (J. Biol. Chem., 1932, **97**, 503—510).—Quince-seed gum on hydrolysis with 0·5*N*-H_2SO_4 leaves an insol. residue (approx. one third) of α-, β-, and γ-cellulose. The hydrolysate contains, in addition to *l*-arabinose, a mixture of methylated and non-methylated aldobionic acids which, on further hydrolysis, yield hexuronic acid and xylose.
F. O. H.

Occurrence of sugar alcohols in marine algæ. II. Sorbitol. P. HAAS and T. G. HILL (Biochem. J., 1932, **26**, 987—990; cf. this vol., 101).—Sorbitol was isolated as the CHPh: and Ac_6 derivatives from *Bostrychia scorpioides*. S. S. Z.

Glucosides from tobacco leaves. I. K. YAMAFUJI (J. Agric. Chem. Soc. Japan, 1932, **8**, 404—410).—*Tabacinin* (0·02%), sinters at 175°, decomp. 227°, gives in EtOH solution a green colour with $FeCl_3$. Acid hydrolysis affords glycuronic acid. *Tabacilin* (0·4—0·5%) on hydrolysis affords nicotine and glucose. CH. ABS.

Reducing and non-reducing sugars and pentosan in red and white ginseng. Y. OSHIMA and S. NOMURA (J. Chosen Med. Assoc., 1931, **21**, 558—561).—Radix primaria of white and red ginseng contain, respectively, 58·05 and 43·17% of total sugar and radices fibrillæ of white 39·34% (reducing sugars 0·93, 6·35, 0·45%). The percentages of pentosan are 6·40, 8·47, 9·03, and of cellulose 5·33, 9·36, 9·14.
CH. ABS.

Inorganic salts in Chosen ginseng. II. S. NOMURA and Y. OSHIMA (J. Chosen Med. Assoc., 1931, **21**, 553—557).—Dry radices fibrillæ of white *Panax ginseng*, C. A. Mey, and of red ginseng, respectively, contain ash 6·14, 6·16%; SO_4 0·537, 0·486; P_2O_5 1·650, 1·635; Fe_2O_3 0·092, 0·159; Al_2O_3 0·125, 0·119; CaO 0·528, 0·466; MgO 0·052, 0·048; SiO_2 0·131, 0·192; Mn trace, trace. CH. ABS.

Acidic constituents of jute fibre. J. K. CHOWDHURY and M. N. MITRA (J. Indian Chem. Soc., 1932, **9**, 291—296).—The fibre is boiled with 0·5% NaOH, delignified with ClO_2, and then extracted with aq. NH_3 (17%) at 45°; the resulting extract contains glycogen and glycuronic, galacturonic, and mucic acids. Extraction of the delignified fibre with 0·5% $(NH_4)_2C_2O_4$ at 85—90° yields pectin; the pectic acid, m.p. 233—235° (decomp.) (darkens at 195—197°), isolated by Candlin and Schryver's method (A., 1928, 1162), is hydrolysed by N-H_2SO_4 at 125—130° to arabinose, galactose, and galacturonic acid, and by 2·5% H_2SO_4 to the two sugars. H. B.

Relationship between natural uronic acids, pentoses, and pentosans. H. Franken (Biochem. Z., 1932, 250, 53—60).—Xylose is detected as a decarboxylation product of glycuronic acid on boiling with 2% H_2SO_4. Arabinose is detected on boiling galacturonic acid with either dil. H_2SO_4, HF, or $H_2C_2O_4$. The amount of pentose is much smaller than corresponds with the CO_2 liberated. P. W. C.

Determination of the acids of plant tissue. I. Nitric acid. G. W. Pucher, H. B. Vickery, and A. J. Wakeman (J. Biol. Chem., 1932, 97, 605—615).—The powdered, air-dried material is treated with $4N$-H_2SO_4 to p_H 0·7—0·9 and extracted with Et_2O. Aq. NaOH is added to the extract, Et_2O removed by distillation, and NO_3' in the residue determined by reduction followed by Nesslerisation, or by pptn. with nitron. F. O. H.

Catechin in the fruit of *Areca catechu*, Lin. R. Yamamoto and T. Muraoka (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 142—143).—The fruit contains *d*-catechin. R. S. C.

Occurrence of lycopene in several tropical fruits (*Erythroxolon novogranatense, Actinophleus macarthurii*, and *Ptychosperma elegans*). J. Zimmermann (Rec. trav. chim., 1932, 51, 1001—1003).—The isolation of lycopene is described. J. W. B.

Carotene in mango fruit (*Magnifera indica*, Lin.). R. Yamamoto, Y. Osima, and T. Goma (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 122—126).—The fresh pulp of mango fruit contains H_2O 81·7, citric acid 0·5, glucose 1·5, fructose 4·9, sucrose 5·5, crude fibre 0·5, N 0·1, ash 0·5, and Et_2O-sol. substances 1·3%. The dried pulp contains 0·1179 g. of carotene (α- and β-), and 0·0785 g. of esterified and 0·0156 g. of free xanthophyll per kg., but these quantities vary with the variety and ripeness of the fruit. R. S. C.

Carotene from the fruits of *Magnifera indica*, Lin. II. R. Yamamoto and G. Kawakami (J. Agric. Chem. Soc. Japan, 1932, 8, 391—393).—Carotene, m.p. 179°, possibly a mixture of α- and β-, from the mango fruit cured avitaminosis-*A* in rats. Ch. Abs.

Carotenoids in fresh tea leaves and fermented tea. R. Yamamoto and T. Muraoka (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 127—131).—Dried tea leaves (1 kg.) of the following varieties contain α-carotene and xanthophyll in the amounts stated: fresh Formosa, 0·1751 and 0·4544 g.; fermenting Formosa 0·1571 and 0·4237 g.; Touchang 0·1681 and 0·4257 g.; Oolong 0·0784 and 0·2441 g.; black 0·0715 and 0·3686 g.; green 0·01571 and 0·4175 g. R. S. C.

Carotene content of ten varieties of carrots. C. E. Bills and F. G. McDonald (Science, 1932, 76, 108).—Data for white, yellow, and orange garden and field carrots are recorded. Garden varieties contain the largest amount of carotene, but traces occur even in white field carrots. L. S. T.

Organic bases of soya bean. K. Sasaki (J. Agric. Chem. Soc. Japan, 1932, 8, 417—420).—Korean soya bean (1930) contained H_2O 11·2, crude fat 16·6, total N 7·03, protein-N 6·48, non-protein-N 0·55%. 5 kg. afforded adenine (picrate) 1·40, guanine 0·31, histidine (dichloride) 0·62, arginine (nitrate) 9·55, choline (Au salt) 25·36, trigonelline (HCl) 0·33, and an unidentified base (from the lysine fraction; m.p. 214°; Pt salt, m.p. 235°; picrate, m.p. 206—208°), 0·80 g. Ch. Abs.

Contents of the rhizomes of *Curcuma domestica* (Temoe Lawak). H. Dieterle and P. Kaiser (Arch. Pharm., 1932, 270, 413—418).—These contain *l*-camphor, *l*-*cyclo*isoprenemyrcene, $[\alpha]_D$ −10·59°, and curcumin. R. S. C.

Existence and distribution of caffeine and theobromine in the organs of the guarana (*Paullinia cupana*). G. Bertrand and P. de B. Carneiro (Ann. Inst. Pasteur., 1932, 49, 381—386).—The leaves and stem bark of guarana contain much theobromine (I) and caffeine (II), the flowers and flower-stalks much (I), but only traces of (II); the seeds, stem wood, and roots contain (II) but no (I). W. O. K.

Alkaloids of Chinese drug Pei-Mu, *Fritillaria Roylei*. T. Q. Chou and K. K. Chen (Chinese J. Physiol., 1932, 6, 265—270).—From the corms of *F. Roylei* have been isolated two cryst. alkaloids: *peimine*, $C_{19}H_{30}O_2N$, m.p. 223°, optically inactive (*hydrochloride*, m.p. 295°; *hydrobromide*, m.p. 288°), and *peiminine*, $C_{18}H_{28}O_2N$, m.p. 135°, $[\alpha]_D^{24}$ −62·5° (*hydrochloride*, m.p. 295°; *hydrobromide*, m.p. 292°). They differ in both mol. formulæ and properties from verticine and verticilline (cf. A., 1930, 227). R. N. C.

Strychnine–brucine ratio of *Nux vomica* and the relative potency of these alkaloids. R. W. Morrison and A. R. Bliss, jun. (J. Amer. Pharm. Assoc., 1932, 21, 648—659, 753—760).—The total alkaloid content of *Nux vomica* (2·000—2·483% in 8 samples, av. 2·272%) is fairly uniform. The average strychnine–brucine ratio of 6 samples was 44—56, one was 49—51, and another 54—46, and these proportions were fairly well maintained in the preps. made from the crude drugs. Failing the double determination of total alkaloid and strychnine, the strychnine content is a more satisfactory standard than the present total alkaloid. E. H. S.

Trimethylamine from spores of *Tilletia lævis*, the stinking smut of wheat. W. F. Hanna, H. B. Vickery, and G. W. Pucher (J. Biol. Chem., 1932, 97, 351—358).—The contents of total volatile base and NH_3 in spores of *T. lævis* and *T. tritici* were determined. The NH_3 content varied from 0·054 to 0·143%. NMe_3 was isolated from the spores of *T. lævis* (0·0036—0·012%) but could not be detected in those of *T. tritici*. F. O. H.

Active substances in pollens of *Gramineæ*. I. Occurrence of a histamine-like substance in

pollen of *Secale cereale*. C. E. Benjamins (Z. Immunität., 1931, 72, 189—211; Chem. Zentr., 1932, i, 2337).—Only rye among the *Gramineæ* pollens contains a substance completely identical in physiological properties with histamine. A. A. E.

Seeds of *Erythrina variegata* var. *orientalis* (L.), Merrill. J. Maranon (Philippine J. Sci., 1932, 48, 563—580).—A morphological and chemical study. Et$_2$O extracts from the seed a fatty oil (15·91%), EtOH an alkaloid (2·5%), identified as hypaphorine (A., 1911, i, 668), 0·1 g. of which is not toxic to guinea-pigs. A. C.

Oil of bittersweet seed. C. Barkenbus and C. F. Krewson (J. Amer. Chem. Soc., 1932, 54, 3993—3997).—Extraction of bittersweet (*Celastrus scandens*) seeds with light petroleum, Et$_2$O, and 95% EtOH gives 36·06, 46·72, and 53·22%, respectively, of extractives. The extracted meal contains H$_2$O 3·05, ash 2·88, protein 18·94, crude fibre 9·14, free invert sugar 0·49, sugar by inversion 1·6, pentosans 5·87, and starch 0·68%. The oil, extracted by Et$_2$O, has d^{20} 0·9772, n^{20} 1·4815, I val. (Hanus) 121·5, SCN-I val. 69·96, sap. val. 297·07, Reichert–Meissl val. 70·86, acid val. 3·98, Ac val. 147·5, unsaponifiable matter 2·96%, and contains glycerides of linoleic 38·46, linolenic 21·03, palmitic 8·42, stearic 1·88, and sol. acids (as AcOH) 15·67%; it is not known whether these acids occur as glycerides. The volatile acids contain HCO$_2$H and a little hexoic acid.

C. J. W. (*b*)

Natural occurrence of methyl *n*-octyl ketone. A. S. Pfau (Helv. Chim. Acta, 1932, 15, 1267—1270).—Spanish and Algerian oil of rue contains small amounts of Me *n*-octyl ketone (I), m.p. 2°, b.p. 89°/10 mm., oxidised by HOI to nonoic acid (p-*phenylphenacyl* ester, m.p. 71°). The m.p. 14° given (A., 1925, i, 514) for (I) is erroneous. The natural occurrence of a ketone with an even no. of C atoms is remarkable, but (I) is related to undecoic acid, which also occurs in nature. R. S. C.

Saponin content of the juice and leaf of the agave plant, Maguey, Manso Fino. H. D. Jones, G. N. Furbeck, and R. Colorado (J. Amer. Pharm. Assoc., 1932, 21, 787—793).—The saponin, [$C_{32}H_{49}O_{16}$(?); Ca 0·41%] from the juice and the dry leaves is described. It has some hæmolytic action and on injection produces diarrhœa.

E. H. S.

Cultivated *Meriandra*. A. M. Borsalino in Semeria (L'Ind. Chimica, 1932, 7, 1205—1208).—The leaves of *M. Benghalensis* grown in Italy are similar in composition to those of the African plant, but differ by containing Mn in the ash. T. H. P.

"Diagnostic wood" of perennial plants (vines) in relation to production. M. E. Vinet (Compt. rend. Acad. Agric. France, 1932, 18, 804—814).—The sum of the % of N, P$_2$O$_5$, and K$_2$O in the "diagnostic wood" (bases of ripened shoots) of vines varies directly with sugar production in the fruit. There is a close proportionality between % of K and sugar production. In general, the PO$_4'''$ content of the wood varies directly and the N content inversely with the no. of grapes produced. A. G. P.

Determination of cellulose in soil. J. A. Daji (Biochem. J., 1932, 26, 1275—1280).—The soil from which lignin has been removed is treated with dil. alkali and acid and then with a solution of NaOCl in the cold. The cellulose is extracted from the residue with Schweitzer's reagent, pptd. with EtOH, and determined by loss of wt. on ignition. S. S. Z.

Localisation of essential oils and pitch resins in pines. G. V. Pigulevski (Bull. Inst. Pin, 1932, 33, 206—210). J. L. D.

Phosphatides of forage grasses. I. Cocksfoot. J. A. B. Smith and A. C. Chibnall (Biochem. J., 1932, 26, 1342—1357).—Considerable phosphatide decomp. takes place during rapid drying of the grass. The presence of lecithin, kephalin, and the Mg or Ca salt of phosphatidic acid has been established. Linoleic and linolenic acids are among the constituent fatty acids of the phosphatides. Oleic acid is absent from this fraction as well as from the glyceride fatty acids. The ratio of saturated to unsaturated acids is <1. S. S. Z.

Nitrogenous nutrition of plants. A. I. Virtanen (Suomen Kem., 1932, 5, 67—74).—In sterile cultures of const. $p_{\rm H}$ aspartic acid was a satisfactory N source for legumes, but not for cereals. The latter utilised asparagine freely. N compounds obtained by diffusion from root nodules of legumes were utilisable by *Gramineæ*. A. G. P.

Arginine metabolism and production of urea in higher plants. G. Klein and K. Tauböck (Biochem. Z., 1932, 251, 10—50; cf. this vol., 101).—By means of a modification of the procedure of Weber (A., 1930, 755) micro-determinations of the free and combined arginine of plants can be made. The species and part of the plant and also the stage of growth affect the amounts greatly. In conifers the content of arginine is high and it plays an unusual part in the metabolism. The urea found in higher plants is probably produced by enzymic degradation of arginine and of similar substances. In the seeds of some species during germination much of the arginine is consumed, in those of others it is liberated from combination but scarcely consumed at all at this stage, whilst in most cases there is moderate consumption and liberation when germination occurs.

W. McC.

Choline metabolism in plants. I. G. Klein and H. Linser (Biochem. Z., 1932, 250, 220—253).—A method is described for determination of small amounts of choline and lecithin in terms of the NMe$_3$ liberated on treatment with conc. NaOH, and applied to the determination of the choline contents of a no. of lecithin preps. and of the EtOH extracts of various organs of a large no. of plants. The total choline content of the seeds of the latter amounts to 0·01—0·10% of the fresh wt. except for the *Leguminosæ*, which contain about twice this amount. The total, lecithin-, and free choline contents of a no. of plants during germination were determined. Etiolated seedlings contain more H$_2$O-sol. (free) choline and less lecithin-choline than green seedlings. The total, lecithin-, and especially the free choline contents of the seedling and of the cotyledon increase during

germination, the cotyledon (*Zea mays*) being often deprived of lecithin-choline in favour of the seedling.
P. W. C.

Utilisation of atmospheric nitrogen by germinating seeds. II. Germinating legumes in presence of alkaloids. N. Vita (Biochem. Z., 1932, 252, 278—291).—Caffeine and strychnine nitrate (1—2% solution) stimulate the utilisation of atm. N_2 by lupins, horse-beans, and peas. The action reaches a characteristic optimum according to the type of seed, the concn. of alkaloid, and the O_2 content of the surrounding atm. (increasing with decreased O_2 content).
P. W. C.

Seasonal changes in the composition of the insoluble nitrogen fraction in the current year shoots of Bartlett pear. A. S. Mulay (Plant Physiol., 1932, 7, 323—327).—The insol. N of bark and wood, respectively, consists approx. of NH_2-N, 40—50, 40; basic N, 20, 12; melanin-N, 10—15, 14; amide-N, 7—9, 10; humin-N, 4—6, 4; EtOH-sol. N, 2, 8; residual N, 5—10, 12%. Seasonal variations in the bark are small, there being an increase in amide- and humin-N at the expense of basic and residual N in the early growing season and a slight fall in NH_2- and a rise in residual N as growth proceeds. In the wood the N distribution is fairly const. except from June to August, when there is a marked decrease in NH_2- and an increase in melanin-N. The residual N tends to increase after actual growth ceases.
A. G. P.

Carbohydrate exchange in nodule-bearing and nodule-free soya beans. E. Rüffer (Z. Pflanz. Düng., 1932, 24A, 129—167).—N fixation by nodule bacteria is largely dependent on the available carbohydrate supply in the plant. Plants grown under sterile conditions with generous N manuring had a lower N content than those inoculated with bacteria but receiving no fertiliser, although the initial intake of N was more rapid. Inoculated plants showed greater assimilation in the early growth stages and a consequent increase in sugar and starch contents. In later stages the carbohydrate content fell below that of sterile plants as a result of utilisation by the nodule organisms.
A. G. P.

Diurnal changes in the temporary accumulation of starch in leaves of green plants. P. P. Stănescu, A. Aronescu, and I. G. Mihăilescu (Bull. Acad. Sci. Roumaine, 1932, 15, 80—83).—No relationship exists between the commencement of starch accumulation and exposure of the plant to light. Diurnal changes vary with the type of plant, and in different leaves of the same plant. Day-to-day variations are considerable.
A. G. P.

Relations between carbohydrates and growth rate in the wild oat, *Avena fatua*. E. C. McCarty (Oscas. Pap. Riverside Jun. Coll., California, 1932, 6, No. 1, 1—32).—The "food march" is inversely proportional to the meristem activity and to the increase in dry wt. The inverse ratio seems to be a fundamental relationship in the growth and development of annual as well as of perennial grasses.
Ch. Abs.

Changes in composition of sunflower seeds with sowing time. S. Rushkovski (Masloboino Zhir. Delo, 1930, No. 9—10, 43—56).—Loss of H_2O by ripe seeds is lower with late than with early sowing; the % hulls in ripe seeds is independent of sowing time. The sol. carbohydrates (of which 50% is reducing) decrease during ripening from 37·5% to 4·5% and are independent of sowing time. The oil content decreases, and the kernel-protein is 10% lower, with late sowing. The hull-protein decreases from 12% to 3—5% with ripening, and is independent of sowing time. The hull-cellulose is higher and -ash lower with early sowing.
Ch. Abs.

Use of expressed sap in determining the composition of maize tissue. J. D. Sayre and V. H. Morris (Plant Physiol., 1932, 7, 261—272; cf. A., 1931, 775).—In successive portions of the expressed sap of maize obtained by steadily increasing pressure the concns. of total and reducing sugars, sucrose, NO_3', and inorg. PO_4''' remain const. The total solids, total N and P (which may include colloidal material) tend to decrease as the pressure rises. The composition of maize tissue with respect to any constituent existing in true solution in the sap may be determined from analyses of the expressed sap. The sucrose content of maize leaves is decreased by freezing the tissue, but not by grinding it.
A. G. P.

Hydrogen-ion concentration and Fe content of tracheal sap from green and chlorotic pear trees. J. Oserkowsky (Plant Physiol., 1932, 7, 253—259).—$[H^{\cdot}]$ and $[Fe^{\cdot\cdot\cdot}]$ are high in the early part of the growing season, but the period of high $[Fe^{\cdot\cdot\cdot}]$ is shorter than that of high $[H^{\cdot}]$. No significant difference exists between the $[H^{\cdot}]$ or $[Fe^{\cdot\cdot\cdot}]$ of green and chlorotic branches from the same orchard.
A. G. P.

Protoplasmic potentials in *Halicystis*. II. Effects of potassium on two species with different saps. L. R. Blinks (J. Gen. Physiol., 1932, 16, 147—156).—The p.d. between the cell-sap of *H. ovalis* (I) and the sea-H_2O in which it is immersed (at p_H 8·1 and 15—20°) exceeds the corresponding figure for *H. Osterhoutii* (II) by about 12 mv. Experiments in which the K content of the surrounding sea-H_2O was varied and in which artificial sap containing K was used as immersion liquid, as well as others in which the K content of the sap in (II) was raised to a level equal to that of (I) (0·3M), indicate that the difference disappears when the difference in K content is balanced or abolished. It is therefore unlikely that the accumulation of KCl in (I) is due to the different mobility of the ions in the protoplasm of the species.
W. O. K.

Kinetics of penetration. IV. Diffusion against a growing potential gradient in models. W. J. V. Osterhout (J. Gen. Physiol., 1932, 16, 157—163).—In a model consisting of (I) an aq. solution of K guaiacoloxide, (III) dil. $KHCO_3$ solution through which CO_2 is bubbled separated by (II) a guaiacol–phenol mixture containing K guaiacoloxide, the K migrates from (I) to (III), whilst a potential is set up opposing the movement. The conditions are analogous to those which probably obtain in certain living cells in which K is accumulated in the sap. W. O. K.

Organic phosphorus compounds in plants and animals. III. Exosmosis of inorganic and organic phosphorus from the cells of plants. H. Magistris (Biochem. Z., 1932, **253**, 64—80; cf. A., 1930, 260).—III. Below 10° the P which passes into the dialysate from vegetables (peas, beans, beet) is almost entirely inorg., but as the temp. is raised (to 30—35°) the amounts of total, org., and inorg. P which dialyse increase. At const. temp. the P which first passes out is chiefly inorg., but after about 10 hr. the amount of org. P which dialyses increases, whilst that of inorg. P decreases. Increase in the amount or renewal of the H_2O used, or irradiation (especially with ultra-violet rays) before or during dialysis, increases the amount of P which dialyses. $CaCl_2$ in the H_2O irreversibly reduces the amount of P (especially org. P) which dialyses, but KCl and $MgCl_2$ first increase, then greatly decrease, this amount. The action of KCl is reversible. The dialysis of inorg. P is greatly, that of org. P completely, inhibited, irreversibly, by heavy metal salts [$Pb(OAc)_2$, $HgCl_2$, $Cu(NO_3)_2$, $AlCl_3$, $ZnSO_4$, $NiSO_4$]. Very low concns. of mineral acid increase, higher concns. decrease, and CO_2 and H_2S greatly and reversibly increase, the dialysis of inorg. and org. P, and it is also increased, apparently in proportion to concn., by org. acids. NH_3 also reversibly increases the dialysis of P, but the investigation of the effect of other alkalis is complicated by their destructive action on the cells. Some of the results of Zaleski and Mordkin (A., 1928, 1061) have been confirmed. W. McC.

Phosphorus compounds of plants. VI. Solubility of compounds of horse-bean meal and phytin–protein complexes. E. Mnich (Bull. Acad. Polonaise, 1931, B, 123—147).—The p_H of the medium determines the proportion of phytin and protein in combination. The p_H at which the concn. of P compounds in solution is min. corresponds with the initial stages of the formation of phytin–protein complexes; with increasing acidity (up to 0·1% HCl) the amount of bound protein increases. Decomp. of the complexes takes place only at a p_H at which denaturation of the protein occurs, the limits of such complex formation being approx. from p_H 6·7 to 1% HCl. P. G. M.

Absorption of the solute from aqueous solutions by the grain of wheat. R. Brown (Ann. Bot., 1932, **46**, 571—582).—Data showing the rate of absorption of H_2O, NaCl, HCl, and I are recorded. The nature of factors influencing the semipermeable system is discussed. A. G. P.

Isoelectric point of plant-cell nuclei. G. Yamaha (Proc. Imp. Acad. Tokyo, 1932, **8**, 315—317).—The isoelectric point of nuclei of cells from the anther of *Lilium tigrinum* is 3·8—3·9. P. W. C.

Iron, manganese, copper, zinc, and iodine contents of some important forage crops. J. S. McHargue, W. R. Roy, and J. G. Pelphrey (J. Amer. Soc. Agron., 1932, 84, 562—565).—Considerable differences are recorded in the amounts of Fe, Mn, Cu, Zn, and I in crops. In general, species having a high proportion of any one element contain unusually low amounts of the others. Liming tends to reduce the Mn contents of crops. A. G. P.

Factors affecting the distribution of iron in plants. C. H. Rogers and J. W. Shive (Plant Physiol., 1932, **7**, 227—252).—Plants in which the composite tissue fluids are of high p_H have very low sol. and high total Fe contents. Those with tissue fluids of low p_H have high sol. and low total Fe. The p_H range over which Fe is pptd. in plant tissues is wider than that of inorg. systems. Diurnal changes in the p_H of tissue fluids resulting from variation of light intensity are associated with corresponding changes in the proportion of sol. Fe. Accumulation of pptd. Fe is greatest in tissues of high p_H lying adjacent to others of low p_H. In plants in which the tissues are uniformly of low p_H, Fe does not accumulate and sol. Fe is evenly distributed throughout the tissues Translocation of Fe from root to leaf occurs principally in the xylem. A. G. P.

Occurrence of small amounts of iodine and fluorine in the organism. II. A. Mayrhofer, C. Schneider, and A. Wasitzky (Biochem. Z., 1932, **251**, 70—86; cf. A., 1929, 478).—By employing another method for the destruction of org. matter the I determination is improved. A description of two methods and an apparatus for the micro-determination of F in org. material is given. The I and F contents of spinach, lettuce, onions, beans, lentils, tea, coffee, and rice (and in some cases of EtOH extracts of these foods) have been determined. Tobacco, tomatoes, and potatoes contain I but no F and cucumber contains only traces of F. In some of the foods the F content is $<$ the I content. W. McC.

Variability of the chemical composition of plants. N. N. Ivanov (Biochem. Z., 1932, **250**, 430—447).—Analytical figures are given in order to emphasise the variability of the protein, fat, carbohydrate, alkaloid, vitamin, etc. contents of plants with the type and strain of plant, the manuring, the climatic conditions (humidity, temp.), and the degree of growth, ripening, and storage. P. W. C.

Effect of fertilisers on the chlorine content of the sap of maize plants. N. A. Pettinger (J. Agric. Res., 1932, **44**, 919—931).—The Cl content and the $[H^{\cdot}]$ of the sap are increased when Cl-containing fertilisers are used, KCl exerting a residual effect even after 15 years. Fertilisers containing S cause little if any accumulation of SO_4'' in the sap. W. G. E.

Effect of thallium on growth of tobacco plants. J. E. McMurtrey, jun. (Science, 1932, **76**, 86).—With 1 p.p.m. of Tl, toxicity is shown as a series of effects which has many of the characteristic symptoms of the typical frenching disease of tobacco. L. S. T.

Radioactivity in plant physiology. D. Montet (Compt. rend., 1932, **195**, 582—584).—The action of radioactive substances on growth, from germination to final development of the plant, can be represented by a smooth curve, indicating a complete parallelism with animal physiology. H. G. R.

Premature flowering in grapefruit from X-rayed seeds. C. N. MOORE and C. P. HASKINS (Science, 1932, 76, 167—168).—Grapefruit seedlings show premature flowering after exposure to radiations from a H_2O-cooled W-target Coolidge tube.
L. S. T.

Pipette manipulator. G. P. C. WANG (Chinese Med. J., 1932, 46, 607—608).—This manipulator works on the principle of a mechanical syringe, avoiding operation by the mouth. H. G. R.

Simple apparatus for absorbing substances from the expired air of laboratory animals. W. MORSE (J. Lab. Clin. Med., 1931, 17, 282—283).
CH. ABS.

Micro-analysis of gases. J. A. CAMPBELL (Nature, 1932, 130, 240).—Krogh's method can be applied to gases from animal tissues by using glycerol containing 20% of H_2O. L. S. T.

Determination of alkali by electrodialysis. C. O. OLDFELDT (Biochem. Z., 1932, 251, 235—245).—The apparatus and method for determination of total alkali in small amounts of tissue by titration of the cathode fluid are described; they have been used successfully for a series of salt solutions and mixtures thereof. The method is finally applied to blood, cat's liver, and urine before and after ashing. P. W. C.

Micro-determination of magnesium in biological material. K. LANG (Biochem. Z., 1932, 253, 215—217; cf. A., 1928, 145).—After removal of protein and of Ca the Mg (0·001—0·002 mg. per c.c. of serum can be determined) is pptd. with tropæolin-*OO*, the ppt. ($C_{36}H_{28}O_6N_6S_2Mg$) dissolved in conc. H_2SO_4, and the Mg content of the solution determined colorimetrically. The error is $<5\%$. The method can be applied gravimetrically in macro-analysis.
W. McC.

Copper and iron in chemistry and biology. A. QUARTAROLI (Annali Chim. Appl., 1932, 22, 517—543).—The co-activation of Fe and Cu in oxidation processes is shown in the ashing of plant materials. Tobaccos of high Fe and Cu content are easily ashed. The mechanism of Fe and Cu co-activation is studied and from these reactions a catalytic method for the determination of traces of Cu (up to 0·0001 mg.) is developed. The method is applied to the determination of Cu in blood, in the body, in foodstuffs, and to the study of the ratio Fe/Cu in the diet.
O. F. L.

Colorimetric micro-determination of copper in organic substances. W. D. McFARLANE (Biochem. J., 1932, 26, 1022—1033).—The coloured Cu salt of diethyldithiocarbamic acid is quantitatively extracted from aq. solution by amyl alcohol, the colour becoming intensified in the latter solvent. The depth of the colour is directly proportional to the amount of Cu present provided the range of Cu concns. is not too great. In alkaline pyrophosphate solution Cu may be determined in the presence of Fe. Previous oxidation of CuS in the cold with saturated $Br-H_2O$ and 10% H_2SO_4 does not interfere with the colour reaction. Procedures for the determination of Cu in biological materials are given. S. S. Z.

Determination of iron in organic substances. I. Microcolorimetry as ferric thiocyanate. II. Potentiometric titration with titanous sulphate. W. D. McFARLANE (Biochem. J., 1932, 26, 1034—1049).—I. In Kennedy's method (A., 1927, 987) when quantities of Fe ranging from 0·007 to 0·022 mg. are determined, the red colour of $Fe(CNS)_3$ is not proportional to the concn. of Fe. It is possible to correct for this deviation so that 0·014 mg. of Fe can be accurately determined.

II. Methods are described by means of which 0·15 mg. of Fe can be determined in org. substances.
S. S. Z.

Gravimetric micro-determination of sulphur in biological material. H. WAELSCH and G. KLEPETAR (Z. physiol. Chem., 1932, 211, 47—56).—The method depends on ashing in an alkaline Benedict–Denis mixture [$Cu(NO_3)_2$, NaCl, NH_4NO_3, and Na_2CO_3 to p_H 7·2] and pptn. as $BaSO_4$. J. H. B.

Iodometric micro-method for determination of chloride. N. BEREND (Biochem. Z., 1932, 252, 362—365).—After pptn. of the Cl with $AgNO_3$ and of the excess of $AgNO_3$ with KIO_3, the excess of KIO_3 is determined in the filtrate iodometrically. The mean error is $\pm 10^{-6}$ g. P. W. C.

Circulation of iodine in nature. B. BLEYER, J. SCHWAIBOLD, and B. HARDER (Biochem. Z., 1932, 251, 87—100).—With the help of an apparatus described the I content of the following materials has been determined: air, snow, and rain in Munich (under varying meteorological and seasonal conditions); Bavarian deep spring water and river water; sewage from Munich. Very great variations were found. W. McC.

Copper reduction values of mannose under certain fixed conditions. P. H. MOORE, R. W. LLOYD, and G. E. BURGET (J. Biol. Chem., 1932, 97, 345—350).—Mannose (I), admixed with proteins from intestinal contents, can be determined by reduction of Benedict's solution to Cu_2O under definite conditions and determination of the Cu in the ppt. by a modification of Peters' electrolytic method. Other methods are inaccurate or inapplicable. A table of Cu equivs. for (I) is given.
R. S. C.

Determination of residual nitrogen by direct Nesslerisation. A. LUBLIN (Klin. Woch., 1932, 11, 110—110; Chem. Zentr., 1932, i, 1557).—A simplification of Folin's method. L. S. T.

Decomposition of rufianates, flavianates, picrates, and picrolonates by means of wool. H. MÜLLER (Z. physiol. Chem., 1932, 209, 207—210).—Ppts. of org. bases with substances capable of dyeing wool-fibre are decomposed on treatment with wool in neutral or alkaline solution at low temp.; the dye is absorbed and the base liberated. The method is specially suitable for biologically active bases. J. H. B.