

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1935.

General, Physical, and Inorganic Chemistry.

Slight correction to the Rydberg constant for hydrogen (H^1). R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1934, [ii], 45, 491). L. S. T.

Triplet $3p$ complex of the hydrogen molecule. G. H. DIEKE (Physical Rev., 1935, [ii], 48, 610—614; cf. this vol., 917).—Many peculiarities in the Fulcher bands of H_2 can be explained by the interaction of the $3p^3\Pi$ with the $3p^3\Sigma$ level (cf. following abstract). N. M. B.

$3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of HD and D_2 . G. H. DIEKE (Physical Rev., 1935, [ii], 48, 606—609; cf. this vol., 555).—Full data for the system in the extreme red and near infra-red are tabulated, and the band consts. are calc. N. M. B.

Vibration and rotation spectrum of the molecule HD. G. C. WICK (Atti R. Accad. Lincei, 1935, [vi], 21, 708—714).—Theoretical and mathematical. O. J. W.

Anomalies in the Zeeman effect of helium. L. E. KINSLER and W. V. HOUSTON (Physical Rev., 1934, [ii], 45, 134). L. S. T.

Photographic record of the resonance line of helium. K. HAIDRICH (Phot. Korr., 1935, 71, 106—107).—The He resonance line at λ 10,830 ($2s-2p$) can be photographed on Ilford I.-R. plates sensitised by neocyanine. The greatest intensity of the line is near the cathode. J. L.

Electric and magnetic effect on the helium lines for perpendicularly crossed fields. W. STEUBING and W. REDEPENNING (Ann. Physik, 1935, [v], 24, 161—182).—The combined Zeeman and Stark effects on the He lines have been investigated. Detailed results are given for the lines $2s-3p$, $2p-nd$ ($n=4, 5, 6$), $2p-ns$ ($n=4, 5, 6$), $2S-nP$ ($n=3, 4$), $2P-nd$ ($n=4, 5, 6, 7$), and $2P-nS$ ($n=4, 5, 6$). A. J. M.

Perturbations in the second positive nitrogen bands. L. GERÖ (Z. Physik, 1935, 96, 669—676). A. B. D. C.

Action of hydrogen bromide on the nitrogen afterglow. W. H. RODEBUSH and M. L. SPEALMAN (J. Amer. Chem. Soc., 1935, 57, 1881—1882).—HBr or Br alters the relative intensity of certain transitions in the afterglow, but the band spectrum of Br was not observed. E. S. H.

Electronic and vibrational absorption in O_4 and O_3 molecules. J. W. ELLIS and H. O. KNESER (Physical Rev., 1934, [ii], 45, 133). L. S. T.

Absorption of oxygen in the extreme ultra-violet. G. B. COLLINS and W. C. PRICE (Physical Rev., 1934, [ii], 45, 561).—Absorption bands below

1000 Å. have been photographed and arranged into three progressions for which formulæ are given. They are due to normal O . Other bands at shorter λ and between 1210 and 1000 Å. have also been measured. L. S. T.

Oxygen in the sun's chromosphere. T. ROYDS (Nature, 1935, 136, 606—607).—The observed infra-red O emission lines 7771, 7774, and 7775 show that O_2 is a normal and probably abundant constituent of the sun's chromosphere. L. S. T.

New emission spectrum of sulphur in the photographic infra-red. M. DESIRANT and J. DUCHESNE (Compt. rend., 1935, 201, 597—598).—Bands at 6650—7765 Å., degraded to the violet, and attributed to S_2 , are described. H. J. E.

Deepest terms in ions of the isoelectronic sequence $Al-Mn$ VIII. P. G. KRUGER and S. G. WEISSBERG (Physical Rev., 1935, [ii], 48, 659—663).—Radiations corresponding with the energy differences between the terms $3p^6\ ^1S_0-3p^54s^3P_1^0, ^1P_1^0$ in Ti v, V vi, Cr vii, Mn viii, and $3p^6\ ^1S_0-3p^55s^3P_1^0, ^1P_1^0$ in V vi and Cr vii, and connecting the upper states with the deepest terms in each ion, have been observed. Series limits and vals. of the deepest terms are calc. N. M. B.

Spectrum of the zinc arc in a vacuum. C. W. HETZLER, R. W. BOREMAN, and K. BURNS (Physical Rev., 1935, [ii], 48, 656—659).—Data for 60 lines in the range 2178—7799 Å. are tabulated. Two new solar Zn lines, λ 4292 and 7799, are reported. A source for obtaining weak lines in vac. is described, and data for the stronger lines of Pb, Cu, Cd, Ag, Sn, Na, K, Rb, Cs, Sr, and Be are given. N. M. B.

Spectrum of doubly-ionised zinc. S. BASU (Indian J. Physics, 1935, 9, 537—544; cf. Bloch, A., 1934, 1051).—Data and analyses for 104 lines and 23 new term vals. are tabulated for the region λ 5513—2387. N. M. B.

Hyperfine structure in selenium, palladium, and gold. L. SIBAIYA (Proc. Indian Acad. Sci., 1935, 2, A, 313—319).—Hyperfine structure analysis of some Se and Pd lines shows that none of the levels examined reveals even isotope displacement. The Se 77 and Pd 105 nuclei have very small magnetic moments, and their spin moment is probably $1/2(h/2\pi)$. The doublet structure ($\Delta\nu=0.224\text{ cm}^{-1}$) in the resonance lines of Au is confirmed by the redoubling of each component due to self-reversal in the source. Evidence points to a single Au isotope of mass 197, indicating that the accepted at. wt. is too high. The

nuclear spin moment of Au is $3/2$, and the $g(I)$ factor is 0.136, agreeing with Landé's theoretical val.

N. M. B.

Quenching of cadmium resonance radiation by foreign gases. H. C. LIPSON and A. C. G. MITCHELL (Physical Rev., 1935, [ii], 48, 625—630).—The quenching of the Cd resonance line λ 3261 by H_2 , D_2 , CO, NH_3 , N_2 , and CH_4 was measured by comparing line intensity from a cell containing pure Cd vapour and one containing Cd vapour and the foreign gas. Applying the Stern-Volmer formula, the quenching cross-sections are: H_2 0.67, D_2 0.19, CO 0.14, NH_3 0.041, N_2 0.021, CH_4 0.012×10^{-16} sq. cm.

N. M. B.

Wave-length shifts of the spectral lines of Sn due to change of pressure. T. YUASA (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, A, 267—277).— λ shifts and modes of appearance of the lines of Sn I, II, III excited at 1 atm. and a few cm. pressure are tabulated. As the inner quantum no. j increased, the shifts and changes in modes of appearance were more marked. Arc lines showed no appreciable shift with pressure increase, but the mode of appearance changed. Effects were comparatively smaller for the principal series in Sn II and Sn III. Results are tabulated also for a no. of unclassified lines.

N. M. B.

Absorption spectrum of diatomic antimony. S. M. NAUDÉ (Physical Rev., 1934, [ii], 45, 280).—Two band systems obtained at different temp. and v.p. of the Sb are described. Some bands show fine structure, and the head corresponding with the mol. $Sb^{121}Sb^{123}$ is more intense than those corresponding with the mols. $(Sb^{121})_2$ and $(Sb^{123})_2$.

L. S. T.

Perturbations of the higher caesium terms by methane hydrocarbons and measurements for the doublet $1s-3p$ of the potassium principal series. C. FÜCHTBAUER and H. J. REIMERS (Z. Physik, 1935, 97, 1—7).— CH_4 , C_2H_6 , and C_3H_8 give red displacement similar to A for the Cs terms, the displacement increasing with perturbing mol. size. Half-width and displacement measurements are given for the K doublet perturbed by these hydrocarbons and inert gases.

A. B. D. C.

Arc and spark spectra of cerium. G. R. HARRISON and W. ALBERTSON (Physical Rev., 1934, [ii], 45, 289).—The Ce arc between 2000 and 5000 Å. has been photographed using a grating of 0.4 Å. per mm.

L. S. T.

Spectrum of singly-ionised europium. W. ALBERTSON (Physical Rev., 1934, [ii], 45, 499—500).

L. S. T.

Emission and absorption from the 2^3P_0 metastable level in mercury. M. L. POOL and O. W. PRASHUN (Physical Rev., 1934, [ii], 45, 124).

L. S. T.

Proportionality of dispersion to field in the Zeeman effect of three mercury levels. G. DUPOUX and P. JACQUINOT (Compt. rend., 1935, 201, 543—544).— $\Delta\nu/H$ is const. for 3P_1 , but increases for 3S_1 and 3P_2 , as the field increases from 30,000 to 50,000 gauss. For 3P_1 $g=1.493$ (cf. this vol., 137).

T. G. P.

Intensity relations in the hyperfine structure of the optically-excited mercury line 5461 Å. E. E. BOGGS and H. W. WEBB (Physical Rev., 1934, [ii], 45, 561).

L. S. T.

Wave-length standards in the extreme ultra-violet. J. C. BOYCE (Physical Rev., 1934, [ii], 45, 289; cf. A., 1934, 1147; this vol., 799).

L. S. T.

Flame and spark-in-flame spectra of rare earths. C. J. RODDEN and O. S. PLANTINGA (Physical Rev., 1934, [ii], 45, 280—281).—Bands given by La, Sm, Pr, Nd, Gd, and Yb when the corresponding rare-earth salts are introduced as a spray in the spark-in-flame method are recorded.

L. S. T.

Current distribution between a small (point) cathode and a large (infinite) anode for glow discharges in different gases. F. KELLER (Z. Physik, 1935, 97, 8—33).—Inert gases give diffusion flow of electrons when electron concn. near the cathode is sufficiently large, and gradient flow when this is small; N_2 belongs to this class. O_2 and H_2O give ionic sheath flow.

A. B. D. C.

Sparking potential of hydrogen at high frequencies. R. ZOUCKERMANN (Compt. rend., 1935, 201, 649—651; cf. A., 1933, 656).—Data are recorded for the effect of Hg vapour on the pressure variation of sparking potential of H_2 in a SiO_2 tube with external electrodes.

H. J. E.

Development of a spark from a glow. E. L. E. WHEATCROFT and H. BARKER (Phil. Mag., 1935, [vii], 20, 562—571).—The transition glow-spark is discussed, and the relations no. of sparks—pressure, crit. pressure—electrode spacing, and crit. pressure—current are examined and plotted.

N. M. B.

Paschen's law at low striking potentials. E. L. E. WHEATCROFT and H. BARKER (Phil. Mag., 1935, [vii], 20, 571—578).—Paschen's law is found to be valid over the glow-spark discharge range. The striking potential curve for air is found. The striking potential is approx. 50—100 volts lower for the spark than for the glow.

N. M. B.

Theory of the glow discharge. E. L. E. WHEATCROFT (Phil. Mag., 1935, [vii], 20, 578—586).—The main features of a glow discharge can be interpreted quantitatively in terms of the breakdown (breakdown potential—pressure \times electrode spacing) curve, and the ionisation conditions.

N. M. B.

Periodic variation of the concentration of neutral atoms in the vapour of an alternating-current sodium lamp. W. UYTERHOEVEN and C. VERBURG (Compt. rend., 1935, 201, 647—649).

H. J. E.

X-Ray line intensities in thick targets of nickel. L. T. POCKMAN, P. KIRKPATRICK, and D. L. WEBSTER (Physical Rev., 1934, [ii], 45, 131).

L. S. T.

Diffuse scattering of X-rays by conduction electrons. C. ZENER (Physical Rev., 1935, [ii], 48, 573—576).

N. M. B.

Soft X-rays and energy states of the conduction electron. H. W. B. SKINNER and H. M. O'BRYAN (Physical Rev., 1934, [ii], 45, 293).—The emission spectra of some lighter metals have been obtained

in the region 40—600 Å. The results are probably characteristic of the pure polycryst. solid. L. S. T.

State of polarisation of continuous X-rays from a thin aluminium anti-cathode. H. P. DE (Indian J. Physics, 1935, 9, 507—516).—A Wilson chamber method of observing the state of polarisation is described, and % polarisations relative to the direction of the cathode particles are given. Results are discussed in relation to available data and theory. N. M. B.

Rotation of the plane of polarisation of a beam of X-rays. R. L. MCFARLAN (Physical Rev., 1934, [ii], 45, 292).—Quartz crystals, 0.75 mm. thick, rotate the plane of polarisation through an angle of approx. $2^\circ 30'$ when a plane polarised beam of X-rays passes through parallel to the optic axis. L. S. T.

Emission [of subsidiary lines] in the $K\alpha$ spectra of the elements between Cu (29) and Rh (45) inclusive. H. HULUBEI (Compt. rend., 1935, 201, 544—547; cf. A., 1916, ii, 509).—Studies of the $K\alpha_{3,4}$ emission of Cu, Zn, As, Se, Br, Rb, Sr, Y (39), and Rh have been made. T. G. P.

Fine structure of the L_{III} absorption discontinuity of the rare earths. V. DOLEJSEK and H. HYLMAR (Compt. rend., 1935, 201, 600—602).—The specimens were prepared by mixing the material with a solution of cellulose nitrate in amyl acetate, and drying the resulting emulsion on paper. Data for Yb, Gd, Sm, Nd, Pr, and Ce are recorded. H. J. E.

Relative intensities of certain L-series X-ray lines of gold (79). F. K. RICHTMYER and S. W. BARNES (Physical Rev., 1934, [ii], 45, 562; cf. this vol., 138). L. S. T.

L emission spectrum of platinum. (MLLE.) Y. CAUCHOIS (Compt. rend., 1935, 201, 598—600).—Data are recorded and classified. H. J. E.

Ratio of fluorescence yields of the L_{11} and L_{22} sub-series of lead. B. E. FOSTER (Physical Rev., 1934, [ii], 45, 130—131). L. S. T.

New satellites of the X-ray line $L\beta_2$. S. KAUFMAN and F. K. RICHTMYER (Physical Rev., 1934, [ii], 45, 562). L. S. T.

Rate of change of electron temperature in the mercury afterglow. R. H. RANDALL and H. W. WEBB (Physical Rev., 1935, [ii], 48, 544—549).—The behaviour of a plasma in which no new ions are found was studied for electron temp. and concn. The rate of cooling of electrons was very rapid at first, decreasing rapidly below 2500° abs. to a const. val. several hundred degrees above that of the vapour. N. M. B.

Back diffusion of and excitation of secondary radiation by slow cathode rays at thin metallic layers. H. W. LANGENWALTER (Ann. Physik, 1935, [v], 24, 273—296).—Thin foils of Ag, Pt, and Pd were bombarded by slow electrons (<100 volts) at 70° incidence. The distribution of velocity amongst the electrons emitted perpendicularly from the foil, and the effect of heating and absorption of gas, were investigated. The different metals give similar curves. Foils which have not been heated

give electrons of two distinct velocity groups separated by a gap. One group consists of unretarded reflected electrons, the other principally of very slow true secondary electrons. On heating the foils, the gap between the two groups disappears, its place being taken by electrons which have diffused back. Treatment of the Pt and Pd foils with H_2 produced a similar effect to heating but smaller. A. J. M.

Electron grouping by concave glowing cathode surfaces revealed by the electron microscope. G. KEMMNTZ, M. KNOLL, and W. WALCHER (Z. Physik, 1935, 96, 612—619).—The electron microscope shows clearly the grouping of emitted electrons at small hollows in the cathode. A. B. D. C.

Mechanism of unimolecular electron capture. F. BLOCH and N. E. BRADBURY (Physical Rev., 1935, [ii], 48, 689—695).—The formation of negative ions by electron capture in gases in which a dissociation process does not occur is explained by a unimol. process involving the excitation of mol. vibrational levels and subsequent loss of energy by collision or resonance. A change of only one vibrational quantum no. must be assumed; this sets an upper limit to the electron affinity. In the case of O_2 this limit is 0.17 volt. N. M. B.

Electron scattering in mercury vapour. A. P. GAGGE (Physical Rev., 1934, [ii], 45, 288).—Results obtained with the magnetic deflexion method are described. L. S. T.

Emission of positrons from radioactive sources. A. I. ALICHANOV, A. I. ALICHANIAN, and M. S. KOSODAEV (Nature, 1935, 136, 719—720).—Measurements of the positron spectrum emitted by a thin-walled Rn tube have been repeated, and a new determination of the ratio of the positron no. to that of the β -particles of Ra-C has been made. When Pb or Al is submitted to rays from a Rn source most of the positrons produced are due to the γ -rays from Ra-C. L. S. T.

Theory of the positron. G. E. UHLENBECK (Physical Rev., 1934, [ii], 45, 290).—Dirac's theory is discussed. L. S. T.

Energy spectra of positrons ejected by artificially-stimulated radioactive substances. S. H. NEDDERMEYER and C. D. ANDERSON (Physical Rev., 1934, [ii], 45, 498—499). L. S. T.

Relation of the positron energy spectrum to the decay constant and to the energy of the bombarding protons. C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1934, [ii], 45, 653—654). L. S. T.

[New] Wilson's cloud chamber and determinations of the ratio of positrons to electrons on transformation of γ -rays in matter. T. BENECKE (Z. Physik, 1935, 96, 571—587). A. B. D. C.

Theory of protons and neutrons. G. WATAHIN (Atti R. Accad. Lincei, 1935, [vi], 21, 703—708).—Mathematical. Dirac's equations are modified for the case of protons and neutrons. O. J. W.

Creation of positive and negative electrons by heavy charged particles. Y. NISHINA, S. TOMO-

NAGA, and M. KOBAYASI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 137—178).—Mathematical. Cross-sections for the creation of pairs of positive and negative electrons by charged particles of high velocity on colliding with at. nuclei are calc. by the method of Weizsäcker (cf. A., 1934, 712). Vals. for Pb are 5.6×10^{-25} cm.² for 10^8 e.v. electrons, and 3.5×10^{-25} cm.² for 10^{11} e.v. protons. The screening effect of outer electrons is examined (cf. Oppenheimer, this vol., 278). N. M. B.

Energy of formation of negative ions in O₂. L. B. LOEB (Physical Rev., 1935, [ii], 48, 684—689).—An attempt to evaluate the energy of attachment of electrons to mols. in O₂, by determining at what energy the electron is detached from the O₂ ion in impact with mols., leads to the val. 0.34 volt. Phenomena of the Loeb electron filter are discussed (cf. Bradbury, A., 1934, 126). N. M. B.

Acceleration of ions. J. W. BEAMS and L. B. SNODDY (Physical Rev., 1934, [ii], 45, 287).—The method of accelerating electrons (*ibid.*, 1933, 44, 784) has been applied to the acceleration of protons. The increase in velocity corresponded with 6 times the max. applied potential of 15,000 volts. L. S. T.

Isotopes. F. W. ASTON (Science, 1935, 82, 235—240).—Address to the British Association, 1935.

Incompleteness of the system of chemical elements. M. DIERSCHKE (Chem.-Ztg., 1935, 59, 833—834).—The probable nature of elements 61, 85, and 87 and the possible existence of other new elements are discussed. A. G. P.

D. I. Mendeleev's elements "X" and "Y" in the light of new ideas. A. M. VASILIEV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 2, 33—34).—The neutron and neutrino are identified with "X" and "Y," respectively. CH. ABS. (e)

Liberation of radon by radioactive cells in drinking-glasses. J. M. A. HOEFLAKE and A. E. KORVEZEE (Rec. trav. chim., 1935, 54, 768—778).—The apparently irregular production of Rn in commercial drinking-glasses fitted with radioactive cells is due to the diffusion of the Rn through the paraffin surface of the cells, irregularities disappearing when measurements are taken at equal intervals. An expression is deduced for the amount of Rn transmitted to the H₂O under various conditions.

J. W. S.
Branching ratio of the actinium family of radioactive elements. M. FRANCIS and CHENG DA-TCHANG (Phil. Mag., 1935, [vii], 20, 623—632; cf. A., 1934, 387).—The ratio is const. at $4.05 \pm 0.1\%$, as determined for 88.7% U₃O₈ Katanga and 42.3% U₃O₈ Canadian pitchblendes and 49.5% U₃O₈ Colorado carnotite, and is the same whether Ta or Zr is used to ppt. the Pa. N. M. B.

Radioactivity of potassium and rubidium. K. SITTE (Z. Physik, 1935, 96, 593—599).—The active isotopes are a very rare K₄₁⁴⁰ and Rb₈₅⁸⁴.

A. B. D. C.
Radioactivity of samarium. H. J. TAYLOR (Nature, 1935, 136, 719).—Using the new technique (this vol., 910), the range of α -particles emitted by

Sm is 1.13 ± 0.02 cm. standard air. In addition to this short-range group, less numerous tracks of max. range approx. 3.5 cm. in air, due to singly-charged particles, have been observed. L. S. T.

Chemistry of polonium. M. LEMARCHANDS (Bull. Soc. chim., 1935, [v], 2, 1699—1700).—The position in the electromotive series allocated to Po by Guillot and Haissinsky (cf. A., 1934, 735, 855) between Te and Ag is confirmed by the relative effects of reducing agents on Po salts. J. W. S.

Segregation of polonium in a bismuth crystal. W. W. EATON (Physical Rev., 1934, [ii], 45, 647—648).—The groups of ranges in α -particles detected by Focke (A., 1934, 1284) have been checked by direct measurements of tracks formed in a Wilson expansion chamber. L. S. T.

L-Absorption constants of protoactinium (91). V. DOLEJŠEK and J. MAREK (Z. Physik, 1935, 97, 70—72). A. B. D. C.

α -, β -, and γ -Rays of the actinium family. A. E. RUARK (Physical Rev., 1934, [ii], 45, 564).—A discussion. L. S. T.

Determination of the decay constant of ionium from the number of α -particles emitted. F. HERNEGGER (Sitzungsber. Akad. Wiss. Wien, 1935, IIa, 143, 367—377; Chem. Zentr., 1935, i, 1658—1659).—The decay const. found was 8096×10^{-6} per year. A new method is given for separating Io from larger amounts of UO₂(NO₃)₂. H. J. E.

α -Particle spectra and the Geiger-Nuttall law. A. E. RUARK (Physical Rev., 1934, [ii], 45, 564).—A discussion. L. S. T.

β -Radiation of polonium. W. BOTHE (Z. Physik, 1935, 96, 607—611). A. B. D. C.

Double β -disintegrations. M. GOEPPERT-MAYER (Physical Rev., 1935, [ii], 48, 512—516).—Mathematical. N. M. B.

Use of electron lenses for β -rays. O. KLEMPERER (Phil. Mag., 1935, [vii], 20, 545—561).—The magnetic field distributions of various electron lenses have been measured and their optical qualities are discussed. A single-lens β -ray spectrograph giving high intensity, and a spectrograph comprising two "lenses" and a deflecting magnetic "prism" between them, giving high intensity and resolving power, are discussed. N. M. B.

Neutron emission. J. R. DUNNING and G. B. PEGRAM (Physical Rev., 1934, [ii], 45, 295; cf. A., 1934, 714). L. S. T.

Scattering of neutrons by protons. M. BRONSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 75—78).—Mathematical. A. J. M.

Emission of neutrons from radioactive sources. C. Y. CHAO (Sci. Rep. Nat. Tsing Hua Univ., 1935, 3, 221—225).—Using a Rn source in Au tubes and irradiating EtI from which the active I is afterwards separated, the no. of emitted neutrons detected was approx. 2 per millicurie per sec., probably emitted by the radioactive nuclei. N. M. B.

Absence of appreciable γ -radiation from the impact of fast neutrons on protons. (MME.) T.

GRIVET-MEYER (Compt. rend., 1935, 201, 658—660).—Lea's results were not confirmed (cf. A., 1934, 235). The increase in the no. of particles is attributed to the action of neutrons on Al used in the construction of the counter. H. J. E.

β -Radioactivity of neutrons. L. MOTZ and J. SCHWINGER (Physical Rev., 1935, [ii], 48, 704—705; cf. Konopinski, this vol., 1048).—Mathematical.

N. M. B.

Neutron-like particles accompanying β -ray emission. G. H. DENISON (Physical Rev., 1934, [ii], 45, 557).—An attempt to detect such particles emitted simultaneously with β -rays failed with Ra-D and -E, KCl, and RbCl. L. S. T.

Possible models of an electrostatic neutron. H. MARGENAU (Physical Rev., 1934, [ii], 45, 559).—Theoretical. L. S. T.

Scattering of slow neutrons. A. C. G. MITCHELL and E. J. MURPHY (Physical Rev., 1935, [ii], 48, 653—656).—Using the radioactivity produced in a Ag foil as a detector of neutrons, curves for the % scattering of slow neutrons as a function of thickness by Fe, Cu, Pb, Sn, and Hg were obtained. The calc. relative cross-sections for scattering are 9.9, 7.7, 7.2, 3.8, and 4.4, respectively. N. M. B.

Velocity of slow neutrons by mechanical velocity selector. J. R. DUNNING, G. B. PEGRAM, G. A. FINK, D. P. MITCHELL, and E. SEGRÉ (Physical Rev., 1935, [ii], 48, 704; cf. this vol., 1186).—A curve is obtained showing the decrease in no. of slow neutrons from a Rn-Be source detected after passing through a Cd-duraluminium two-shutter system as the speed of the sectors changed. N. M. B.

γ -Rays due to absorption of slow neutrons. F. RASETTI (Z. Physik, 1935, 97, 64—69).—Results are given for energy associated with γ -rays emitted from Cl, Co, Y, Ag, Cd, Ir, and Hg. A. B. D. C.

Slow neutrons. P. LUKIRSKY and T. ZAREWA (Nature, 1935, 136, 681—682).—The increased radioactivity induced in Ag irradiated by slow neutrons on cooling the paraffin wax to the temp. of liquid air has been confirmed (cf. this vol., 802). With thick layers of wax, however, no temp. effect is observed owing to loss of neutrons by absorption in the wax. Absorption increases with a decrease in velocity of thermal neutrons. The calc. effective cross-section of neutrons is approx. 10^{-24} cm.² L. S. T.

Application of radioactive bromine to the investigation of the mechanism of chemical reactions. S. ROGINSKY and N. GOPSTEIN (Physikal. Z. Sovietunion, 1935, 7, 672—676).—Org. Br linked to C shows scarcely any interchange with radioactive Br in Br₂, HBr, KBr, or CuBr₂. Passage of radioactive Br vapour over heated aq. KBr, or dissolution and subsequent evaporation of radioactive Br from aq. KBr, leads to complete distribution of the activity. At high temp. HgBr₂ and AlBr₃ show complete interchange of Br with the vapour phase. Heating of CuBr₂ containing radioactive Br, to form CuBr, followed by re-conversion into CuBr₂ in non-radioactive Br causes < theoretical

loss of activity, and after 5 cycles 50% of the activity remains, indicating that the valencies are unequal.

J. W. S.

Proton source for atomic disintegration experiments. S. N. VAN VOORHIS, J. B. H. KUPER, and G. P. HARNWELL (Physical Rev., 1934, [ii], 45, 492—493).—A focussed beam of ions of 20—50 microamp. consisting mainly of protons has been obtained from a modified Lamar-Luhr low-voltage arc (A., 1934, 1052). L. S. T.

Detection of nuclear disintegration products. H. A. BARTON and D. W. MUELLER (Physical Rev., 1934, [ii], 45, 650—651).—An arrangement for detecting disintegration products by means of tracks in a photographic emulsion is described. L. S. T.

Disintegration of Li⁶ by protons and deutons. T. Y. WU and G. E. UHLENBECK (Physical Rev., 1934, [ii], 45, 553—554; cf. A., 1934, 343).—Bombardment of ordinary Li by protons gives, in addition to the 8.4-cm. group, two groups of α -particles with ranges of 6.5 and 11.5 mm. The 6.5-mm. group may be ascribed to ${}^6_3\text{Li}$. Bombardment of ${}^6_3\text{Li}$ with deuterons gives α -particles of 13.2 cm. range and protons of 30 cm. range; the latter are explained by assuming the reaction ${}^6_3\text{Li} + {}^2_1\text{H} \rightarrow {}^7_3\text{Li} + {}^1_1\text{H}$. L. S. T.

Transmutation of lithium by deuterons and its bearing on the mass of the neutron. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 550—552).—Experiments showing that γ -rays are not produced in the disintegration of Li by deuterons are described. Hence, previous calculations of the mass of the neutron are not invalidated by this assumption. The val. given for this mass is 1.0068. L. S. T.

Artificial radioactivity produced by deuteron bombardment. M. C. HENDERSON, M. S. LIVINGSTON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 428—429).—With the possible exception of C, no radioactivity was induced in Ca and in the elements from Li to Cl (Ne and S not included) by bombardment with 1.5×10^6 volt protons. With 3×10^6 volt deuterons, each element emitted both γ -radiation and ionising particles, presumably positrons, of approx. electronic mass. The half-lives of the radioelements produced in the following targets were: CaF₂ 40 sec., CaCl₂ 13 min., B₂O₃, Na phosphate, Li₂CO₃, and NH₄NO₃, approx. 2 min., Al 3 min., Mg 9 min., Be 9 min. and possibly 3 min., and C 12 min. L. S. T.

Further experiments with artificially-produced radioactive substances. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 497—498).—When bombarded by protons, C and B₂O₃ show an activity which decays at the same rate as that produced by deuterons (see below). The intensities are approx. 10 and 20%, respectively, of those produced by deuterons. Alternative reactions are discussed. After deuteron bombardment of B₂O₃ the active material appears to be a gas which rapidly diffuses from the target. It is concluded that most of the C¹¹, assumed to be the radio-element formed, exists in the target as CO or CO₂ and little, if any, as C. L. S. T.

Disintegration of boron by deuterons and by protons. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 493—495; cf. A., 1934, 579).—The radiation obtained from B bombarded with a mixed beam of deuterons and protons has been analysed. In addition to neutrons there is a large component of γ -radiation of energy 1.6×10^6 e.v. The γ -rays are probably associated with the same transformation which produces the neutrons. This is assumed to be $B^{11} + H^2 \rightarrow C^{12} + n^1 + \gamma$, and the val. 1.6×10^6 e.v. probably corresponds with an excitation level in C^{12} . L. S. T.

γ -Rays from carbon bombarded by deuterons. C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 45, 345—346; cf. A., 1934, 579).

L. S. T.

Radioactivity from carbon and boron oxide bombarded with deuterons and the conversion of positrons into radiation. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 430—432).—Additional data (cf. A., 1934, 579) are recorded and evidence for the assumption that the γ -rays originate from the annihilation of positrons together with electrons is advanced. C appears to be transformed by deuterons in two ways: ${}_6C^{12} + {}_1H^2 \rightarrow {}_6C^{13} + {}_1H^1 + \gamma$, ${}_6C^{12} + {}_1H^2 \rightarrow {}_7N^{13} + {}_0n^1$ and ${}_7N^{13} \rightarrow {}_6C^{13} + (+\epsilon)$. The first process is 10 times as frequent as the second. With B the supposed transformations are ${}_5B^{10} + {}_1H^2 \rightarrow {}_6C^{11} + {}_0n^1$ and ${}_6C^{11} \rightarrow {}_5B^{11} + (+\epsilon)$.

L. S. T.

Investigation of nuclear disruption of aluminium by the photographic method. M. BLAU and H. WAMBACHER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 401—410; Chem. Zentr., 1935, i, 1658).—Investigation by the photographic method confirmed the presence of particle groups found by Chadwick and Constable, and revealed a new group of range 35—50 cm. J. S. A.

Secondary emission from elements of medium mol. wt. under action of radiation from Po+Be. Z. OLLANO (Ric. sci. Prog. tec. Econ. naz., 1934, 2, 374—376; Chem. Zentr., 1935, i, 1821).—Heavy elements, except Sn and Sb, have a relatively lower absorption per mol. than light elements toward radiation from Po+Be. Sn emits soft radiation of great energy. J. S. A.

Nuclear evolution of iron, cobalt, and nickel. H. J. WATKES (Phil. Mag., 1935, [vii], 20, 738—739; cf. this vol., 427).—The isotopes ${}_{26}Fe^{58}$ and ${}_{26}Fe^{59}$ are missing, and ${}_{26}Fe^{57}$ and ${}_{28}Ni^{58}$ are stable. The schemes proposed are: ${}_{26}Fe^{58} \rightarrow \beta \rightarrow {}_{27}Co^{58} \rightarrow \beta \rightarrow {}_{28}Ni^{58}$, and ${}_{26}Fe^{59} \rightarrow \beta \rightarrow {}_{27}Co^{59}$. N. M. B.

Atomic fragment of short range from heavy inert gases. H. PETTERSSON and J. SCHINTLMEISTER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 385—399; Chem. Zentr., 1935, i, 1657—1658).—Investigation of very short-range particles by means of a tube electrometer reveals the presence of such particles in addition to elastically scattered α -particles from Xe and Kr but not from Ni or I. J. S. A.

Corpuscular theory of primary cosmic radiation. W. F. G. SWANN (Physical Rev., 1935, [ii],

48, 641—648).—A survey co-ordinating available data and theory. N. M. B.

Effect of primary cosmic-ray energy on burst production. W. F. G. SWANN and D. B. COWIE (Physical Rev., 1935, [ii], 48, 649—652).—The intensity of burst-production was much greater for vertical rays than for rays limited to a direction of 45° , in agreement with the corresponding increase with altitude as compared with ray intensity. N. M. B.

Diurnal variation of cosmic-ray intensity and *Nova Herculis*. J. BARNÓTHY and M. FORRÓ (Nature, 1935, 136, 680—681). L. S. T.

Positive and negative ions in the primary cosmic radiation. H. J. WATKES (Nature, 1935, 136, 681).—Since equal nos. of positive and negative ions probably occur in the cosmic rays, the observed east-west asymmetry of cosmic radiation must be explained in terms other than those of an unbalanced positive component. L. S. T.

Vertical intensity of cosmic rays by threefold coincidences in the stratosphere. E. REGENER and G. PROTZER (Nature, 1935, 136, 718—719). L. S. T.

Neutrons of high energy from cosmic-ray bursts in aluminium. G. L. LOCHER (Physical Rev., 1934, [ii], 45, 235; cf. A., 1934, 235). L. S. T.

Secondary photons in cosmic-ray showers. C. D. ANDERSON and S. H. NEDDERMEYER (Physical Rev., 1934, [ii], 45, 295). L. S. T.

Possible explanation of the frequency distribution of the size of Hoffmann Stösse. C. G. MONTGOMERY (Physical Rev., 1934, [ii], 45, 294). L. S. T.

Further geographic studies of cosmic rays. A. H. COMPTON, J. M. BENADE, and P. G. LEDIG (Physical Rev., 1934, [ii], 45, 294—295). L. S. T.

Comparison of absorption coefficients of different elements for cosmic rays. J. C. STEARNS and C. HEDBERG (Physical Rev., 1934, [ii], 45, 294).—The cosmic-ray energy absorbed by 6 in. of Al, Cu, Pb, and Zn, respectively, has been determined. L. S. T.

Hypothesis of the instability of the deuteron. G. N. LEWIS, M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 497).—An alternative explanation for previous results (A., 1934, 471) is discussed. L. S. T.

Excitation and disintegration of protons and the neutret. R. M. LANGER (Physical Rev., 1934, [ii], 45, 495—496).—Theoretical. L. S. T.

Emission of fast particles. K. C. KAR (Current Sci., 1935, 4, 154—155).—A modification of the wave-statistical formula for the emission of fast particles from radioactive elements is proposed. W. R. A.

Collisions of very fast heavy particles. W. BRAUNBEK (Z. Physik, 1935, 96, 600—606).—Theoretical. A. B. D. C.

Theory of elementary particles. II. Electromagnetic whirls and elementary particles. N. S. JAPOLSKY (Phil. Mag., 1935, [vii], 20, 641—706; cf.

ibid., 417).—Mathematical. It is suggested that the elementary particles electrons, protons, positrons, light quanta, etc. can be considered as "whirls" or certain systems of Maxwell electromagnetic waves. In this way the quantum and relativity relationships, the de Broglie formula, and gravitation can be explained on classical electrodynamics. The theory leads to a proton-electron mass ratio agreeing with experiment. N. M. B.

Ionising effects of meteors. A. M. SKELLETT (*Proc. Inst. Radio Eng.*, 1935, 23, 132—149).—A meteor of average velocity has sufficient velocity to cause ionisation of atm. gases by impact. CH. ABS. (e)

Nuclear energies of aluminium and beryllium. H. A. WILSON (*Physical Rev.*, 1934, [ii], 45, 430).—Bombardment data for Al and Be indicate that the nuclei of the atoms of the elements have possible energies equal to $3.85n$ or $3.85n + a \text{ const.}$, where n is 0 or an integer. L. S. T.

Energy levels of inert gas configurations. C. L. BARTBERGER (*Physical Rev.*, 1935, [ii], 48, 682—683).—A more accurate calculation of the energy levels for the configuration n^2p^2np is made (cf. Shortley, A., 1933, 1226; this vol., 556), taking account of the electrostatic interaction between groups. N. M. B.

Values of Planck's constant. K. SHIBA (*Bull. Inst. Phys. Chem. Res. Japan*, 1935, 14, 897—908).—The most probable vals. of e , e/m , and h are recalculated to be (cf. A., 1933, 884) $(4.8032 \pm 0.02\%) \times 10^{-10}$ e.s.u., $(1.7582 \pm 0.02\%) \times 10^7$ e.m.u., and $(6.6271 \pm 0.04\%) \times 10^{-27}$ erg/sec., respectively. R. S. B.

Field between an α -particle and an atomic nucleus. L. SCHAMES (*Arch. Sci. phys. nat.*, 1935, [v], 17, Suppl., 102—103).—Mathematical. The field is expressed in terms of the mass and radius of the neutron and the elementary charge. Up to a distance of 3×10^{-13} cm. the difference between the fields of H and of D is calc. to be negligible, in accordance with experiment. S. J. G.

Fundamental difference between material mass and electromagnetic mass. L. SCHAMES (*Arch. Sci. phys. nat.*, 1935, [v], 17, Suppl., 103—104).—The mass of both positron and electron is electromagnetic and is annihilated when the two particles collide. The mass of the neutron is material and cannot be destroyed, but obeys the law of conservation of mass. S. J. G.

Bands in the neighbourhood of spectral lines in the ultra-violet. F. DUSCHINSKY (*Compt. rend.*, 1935, 201, 542—543).—Bands described by Hulubei (A., 1931, 993) are due to interference. T. G. P.

Green flame of phosphorus hydride. E. B. LUDLAM (*J. Chem. Physics*, 1935, 3, 617—620).—The spectrum of the green flame of burning P has been photographed. The moment of inertia of the emitter calc. from the rotational structure of the bands ($\Sigma-\Sigma$) indicates that it is PH. T. G. P.

Absorption spectra of solutions in liquid ammonia. I. Solutions of metallic complex salts. H. SHIBA and T. INOUE (*J. Chem. Soc.*

Japan, 1935, 56, 213—220).—Solutions of complex salts of Co, Ni, and Cr in liquid NH_3 show absorption bands similar to those in aq. solution. CH. ABS. (e)

Ultra-violet absorption and colour centre formation of alkali halide crystals. E. REXER (*Physikal. Z.*, 1935, 36, 602).—Pressure-deformation of pure KBr with 800 g. per sq. mm. raises the absorption coeff. at 203 $\text{m}\mu$ from 0.250 to 0.750 mm^{-1} . A. B. D. C.

Spectra of strontium hydride. W. R. FREDERICKSON, M. E. HOGAN, jun., and W. W. WATSON (*Physical Rev.*, 1935, [ii], 48, 602—606).—Full data and quantum analyses of the SrH band systems, photographed at high dispersion, are reported. N. M. B.

Emission band spectrum of the OD molecule. Y. OTA (*Mem. Fac. Sci. Agric. Taihoku*, 1935, 15, 181—191).—The spectrum excited by an electrical discharge through H_2O vapour containing 65% of combined D was photographed, and full data for the (0,0) OD band of the $2\Sigma^+ \rightarrow 2\Pi$ transition are tabulated. From the relative intensity of lines in the P_1 , P_2 , Q_1 , and Q_2 branches the nature of the abnormal rotation of the excited OD mol. is discussed in comparison with the corresponding OH band. N. M. B.

Absorption spectra of iodine solutions and the influence of the solvent. O. J. WALKER (*Trans. Faraday Soc.*, 1935, 31, 1432—1438).—The mol. extinction coeff. for violet solutions of I in eight chlorinated hydrocarbons has been measured. In non-polar solvents λ_{max} is at 516—518 $\text{m}\mu$, and in others is displaced towards shorter λ to an extent which increases with the dipole moment. The types of interaction between I and the solvent are discussed. F. L. U.

Absorption spectrum of Eu^{+++} in crystalline $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. E. J. MIEHAN (*J. Chem. Physics*, 1935, 3, 621—627; cf. Spedding *et al.*, this vol., 144).—The absorption has been studied from 14° to 290° abs. Variations in intensity with temp. establish levels 21 cm^{-1} and 41 cm^{-1} above the basic one, and indicate others of 67 cm^{-1} , 86 cm^{-1} , and higher levels. Unusual const. energy differences exist between lines at the lowest temp. T. G. P.

Absorption spectrum of selenium dioxide. L. BLOCH, E. BLOCH, and C. S. PIAW (*Compt. rend.*, 1935, 201, 654—655).—A series of absorption bands, degraded to the red, was observed at λ 2400—3200 Å. in the vapour of SeO_2 heated in vac. to 250°. With rise in temp. other bands were observed at approx. λ 3700—4300 Å. H. J. E.

Optical absorption and double linking. V. Absorption at low temperatures of compounds with conjugated doubly-linked carbon atoms. K. W. HAUSER, R. KUHN, and G. SEITZ. VI. **Fluorescence of diphenylpolyenes.** K. W. HAUSER, R. KUHN, and E. KUHN (*Z. physikal. Chem.*, 1935, B, 29, 391—416, 417—454; cf. this vol., 1300).—V. The position of the absorption bands of the diphenylpolyenes (I), polyenecarboxylic acids, and lycopene in solution at -196° is given by $\nu = (\nu_0 + 37.0l + 47.1m) \times 10^{12} \text{ sec}^{-1}$, where l , $m =$

0, 1, 2. . . (I) have other bands at shorter λ , which are similar to bands of Ph_2 in position and structure and are attributed to the Ph groups; the height of the max. do not vary with the no. of C:C linkings. The spectra of diphenylacetylenes differ in type from those of (I). Fundamentally the spectra of the porphyrins are similar to those of the aliphatic polyenes, but on these bands other vibrations are superimposed.

VI. The absorption and fluorescence spectra of the diphenylpolyenes, $\text{Ph} \cdot [\text{CH}:\text{CH}]_n \cdot \text{Ph}$, are in the relation of object to mirror image in respect of the position, but not of the height, of the bands. With increase in n the fluorescence bands shift more than the absorption bands and the heights of the max. fall. At -196° the positions of the fluorescence bands are given by ν (cm^{-1}) $= \nu_0 - 1550\nu_1'' - 1160\nu_2''$, where ν_0 is the position of the band of shortest λ and ν_1'' , $\nu_2'' = 0, 1, 2, 3, \dots$. The band separations 1550 and 1160 cm^{-1} correspond with the strongest lines in the Raman spectra and represent frequencies of the C:C linking. The variation of fluorescence with concn., solvent, temp., and state of aggregation agrees with the theory of quenching collisions (cf. A., 1925, ii, 474). The fluorescence of dodecapentanoic acid and isomethylbixin proves that ring closure is not essential for fluorescence; they have almost the same fluorescence spectra. R. C.

Optical absorption of porphyrins. II. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1935, 174, 81—103; cf. this vol., 10).—Absorption in dioxan solution has been determined. Comparison of the absorption spectra of porphyrins with those of the corresponding chlorins supports the view that in the latter the porphin framework has changed into a dihydroporphin (cf. *ibid.*, 871). Substances with a structure based on dihydroporphin, such as chlorins, pyrophæophorbide-*a*, and methylphæophorbide-*a*, have very similar visible absorption spectra. Uroporphyrin Petry, uroporphyrin Pteris, and Me_8 1:3:5:7-tetramethylporphin-2:4:6:8-tetrasuccinate are spectroscopically identical. The absorption curve of hæmin solution has been determined. R. C.

Absorption spectra of tervalent halides dissolved in ether and their dissociation products. S. KATO and F. SOMENO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 95—111).—The absorption spectra in range 2000—7000 Å. of solutions of trihalides of As, Sb, Bi, Fe, and Tl in Et_2O , and of the vapours of As, Sb, and Bi trihalides, have been determined. The Raman spectra of AsCl_3 , AsBr_3 , and SbCl_3 in Et_2O are similar to the spectra with the liquid salts, but differ from those with the crystals. Photo-dissociation with light from a Hg-vapour lamp or C arc has been studied chemically, the products being lower halides or metal, except with AsI_3 (As_2O_3), SbI_3 (SbOI), and BiI_3 (BiOI). The mols. of salt in Et_2O are in the ground state, but are deformed by the solvent. R. S. B.

Ultra-violet absorption spectra of certain compounds derived from living cells. F. F. HEYROTH and J. R. LOOFBOUROW (Physical Rev., 1934, [ii], 45, 126; cf. A., 1934, 1112). L. S. T.

Two new bands of CO_2 in the photographic infra-red. G. HERZBERG and H. VERLEGER (Physical Rev., 1935, [ii], 48, 706).—New bands at 1.2031 and 1.2178 μ , showing fine structure, have been photographed. Results agree with the predictions of Adel (cf. A., 1933, 661, 885). N. M. B.

Rotation spectra of ammonia and ND_3 . R. B. BARNES, W. S. BENEDICT, and C. M. LEWIS (Physical Rev., 1934, [ii], 45, 347; cf. this vol., 806). L. S. T.

Absorption spectra, in the near infra-red, of amines and amides. Use of the phenomenon of "dissimulation" in studying amphoteric ions. Influence of neighbouring groups. (MME.) M. FREYMAN and P. RUMPF (Compt. rend., 1935, 201, 606—608; cf. this vol., 563).—The NH absorption band at approx. 1.04 μ is not observed in a 20% aq. solution of glycine, or in saturated aq. taurine, but is observed in solutions of the Na and Li salts, respectively. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ does not show the band, but its Na derivative does. N has a co-ordination no. of 4 when the band is not observed. Data for the position of this NH band in various amides are recorded. The structure of these compounds is discussed. H. J. E.

Absorption of simple substituted hydrocarbons in the near infra-red. I. Influence of state of aggregation. (Gas-liquid comparison.) R. MECKE and O. VIERLING (Z. Physik, 1935, 96, 559—570).—Absorption spectra of the third CH overtone were obtained for MeCl, MeBr, EtCl, vinyl chloride, and $(\text{CH}_3)_2\text{O}$ in the gas and liquid phases, and data are summarised for $n\text{-C}_6\text{H}_{14}$, cyclo-hexane and hexanol, C_6H_6 , and dioxan. Condensation to the liquid state always lowers the frequency of vibration in a series of overtones by the amount $\Delta\nu$, where $\Delta\nu/\nu$ is a const. Closure of a ring also decreases the frequency, as does an increase in ring size. A. B. D. C.

Infra-red spectrum of hexadeutero benzene and the structure of benzene. W. R. ANGUS, C. R. BAILEY, C. K. INGOLD, A. H. LECKIE, C. G. RAISIN, J. W. THOMPSON, and C. L. WILSON (Nature, 1935, 136, 680; cf. this vol., 914).—The principal frequencies of the infra-red spectra of C_6D_6 and C_6H_6 are compared. The new measurements for C_6D_6 agree, on the whole, with those of Barnes and Brattain (this vol., 1189). Coincidences between certain frequencies of the Raman and infra-red spectra of C_6H_6 and of C_6D_6 , which led to the rejection of the plane hexagonally symmetrical C_6H_6 model, are now regarded as accidental; the model is retained. L. S. T.

Structure and interpretation of the infra-red absorption spectra of crystals. R. B. BARNES, R. R. BRATTAIN, and F. SEITZ (Physical Rev., 1935, [ii], 48, 582—602).—A detailed investigation of the absorption spectrum of MgO in the near infra-red is reported; the fundamental absorption is accompanied by much secondary structure. Results are interpreted on the basis of a quantum-mechanical treatment of anharmonic potential forces, and show that the absorption spectra of a MgO-type cubic crystal should have a very complicated secondary structure. N. M. B.

Infra-red absorption by Rochelle salt crystals. J. VALASEK (Physical Rev., 1934, [ii], 45, 654—655).—Optical measurements indicate that the unusually large ϵ of these crystals is not due to the polarisation of the H_2O mols. L. S. T.

Rayleigh scattering in crystals. F. MATOSI (Z. Physik, 1935, 96, 698).—Corrections (cf. this vol., 146). A. B. D. C.

Doppler effect in light scattering in liquids. II. Polarisation of the transversely scattered radiations. B. V. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 236—241; cf. this vol., 1053).—For light scattered transversely by CCl_4 , PhMe, and CS_2 , the two Doppler components are completely polarised, and the central component is almost completely polarised. N. M. B.

Bibliography of the Raman effect. III. S. C. SIKKAR and D. CHAKRAVARTY (Indian J. Physics, 1935, 9, 553—622; cf. A., 1933, 445).—A complete list of papers classified under subject headings, authors, and substances studied is given. N. M. B.

Intensity of Raman effect. A. CARELLI (Rend. Accad. Sci. Napoli, 1933, [iv], 3, 156—160; Chem. Zentr., 1935, i, 1827).—The ratio of intensity of the Raman line of CCl_4 , $\Delta\nu$ 1550 cm^{-1} , to its first overtone is 1 : 10. An explanation is advanced. J. S. A.

Raman spectrum of (A) deuterium and (B) hydrogen deuteride. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 303—309, 310—312).—(A) Using the λ 4358 Hg line as incident radiation, and 17 atm. pressure, rotation lines ± 179.5 , ± 297.4 , 415.2, 530.8, and 643.5 cm^{-1} , and a vibration line of shift 2992.7 were observed. Results agree with available mol. const. data. Relative rotational intensities agree with a nucleus of one unit spin and obeying the Bose-Einstein statistics. Intensity distribution agrees qualitatively with the theory of rotational Raman scattering in diat. mols.

(B) With λ 4358, HD showed a spectrum containing 267, 442, and 618 cm^{-1} , arising respectively from the rotational transitions $0 \rightarrow 2$, $1 \rightarrow 3$, and $2 \rightarrow 4$, and agreeing with calc. vals. The anti-Stokes line due to the transition $2 \rightarrow 0$ was found. Alternating intensities were not observed, and the line corresponding with $1 \rightarrow 3$ is the most intense. N. M. B.

Raman spectrum of heavy water. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 291—302).—The spectrum shows a strong band with three imperfectly resolved components of frequency shifts 2363, 2515, and 2662 cm^{-1} , and a sharp band with frequency shift 1235 cm^{-1} with a feeble companion at about 1110 cm^{-1} , and a strong low-frequency band 175 cm^{-1} . Comparison of H_2O and D_2O spectra shows many similarities. The valency angles and force consts. do not alter much in passing from H_2O to D_2O . The triple structure of the principal band indicates polymerisation similarly to H_2O . The low-frequency band is connected with the nature of the liquid state. N. M. B.

Raman spectrum of liquid heavy water. E. BAUER and M. MAGAT (Compt. rend., 1935, 201,

667—669).—The Raman shifts observed for D_2O were 170, 350, approx. 500, 1207, 2389, and 2509 cm^{-1} , the corresponding vals. for H_2O being 176, 500, 700, 1659, 3221, and 3435 cm^{-1} . H. J. E.

Constitution of water in solutions of non-electrolytes. I. Acetone. C. S. S. RAO (Phil. Mag., 1935, [vii], 20, 587—594; cf. this vol., 295).—The intensity distribution along the Raman H_2O band was investigated in solutions of 0, 25, 50, and 75% $\text{C}_2\text{H}_5\text{O}$. The band becomes sharper with increasing concn. of dissolved substance; the intensity max. does not shift with change of concn. as in the case of strong and weak electrolytes; the smaller frequency branch of the intensity curve shifts and changes in shape with increasing concn. of $\text{C}_2\text{H}_5\text{O}$. Results indicate a preponderance of double H_2O mols. and double hydrates over the other types, especially at high concns. of the dissolved substance. N. M. B.

Molecular clustering in binary liquid mixtures. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 221—231; cf. this vol., 11).—A comparative study of the intensity, by the photo-electric method, and the depolarisation of light scattered transversely by mixtures of PhOH and H_2O in different proportions and at different temp. was made. The lowest vals. for the depolarisations of light unpolarised, and perpendicularly and horizontally polarised, were found with the crit. composition mixture (34% PhOH) at the crit. solution temp. The intensity of scattering increases considerably for the 34% mixture as the crit. temp. is approached. The tendency for the formation of, and size of, clusters depend on the temp. and composition of the mixture. These phenomena are most pronounced for the crit. mixture at the crit. temp. The relation of results to anomalies of viscosity, magnetic birefringence, etc. is examined. N. M. B.

Raman spectrum of phosphorus. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 260—264).—Data for solid, liquid, vapour, and solution in CS_2 are given. Only small changes in frequency are found in passing from one state to another, indicating the non-polar character of the mol. In all cases a strong fluorescence band extends from 6230 to 6550 Å. N. M. B.

Raman spectra of heavy and light phosphine. M. DE HEMPTINNE and J. M. DELFOSSE (Bull. Acad. roy. Belg., 1935, [v], 21, 793—799).—The Raman spectra of PH_3 and PD_3 in the liquid and solid state have been investigated. Liquid PD_3 gave lines 1664, 807, and 740 cm^{-1} . The most intense lines are: PH_3 (liq.) 2306, (gas) 2327; PD_3 (liq.) 1664, (gas) 1684; PHD_2 1825; PDH_2 1755 cm^{-1} . A. J. M.

Raman spectrum of nitrogen pentoxide. J. CHÉDIN (Compt. rend., 1935, 201, 552—554).—Raman spectra of N_2O_5 in HNO_3 , H_2SO_4 , CCl_4 , and CHCl_3 are recorded. T. G. P.

Raman spectrum and constitution of fuming sulphuric acid. N. G. PAI (Phil. Mag., 1935, [vii], 20, 616—623).—Raman data obtained for four concns. of fuming H_2SO_4 indicate that at low concn. all the SO_3 mols. go into combination, forming $\text{H}_2\text{S}_2\text{O}_7$, and the H_2SO_4 lines weaken in intensity;

at higher concn. much free SO_3 and S_2O_6 are present; in 71% acid their relative proportions are approx. as in a SO_3 - S_2O_6 mixture in equilibrium; in 80% acid a small concn. of free H_2SO_4 mols. exists.

N. M. B.

Influence of intermolecular action on the Raman effect for liquids. W. BUCHHEIM (Physikal. Z., 1935, 36, 694—711).—The theoretical effect of an electric field on Raman scattering is considered. The Raman lines should increase in width with increasing field strength, owing to alteration of mol. vibrations by the effect on the electron charge cloud. A displacement of the lines is also to be expected. Lines forbidden by mol. symmetry may appear on application of a field. The widening of the lines due to infra-red active vibrations by electrodynamic interaction is considered. The variation in intensity of the Raman spectrum of a substance on mixing with another was investigated in the following cases: C_6H_6 mixed with C_6H_{14} and with CHCl_3 ; CCl_4 in COme_2 mixed with C_6H_6 ; CHCl_3 in C_6H_6 mixed with C_6H_{14} .

A. J. M.

Raman spectra of methyl deuteride. G. E. MACWOOD and H. C. UREY (J. Chem. Physics, 1935, 3, 650—651).—Vibrational frequencies of MeD in the Raman spectra have been measured. They are higher (max. +30 cm^{-1}) than those calc. by Dennison and Johnston (Physical Rev., 1935, [ii], 47, 93). No rotational structure was observed.

T. G. P.

Raman spectrum of neopentyl deuteride. D. H. RANK, E. R. BORDNER, and K. D. LARSEN (Physical Rev., 1934, [ii], 45, 566).—The results show that the vibrational degeneracy of the neopentane mol. is partly removed by the substitution of a D for a H. The C-D vibration becomes evident through the appearance of a line at 2179 cm^{-1} .

L. S. T.

Raman spectra of dioxan and tetralin. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 279—290).—Full data, obtained with the filters used, are tabulated. The spectrum of dioxan consists of 24 lines, 14 being new, and closely resembles that of *cyclohexane*. Tetralin gave 11 new lines. Results are discussed with reference to mol. structure.

N. M. B.

Raman spectra of *cis*- and *trans*-decalins. S. K. K. JATKAR (Indian J. Physics, 1935, 9, 545—551).—Using a sample containing 36% of *cis*-form prepared by fractional distillation, and a sample containing mostly *trans*-form prepared by keeping ordinary decalin in contact with AlCl_3 for 24 hr., Raman data are tabulated, and results are discussed in relation to mol. structure.

N. M. B.

Chemical reactivity and Raman spectra of the eugenols, vanillins, and safoles, and of piperonal, estragol, and anethole. B. SUSZ, E. PERROTTET, and E. BRINER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 133—134).—The oxidation of the above compounds by O_3 has been studied and their Raman spectra have been determined. All show the characteristic frequencies of the C_6H_6 nucleus, and C=O and C=C linkings where present.

S. J. G.

Raman spectra of solutions of pyrogallol, gallic acid, and tannin. E. BRINER, S. FRIED, and B. SUSZ (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 178—180).—Raman frequencies of pyrogallol and of gallic acid in EtOH solution and of tannin in aq. solution are recorded.

S. J. G.

Coloration of compounds of different elements by cathode rays. H. NAGAOKA and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 77—94).—The intensity of the coloration produced when cathode rays of 0—10⁴ volts impinge on various metallic salts has been determined. It is inferred that the colours are due to dissociation of mols. near the surface, the metallic atoms produced being protected by a surface layer of undissociated salt.

R. S. B.

Phosphorescent beryllium nitride. S. SATOH (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 920—924).—Phosphorescent Be_3N_2 , activated by Al, gives a cathode-ray spectrum with a continuous band at 4200—4900 Å., max. at 4650 Å.

R. S. B.

Fluorescence in *cyclohexane*. R. PADMANABHAN (Proc. Indian Acad. Sci., 1935, 2, A, 209—212).—Using an improved continuous distillation apparatus, pure *cyclohexane* has no fluorescence; that reported by Haberl (cf. this vol., 11) is due to photochemical decomp. in which the region λ 2400—2600 is active.

N. M. B.

Comparison of effect of ordinary and *geno*-alkaloids on the fluorescence of uranine solutions. C. ACHARD, A. BOUTARIC, and J. BOUCHARD (Compt. rend., 1935, 201, 629—631).—The *geno*-alkaloids (e.g., *geno*-strychnine hydrobromide) do not inhibit the fluorescence of aq. uranine in the same way as the normal alkaloid.

H. J. E.

Spray electrification of liquids. S. CHAPMAN (Physical Rev., 1934, [ii], 45, 135—136).—Data correlating drop size, sign and magnitude of the charge, γ , and ϵ are given for H_2O , glycerol, NH_2Ph , PhNO_2 , and "ameroil." In general, larger drops (4 — 5×10^{-4} cm. radius) have the greater charges, and the greater is ϵ the higher is the charge val.

L. S. T.

Contact potential difference between clean and oxygenated tungsten. A. L. REIMANN (Phil. Mag., 1935, [vii], 20, 594—607).—The contact p.d. at room temp. between slightly electronegatively contaminated W and W when O_2 -covered, for most effectively raising the work function was 1.70 volts. The calc. p.d. at 1500° abs. between clean W and W less effectively O_2 -covered than above is 1.75 volts. Loss of electronegateness of oxygenated W by evaporation of O_2 was detected at 1300° abs., and beyond this the rate of evaporation increased rapidly with rise of temp. A clean W surface oxygenated when hot or cold showed no difference in electronegateness or volatility of O_2 . The most complete O_2 -covering (of the degrees of covering stable in vac.) most effectively raises the work function.

N. M. B.

Photo-electric properties and electrical resistance of metallic films. D. ROLLER and D. WOOLDRIDGE (Physical Rev., 1934, [ii], 45, 119—120).—As the average thickness of a Cd film decreases, the electrical resistivity increases from the val. charac-

teristic of the metal in bulk at first slowly and then more rapidly, until just beyond a crit. thickness it rapidly approaches an infinite val. L. S. T.

Photosensitive layers of the photo-electric conductive thallium cell. (MRS) C. ASAI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 797—832).—Heating of a film of Tl in air yields Tl_2O , Tl_2O_3 , etc. Distillation of Tl_2S gives the amorphous or cryst. form according to conditions of distillation, the former being converted into the latter by annealing. The photo-electric sensitivity is high when Tl_2O and Tl are disseminated in cryst. Tl_2S , so the conductivity is explicable on the impurity theory of semiconductors. J. W. S.

Spectral photo-electric poly-selectivity of various surface layers. W. KLUGE (Z. Physik, 1935, 96, 691—697).—Decrease in sensitivity due to adsorption of O_2 has been studied at λ from 200 to 1100 $m\mu$ for the layers $Ag-Cs_2O-Cs$, $Cu-Cs_2O-Cs$, and Cs . A. B. D. C.

Dielectric loss in electrolytic barrier layers at high field intensities to 10^7 volts per cm. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1935, 96, 686—690).—The loss angle for Al_2O_3 is 0.02, and for Ta_2O_5 is 0.075, both at 50 cycles; its variation with time of measurement, formation voltage, field intensity, time of formation, age, and frequency is also given. A. B. D. C.

Measurement of the variation of the dielectric constant of water with extent of adsorption. G. H. ARGUE and O. MAASS (Canad. J. Res., 1935, 13, B, 156—166).—Apparatus and technique for determining the dielectric const. of cellulose containing various amounts of adsorbed H_2O are described. Dielectric const. of the adsorbed H_2O have been calc. for the concn. range 0—18%. The dielectric const. of H_2O initially adsorbed is > 0.25 of that of liquid H_2O , but increases with increasing amount of adsorption until it approximates to that of liquid H_2O as the fibre becomes saturated. E. S. H.

Structure of the naphthalene nucleus. N. NAKATA (Bull. Chem. Soc. Japan, 1935, 10, 318—323; cf. A., 1931, 1281).—Dipole moments of a no. of $C_{10}H_8$ derivatives are given. Only the α -positions appear to be aromatic, and centrosymmetry is indicated. R. S.

Dipole moment of tetralin. M. A. G. RAO and S. S. RAO (Proc. Indian Acad. Sci., 1925, 2, A, 232—235).—The val. as measured in C_6H_6 as solvent is $0.4-0.5 \times 10^{-18}$. N. M. B.

Physical chemistry of betaines and related substances. I. Dielectric constants and apparent molal volume. J. T. EDSALL and J. WYMAN, jun. (J. Amer. Chem. Soc., 1935, 57, 1964—1975).—Data are recorded for betaines and for *N*-dimethylantranilic acid (I) and its Me ester (II) in H_2O , $EtOH$, C_6H_6 , and their mixtures. Approx. dipole moments have been calc. for the relatively rigid benzbetaines. In solvents of low dielectric const., the dielectric increments (and probably the moments) of all the betaines studied are much $<$ their vals. in H_2O , an effect which appears to be

due to deformation rather than association. (I) exists largely as a zwitterion in all the solvents; in C_6H_6 its dipole moment is 3 times that of (II). The electrostriction of the solvent produced by betaines in H_2O is $<$ that produced by similar NH_2 -acids; the electrostriction in solvents of low dielectric const. is much $>$ in H_2O . E. S. H.

Electric moments of organic compounds. J. N. PEARCE and L. F. BERHENKE (J. Physical Chem., 1935, 39, 1005—1010).—The dielectric const. and d of dil. solutions of *p*-bromo-, *p*-hydroxy-, and *p*-methoxy-benzaldehyde, *p*-tolualdehyde, β -ethylhexan- α -ol, α -ethylhexaldehyde, tri-, di-, and mono-hydroxyethylamine in C_6H_6 and dioxan have been determined at 25°. The total polarisation and dipole moments have been calc. E. S. H.

Constitution of [alkyl] polysulphides. I and II. S. BEZZI (Gazzetta, 1935, 65, 693—703, 704—723).—I. Measurements of d , b.p., refractive index, and of mol. wt. in C_6H_6 have been made for Et, Pr, Bu, and isohexoyl mercaptides, sulphides, disulphides, and tetrasulphides. The at. refraction of S increases from 7.95 in the mercaptides to 8.76 in the tetrasulphides.

II. Viscosity measurements for the above-mentioned substances are recorded. The viscosity of the pure substances is a function of the mol. wt., and is independent of the constitution. From the viscosities of dil. solutions of these substances in $CHCl_3$ and in Et_2O it is shown that the length of the mol. is the same (for a given alkyl radical) in the mono-, di-, and tetra-sulphides, and that, therefore, chains of S atoms are not present. O. J. W.

Behaviour [rotation] of benzylamine tartrate in acetic acid. E. DARMOIS and I. PEYCHÈS (Bull. Soc. chim., 1935, [v], 2, 1656—1668).— $[\alpha]$ was determined, using Hg lines, for benzylamine tartrate (I) and tartaric acid (II) at different concns. in $AcOH$. $[\alpha]$ for the tartrate ion is independent of concn. for (II), but increases linearly with the (concn.) $^{1/3}$ for (I). The effect of the addition of H_2O on the val. of $[\alpha]$ is discussed. Vals. of electrical conductivity for solutions of (I) and NMe_4 tartrate in $AcOH$ and with added H_2O are also given. F. R. G.

Anomalous rotatory dispersion of *l*- β -pinene. I. R. PADMANABHAN and S. K. K. JATKAR (J. Indian Chem. Soc., 1935, 12, 518—526).—Tests on samples of purified β -pinene indicate that the anomaly in rotatory dispersion at about 2800 Å. is due to a closely associated impurity which is difficult to remove. The anomaly in the ultra-violet region is a characteristic of β -pinene. This is confirmed by the Raman spectra of the fractions on distillation. As there is no evidence of absorption in the region of anomaly, the latter is not due to a Cotton effect, but is attributable to a superposition effect caused by a second rotation of opposite sign and different dispersion. This second rotation is not due to induced dissymmetry of the semicyclic double linking, because camphene, of similar structure, has normal dispersion. J. W. S.

Magneto-optical rotation of uranyl salts. S. S. BHATNAGAR, P. L. KAPUR, and N. R. VERMA (J.

Indian Chem. Soc., 1935, 12, 514—518).—The mol. rotation of UO_2^{++} , determined from the magneto-optical rotations of $\text{UO}_2(\text{NO}_3)_2$ and UO_2Cl_2 solutions, is about -8 , whereas the val. from measurements on UO_2SO_4 solutions is about -11 , the difference being attributed to the formation of complexes between UO_2^{++} and H_2SO_4 . J. W. S.

Magnetic double refraction and light scattering in fused nitrates. V. N. THATTE (Proc. Indian Acad. Sci., 1935, 2, A, 244—248; cf. A., 1934, 942).—Data for $\text{Zn}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ are given. The calc. magnetic and optical anisotropies of the NO_3 are the same as for the NO_3 in HNO_3 and in cryst. nitrates. N. M. B.

Influence of substituents in bases and anions on the co-ordination number of a metal. VII. Influence of electric moment on the number of molecules of base fixed by a salt. A. ABLOV (Bull. Soc. chim., [v], 2, 1724—1736; cf. A., 1934, 755).—If the dipole moment of a negative group substituted in the *p*-position in NH_2Ph is $\approx 1.5 \times 10^{-18}$ it increases the no. of mols. of base co-ordinated by $(\text{CCl}_3\text{CO}_2)_2\text{Ni}$ and $(\text{CHCl}_2\text{CO}_2)_2\text{Ni}$, whilst the same group in the *o*-position has the reverse effect. The results are discussed with reference to the electrostatic theory of valency. J. W. S.

Concentration of H^3 and O^{18} in heavy water. W. BLEAKNEY and A. J. GOULD (Physical Rev., 1934, [ii], 45, 281—282).—Results obtained with heavy water containing 70—98% D show that the ratio $\text{H}^3 : \text{D}$ is < 1 in 10^5 . Hence, in ordinary H_2 the ratio $\text{H}^3 : \text{H}^1$ is probably < 1 in 5×10^8 . In O_2 obtained by electrolysis of nearly pure D_2O yielding 98% D_2 , no increase in the ratio $\text{O}^{18} : \text{O}^{16}$ was detected. L. S. T.

H^3 in heavy hydrogen. W. W. LOZIER, P. T. SMITH, and W. BLEAKNEY (Physical Rev., 1934, [ii], 45, 655).—Measurements with a more sensitive apparatus give an abundance ratio $\text{H}^3 : \text{D}$ of $5 : 10^6$ in 99% D_2 obtained by electrolysis of D_2O . The ratio $\text{H}^3 : \text{D}$ in natural H is probably $\approx 1 : 10^9$. L. S. T.

Stable hydrogen isotope of mass three. M. A. TUVE, L. R. HAFSTAD, and O. DAHL (Physical Rev., 1934, [ii], 45, 840—841).—Range measurements indicating H^3 nuclei from stable H^3 atoms present in the order of 1 in 10^6 in 98% D_2 are described. L. S. T.

Wandering of adsorbed atoms along the surface of solid bodies. A. GEHRTS (Z. tech. Phys., 1934, 15, 456—461; Chem. Zentr., 1935, i, 1344).—Activation and deactivation processes are interpreted in terms of Volmer's conception of atom wandering. J. S. A.

Affinity factors in molecular collisions. A. EUCKEN (Oesterr. Chem.-Ztg., 1935, 38, 162—166).—A lecture. F. L. U.

Calculation of vibrational isotope effect in polyatomic molecules by a perturbation method. E. B. WILSON, jun. (Physical Rev., 1934, [ii], 45, 427).—Mathematical. L. S. T.

Proper vibrations of heavy acetylene and ethylene halides. Y. MORINO and S. MIZUSHIMA

(Physikal. Z., 1935, 36, 600—602).—Assuming the C-H equilibrium separation 1.01 \AA . and the C-C 1.226 \AA ., together with two observed valency and deformation frequencies for C_2H_2 , frequencies are calc. for C_2HD , and C_2D_2 . Similar calculations are made for $\text{C}_2\text{H}_4\text{Cl}_2$ and $\text{C}_2\text{H}_4\text{Br}_2$, and compared with Raman displacements. A. B. D. C.

Analytical representation of the potentials of diatomic molecules and their determination from spectroscopic data. I. General theory. II. Application to CdH and N_2 . E. A. HYLLERAAS (Z. Physik, 1935, 96, 643—660, 661—668).—I. A general expression for the potential-nuclear separation curve is given; it includes those of Morse and of Rosen and Morse as particular cases, and is determined from D, $h\nu_e$, and rotation consts. An energy formula for vibrational levels is deduced.

II. The above formula is applied to the $^2\Sigma$ -state of CdH and gives excellent reproduction of Rydberg's curve (cf. A., 1932, 104). It also gives improved results for the $1^1\Sigma$ -state of N_2 . A. B. D. C.

Potential curve for diatomic homopolar molecules. Application to CdH and N_2 . E. A. HYLLERAAS (Physikal., 1935, 36, 599—600).—Preliminary notes (cf. preceding abstract). A. B. D. C.

(C·C)_{diam.} linking energy. H. GERSHINOWITZ (J. Physical Chem., 1935, 39, 1041).—A criticism (cf. this vol., 1058). E. S. H.

Moments of inertia and the shape of the ethylene molecule. R. M. BADGER (Physical Rev., 1934, [ii], 45, 648).—Available spectroscopical data agree with a plane symmetrical structure, and the moments of inertia calc. are 33.2×10^{-40} , 27.5×10^{-40} , and $5.70 \times 10^{-40} \text{ g. cm}^2$, respectively, in the ground state. Vals. for the C-C and C-H distances and for the angle between the C-H linkings consistent with these moments are 1.37 \AA ., 1.04 \AA ., and 126° , respectively. L. S. T.

Periodic unequal potential minima and torsion oscillation of molecules. T. Y. WU (Physical Rev., 1934, [ii], 45, 66—67).—The torsion oscillation of mols. of the *cis*- and *trans*-forms of $\text{C}_2\text{H}_2\text{Cl}_2$ is discussed. L. S. T.

Suggested improvements of Morse's rule. C. H. D. CLARK and J. L. STOVES (Nature, 1935, 136, 682).—The modification of Morse's rule previously suggested (A., 1934, 833) gives better approximations to experimental vals. than those of other workers (cf. this vol., 685). L. S. T.

Potential energy curves and structure of the alkaline-earth oxides. P. C. MAHANTI (Indian J. Physics, 1935, 9, 517—536).—Curves for the different electronic states of BeO, MgO, BaO, CaO, and SrO are drawn according to Morse's function. The electronic configuration, dissociation energy, and the products of dissociation in each state are discussed, and similarities in the spectra of the different members are traced. N. M. B.

Extra negative term in the incoherent part of the diffuse scattering of X-rays from neon-like crystals. G. E. M. JAUNCEY and J. H. DEMING

(Physical Rev., 1935, [ii], 48, 577—581; cf. A., 1934, 1148).—Measurements of the scattering vals. of NaF, MgO, and SiC at 295° abs. lead to results in good agreement with the Waller-Hartree theory of the extra negative term, and give evidence for the operation of the Pauli exclusion principle on the outer shell electrons. N. M. B.

Stress analysis by X-ray diffraction. C. S. BARRETT and M. GENSAMER (Physical Rev., 1934, [ii], 45, 563).—Mathematical. L. S. T.

Selective X-ray diffraction from artificially stratified metal films deposited by evaporation. J. W. M. DuMOND and J. P. YOUTZ (Physical Rev., 1935, [ii], 48, 703).—Stratified films deposited on glass consisting of 100 layers of Au alternating with 100 layers of Cu, and giving selective X-ray diffraction of Mo K radiation in the first order, have been produced. The total thickness is approx. 10,000 Å. and the "grating const." 100 Å. N. M. B.

Ultra-soft Röntgen radiation and lattice binding forces. H. BROILI, R. GLOCKER, and H. KLESSIG (Ergeb. Tech. Röntgen., 1934, 4, 94—99; Chem. Zentr., 1935, i, 1500).—The K α line of graphite differs from that of diamond in the distribution of intensity amongst its 4 components. The difference is attributed to the lattice forces, four homopolar linkings being present in diamond, and three homopolar and one very loose quasi-metallic linking in graphite. SiC resembles diamond, but the C line of Be carbide shows a typical heteropolar linking. The structure of the Be line indicates complete mobility of the conductivity electrons (electron gas state). J. S. A.

Precipitation-hardening and secondary structure. K. H. MOORE (Physical Rev., 1934, [ii], 45, 296).—A preliminary report on the use of polarised light in investigating a possible connexion between pptn.-hardening and the secondary or mosaic structure of crystals, with special reference to a Cu-Be (2.5% Be) alloy. L. S. T.

Bitter's powder patterns. K. J. SIXTUS (Physical Rev., 1934, [ii], 45, 565).—Three different types are distinguished in the Bitter powder patterns (A., 1932, 1077) of single crystals of Si-Fe (3.5% Si). The different directions of the patterns can be explained by the present theory of the magnetisation process. L. S. T.

Molecular field of liquids. J. WEIGLE (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 105—107).—Mathematical. An expression is derived on the assumption that a liquid has a pseudo-cryst. structure, one mol. being imagined fixed and the others arranged somewhat as in a crystal lattice blurred by thermal agitation. S. J. G.

Crystallisation of melts. III. J. MEYER and W. PROFF (Z. anorg. Chem., 1935, 224, 305—314; cf. this vol., 811).—Supercooling of H₂O and C₆H₆ is shown to depend on the presence of nuclei, the nature of the surface of the containing vessel, and purity. Distilled H₂O, filtered through collodion into a quartz vessel and covered with paraffin, was kept liquid at -33°. The growth of single crystals

of ice from the surface of supercooled H₂O into the air-free space above is discussed. T. G. P.

Sub-boundaries in a crystal grown by the Bridgman method. W. H. GEORGE (Nature, 1935, 136, 392).—A photomicrograph of a single crystal of Cu grown by the Bridgman method and etched with HNO₃ suggests that the crystal has broken down into a large no. of smaller ones, the outlines of which appear as curved lines. The markings are similar to the "sub-boundary" or "veined" structures observed in many metals. L. S. T.

Polymorphism from viewpoint of Röntgen investigation II. Polymorphism and atomic structure of elements. Polymorphism of inorganic compounds. H. STINTZING (Ergeb. tech. Röntgen., 1934, 4, 113—129; Chem. Zentr., 1935, j, 1814—1815).—Elements with crystal lattices other than cubic face- or body-centred, or hexagonal close-packed, and particularly those with lattices of low co-ordination no., are especially prone to polymorphism. Only elements for which $\log d/(n-1)$ is $<$ that for the inert gases exhibit polymorphism (d = interat. lattice distance and $n-1$ = principal quantum no. of the highest filled electron shell). Polymorphism in inorg. compounds is a constitutive property, and occurs only when one element is highly polymorphic, especially with O or S. J. S. A.

Stereochemistry of solid substances. W. BILTZ (Ber., 1935, 68, [A], 91—108).—A lecture. H. W.

Large artificial crystals of graphite. K. S. KRISHNAN (Physical Rev., 1934, [ii], 45, 115).—The crystal flakes composing the large artificial crystals prepared by Goetz *et al.* are not necessarily parallel to one another (cf. A., 1933, 1128). L. S. T.

Production of "colloidal single crystals." A. GOETZ (Physical Rev., 1934, [ii], 45, 282—283).—A reply to criticism (see above). L. S. T.

Attempts to produce relief patterns by the direct electrographic effect. E. WILCOX and P. H. CARR (Physical Rev., 1934, [ii], 45, 286).—Partial success in producing relief patterns by taking advantage of the direct electrographic effect, *i.e.* the partial inactivity in metallic surfaces towards corrosive vapours produced by exposure to cathode rays, is described. L. S. T.

X-Ray determination of the chemical composition of oxide-coated cathodes. W. P. JESSE (Physical Rev., 1934, [ii], 45, 563; cf. A., 1933, 345).—The changes which occur on heating mixtures of BaCO₃+SrCO₃ coated on a Ni ribbon cathode have been followed by means of X-ray photographs. At 800°, the mixed carbonates are converted into the individual oxides, and at 960° a slow transformation into a solid solution, BaO-SrO, occurs. L. S. T.

Structure and physical properties of thin films of metal on solid surfaces. E. N. DA C. ANDRADE and J. G. MARTINDALE (Phil. Trans., 1935, A, 235, 79—100).—Uniform and reproducible films of Ag and Au (30—100 atoms thick) have been obtained by slow cathodic sputtering on a cooled surface. With films of 50 atoms thickness the first

stage of crystallisation, observed at 230° for Ag and > 230° for Au, consists in the formation of small aggregates, which show a characteristic figure in polarised light. This change is independent of the nature of the non-metallic surface supporting the film. The aggregates are formed by the motion of the upper layers of the film only, which must move freely at a temp. 700° below the m.p. Rapid growth of the aggregates follows prolonged heating at about 100° > the temp. at which they are formed, leading to the formation of well-defined, cubic crystals, which are arranged with their (111) faces parallel to the supporting surface. The thinner is the film of metal the higher is the temp. required to initiate crystallisation. Variations of colour and other properties found by previous observers under apparently identical conditions are ascribed to uncontrolled heating of the film during prep. E. S. H.

Recrystallisation of thin metallic layers. A. B. C. ANDERSON and A. GOETZ (Physical Rev., 1934, [ii], 45, 293).—Resistivity measurements of thin layers of Ag deposited on amorphous and cryst. surfaces (calcite) by evaporation in a vac. are discussed. The tendency of the isolated atoms to form aggregates is independent of the no. of atoms present. The resistance per layer decreases suddenly when a definite statistical thickness is reached, indicating the formation of cryst. groups of 10^{-5} – 10^{-4} cm. in diameter. L. S. T.

Lattice constants of five elements possessing hexagonal structure. E. A. OWEN, L. PICKUP, and I. O. ROBERTS (Z. Krist., 1935, 91, 70–76).—Precision measures are given for Zn, Mg, Be, Ru, and Os. The annealing technique necessary for undistorted crystals and hence for good X-ray definition is described. B. W. R.

Energy bands in copper. H. M. KRUTTER (Physical Rev., 1935, [ii], 48, 664–671).—The general method of obtaining energy bands and wave functions for a face-centred lattice is applied to a Cu lattice using a corr. Hartree potential field, and energy bands are calc. as a function of internuclear distance. Electron assignment to the lowest energy bands explains the good conductivity of Cu. The various energy bands in the directions 100, 110, and 111 are correlated. N. M. B.

Structure of solid oxygen. L. VEGARD (Nature, 1935, 136, 720–721).—X-Ray powder diagrams of γ -O₂ indicate a lattice with rotating mols. The cryst. structure may be represented by a cubic cell, a 6.83 Å., containing 8 mols. grouped into pairs (O₂–O₂); space-group T_h^6 . The distance between the 2 mols. of a rotating pair, 3.48 Å., is slightly < the min. distance, 3.68 Å., between neighbouring pairs. The centres of the O₂–O₂ pairs form a face-centred lattice, and γ -O₂ thus forms a closest cubical packing of pairs of O₂ mols. Its structure is similar to that of α -N₂ and α -CO. L. S. T.

Structure of electrolytic chromium. L. WRIGHT, H. HIRST, and J. RILEY (Trans. Faraday Soc., 1935, 31, 1253–1259).—The existence of hexagonal Cr in deposits obtained from aq. HCrO₄ + H₂SO₄ has been confirmed. The at. distance is

2.717 Å. and $c/a=1.626$. The hexagonal form is converted into the body-centred cubic form by heating in vac. at 800° for 1.5 hr. The factor influencing the formation of the hexagonal allotrope is the amount of Cr existing in the cation in the reduced solutions. E. S. H.

Crystal structure of γ -Fe₂O₃ and γ -Al₂O₃. E. J. W. VERWEY (Z. Krist., 1935, 91, 65–69).—Powder photographs of Fe₂O₃ and γ -Fe₂O₃, and MgAl₂O₄ and γ -Al₂O₃ (the former of each pair having the known spinel structure), are compared. In the γ -oxides, 21 $\frac{2}{3}$ cations, 32 O atoms, and 2 $\frac{1}{3}$ vacant spaces form statistically a spinel structure. B. W. R.

Structure of silicon disulphide. W. BÜSSEM, H. FISCHER, and E. GRUNER (Naturwiss., 1935, 23, 740).—SiS₂ is rhombic (a 9.57, b 5.65, c 5.54 \pm 0.01 Å.), 4 mols. in the unit cell. The Si are surrounded by S atoms at the apices of a tetrahedron, the tetrahedra having two S in common. In the c -direction the crystal forms a unidimensional, infinite chain mol. The structural principle for silicates, viz., that the anionic tetrahedra can only have apices in common, is broken in this case owing to the large diameter of S²⁻. A. J. M.

Crystallography of magnesium sulphite. H. A. KLASSENS, W. G. PERDOK, and P. TERPSTRA (Rec. trav. chim., 1935, 54, 728–732).—MgSO₃.6H₂O has a rhombohedral lattice; unit cell contains 1 mol. J. W. S.

Triphosphonitric chloride. K. H. MEYER and G. W. PANKOW (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 139).—(PNCl₂)₃ when heated polymerises to a rubbery product. Stretching makes it birefringent and yields an X-ray diagram, which disappears on releasing the tension. It crystallises in a rhombic elementary cell, period 5.16 Å. A chain structure is suggested. S. J. G.

Structure of potassium hexachlorothallate dihydrate. J. L. HOARD and L. GOLDSTEIN (J. Chem. Physics, 1935, 3, 645–649).—X-Ray data show that K₂TlCl₆.2H₂O has compact, body-centred tetragonal lattice unit with α_0 15.841, c_0 18.005 (\pm 0.020) Å., containing 14 mols. Rb₃TlBr₆.²H₂O has a similar structure. T. G. P.

Crystal structures of rubidium and ammonium fluoborates. J. L. HOARD and V. BLAIR (J. Amer. Chem. Soc., 1935, 57, 1985–1988).—X-Ray data show that RbBF₄ has a 9.07, b 5.60, c 7.23 Å.; NH₄BF₄ has a 9.06, b 5.64, c 7.23 Å. These compounds crystallise with the BaSO₄ type of structure, space-group V_1^2 - $Pnma$, and are aggregates of BF₄ tetrahedra and Rb⁺ or NH₄⁺ ions. E. S. H.

Crystal structure of ammonium uranyl acetate. I. FANKUCHEN (Physical Rev., 1934, [ii], 45, 563).—NH₄ uranyl acetate, tetragonal, a 13.79, c 27.60 Å., body-centred, has 16 mols. in the unit cell; d (calc.) 2.33 (lit. 2.219); space-group probably $I4_12$ (D_{4h}^{10}). L. S. T.

Possibility of a secondary structure in calcite. S. HARRIS (Physical Rev., 1934, [ii], 45, 646–647).—A discussion. L. S. T.

Lattice constants and m.p. of berzeliites. W. BUBECK (Geol. Fören. Stockholm, 1934, 56, 525—530; Chem. Zentr., 1935, i, 1677).— a varied with the Mn content from 12.35 Å. with 2.3% MnO to 12.46 Å. with 19.4% Mn. Corresponding m.p. were 1090° and 1180°, respectively. Vegard's rule is not obeyed.

J. S. A.

Atomic arrangement in vitreous silica and germanium dioxide. B. E. WARREN (Physical Rev., 1934, [ii], 45, 292).—The at. arrangement in the two glasses is the same: each cation is tetrahedrally surrounded by 4 O and each O is shared between two tetrahedral groups. The orientation about the direction of linking is random, and the resulting network non-repeating, distinguishing the vitreous from the cryst. state. The interat. distances in the glass and crystal are equal.

L. S. T.

Orientation of the oxalate group in oxalic acid and some of its salts. S. B. HENDRICKS (Z. Krist., 1935, 91, 48—64).—Lattice consts. and optical properties are determined for α and β anhyd. $\text{H}_2\text{C}_2\text{O}_4$, and for several Na, Rb, and K oxalates; complete structure determinations are made for the acids, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, KHC_2O_4 , and RbHC_2O_4 . The C_2O_4 group has coplanar atoms, and when perfect cleavage occurs it is in planes not cutting C_2O_4 groups or O·H·O linkings.

B. W. R.

Structure of cyanuric triazide. E. W. HUGHES (J. Chem. Physics, 1935, 3, 650).—A reply to Knaggs (this vol., 434).

T. G. P.

Structure of benzil. K. BANERJEE and K. L. SINHA (Sci. and Cult., 1935, 1, 301).—Rotation photographs show 3 mols. per unit cell, confirming a hexagonal basic lattice; space-group D_{3h}^1 . Reflexion intensity measurements indicate that the mol. has its two C_6 rings in parallel planes.

N. M. B.

Crystal structure of ergotamine. H. BRASSEUR (Bull. Soc. Chim. biol., 1935, 17, 1462—1464).—By means of the polarising microscope and the X-ray diffraction method ergotamine cryst. from aq. COMe_2 is shown to be monoclinic, with negative birefringence. Lattice dimensions are a 20.30, b 18.65, c 10.11 Å., β 90°.

A. L.

X-Ray examination of the transformation of sodium cellulose by the action of carbon disulphide.—See this vol., 1486.

X-Ray examination of the effect of removing non-cellulosic constituents from vegetable fibres. W. T. ASTBURY, R. D. PRESTON, and A. G. NORMAN (Nature, 1935, 136, 391—392).—X-Ray examination of the effect of the progressive removal of the xylan (I) of cellulose fibres from Manila hemp reveals no fundamental change; only a more perfect state of crystallisation is indicated, supporting the view that the incorporation of (I) is a kind of mixed crystallisation. Removal of lignin and encrusting hemicelluloses clarifies the X-ray photograph and leads to improved definition through a sharpening of the crystallite orientation.

L. S. T.

Structure of humic acid and its relation to lignin and coal. J. SEDLETZKI and B. BRUNOVSKI (Kolloid-Z., 1935, 73, 90—91).—The X-ray diagram

of humic acid is compared with those of lignin, coal, and graphite. The genetic relation of these substances is discussed.

E. S. H.

Structure of seed-globulins.—See this vol., 1433.

Process of stretching of highly polymerised substances. H. MARK (Ergeb. tech. Röntgen., 1934, 4, 75—79; Chem. Zentr., 1935, i, 1852).—On the basis that long-chain polymerides exhibit mobility corresponding with all the degrees of freedom of oscillation and rotation present, and that in a swollen gel the polymeride chains, or bundles thereof, are slowly oriented on deformation, a quant. statistical theory of elastic extension is derived. In the most probable orientation, the chain length is $<$ total length of the constituent units, corresponding with bent chains. Alteration of the most probable state involves work of extension or compression.

J. S. A.

Electron diffraction by highly polymerised substances. H. MARK and J. J. TRILLAT (Ergeb. tech. Röntgen, 1933, 4, 69—74; Chem. Zentr., 1935, i, 1852).—Thin films (10^{-5} to 10^{-6} cm.) of unstretched caoutchouc gave an "amorphous" diagram which changed to that of an orthogonal lattice, periods 8.1 and 12.4 Å., on 100% extension, in agreement with X-ray results. Cellulose acetate and nitrate give diffraction rings when fresh due to small crystallites of size 30—60 Å. On ageing, growth of crystallites occurs. For the nitrate, periods a 4.7, b 7.1, c 5.0 Å. were obtained.

J. S. A.

New interference phenomenon on the passage of rapid electrons through crystals. F. KIRCHNER and H. LASSEN (Ann. Physik, 1935, [v], 24, 113—123).—When rapid electrons fall on very thin Ag layers (approx. 10^{-6} cm.) the interference spots at the edges of the zero principal max. resolve themselves into cross-like patterns, which are due to a surface lattice effect. The same effect is obtained with reflexion photographs, and it is deduced that the interference is due to very small Ag crystals with exactly parallel orientation, on the surface.

A. J. M.

Crystal structure and electron configuration of transition and univalent metals. U. DEHLINGER (Z. Physik, 1935, 96, 620—633).—The crystal structures of transition metals are arranged symmetrically about the column Cr, Mo, W; only the last three metals have cube-centred lattices, the others having cubic or hexagonal lattices of closest spherical packing. The structures of the transition metals are therefore due to a gradual building up of the d -shell, all having only one s outer electron. The exception of ferromagnetic Fe is due to preponderance of spin valency over orbital valency to produce the cube-centred lattice at low temp.

A. B. D. C.

Electron-optical observation of transformations of iron between 500° and 1000°. E. BRÜCHE and W. KNECHT (Z. tech. Phys., 1934, 15, 461—463; Chem. Zentr., 1935, i, 1336).—The electron emission at 1050° was employed (cf. A., 1934, 859), using Fe specimens annealed at 1050°, heat-treated at temp. between 500° and 1000°, and then rapidly reheated to 1050°. Structural changes were

observed between 665° and 725° , and between 615° and 665° . J. S. A.

Intensity of diffraction of electrons by ZnO. H. J. YEARIAN (Physical Rev., 1935, [ii], 48, 631—639).—Electron diffraction patterns of ZnO powder were obtained in the range 10—80 kv. The intensity distribution shows marked deviations from that of the corresponding X-ray pattern. Numerous considerations fail to explain the anomaly. Agreement between experimental and calc. curves for the scattering factor is obtained by assuming a distortion of the electron cloud (M shell of the Zn and L shell of the O) resulting in a different parameter for the distances Zn nucleus—O nucleus, and Zn electrons—O electrons. An expression for the structure factor is found. N. M. B.

Diffraction of electrons by metals and organic polymerides. J. J. TRILLAT and H. MOTZ (Ann. Physique, 1935, [xi], 4, 273—304).—The electron diffraction patterns obtained with cellulose nitrate and acetate, polyoxymethylenes, synthetic resins, rubber, etc. are closely similar and are attributable to thin oriented surface films of fatty materials (fatty acids, waxes, or paraffins). The same phenomenon with metallic surfaces is due to the presence of long aliphatic mols. oriented perpendicular to the surface. J. W. S.

"Extra" rings in electron diffraction patterns. G. I. FINCH and A. G. QUARRELL (Nature, 1935, 136, 720).—The spacings of extra rings due to grease are found to be independent of the nature of the metal, confirming the results of Mark *et al.* (this vol., 813). Measurements recorded for Au show that the rings obtained by heating a metal in a gas depend on the metal, the gas, and the nature of the heat-treatment. Amalgamation also produces extra ring systems which have spacings dependent on the metal. L. S. T.

Electronic structures of molecules. XIII. Diborane and related molecules. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 635—645; cf. this vol., 1306).— B_2H_6 is shown to have 11 low-energy electron states within an energy range of 1.5 volts, belonging to three electron configurations, in general agreement with the suggestions of Sidgwick *et al.* (A., 1931, 1356). The three H atoms in each BH_3 are held by two [S] and three [π] electrons shared equally. The same equal sharing occurs, *e.g.*, in $B_2H_2Me_4$. The absence of dimeric BCl_3 is discussed. T. G. P.

Fundamental problems of the modern theory of metals. L. E. GUREVITSCH (Trans. Lenin. Ind. Inst., 1934, 5, No. 3, 125—147).—A review.

Refinement of the Heisenberg theory of ferromagnetism applicable to simple cubic crystals. C. H. FAX (Proc. Nat. Acad. Sci., 1935, 21, 537—542).—A new method gives results in agreement with the simple Heisenberg theory, but at variance with the approx. method of Heisenberg using Gaussian distribution of coupling energies. A. J. M.

Negative hysteresis in nickel. S. SHARAN (Current Sci., 1935, 4, 157).—The influence of an alternating circular or longitudinal field on the

intensity of magnetisation of soft Fe and Ni under const. magnetic field is examined. Ni exhibits negative hysteresis under the influence of an alternating circular field but not with an alternating longitudinal field. W. R. A.

Validity of Becker's relation for initial permeability of highly strained nickel wires. G. SCHARFF (Z. Physik, 1935, 97, 73—82).—Temp. variation of initial permeability of Ni under load confirms Becker's theory of magnetisation (A., 1930, 844). A. B. D. C.

Negative Matteucci effect. E. ENGLERT (Z. Physik, 1935, 97, 83—93).—Results are given for wires of Ni and of Fe-Ni (92:8%). A. B. D. C.

Displacement of the Curie point by tension. E. ENGLERT (Z. Physik, 1935, 97, 94—96).—No such effect could be found (cf. Ray-Chaudhuri, A., 1931, 1216). A. B. D. C.

Interior magnetic field in iron. L. ALVAREZ (Physical Rev., 1935, [ii], 45, 225—226, 566).—Data obtained from the passage of β -rays from Ra-C through Fe after focussing in a magnetic field disagree with the classical theory of magnetisation. L. S. T.

Comparison of theoretical and measured Hall coefficients. K. K. SMITH and N. A. HEDENBURG (Physical Rev., 1934, [ii], 45, 122). L. S. T.

New substance with the electrical properties of Rochelle salt. G. BUSCH and P. SCHERRER (Naturwiss., 1935, 23, 737).— KH_2PO_4 shows a variation of dielectric const., ϵ , with temp. similar to Na K tartrate (I), although ϵ is $<$ for (I). The principal dielectric const., ϵ_{33} , increases with decrease of temp. attaining a max. of 155 at -130° . Like (I) it has two Curie points (-130° and -195°). Qual. investigation of the piezo-electric activity shows that this varies with temp. in an analogous manner to ϵ . X-Ray analysis indicates no structural change at the upper Curie point. A. J. M.

Dielectric anomalies of Rochelle salt. H. STAUB (Naturwiss., 1935, 23, 728—733).—A review. A. J. M.

Further studies on the double refraction of interfacial layers of the normal aliphatic acids. A. KING (Physical Rev., 1934, [ii], 45, 562).—Measurements on tridecoic and palmitic acids confirm previous results (cf. A., 1933, 889, 1104). L. S. T.

Effect of photochemical coloration on the elastic limit and strength of single crystals of rock-salt. M. PODASCHEVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 71—74).—Uniformly coloured crystals show a considerable increase in the elastic limit and strength. A. J. M.

Cinematographic record of the $\alpha \rightleftharpoons \gamma$ iron transition, as seen by the electron microscope. W. G. BURGERS and J. J. A. PLOOS VAN AMSTEL (Nature, 1935, 136, 721).—The growth of crystals of α -Fe in the original γ -Fe near the transition temp. 900° has been recorded by means of an electron microscope with one magnetic lens. L. S. T.

Allotropy investigations with very pure calcium. A. SCHULZE (Physikal. Z., 1935, 36,

595—598).—Cooling curves, electrical resistance, thermal expansion, and X-ray data all show the presence of two allotropic forms of Ca. The α - β transition lies near 300°, and the β - γ near 450°.

A. B. D. C.

Syntax and polytypy. H. UNGEMACH (Z. Krist., 1935, 91, 1—22).—Special forms of polymorphism are discussed in relation to coquimbite, carborundum, parasite, and other minerals.

B. W. R.

Pressure effect of electrical resistance of metals. N. K. SAHA (Indian J. Physics, 1935, 9, 623—635).—The pressure coeff. of electrical resistance and the change in resistance at different pressures are calc. on the rigid ionic model of Nordheim, using a screened Coulombian form of potential. Good agreement is found for metals having low compressibility. Results are compared with those of Kroll using Fermi's statistical form of ionic potential. The sp. resistances of Au, Ag, Cu, Na, K, and Li are calc. using the two forms of potential on the rigid ionic model. Results on Fermi's potential are less consistent. For the highly compressible alkali metals neither form is satisfactory.

N. M. B.

Diamagnetism of the tervalent bismuth ion. S. S. BHATNAGAR and B. S. BAHL (Current Sci., 1935, 4, 153—154).—Experimental vals. for the diamagnetic susceptibilities of 10 salts of Bi⁺⁺⁺ are recorded. From known vals. for the susceptibilities of the anions the val. 41.24 for Bi⁺⁺⁺ is obtained, compared with 43.8 calc. from theory.

W. R. A.

Magneto-chemical investigations. XVII. Magnetic behaviour of chalcogenides of bivalent chromium. H. HARALDSEN and E. KOWALSKI (Z. anorg. Chem., 1935, 224, 329—336; cf. Henkel *et al.*, this vol., 436).—The susceptibilities of CrS, CrSe, and CrTe have been measured. CrS and CrSe are paramagnetic between 90° and 600°. CrTe is ferromagnetic below 70°. The results confirm the presence of at. linkings between the metallic ions (A., 1934, 1294) in certain compounds of the transition elements.

T. G. P.

Diamagnetism of alkyl acetates. D. B. WOODBRIDGE (Physical Rev., 1935, [ii], 48, 672—682).—Susceptibility measurements on the first five primary alkyl acetates and on MeOH for the range 5—70° show very slight variation of susceptibility with temp. and indicate increasing temp. dependence for higher members of the series. The mol. susceptibility of CH₃ is additive, in agreement with Pascal's law. The magnetic properties of NiCl₂ solutions are discussed.

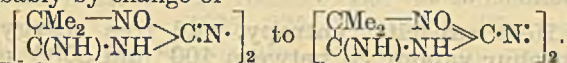
N. M. B.

Magneto-chemical investigations of organic substances. IV. Magnetic behaviour of free radicals. E. MÜLLER, I. MÜLLER-RODLOFF, and W. BUNGE (Annalen, 1935, 520, 235—255; cf. this vol., 689, 1116).—Susceptibilities of the following paramagnetic substances have been determined at temp. down to -183°: C₁₈H₂₁O₂N₂ (I) (cf. A., 1932, 324); (*p*-OMe·C₆H₄)₂N·O (II); NPh₂·N·C₆H₄(NO₂)₃ (III); C(C₆H₅Ph)₃ (IV). (I) and (II) obey Curie's law exactly, whilst (II) shows a slight, and (IV) a somewhat larger, deviation at

low temp. The calc. magnetic moments correspond with one unbalanced electron in each of the substances. (I) and (II) are entirely, and (III) is preponderantly, monomeric both in the solid state and in solution at all temp., whilst (IV) may be slightly associated at low temp.

F. L. U.

Magneto-chemical investigations of organic substances. V. Magnetic behaviour of porphyrexide and porphyrindin. VI. Determination of the degree of dissociation of hexa-aryl substituted ethanes. E. MÜLLER and (FRL.) I. MÜLLER-RODLOFF (Annalen, 1935, 521, 81—89, 89—94; cf. preceding abstract).—V. Porphyrexide shows the expected (Σ -condition) magnetic behaviour. Porphyrindin is a mixture of dia- and para-magnetic mols., the former being favoured by lower temp., probably by change of



VI. Free radicals should have a paramagnetic susceptibility, $\chi_{\text{mol.}}$, +2.1270 $\times 10^{-6}$ at 20°. Differences are due to incomplete dissociation, the degree of which can be calc. The method is applicable only for highly dissociated compounds or for high concns. of those slightly dissociated, e.g., for C₂Ph₆ at > 4%. C₂Ph₆ is found to be 2.1% dissociated at 20° in 4% solution, the heat of dissociation being -11.6 \pm 1.7 g.-cal.

R. S. C.

Change of magnetic susceptibility of metals during melting and allotropic transformation. K. HONDA and Y. SHIMIZU (Nature, 1935, 136, 393).—New measurements, in a vac., of the change in magnetic susceptibility during the melting of Sn, Cu, Ag, and Au, and the allotropic change of Sn, are recorded.

L. S. T.

Diamagnetism of copper. S. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 249—259; cf. this vol., 19).—Colloidal Cu was prepared in vac. by an electrical method in a dispersing medium of C₆H₆ or PrOH. The diamagnetic susceptibility, determined by a sensitive Curie method, was 0.080 for mass Cu, and increased as the size of the particles was reduced, the crit. diameter below which large changes occurred being 0.8 μ . The conclusions of Honda (cf. this vol., 287) are confirmed. The thickness of the surface layer is approx. 300 Å., and its diamagnetic susceptibility 0.200. The density of the surface layer is 8.404 as against 8.943 for mass metal.

N. M. B.

Magnetic anisotropy of crystals of Sn, and of Sn with added Sb, Cd, or Ga. H. J. HOGE (Physical Rev., 1935, [ii], 48, 615—619).—The principal magnetic susceptibilities of single crystals of white (tetragonal) Sn, grown by the travelling furnace method, were measured. Relative to the tetragonal axis the susceptibilities per unit vol. were: k_{\perp} 0.197 $\times 10^{-6}$ and k_{\parallel} 0.176 $\times 10^{-6}$. The ratio k_{\perp}/k_{\parallel} is strongly influenced by the addition of traces of certain elements; for pure Sn the val. is 1.120, 0.6% Sb gives 1.200, 0.76% Cd gives 0.923, and 0.89% Ga gives 0.897. The relation between the change in this ratio and the no. of valency electrons of the added element is compared with data for Bi (cf. Goetz, A., 1934, 353).

N. M. B.

Paramagnetism of metallic gadolinium above its Curie point. F. TROMBE (Compt. rend., 1935, 201, 652—653).—Measurements of χ are recorded from 16° to 360°. The ferromagnetic and paramagnetic Curie points are at 16° and 29.5°, respectively.

H. J. E.

Absolute temperature of the normal freezing point of water. The ψ_0 -limiting value. W. JACYNA (Z. Physik, 1935, 97, 107—112).—This is 273.22° abs.

A. B. D. C.

Anomaly in specific heat of lithium. G. W. PANKOW and P. SCHERRER (Helv. phys. Acta, 1934, 7, 644—647; Chem. Zentr., 1935, i, 1832).—Between room temp. and -190° the energy supplied to Li goes entirely to at. vibration, and not to a quantum jump. The characteristic temp., θ , is given by three methods as 350—370°.

J. S. A.

Heat capacity, entropy, and free energy of sulphur vapour S_2 between 100° and 5000° abs. I. GODNEV and A. SVERDLIN (Z. Physik, 1935, 97, 124—130).—Heat capacity, entropy, and free energy are deduced from spectroscopic data.

A. B. D. C.

Specific heats of liquid deuterium oxide. R. S. BROWN, W. H. BARNES, and O. MAASS (Canad. J. Res., 1935, 13, B, 167—169).—The mean sp. heats over the ranges 4—26°, 26—45°, and 26—65° are 1.018, 1.003, and 1.008, respectively.

E. S. H.

Anomaly of specific heat of Seignette salt. A. A. RUSTERHOLZ (Helv. phys. Acta, 1934, 7, 643—644; Chem. Zentr., 1935, i, 1832).—The dielectric behaviour is abnormal below 25°, ϵ being very high. The variation of mol. heat with temp. in that region resembles that of ferromagnetic substances, corresponding with a work of electrification of 2.1 g.-cal. per mol.

J. S. A.

Latent heat of vaporisation of water in the pressure range 100—200 kg. per sq. cm. W. KOCH (Forsch. Ing., 1934, A, 5, 257—259; Chem. Zentr., 1935, i, 1672).—The latent heat for H_2O between 100 and 200 atm. is given by $r=59.5(374.11-t)^{0.4}+0.025(374.11-t)$.

J. S. A.

Heat of vaporisation of water and specific volume of saturated vapour up to 200 kg. per sq. cm. (365°). M. JAKOB and W. FRITZ (Physikal. Z., 1935, 36, 651—659).—The heat of vaporisation of H_2O has been determined calorimetrically up to 202 kg. per sq. cm. pressure (365°). An empirical formula for the heat of vaporisation and sp. vol. embodying these results and those of previous workers is deduced.

A. J. M.

Latent heat of condensation of metals. D. S. KOTHARI and N. K. SAHA (Sci. and Cult., 1935, 1, 300—301).—The electron gas theory is extended to calculate the latent heat of fusion of metals. Results for Li, Na, K, Rb, Cs, Ag, Cu, Au, and Cd agree with experimental data only in order of magnitude; those for Hg and Zn diverge widely.

N. M. B.

Expression of the second law of thermodynamics in terms of Clifford's numbers. A. MERCIER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 112—113).—Mathematical.

S. J. G.

I-T diagram for methane. A. EUCKEN and W. BERGER (Z. ges. Kalte-Ind., 1934, 41, 145—152; Chem. Zentr., 1935, i, 1346).—The complete enthalpy-temp. diagram of CH_4 is given between 110° and 290° abs. C_p and the molar heat of evaporation are given as functions of T .

J. S. A.

Vapour pressure of deuterium. F. G. BRICKWEDDE, R. B. SCOTT, H. C. UREY, and M. H. WAHL (Physical Rev., 1934, [ii], 45, 565; cf. A., 1934, 1164).

L. S. T.

Pressure-volume-temperature relations of the liquid, and the phase diagram of heavy water. P. W. BRIDGMAN (J. Chem. Physics, 1935, 3, 597—605).—Pressure-vol.-temp. relations of liquid D_2O and H_2O have been measured between -20° and 95° and up to 12,000 kg. per sq. cm., and the transition parameters of the liquid and solid modifications of D_2O in the range -60° to 20° and up to 9000 kg. per sq. cm. An unstable modification IV of solid D_2O occurs in the field of stability of V, which confirms the existence of the corresponding modification in solid H_2O (A., 1913, ii, 39). D_2O and H_2O behave similarly, and differ in the direction suggested by the greater zero-point energy of H_2O : the mol. vol. of D_2O is > of H_2O at the same temp. and pressure; the transition lines of D_2O always run at higher temp. In detail the differences are irregular, and considerations other than zero-point energy are necessary for complete explanation.

T. G. P.

Baur and Brunner's measurements of vapour pressure of high-boiling metals. J. FISCHER (Helv. Chim. Acta, 1935, 18, 1028—1029; cf. A., 1934, 1301).—Baur and Brunner's vals. for the b.p. of Pb and Ag disagree with accepted vals. Defects in the method are pointed out.

H. J. E.

Measurements of vapour pressure of high-boiling metals. E. BAUR and R. BRUNNER (Helv. Chim. Acta, 1935, 18, 1030; cf. preceding abstract).—A reply.

H. J. E.

Vapour pressure of barium. E. RUDBERG and J. LEMPET (J. Chem. Physics, 1935, 3, 627—631; cf. this vol., 22).—The v.p. of Ba, determined between 525° and 750° by mol. effusion, gives $\log p(\text{mm.})=6.99-8980/T$, and $L=40.9$ kg.-cal. per mol.

T. G. P.

Ratio of the thermal coefficient of expansion to the specific heat at constant pressure for tungsten. W. J. JACKSON (Physical Rev., 1934, [ii], 45, 285).—The ratio is const. for only a limited temp. range; above 200°, it increases with rise of temp. up to 500°, where the validity of the empirical relationships ceases.

L. S. T.

Principal expansion coefficients of single crystals of mercury. D. M. HILL (Physical Rev., 1935, [ii], 48, 620—624).—Expansion coeffs. measured at 5° intervals from -115° to -160°, and mean vals. found from -160° to -190°, are tabulated and plotted. A recrystallisation process sets in between -115° and -110°. Relative to the trigonal axis, α_{11} is larger and increases more rapidly with rise of temp. than α_1 . The vol. coeff. is given from the m.p. to -160°, where the coeff. decreases rapidly with fall of temp.

N. M. B.

Thermal conductivity of carbonic acid. R. PLANK and O. WALGER (Forsch. Ing., 1934, A, 5, 289; Chem. Zentr., 1935, i, 1670).—Sellschop's val. (this vol., 574) is confirmed. J. S. A.

Thermal conductivity of various liquids. R. PLANK (Z. ges. Kälte-Ind., 1934, 41, 214; Chem. Zentr., 1935, i, 1506).—The val. of Kardes (A., 1934, 1300) for CO_2 is too high, due to convection effects. Data for other liquids are not so affected. J. S. A.

Thermal expansion of calcite. H. SAINI (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 108—109).—Determinations of coeff. of expansion of the same crystal of calcite by an optical interference method and by an X-ray method agreed between 25° and 100° . S. J. G.

Density and compressibility of silicane and silicoethane. K. L. RAMASWAMY and G. G. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 213—220).—Using an apparatus for the simultaneous measurements of density and approx. compressibilities, vals. were obtained for SiH_4 at room temp. and -79.8° , and for Si_2H_6 at room temp. The calc. mean mol. wts. are 32.13 and 62.74, respectively. Corresponding at. wts. of Si are compared with those of other authors. N. M. B.

Variation of the viscosity of gases with temperature over a large temperature range. A. B. VAN CLEAVE and O. MAASS (Canad. J. Res., 1935, 13, B, 140—148).—Data are recorded for NH_3 , C_3H_8 , C_2H_4 , and Me_2O between 23° and -80° , with a relative accuracy of 0.1%. The validity of different viscosity-temp. relations has been tested with the present data; an empirical equation, which adequately represents the results, is suggested, but it fails at high temp. for all gases and at low temp. for H_2 , air, and C_2H_4 . The viscosity-temp. curves for CO_2 , SO_2 , NH_3 , Me_2O , and C_3H_8 show an inflexion point, which is related to the polarity of the mol. and the crit. temp. E. S. H.

Viscosity of air and the electronic charge. G. KELLSTRÖM (Nature, 1935, 136, 682—683).—For dry air η_{20° , determined by the rotating-cylinder method, is $(1820.0 \pm 3.0) \times 10^{-7}$, corresponding with $\eta_{23^\circ} = (1834.8 \pm 3.0) \times 10^{-7}$, a val. different from that used by Millikan in determining e . The new val. gives $(4.818 \pm 0.012) \times 10^{-10}$ e.s.u. for e , the same val. as calc. from X-ray measurements. L. S. T.

Influence of a magnetic field on the coefficient of viscosity of liquids. H. S. VENKATARAMIAH (Current Sci., 1935, 4, 156).—The results of experiments (in 1932) on the influence of a magnetic field on the viscosity of C_6H_6 are published (cf. Raha *et al.*, this vol., 1198). W. R. A.

Influence of the proximity of a solid wall on the consistency of viscous and plastic materials. IV. R. K. SCHOFIELD and G. W. S. BLAIR (J. Physical Chem., 1935, 39, 973—981; cf. B., 1930, 844; 1931, 825).—The rate of flow of an aq. paste of BaSO_4 through tubes of the same radius under the same pressure gradient is independent of the length of the tube, but with tubes of different radii the velocity gradient does not appear to depend only on the shearing stress. The proximity of the tube wall

apparently causes a sheath of material to shear more easily than does the bulk of the material. E. S. H.

Mixed crystal formation with tin oxide. E. HAYEK (Monatsh., 1935, 66, 197—200).—Pptn. of SnO in presence of salts of Pb, Mn, Fe, Zn, Cd, and Ca gives mixed crystals, but Co, Ni, Mg, Sr, and Ba do not enter the SnO lattice. The mixed crystals have characteristic colours. Their homogeneity has been confirmed by X-ray photographs. SnO shows passivity. T. G. P.

Nature of a solid solution. K. HONDA (Metal Progr., 1934, 26, No. 3, 42—43).—Experimental vals. of d for a 4.5% Al-Ag alloy agree within 0.3% with the val. calc. from the displacement of the Ag lattice by Al in solid solution. CH. ABS. (e).

Equilibrium diagram of the system magnesium-lithium. P. SALDAU and F. SCHAMRAY (Z. anorg. Chem., 1935, 224, 388—398).—Thermal analysis of Mg-Li mixtures, supported by microscopical observations, indicates the formation of three solid solutions, the limits of which have been established. The compound LiMg_2 (not Li_2Mg_5 ; cf. this vol., 591) melts without change. F. L. U.

X-Ray study of aluminium-zinc alloys at elevated temperatures. E. A. OWEN and L. PICKUP (Phil. Mag., 1935, [vii], 20, 761—777; cf. A., 1934, 356).—Arrangements are described for obtaining rotation powder photographs of metals and alloys at high temp. in vac., with special reference to the β -phase in Al-Zn alloys which decomposes spontaneously below 270° . Equilibrium diagrams and accurate measurements of parameter vals., temp., and phase-boundaries above the eutectoid temp. are given, and results compared with previous data. The γ -phase parameter in the $\beta+\gamma$ region decreases with rising temp.; the transformation temp. (272°), and the $(\beta+\gamma)-\gamma$ boundary are derived from the thermal "expansion" curves of the γ -phase in certain alloys. N. M. B.

X-Ray investigation of the system iron-chromium-nitrogen. S. ERIKSSON (Jernkont. Ann., 1934, 118, 530—543; Chem. Zentr., 1935, i, 2069—2070).—The existence of an intermediate α' -phase in the Fe-Cr system (approx. formula FeCr) is confirmed (cf. Wever, B., 1932, 469). In the system Cr-N the hexagonal β -phase has a "superstructure," the cell vol. of which is three times as large as that of the hexagonal close-packed lattice. The upper and lower limits of the region of homogeneity of the β -phase are 11.9% N (Cr_2N) and 9.3% N, respectively. Lattice dimensions are recorded. Results are given for the chief phases in the Fe-Cr-N diagram at 700° and 400° . H. J. E.

Metals and alloys. XV. X-Ray analysis of lithium-zinc alloys. E. ZINTL and A. SCHNEIDER. XVI. Structure of platinum-thallium alloys. E. ZINTL and A. HARDER. XVII. X-Ray analysis of lithium amalgams. E. ZINTL and A. SCHNEIDER (Z. Elektrochem., 1935, 41, 764—767, 767—771, 771—774; cf. this vol., 692).—XV. Examination of the phases existing at room temp. confirms the results obtained by thermal analysis and electrical conductivity measurements (cf. A., 1934, 21).

XVI. Pt dissolves up to 1.5% of Tl with widening of the space lattice. The solid solubility of Pt in Tl is very small. The system includes the compound PtTl, the structure of which has been determined.

XVII. The results confirm the existence of the compounds LiHg_3 , LiHg_2 , LiHg , Li_2Hg , and Li_3Hg , the structures of which are discussed. E. S. H.

Irreversibility of iron-nickel alloys and their equilibrium diagram. E. SCHEIL (Arch. Eisenhüttenw., 1935—1936, 9, 163—166).—The irreversible range of Ni steels has an appreciable width for the temp. interval in which place interchange of the atoms takes place, and in this interval the α - γ transformation occurs throughout the irreversible range, provided that the time of annealing is sufficiently prolonged. Transformation in the irreversible range requires not only a change in the lattice structure, but also a diffusion of the Ni atoms to produce a γ -phase which is richer in Ni than the still unconverted α ; the first occurs with great rapidity, but the second only very slowly. Measurements of the Acl, Ar1, and Ar2 points of a 4.8% Ni steel after annealing at 665–725° and of the resulting degree of transformation show that the α - γ range in Fe alloys containing up to 10% Ni is probably bounded by two curved lines convex to the origin, one joining the points 900°, 0% Ni; 725°, 4.8% Ni; and 630°, 10% Ni, and the other the points 900°, 0% Ni; 600°, 4.8% Ni, and 520°, 10% Ni. A. R. P.

Alloys of palladium with manganese. A. T. GRIGORIEV (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 75—88; cf. A., 1933, 18).—Pd-Mn alloys (5–95% Pd), cast or tempered at 900° for 16 hr., and at 300° for 7 days, form on cooling a continuous series of solid solutions. Alloys with 39.3–45% of Pd have a min. m.p. With fall in temp. the solid solution is converted into the compound PdMn. The thermal changes shown by alloys rich in Mn at 1040–1089° and 730–797° are conditioned, respectively, by the Mn transformations $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$. CH. ABS. (c)

Alloys of praseodymium and copper. G. CANNERI (Met. ital., 1934, 26, 869–871; Chem. Zentr., 1935, i, 1816).—The following compounds were found: PrCu_6 , m.p. 962°; PrCu_4 , transition point 824°; PrCu_3 , m.p. 841°; PrCu , transition point 563°. Eutectics occur at 891°, 15% of Pr; 792°, 45% Pr; 472°, 82.5% Pr. The alloys are hard and brittle. J. S. A.

X-Ray and electrical investigation of Pd-Ag-H alloys. G. ROSENHALL (Ann. Physik, 1935, [v], 24, 297–325).—Errors in deducing the [H] of Pd-H alloys from the current passed during electrolysis of aq. KOH, using the Pd as cathode, are discussed. Addition of > 27% of Ag to the Pd leads to the production of single-phase alloys at all [H]. The resistance of such alloys decreases for about four days after prep., this representing the time required to reach equilibrium. The Pd-Ag-H alloys have in all cases face-centred cubic lattices of which the const. varies with composition. The solubility of H_2 in Pd-Ag alloys (30–100% Pd) shows a max. only at pure Pd. X-Ray data can be explained on

either the hydride or the absorption hypothesis, but resistance min. observed favours the PdH hypothesis. J. W. S.

Theory of superlattice structures in alloys. W. HUME-ROTHERY and H. M. POWELL (Z. Krist., 1935, 91, 23–47).—Superlattices of various types are defined, which are intermediate between the random solid solution of A and B and the normal intermetallic compound A_mB_n . The concept of “zones” characterised by different distances between the atoms A and their nearest B neighbours is used to discuss the stability and formation of different superlattices, the lattices FeAl and CuAu being examined in detail. B. W. R.

Diffusion coefficients in alcohol-water mixtures. H. MOUQUIN and W. H. CATHCART (J. Amer. Chem. Soc., 1935, 57, 1791–1794).—Apparatus and technique are described, and results given for crystal-violet. A break in the composition curve occurs at 65% EtOH. E. S. H.

Apparent volumes and apparent compressibilities of solutes in solution. II. Concentrated solutions of lithium chloride and bromide. A. F. SCOTT and G. L. BRIDGER (J. Physical Chem., 1935, 39, 1031–1039; cf. this vol., 31).—Irregularities are discussed in the light of the data recorded and previous measurements. E. S. H.

Volume changes in mixtures of benzene and chloroform. G. BOTECCIA (Atti R. Ist. Veneto Sci., Lett. Arti, 1934, 93, 567–572; Chem. Zentr., 1935, i, 1688; cf. A., 1933, 1110).—The vol. increase shows a max. at 20 mol.-% CHCl_3 . A pressure of 76 atm. is required to restore the vol. to the sum of the vols. of the components. H. N. R.

Variation of vapour pressure of the isotopic mixture of hydrogen with time at 20.38° abs. K. STEINER (Physikal. Z., 1935, 36, 659–660).—The v.p. at 20.38° abs. of samples rich in D_2 decreases with time. The results are discussed. A. J. M.

Critical data of light and heavy water and their density-temperature diagram. E. H. RIESENFELD and T. L. CHANG (Z. physikal. Chem., 1935, B, 30, 61–68).—The crit. temp., t_c , of mixtures of H_2O and D_2O can be calc. with considerable exactness by the mixture rule, being given by $t_c = 374.2 - 2.7n$, where n is the mol. fraction of D_2O . The crit. data for D_2O are t_c 371.5°, p_c 218.6 atm., d_c 0.363 g. per c.c. H_2O and D_2O have the same d at 49.5° (saturated vapour) and also at 370.0° (liquid). R. C.

Mixed m.p. in eutropic series. H. D. K. DREW and J. K. LANDQUIST (J.C.S., 1935, 1480–1482).—The series CPh_3 , SiPh_4 , GePh_4 , SnPh_4 , and PbPh_4 show a continuous fall in m.p., viz., 285°, 237.5°, 233.4°, 229.2°, and 227.8°, respectively. A mixture containing equimol. proportions of each has m.p. 220–221°. The m.-p. depression of binary mixtures suggests a change in some function, possibly in the valency angle, on passing from Ge to Sn. The m.-p. depressions for binary mixtures of NPh_3 , PPh_3 , AsPh_3 , SbPh_3 , and BiPh_3 indicate that N and Bi diverge from the other elements, and that only P and As are compatible with one another. Austin's

formula for m.p. in org. homologous series (A., 1930, 675) is inapplicable to the eutropic series. J. W. S.

Mutual solubility of heavy water and organic liquids in systems with a negative saturation curve. J. TIMMERMANS and G. POPPE (Compt. rend., 1935, 201, 608—610; cf. this vol., 1314).—Replacement of H_2O by D_2O extends the region of non-miscibility of a H_2O - α -picoline mixture. With 33.2% of α -picoline the lower and upper crit. solution temp. are 92° and 112.5° , respectively. With increasing pressure these limits approach one another, the liquids being miscible at all temp. for pressures > 90 kg. per sq. cm. For D_2O - Bu°OH mixtures a smaller KCl addition is needed to produce two phases than with H_2O . H. J. E.

Ternary system isoamyl alcohol-propyl alcohol-water. J. COULL and H. B. HOPE (J. Physical Chem., 1935, 39, 967—971).—Miscibility, d , and n have been determined at 25° . E. S. H.

Solubility of barium iodate in salt solutions. G. MACDOUGALL and C. W. DAVIES (J.C.S., 1935, 1416—1419).—Conductivity measurements on aq. $\text{Ba}(\text{IO}_3)_2$, and solubility measurements at 25° for $\text{Ba}(\text{IO}_3)_2$ in aq. KCl, KNO_3 , KClO_4 , CaCl_2 , and KClO_3 solutions are recorded. The results, when corr. for ionic association, are in accord with the Debye-Hückel limiting formula. The dissociation const. of BaIO_3 is 0.083, and that of BaClO_3 , deduced from solubility measurements of $\text{Ba}(\text{IO}_3)_2$ in KClO_3 , is about 0.2. J. W. S.

Nitrates of neodymium and praseodymium and their solubilities in water. J. N. FRIEND (J.C.S., 1935, 1430—1432; cf. this vol., 928).— $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ exists in α - and β -forms, the latter having m.p. 67.5° . The transition point is about 22° . $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, like the La and Nd salts, is probably isodimorphous with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and has m.p. 56° . The solubilities of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ between 0° and the m.p. and of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ between 15.8° and the m.p. are recorded. The solubilities of the Nd, Pr, and La salts are all too close to permit good separation in neutral solution. J. W. S.

"Salting-in" of hydrogen peroxide by electrolytes. M. H. GORIN (J. Amer. Chem. Soc., 1935, 57, 1975—1978).—The solubility of H_2O_2 , as determined by its distribution between H_2O and amyl alcohol, is increased in the aq. phase by addition of NaCl, NH_4Cl , KCl, NaNO_3 , NH_4NO_3 , KNO_3 , and NH_4ClO_4 , but decreased by H_2SO_4 . The apparent displacement of H_2O of hydration by H_2O_2 mols. can be explained if the H_2O_2 mol. has a higher dipole moment than that of H_2O in the neighbourhood of the ion. A structure for H_2O_2 , which would yield the necessary high dipole moment, is discussed. E. S. H.

Systems naphthalene-acetone and diphenylacetone and the solubility of a third substance in them. P. SPINOGLO and G. RAVENNA (Gazzetta, 1935, 65, 668—678).—For a given sample of COMe_2 , the solubility of CdI_2 in C_{10}H_8 - COMe_2 and in Ph_2 - COMe_2 mixtures of various concns. is const. when referred to a fixed wt. of COMe_2 . The

actual val. of the solubility varies with the small amounts of H_2O present even in carefully distilled COMe_2 . O. J. W.

Densities of adsorbed gases. I. Carbon dioxide on charcoal. T. DE VRIES (J. Amer. Chem. Soc., 1935, 57, 1771—1774).—He has been used as the displaced fluid to determine, before and after CO_2 adsorption, the unoccupied vol. in a tube containing C at 30° . He does not penetrate the CO_2 layer when d is > 0.09 mg. per ml. Polanyi's theory gives d for the adsorbed layer equal to the observed vals. if it is assumed that He penetrates the outer portion of the adsorbed layer. E. S. H.

Active charcoal. IX. Curves of sorption isotherms and their properties. X. Non-reducible sorption equilibrium, hysteresis, drift, and residual sorption. XI. Sorption and capillary condensation; their mechanism. O. KAMIKE. XII. Preparation of active charcoal by the zinc chloride process. Y. IMAI. XIII. Velocity of sorption of vapour in a dilute current of inert gas. S. TAMARU and Y. IMAI (J. Chem. Soc. Japan, 1935, 56, 114—123, 124—132, 133—141, 142—152, 153—177).—IX. A summary of previous work.

X. Hysteresis and drift are different phenomena. The former can be observed at relatively high vals. of v.p.

XI. Org. substances, notably AcOH, are the more readily adsorbed by active C. The radius of the capillary is calc.

XII. Active C of good quality is obtained by dipping a specimen of *Quercus glandulifera* in 30% aq. ZnCl_2 , treating with HCl at 90° (16 hr.), and igniting at 700° .

XIII. Relations between the amount of gas absorbed, time of contact, and dilution are examined.

CH. ABS. (p)

Adsorption of methane by coal. J. B. SUTTON and E. C. H. DAVIES (J. Amer. Chem. Soc., 1935, 57, 1785—1787).—The Freundlich equation is applicable to the results obtained at 10.94° , 17.77° , and 24.60° . The calc. heats of adsorption are 4700—5200 g.-cal. per mol. for x/m vals. between 1.5 and 3.5.

E. S. H.

Sorption of dimethyl ether on alumina. J. EDWARDS and O. MAASS (Canad. J. Res., 1935, 13, B, 133—139).—The investigations cover the ranges 0.5 — 52 atm. and 25 — 135° . No discontinuity in sorption accompanies the transition of sorbate from vapour to gas at the crit. temp. With increasing pressure the initially-formed unimol. layer is followed by a multimol. layer; it is, however, unlikely that condensation to liquid occurs in the pores, except at high pressures. The increase in crit. temp. of such a liquid must be very great to account for the continuous form of the isobars up to 135° . E. S. H.

Heat of adsorption of gases on zinc oxide and $\text{ZnO-Cr}_2\text{O}_3$ at low pressures and room temperatures. W. E. GARNER and F. J. VEAL (J.C.S., 1935, 1487—1495; cf. A., 1931, 904).—The heats of adsorption on oxidised or reduced surfaces of ZnO and $\text{ZnO-Cr}_2\text{O}_3$ catalysts decrease as the surfaces become covered with gas, particularly with oxidised surfaces. The adsorption of CO and H_2 on oxidised

$\text{ZnO-Cr}_2\text{O}_3$ occurs irreversibly, and with liberation of 45 kg.-cal. per mol. The surface undergoes simultaneous reduction, the gases being adsorbed on the reduced areas with heats of 10–15 kg.-cal. per mol. O_2 is also adsorbed on the reduced areas, a 2:1 CO-O_2 mixture being adsorbed completely by oxidised $\text{ZnO-Cr}_2\text{O}_3$. CO , H_2 , C_2H_4 , and C_2H_6 are adsorbed reversibly on the reduced surface with heats of 10–25 kg.-cal. per mol., but only when no penetration of capillaries occurs can desorption be completed in a short time at room temp. The behaviour on desorption is discussed with reference to the energies of activation of the adsorption process. It is suggested that the adsorption on the reduced surface is chemisorption. J. W. S.

Kinetics of absorption of oxygen by pyrocatechol. M. A. JOSLYN and G. E. K. BRANCH (J. Amer. Chem. Soc., 1935, 57, 1779–1785).—The dependence of reaction rate on p_{H} , pyrocatechol concn., partial pressure of O_2 , temp., and surface has been studied in buffered and unbuffered solutions. The heats of activation in NaOH solutions and in phosphate buffers have been determined at 20–35°. E. S. H.

Special cases of propagation of capillary action. C. E. GUYE (Helv. phys. Acta, 1934, 7, 850–855; Chem. Zentr., 1935, i, 1987; cf. this vol., 581).—Mathematical. J. S. A.

Dimensions of soap molecules as supposedly deduced from surface tension measurements. H. M. CASSEL (J. Amer. Chem. Soc., 1935, 57, 2009).—A criticism (cf. du Nouÿ, A., 1925, ii, 109). E. S. H.

Properties of detergent solutions. I. Influence of hydrogen-ion concentration on the surface tension of soap solutions. J. POWNEY (Trans. Faraday Soc., 1935, 31, 1510–1521).—Surface tensions of Na and K laurate, myristate, and oleate have been measured at 20° in presence of atm. CO_2 and of different concns. of added alkali. The effect of the latter is most marked with the laurate, and in all cases depends on soap concn. The results are discussed. F. L. U.

Inter-phase energies in systems of pure electro-neutral phases. H. HOHN and E. LANGE (Physikal. Z., 1935, 36, 603–624).—A discussion of thermodynamic and empirical relations shown by inter-phase energies in phenomena such as wetting, spreading, and cohesion. A. B. D. C.

Surface potential differences of unimolecular films of fatty acids. Y. YAMAGUCHI and S. MIZUNO (Bull. Chem. Soc. Japan, 1935, 10, 453–464).—The p.d. between air and 0.1N-KCl or 0.1N-HCl with a thin film of fatty acid on the substrate has been measured at 17–20° using X-rays to ionise the air gap. The p.d. rises with surface concn. to a const. val. of approx. 350 mv. for $\text{Me}[\text{CH}_2]_n\text{-CO}_2\text{H}$, where $n=12, 14$, and 16, and a const. val. of approx. 240 mv. for $\text{Me}[\text{CH}_2]_7\text{-CH:CH}[\text{CH}_2]_7\text{-CO}_2\text{H}$ (I), the change to a condensed film occurring at an area per mol. of approx. 27 \AA^2 for all acids. The mean vertical component of the dipole moment is 1.89, 1.37, 2.68, and 1.27×10^{-18} e.s.u. for the acids in the order given. It is suggested that (I) is folded at C'C. R. S. B.

Properties of thin layer of clay-water solution interposed between solid surfaces. H. TAKO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 909–919).—The coeff. of friction between a rubber plate (wetted with an aq. suspension of clay) and a plane surface decreases with concn. (c) of clay. With moving surfaces separated by a clay- H_2O film the resisting force is a min. for a velocity (v_0) approx. $\propto c^{1/2}/\eta$ (η apparent viscosity). ηv_0 is approx. insensitive to the addition of CuSO_4 and AlCl_3 , although η increases considerably. R. S. B.

Physical chemistry of flotation. VI. Adsorption of amines by sulphide minerals. E. E. WARK and I. W. WARK (J. Physical Chem., 1935, 39, 1021–1030; cf. B., 1935, 671).—The contact angle between the mineral and aq. solutions of several amine hydrochlorides is the same (about 60°) for all the amines investigated. The Cu minerals respond most readily and the quaternary NH_4 salts are most readily adsorbed. Using hexylamine, sphalerite can be floated away from galena. In a homologous series of amines the efficiency at a given concn. increases with increasing no. of C atoms; the activity increases in the order primary, sec., tert. Contact tests are closely parallel to flotation tests in the same solutions. The contact induced at certain mineral surfaces by some amines is prevented by addition of alkali or acid. E. S. H.

Electro-osmosis with some ceramic diaphragms. A. VAŠIČEK (Sborn. Škol. Tech. Brně, 1934, 8, No. 32; Chem. Zentr., 1935, i, 1350).—Electro-osmotic properties of ceramic diaphragms in aq. KCl have been examined. Surface conduction and electro-osmosis take place in solutions $\geq 0.02\text{--}0.05N$. Electrokinetic potential and surface conduction are dependent on the structure of the diaphragm. J. S. A.

Application of an empirical correction to the Donnan effect in the determination of mol. wts. of proteins by osmotic pressure measurements. D. R. BRIGGS (J. Physical Chem., 1935, 39, 983–995).—The relation between the observed osmotic pressure, P_o , and that calc. on the basis of unequal distribution of diffusible ions, P_c , is given by $E\alpha'([+])^x/(P_o - P_o - P_p) = \text{const.}$, where P_p is the osmotic pressure (calc.) due to protein of mol. wt. M , $E=59.1$ ($pH_o - pH_i$) = the membrane potential, α' = equiv. of diffusible ion derived from unit mass of the protein, $[+]$ = concn. of all ions bearing the same sign of charge as the protein, in the colloid-containing solution, and x is const. for a given colloid. Calculations of M gave 35,000, 60,000, and 80,000 (\pm about 15%) for cryst. ovalbumin, non-cryst. cow-serum albumin, and cryst. horse-serum albumin, respectively. E. S. H.

Cryoscopic study of trichloroacetic acid and its hydrate in benzene and in dioxan solution. R. P. BELL and M. H. M. ARNOLD (J.C.S., 1935, 1432–1435).—Cryoscopic measurements have been made with solutions of $\text{CCl}_3\text{-CO}_2\text{H}$ (I) and $\text{CCl}_3\text{-CO}_2\text{H.H}_2\text{O}$ (II) in C_6H_6 . The solid phase contains a little (I), probably adsorbed, but insufficient to prevent interpretation of the results. (I) is present in C_6H_6 solution as double mols. throughout the concn. range investigated.

(0.01—1.5 mol.). (II) occurs entirely as single mols. in dil. solution, but probably forms double mols. at higher concn. Structures are proposed for single and double mols. (I) occurs entirely as single mols. in dioxan solution, probably owing to association with solvent mols. On addition of an equiv. amount of H_2O only incomplete formation of (II) occurs.

J. W. S.

Cryoscopic study of the total hydration of the ions of sodium bromide. (MLLE.) O. HUN (Compt. rend., 1935, 201, 547—549; cf. A., 1933, 460).—The total hydration in N and in $0.5N$ solution corresponds with 12.9 and 15.3 mols. H_2O , respectively.

T. G. P.

Cryoscopic determination of the total hydration of ions of sodium nitrate. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1935, 201, 660—662; cf. A., 1934, 728).—Hydration corresponds with $NaNO_3 \cdot 9.3H_2O$ and $NaNO_3 \cdot 11.1H_2O$ in $1.0M$ and $0.5M$ solutions, respectively.

H. J. E.

Effect of light on Brownian motion. R. FÜRTH and O. ZIMMERMANN (Ann. Physik, 1935, [v], 24, 183—208).—Unpolarised light of intensity 0.00062—2.6 watt per sq. cm. has no effect on particle size or Brownian motion, irrespective of the material, particle size, or λ of light. The Brownian motion is the same in the direction of the light and perpendicular to it. When linearly polarised light is used, the mean square of the displacement in the direction of the magnetic vector of the light vibration is independent of the particle size and material, but is 7—11% > in the direction of the electric vector or in the direction of propagation of the light. The effect disappears if the short-wave part of the light is filtered out. The results disagree with those of Pospíšil (A., 1927, 823; 1930, 412), and a systematic error in his work is suggested. An explanation of the effect is attempted on the basis of photo-electric theory.

A. J. M.

State of aggregation of colloids and calculation of mol. wt. F. F. NORD and F. E. M. LANGE (Naturwiss., 1935, 23, 722).—When solutions of lyophilic and lyophobic colloids of concn. 10^{-6} —5% are submitted to temp. $< 0^\circ$, the particles are either condensed or further dispersed according to the concn. The size of the particle depends on the previous physical treatment of the solution, and hence the mol. wt. of a colloid has little chemical significance.

A. J. M.

Colloidal systems of three components. I. Colloidal behaviour of the critical mixture of three fluids. N. SATA and O. KIMURA (Bull. Chem. Soc. Japan, 1935, 10, 409—420).—The crit. blue opalescence with 3-component mixtures of H_2O and various org. fluids has been studied at 30° . The system C_6H_6 — H_2O — $EtOH$ or $MeOH$ gives emulsoids with the greatest range of stability. When C_5H_{12} or C_6H_{14} replaces C_6H_6 , or when $COMe_2$ replaces $EtOH$, no opalescence occurs. With C_6H_6 — H_2O — $EtOH$ at approx. 20 — 40° opalescence is stable for an interval of approx. 10° . Mixtures poor in H_2O are stable at a lower temp. than those rich in H_2O . The disperse phase is rich, and the dispersion medium poor, in C_6H_6 .

R. S. B.

Hydrous thorium hydrosols considered as polynuclear basic thorium complexes. A. W. THOMAS and C. B. KREMER (J. Amer. Chem. Soc., 1935, 57, 1821—1824).—The p_H of $Th(OH)_4$ sols is raised by adding K salts. The effect is ascribed to displacement of co-ordinated OH groups by the anion of the added salt, the anion then becoming co-ordinately bound. The dialysed sols rapidly become more acid when kept at room temp., the rate increasing at higher temp. The heated sols are less sensitive to p_H change on addition of salts. A polyolated or oxolated structure of the micelle is assumed.

E. S. H.

Basic zirconium chloride hydrosols. A. W. THOMAS and H. S. OWENS (J. Amer. Chem. Soc., 1935, 57, 1825—1828).—The p_H of the sols is raised on adding K salts by a process similar to that observed with $Th(OH)_4$ sols (cf. preceding abstract).

E. S. H.

Absorption spectra of metallic and organic colloidal solutions and the absorption of metal films. A. T. WILLIAMS (Compt. rend., 1935, 201, 665—667; cf. A., 1932, 691).—Data are recorded for colloidal solutions of Ag, Au, and Pt. The ultraviolet absorption band (2270—2820 Å.) is independent of the method of preparing the colloid. The absorption spectra of colloidal solutions of org. mols. resemble those of true solutions.

H. J. E.

Viscosity of titanium dioxide sol in presence of electrolytes. S. M. MEHTA and (MISS) O. JOSEPH (J. Indian Chem. Soc., 1935, 12, 552—559).—The change of viscosity of TiO_2 sol. dialysed and diluted to different extents, on the addition of salts, has been studied by the method described previously (A., 1932, 693). The viscosity of the sol increases with time, and the viscosity-time curves are periodic or discontinuous in the slow region (cf. A., 1934, 1171). The sp. conductivity and $[H^+]$ of the sol diminishes on dilution and on dialysis, and the increased rapidity of coagulation is attributable to decrease of peptising ions. The autocatalytic nature of the coagulation process disappears as the sol is dialysed.

J. W. S.

Viscosimetric investigation of benzene solutions of ethyl- and benzyl-cellulose. S. LEE and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 436—438B).—Vals. are recorded for η_{sp}/c (when $c=0$), the form and charge factor, and the sp. vol. for solutions of ethyl- (I) and benzyl-cellulose (II) in C_6H_6 at 10 — 60° . η/c for (I) is 0.885 at 20° and 0.74 at 50° , and for (II) is 1.2 at 10° and 0.77 at 60° .

A. G.

Influence of gases on silver sols. T. I. TAYLOR and W. H. CONE (J. Physical Chem., 1935, 39, 997—1003).—The effect of O_2 , N_2 , H_2 , CH_4 , and C_2H_4 on the pptn. vals. (for $NaNO_3$), electrophoretic velocities, and conductances of Ag sols has been investigated. The gases have a stabilising effect on those sols which are on the border line of stability and apparently contain secondary particles. The electrophoretic measurements show no increase in the average charge of the particles.

E. S. H.

Properties of silver halides peptised by ultrasonic waves in gelatin. H. W. DANGERS (Z. Physik, 1935, 97, 34—45).—Peptisation under varied

conditions has been studied, and it is shown that this treatment can produce a max. colour-sensitivity.

A. B. D. C.

Comparative investigations on caramel and molasses colloids.—See this vol., 1485.

Relations between colloid and constitutive changes of proteins. IV. Heat-coagulation and colloid structure of albumins. W. PAULI and J. WEISSBROD (*Kolloid-Beih.*, 1935, 42, 429—462; cf. this vol., 823).—Neutral salts raise the coagulation temp. of serum albumin. The effect is detectable at a concn. of 0.001*N*, and varies with the anion according to the Hofmeister series; SCN has the greatest effect. Sucrose and CO(NH₂)₂ at high concns. have a similar effect. The coagulation temp. of ovalbumin is raised by electrolytes only at low concns. (<0.001*N*); at higher concns. the coagulation temp. is lowered. The order of effectiveness of different anions is that usually observed with positively-charged colloids; sucrose and CO(NH₂)₂ act as with serum albumin, but the effect of glycine is similar to that of a neutral salt. Complex relations are observed with mixed albumin sols. The mechanism of these phenomena is discussed.

E. S. H.

Combination of bivalent manganese with certain proteins, amino-acids, and related compounds. R. K. MAIN and C. L. A. SCHMIDT (*J. Gen. Physiol.*, 1935, 19, 127—147).—Partition, electrophoretic, and anomalous titration data show that Mn⁺⁺ forms complexes with H₂SO₄, H₃PO₄, nucleic and glycerophosphoric acids, with dicarboxylic, hydroxy-mono-, -di-, and -tri-carboxylic acids, dicarboxylic NH₂-acids, and certain enol sulphonic acids; also with certain proteins (casein, edestin, gelatin).

F. A. A.

Lecithin as a dispersing agent for dibenzanthracene. H. D. BARNES (*Nature*, 1935, 136, 756).—Two methods for obtaining colloidal dispersions of dibenzanthracene using lecithin as dispersing agent are described.

L. S. T.

Swelling of structured proteins.—See this vol., 1522.

Electrophoresis of sterols.—See this vol., 1523.

Factors influencing electrophoretic mobilities and apparent critical potentials. H. L. WHITE and B. MONAGHAN (*J. Physical Chem.*, 1935, 39, 925—934).—In very dil. electrolyte solutions the electrophoretic mobility of small glass particles is < the electro-osmotic mobility at a glass surface, but at 0.01*M* the mobilities are identical. The same holds for gelatin surfaces. The effect is traced to a retardation of the particles in very dil. solutions, chiefly through polarisation of the double layer by the applied field. The apparently lower crit. potential obtained with electrolytes which coagulate in low concns., and kindred phenomena are explained.

E. S. H.

Comparison of the electrokinetic potentials at fused and unfused glass surfaces. B. MONAGHAN and H. L. WHITE (*J. Physical Chem.*, 1935, 39, 935—939).—The prep. of glass spheres 3 μ or less in diameter is described. The electrophoretic velocity of Pyrex glass spheres in aq. KCl is the same as that

of unfused Pyrex particles and < the electro-osmotic velocity at a fused Pyrex surface.

E. S. H.

Thermal equilibrium between ethylene iodide, ethylene, and iodine. G. R. CUTHBERTSON and G. B. KISTIAKOWSKY (*J. Chem. Physics*, 1935, 3, 631—634).—Results obtained between 50° and 125° agree with the extrapolation of Mooney and Ludlam's data (*A.*, 1929, 766) for lower temp., but disagree with their high-temp. data. The heat of dissociation of C₂H₄I₂ is 13.4±0.5 kg.-cal. per mol. The position of equilibrium is given by log *K* (atm.)=8.17—13,400/4.58*T*.

T. G. P.

Exchange of heavy hydrogen atoms between hydrogen and ammonia. K. WIRZ (*Naturwiss.*, 1935, 23, 721—722).—*K* for the reaction NH₃+HD=NH₂D+H₂ is 1.9 at 300°.

A. J. M.

Fourth ionisation constant of ferrocyanic acid. I. M. KOLTHOFF and W. J. TOMSICEK (*J. Physical Chem.*, 1935, 39, 955—958).—The val. 5.6×10⁻⁵ at 25° has been derived from a study of the effect of H⁺ on the oxidation potential of a mixture of K₄Fe(CN)₆ and K₃Fe(CN)₆ at known ionic strengths.

E. S. H.

Titration curves and dissociation constants of *l*-ascorbic acid (vitamin-C) and diethyl dihydroxymaleate. W. D. KUMBLER and T. C. DANIELS (*J. Amer. Chem. Soc.*, 1935, 57, 1929—1930).—The results show that *l*-ascorbic acid is 1000 times as strong as Et₂ dihydroxymaleate.

E. S. H.

Interaction of amino-acids and salts. I. Zinc chloride. II. Sodium chloride and thallous chloride. N. R. JOSEPH (*J. Biol. Chem.*, 1935, 111, 479—487, 489—499).—The addition of various NH₂-acids decreases the activity coeffs. of ZnCl₂, TlCl, and NaCl in concn. cells without liquid junction. Comparison is made with results obtained by other methods. These indicate that "salting-out" forces of opposite sign are present, which become relatively greater with increase in the length of the hydrocarbon chain of the NH₂-acid and the dielectric const. of the solvent.

F. A. A.

Association in the dissociation of simple straight-chain sulphonic acids in water. I. Conductivity. II. F.p. III. Electromotive force. J. W. McBAIN and M. D. BETZ. IV. Comparison of results, and so-called "Hammarsten effects." J. W. McBAIN (*J. Amer. Chem. Soc.*, 1935, 57, 1905—1909, 1909—1912, 1913—1916, 1916—1920).—I. In very dil. solutions the straight-chain sulphonic acids behave as simple, partly dissociated electrolytes. Conductivity is at a min. in 0.05*N* solutions and increases greatly at higher concns. This is explained by the association of like ions to form ionic micelles, the equiv. conductivity of which in conc. solutions attains that of OH⁻. This effect predominates over the ordinary features of interionic attraction.

II. F.-p. data support the above results.

III. E.m.f. data for sulphonic acids and their mixtures with HCl show that the ionic micelles of the sulphonic acids cannot be regarded as equiv. to multivalent ions in which the charges are conc. at

one point. The degree of dissociation of sulphonic acids in conc. solution remains const. or tends to increase.

IV. The above results are discussed. The dissociation of the colloidal electrolyte is about 50%. An explanation of the Hammarsten effect, based on steric hindrance to close packing, is given.

E. S. H.

Thermodynamic properties of methyl bromide.

S. SUGAWARA (J. Inst. Mech. Eng. Tokyo, 1935, 38, 87—88).

CH. ABS. (e)

Thermodynamic properties of uni-univalent halide mixtures in aqueous solution. H. S. HARNED (J. Amer. Chem. Soc., 1935, 57, 1865—1873).—E.m.f. of the cells $H_2|HCl(0.01), NaCl(m)|AgCl|Ag$ have been determined at 5° intervals from 0° to 60°. The results are considered in relation to the law of linear variation of the logarithm of the activity coeff. at const. ionic strength for such halide mixtures.

E. S. H.

Thermodynamics of ionised water in sodium chloride solutions. H. S. HARNED and G. E. MANNWEILER (J. Amer. Chem. Soc., 1935, 57, 1873—1876).—The ionic activity coeff. product of H_2O in aq. $NaCl$ has been calc. from e.m.f. measurements of the cells $H_2|NaOH(0.01), NaCl(m)|AgCl|Ag$ and $H_2|HCl(0.01), NaCl(m)|AgCl|Ag$ from 0° to 60°. The logarithm of the ionisation in alkaline halide solutions at a given concn. varies nearly linearly with the sum of the reciprocal of the ionic radii. The total heat change for the ionisation of H_2O and the relative partial mol. heat content of H^+ and OH^- in aq. $NaCl$ have been determined from 0° to 60°.

E. S. H.

Neutral salt action in non-aqueous solutions.

P. P. KOZAKEVITSCH (Bull. Soc. chim., 1935, [v], 2, 1631—1655).—The thermodynamic activity of CO_2 , CCl_4 , $CHCl_3$, NH_4Et_2 , $C_{10}H_8$, and camphor in $MeOH$ solution is increased by addition of salts to almost the same extent as in aq. solution. The distribution coeff. of these substances between vaseline oil and $MeOH$ is independent of their concn. but varies with the neutral salt concn. Setschenov's equation holds for $MeOH$ solutions of most metal halides except Li salts. The relative effects vary with the nature of the ions present and are discussed with reference to the action of undissociated mols. and the structure of the solvent. The electrostatic effect of the ions extends probably only to a unimol. layer of $MeOH$ mols. The anomalous behaviour of $HgCl_2$ and CdI_2 in presence of camphor indicates the existence of compounds $C_{10}H_{16}O, HgCl_2$ and $C_{10}H_{16}O, CdI_2$. There is also evidence of complex formation between several salts and $C_{10}H_8$.

J. W. S.

Application of equations for the chemical potentials to partially miscible solutions. G. SCATCHARD and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 1805—1809).—Equations for the free energy of mixing are computed from the mutual solubilities of partly miscible substances; the vapour compositions and pressures calc. from these equations agree satisfactorily with experiment.

E. S. H.

Application of equations for the chemical potentials to equilibria between solid solution

and liquid solution. G. SCATCHARD and W. J. HAMER (J. Amer. Chem. Soc., 1935, 57, 1809—1811).—Theoretical. Simple equations for the change in chemical potentials on mixing are applied to the equilibria between solid and liquid solutions of the $Ag-Pd$ and $Au-Pt$ systems.

E. S. H.

Vapour pressure and thermal dissociation of orthoboric acid. S. BEZZI (Gazzetta, 1935, 65, 766—772; cf. A., 1933, 120).—The v.p. of H_3BO_3 , measured at various temp. by a dynamic method, is independent of the partial pressure of H_2O in the transporting gas and equal to the v.p. of its saturated solutions. H_3BO_3 is therefore volatile in steam on account of its own v.p., and not because it forms volatile compounds with H_2O . The equilibrium pressures of the system $H_3BO_3 \rightleftharpoons HBO_2 + H_2O$ have been determined.

O. J. W.

Two compounds of titanium tetrachloride and hydrogen chloride. A. CHRÉTIEN and G. VARGA (Compt. rend., 1935, 201, 558—560).—Thermal analysis of the system $TiCl_4-HCl$ reveals $TiCl_4 \cdot 6HCl$, m.p. -86° , and $TiCl_4 \cdot 2HCl$, m.p. -30.8° , and the corresponding three eutectics.

T. G. P.

System water-sulphuric acid-nickel sulphate. R. ROHMER (Compt. rend., 1935, 201, 672—674).—Equilibrium data at 25° and 50° are recorded. In presence of H_2SO_4 , both $NiSO_4 \cdot H_2O$ (I) and $NiSO_4$ (II) may be prepared at 25°. $NiSO_4 \cdot 4H_2O$, which is metastable, exists at 25° in contact with solutions containing <43% of H_2SO_4 . Above 84.8° only (I) and (II) occur as stable solid phases.

H. J. E.

Ternary system $K_2SO_4-(NH_4)_2SO_4-H_2O$. E. BOVALINI and E. FABRIS (Gazzetta, 1935, 65, 617—623).—The isotherms at 0°, 35°, 50°, 70°, and 96.5° have been studied. At all temp. the salts form a continuous series of mixed crystals.

O. J. W.

Singular elements in the ternary system: lithium oxide-nitric anhydride-water. Effect of hydration. M. I. RAVITSCH (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 235—244; cf. A., 1932, 469).—Isotherms have been determined at 0°, 15°, 25°, 28.5°, 65°, and 130°.

CH. ABS. (e)

Singular fold in the ternary system: sodium chloride-platinum chloride-water. N. S. KURNAKOV and M. I. RAVITSCH (Ann. Inst. Anal. phys.-chim. U.S.S.R., 1935, 7, 225—233; cf. A., 1933, 1013).—The singular points of the ice field and the cryohydric lines are described. The results are compared with other ternary systems. Na_2PtCl_6 behaves as a complex salt.

CH. ABS. (e)

System $K_2SO_4-MgSO_4-CaSO_4$. L. S. RAMSDELL (Amer. Min., 1935, 20, 569—574).—X-Ray examination of fused mixtures of K_2SO_4 , $MgSO_4$, and $CaSO_4$ show the existence of a continuous isomorphous series with $K_2Mg_2(SO_4)_3$ (langbeinite) and $K_2Ca_2(SO_4)_3$ as end-members, no other compounds being formed. The lattice is a simple cube, 4 mols. per unit cell; the cube edge varies from 9.96 Å. for the Mg to 10.37 Å. for the Ca end-member. Polyhalite (I) calcined at approx. 475° for a short period gives a product of low d from which practically complete extraction of K_2SO_4 and $MgSO_4$ is obtained by hot

H₂O. The CaSO₄ residue is rapidly converted into gypsum by cold H₂O, but X-ray photographs show that it is normal anhydrite. Calcination at higher temp. or for longer periods reduces the yield. The mechanism of dehydration of (I) is discussed.

L. S. T.

Alkali aluminium silicates. X. System ultramarine silicate-sulphur. E. GRUNER and J. FÖRSTER (Z. anorg. Chem., 1935, 224, 369—387; cf. this vol., 1470).—Pressure-S content curves representing the isothermal decomp. of blue and green ultramarine between 600° and 1050° have the same form as those of substances containing "zeolitic" H₂O. The residue left when all S has been expelled by heat shows the lattice of nephelite. The constitution of ultramarine is discussed.

F. L. U.

Dissociation energy of carbon monoxide and the heat of sublimation of carbon. H. LESSHEIM and R. SAMUEL (Nature, 1935, 136, 606).—The val. calc. for the heat of dissociation of CO is 10.45 v.e. (cf. this vol., 925), giving 155.7 kg.-cal. per mol. for the heat of sublimation of β -graphite at 25°.

L. S. T.

Heat of dilution of cadmium chloride. (MLLE.) M. QUINTIN (Compt. rend., 1935, 201, 549—550).—Calculations are made from previous data (this vol., 826).

T. G. P.

Free energy change that accompanies hydrogenation of pyridine to piperidine. G. H. BURROWS and L. A. KING, jun. (J. Amer. Chem. Soc., 1935, 57, 1789—1791).—The equilibrium between C₅H₅N, C₅H₁₁N, and H₂ at 150°, 170°, and 180° has been determined; the heat of reaction and accompanying free energy changes have been calc.

E. S. H.

Conductivities of acids and other solutes in pyridine. M. M. DAVIES (Trans. Faraday Soc., 1935, 31, 1561—1567).—Conductivities of HClO₄, HNO₃, and HI in C₅H₅N at 25° have been measured. The dissociation const. are, respectively, 7.55×10^{-4} , 4.96×10^{-5} , and 5.9×10^{-4} . Results obtained by addition of C₅H₅N to solutions of CPh₃Cl and of C₆H₂Cl(NO₂)₃ in PhNO₂ indicate the formation of complexes with C₅H₅N. C₆H₃(NO₂)₃ behaves as a weak acid in C₅H₅N, whilst C₆Me₃(NO₂)₃ does not.

F. L. U.

Conductance of non-aqueous solutions. I. Sodium triphenylboron and disodium tri- α -naphthylboron in diethyl ether. H. E. BENT and M. DORFMAN (J. Amer. Chem. Soc., 1935, 57, 1924—1927).—Equiv. conductances have been determined at 0° and 25° from 10^{-1} to 10^{-7} mol. per litre. The structure of B(C₁₀H₇- α)₃ is discussed in the light of the results.

E. S. H.

Transport number and valency of silver in silver amalgam. K. SCHWARTZ (Monatsh., 1935, 66, 218—219).—Ag in Ag amalgam is a bivalent anion for which transport no./concn. = 4.0×10^{-4} and diffusion const. = 1.0×10^{-5} cm. per sec.

T. G. P.

Cathode-ray oscillograph method of investigating the Wien effect in electrolytes. W. HÜTER (Ann. Physik, 1935, [v], 24, 253—272).—The oscillographic method clearly indicates the Wien effect, and

allows the varying magnitude of the effect with field strength to be rapidly determined. A. J. M.

Behaviour of oxygen electrodes in carbonate melts. E. BAUR and R. BRUNNER (Z. Elektrochem., 1935, 41, 794—796).—The construction of O₂ electrodes for use at 450—1000° is described. C.d.-p.d. curves covering this temp. range have been determined.

E. S. H.

Oxidation potential of the system potassium ferrocyanide-potassium ferricyanide at various ionic strengths. I. M. KOLTHOFF and W. J. TOMSICEK (J. Physical Chem., 1935, 39, 945—954).—The normal electrode potential is 0.3560 volt at 25°. In very dil. solution the variation of potential with increasing ionic strength is > calc. on the basis of the simple Debye-Hückel expression. For the same valency type of salts the anion effect on the potential is the same for different anions at the same ionic strength. The cation effect of the alkaline-earth ions is > that of the alkali ions, which decreases in the order Ca > Rb > K = NH₄ > Na = Li.

E. S. H.

Junction potentials between solutions of sugars and potassium chloride. J. M. ORT and M. H. ROEPKE (J. Physical Chem., 1935, 39, 941—943).—A saturated aq. KCl bridge eliminates all significant liquid junction potentials, even in the most conc. sugar solutions, if the sugar solution has $p_H > 10$ and does not contain a large amount of ionised decomp. products.

E. S. H.

Electromotive forces due to the combination of metal [electrodes] in gelatin and the importance of the Volta effect in cells. S. VEIL (Compt. rend., 1935, 201, 551—552).—The p.d. between electrodes of Zn, Cd, Fe, Pb, Ni, and Cu and a Pt wire in gelatin have been measured with a quadrant electrometer (cf. this vol., 822).

T. G. P.

Polarographic studies with the dropping mercury cathode. LII. Electro-reduction of benzaldehyde. M. TOKUOKA. LIII. Electro-reduction of ferric-mannitol complexes in alkaline solutions. K. KOMÁRAK. LIV. Electro-reduction of formaldehyde. F. G. JAHODA (Coll. Czech. Chem. Comm., 1935, 7, 392—403, 404—414, 415—423).—LII. Polarographically recorded current-voltage curves show that the reduction occurs in two stages, each of which requires one F per mol. of PhCHO. The first stage of reduction probably yields free radicals, $\cdot\text{CHPh}\cdot\text{OH}$, which may subsequently form hydrobenzoin; the second stage leads to CH₂Ph-OH and does not involve the deposition of H⁺ or an alkali metal. As the p_H is increased, the potential for the first stage becomes more negative and that for the second stage slightly more positive. The potentials coincide at $p_H > 6$ and decrease by approx. -0.025 volt per unit rise of p_H . These results are, in general, independent of the type of buffer solution used. The reduction potential is approx. -1.5 volt, with respect to the $N\text{-Hg}_2\text{Cl}_2$ electrode in neutral aq. MCl (M=Na, K, NMe₄), but is raised slightly by Sr⁺⁺, Ca⁺⁺, NH₄⁺, NH₂Me⁺, NH₂Me₂⁺, and NHMe₃⁺, which also increase the

diffusion current. Electro-reduction of BzOH in presence of NMe_4^+ occurs at -2.3 volt.

LIII. Mannitol does not affect the current-voltage curve obtained with slightly acid solutions of Fe^{II} , but in alkaline solutions, especially in absence of O_2 , two saturation currents ("waves") are observed. Glycerol, sucrose, lactic and citric acids give similar results if added before the solution is made alkaline. The "waves" correspond with the successive electro-reductions: Fe^{III} -org. mol. complex $\rightarrow \text{Fe}^{II}$ -org. mol. complex $\rightarrow \text{Fe}$, and the ratio of the heights of the waves decreases from 1:2 to 1:1 as the alkali is neutralised. The origin of the last phenomenon is discussed. The affinity of the Fe^{III} -mannitol complex is small.

LIV. The saturation current, i , is a linear function of $[\text{CH}_2\text{O}]$ and the "mol. reduction potential" is -1.50 volt. Reduction of 1 mol. of CH_2O requires $2F$. i is increased in alkaline solutions and by rise of temp., indicating dissociation of polymerisation products. The max. of current-voltage curves and i decrease with increasing age of CH_2O solutions. At 90° , 7×10^{-8} g. of CH_2O in 1 c.c. can be determined polarographically to within 10% in presence of other aliphatic aldehydes, ketones, esters, and org. acids. Minute traces of CH_2O in coal gas are inferred.

J. G. A. G.

Electrolytic reduction potential of organic compounds. XXII. Mechanism of electrolytic reduction. I. TACHI (J. Agric. Chem. Soc. Japan, 1935, 11, 734—740).—Small drops of H_2O -insol. org. compounds placed on a Hg cathode having a small surface at first become flat owing to polarisation, but further polarisation tends to restore the original form. The angles of contact between drop and Hg and the changes which these undergo when polarisation occurs vary with the compound used and with the nature of the dissolved electrolyte. Camphor oil drops become flatter than do those of PhNO_2 and CCl_4 . PhNO_2 drops become flatter in alkaline than in acid media.

W. McC.

General properties of electrodes of photo-sensitive organic substances. (Miss) H. T. NGA (J. Chim. phys., 1935, 32, 564—584).—Electrodes were prepared by immersing Cu (or Pt) in collodion and then in aq. solutions of various coloured substances. The photo-potential (E_p) varies with the nature, and diminishes to a steady val. with increasing concn., of the electrolyte. Oxidising or reducing agents diminish E_p irreversibly. The temp. coeffs. of the electrodes are generally negative; for pyronine it is positive, and for crystal-violet zero. The log. variation of E_p with light intensity has been confirmed. The variations of E_p (for different λ) with the polarisation of the electrodes indicate that photo-electric and not electronic processes play the major part. E_p bears no discernible relation to photo-conductivity, is sensibly zero in non-aq. solvents, and \propto the % of H_2O in aq. glycerol. The properties of org. and inorg. photo-electrodes are thus very similar.

T. G. P.

Dependence of the electrochemical properties of an element on the state of aggregation. II. Polarisation relations in the electrolytic de-

position and dissolution of gallium and their dependence on temperature near the m.p. O. STELLING (Z. Elektrochem., 1935, 41, 779—789; cf. this vol., 1325).—Further studies of the anodic and cathodic behaviour of Ga in dil. HCl and NaOH confirm that liquid Ga behaves as a nobler metal than solid Ga.

E. S. H.

Electrode dispersion of noble metals. A. VOET (Trans. Faraday Soc., 1935, 31, 1488—1491).—Anodic disintegration of Au, Pt, and Pd is observed when acid, alkaline, or neutral solutions are electrolysed at 100 volts and high c.d. It is always accompanied by periodicity of the current, and is not due to the Wehnelt effect. An explanation based on the formation and disruption of an oxide layer is given.

F. L. U.

Passivity of iron and steel in nitric acid solution. VII. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 925—964; cf. this vol., 827).—The passivation of Fe in conc. HNO_3 is more difficult to effect when the test piece has suffered internal stress by twisting.

R. S. B.

Quantum mechanics and kinetics of reactions in organic chemistry. C. N. HINSHELWOOD (Bull. Soc. chim., 1935, [v], 2, 1786—1799).—A lecture.

General method of statistics and its application to chemical energetics. G. ALLARD (Ann. Physique, 1935, [xi], 4, 305—377).—Mathematical.

J. W. S.

Kinetics of slow reactions and their entropy changes. F. G. SOPER (J.C.S., 1935, 1393—1395).—On the hypothesis that the decomp. of the crit. complex into the products and reagents \propto the relative thermodynamic probabilities of the three states, a factor representing the fraction of crit. complexes which decompose to reaction products has been introduced into the velocity equation. The modified equation is of correct thermodynamic form, and reduces to $k = Ze^{-E/RT}$ when the reaction is attended by an increase of entropy, but gives greatly diminished rates when the entropy change is negative. Existing data show that, with one exception, the classification of reactions as "normal" and "slow" is in general agreement with that based on the sign of entropy change. The factor affects only slightly the existing agreement between observed and calc. velocities of reactions associated with small decreases of entropy, e.g., $2\text{HI} \rightarrow \text{I}_2 + \text{H}_2$; $\text{NH}_4\text{CNO} \rightarrow \text{CO}(\text{NH}_2)_2$.

J. G. A. G.

Photographic investigation of flame movements in gaseous explosions. VII. Phenomenon of spin in detonation. W. A. BONE, R. P. FRASER, and W. H. WHEELER (Phil. Trans., 1935, A, 235, 29—68; cf. A., 1932, 232).—The spiral track formed by the rotation of the "head" of detonation in the system moist $2\text{CO} + \text{O}_2$ has been studied in relation to the influence of dimensions and shape of the explosion tube and the addition of small amounts of H_2 or $\text{Fe}(\text{CO})_5$. Drying the mixture with P_2O_5 increases the flame speed and stabilises the spin. In a moist mixture the flame speed is reduced in passing through a powerful axial magnetic field, and both spin and detonation can be suppressed when

the detonation traverses a sufficiently strong electric field in a negative to positive direction. A new view of the detonation wave is advanced. It is viewed as two separable components, an intensively radiating flame-front with an invisible shock wave immediately ahead of it; whether persistent spin is developed or not depends on the stability of their association.

E. S. H.

Ignition of gases. IX. Ignition by a heated surface. Mixtures of methane and air at reduced pressures. C. A. NAYLOR and R. V. WHEELER (J.C.S., 1935, 1426—1430).—In general, the upper ignition temp., T , of CH_4 -air mixtures in a SiO_2 vessel rises as the proportion of CH_4 is raised from 5.3 to 12.5%, but the variation of T with total pressure ($P=263$ —760 mm.) is not uniform. With $> 10.7\%$ of CH_4 , T decreases progressively as P increases, but with less CH_4 , two pressure limits are found for each val. of T (cf. A., 1933, 129). The data do not conform to the Semenov relation between T and P . The lag before ignition decreases as P is raised and as the % of CH_4 is decreased. The results accord with earlier work (A., 1931, 1240) and an interpretation is suggested.

J. G. A. G.

Kinetics of the thermal decomposition of acraldehyde. H. W. THOMPSON and J. J. FREWING (J.C.S., 1935, 1443—1451).—The thermal decomp. of 5—650 mm. of acraldehyde at 490—570° is essentially homogeneous and affords C_4H_8 , C_2H_4 , CO , C_2H_6 , CH_4 , and H_2 . The proportion of C_4H_8 increases with increase of initial pressure and decreases during the course of a run. C_2H_6 , CH_4 , and H_2 are also primary products. The plot of the reciprocal of the period of half change against the initial pressure, P_0 , is segmented and the reaction probably consists of several independent quasi-unimol. processes superposed on a bimol. reaction. The energy of activation increases with decrease of P_0 .

J. G. A. G.

Velocity of thermal decomposition of chloropicrin. D. RĂDULESCU and G. ZAMFIRESCU (Bull. Soc. Chim. România, 1935, 17, 87—92).—The decomp. is unimol. up to 160° and has a large temp. coeff. Photodecomp. is inhibited by the NOCl produced, which absorbs the light.

R. S.

Diabatic reactions and primary chemiluminescence. R. A. OGG, jun., and M. POLANYI (Trans. Faraday Soc., 1935, 31, 1375—1384; cf. this vol., 452).—An outline of the theory of ionogenic reactions and a list of its applications are given. Luminescence accompanying a primary chemical change is described as the inverse of predissociation.

F. L. U.

Mechanism of ionic reactions. Heat of ionic substitution reactions. R. A. OGG, jun. (Trans. Faraday Soc., 1935, 31, 1385—1392; cf. preceding abstract).—Estimates of the heat (H) involved in reactions between MeX ($\text{X}=\text{Cl}$, Br , I) and a negative ion other than halogen show that ionic interchange reactions having large positive H are characterised by small energies of activation. Examples are given and discussed.

F. L. U.

Steric factor of bimolecular association reactions. C. E. H. BAWN (Trans. Faraday Soc., 1935, 31, 1536—1547).—Consideration of the reaction

velocity coeff. by means of the transition state method indicates that the steric factor of bimol. association reactions is related to the probability of the transition state. The theoretical results are applied to the cracking of long-chain hydrocarbons.

F. L. U.

Velocity of oxidation of sulphides and sulphoxides by peracetic acid. J. BÖESEKEN and (Mlle.) E. ARRIAS (Rec. trav. chim., 1935, 54, 711—715).—The reaction between Ph_2SO and AcO_2H in AcOH is bimol. and its velocity coeff. increases considerably with increasing $[\text{AcO}_2\text{H}]$, possibly owing to spontaneous decomp. of the AcO_2H and an accelerating influence of the change of medium. The oxidation of Ph_2S by AcO_2H occurs in two stages, the bimol. oxidation to Ph_2SO being complete in 3 min. and being followed by oxidation of the Ph_2SO to Ph_2SO_2 . Oxidation of $(p\text{-C}_6\text{H}_4\text{Br})_2\text{S}$ is similar, but the velocity of reaction is less. The results are compared with those for the oxidation of unsaturated hydrocarbons.

J. W. S.

Decomposition of polythionate solutions. A. KURTENACKER, A. MUTSCHIN, and F. STASTNY (Z. anorg. Chem., 1935, 224, 399—419; cf. A., 1934, 160).—The different modes of decomp. of aq. solutions of $\text{K}_2\text{S}_n\text{O}_6$ ($n=3$ —6) are discussed. Velocities of decomp. have been measured, mostly at 50°, and the influence of $[\text{H}^+]$ has been studied. All the decomp. can be represented by a unimol. coeff., except for tetra-, penta-, and hexa-thionates within the range p_H 4—9, where they may be markedly autocatalytic.

F. L. U.

Critical increment of ionic reactions. Influence of dielectric constant and ionic strength. W. J. SVIRBELY and J. C. WARNER (J. Amer. Chem. Soc., 1935, 57, 1883—1886).—Assuming that the rates of ionic reactions are functions only of temp., dielectric const., and ionic strength, equations are derived which predict the influence of dielectric const. and ionic strength on crit. increments. Experimental data for the reaction between NH_4^+ and CNO^- in H_2O and $\text{EtOH-H}_2\text{O}$ are in agreement with the theory.

E. S. H.

Mechanism and thermal effect of fulminic acid polymerisation. K. SENNEWALD and L. BIRCKENBACH (Annalen, 1935, 520, 201—234; cf. A., 1934, 994).—The heat of polymerisation of fulminic acid (I) in 0.4*N* aq. solution has been measured in presence of H_2SO_4 at various concns. When the $[\text{H}_2\text{SO}_4] \geq 0.01*N*$ the heat produced is 20% $>$ when $[\text{H}_2\text{SO}_4]$ is $> 0.15*N*$. In the latter case the reaction is bimol., whilst in the former it is of no simple order. These results, in conjunction with chemical observations, indicate that in neutral ($< 0.01*N*$ -acid) solution cyano-oximinoacetohydroxamic acid is formed as the final, with metafulminuric acid as an intermediate, product. In acid ($> 0.15*N*$) solution the primary product is dicarbonyldioxime (II), a small part of which combines with a mol. of (I) to form a trimeride, whilst a larger part undergoes polymerisation to *isocyanilic acid*. The following [from (II) and aq. halogen acid] are described: *bromoglyoxime*, m.p. 173° (decomp.); *iodoglyoxime*, m.p. 163° (decomp.); also *bromoglyoxime anti-diacetate*, m.p. 100°. F. L. U.

Reactivity of halogen compounds. III. Velocities of reaction, energies of activation, and probability factors for the reaction between 2:4-dinitrobromobenzene and aromatic primary amines. IV. Effect of addition of inactive substances on the rate of reaction, energy of activation, and probability factor. A. SINGH and D. H. PEACOCK (J.C.S., 1935, 1410—1411, 1411—1412).—III. Velocity coeffs. of the reaction between 1:2:4- $C_6H_3Br(NO_2)_2$ (I) and NH_2Ph , *m*- and *p*-toluidine in EtOH at 35° and 45° are > with 1:2:4- $C_6H_3Cl(NO_2)_2$ (II), probably owing to a higher probability factor (J.C.S., 1923, 123, 3099).

IV. The rate of reaction of NH_2Ph with (I) and (II) is retarded by added C_6H_6 derivatives, but cyclohexane has no effect. The results negative an earlier hypothesis (A., 1926, 691). J. G. A. G.

Influence of substituents on the additive reactivity of ethylene derivatives. III. Addition of bromine in solution. S. V. ANANTAKRISHNAN and C. K. INGOLD (J.C.S., 1935, 1396—1398; cf. this vol., 1103).—Data are recorded concerning the effect of substituting Me, Ph, and CHO in C_2H_4 on the rate of addition of Br in CH_2Cl_2 solution. The rate is increased with the no. of Me groups, in agreement with the theory (A., 1931, 1267), but in each case the CHO increases the rate, indicating an enforced reversal of the anticipated functions of the reagent.

J. G. A. G.

Steric course of two diene syntheses.—See this vol., 1500.

Hydrolysis of phenylalanine. E. BAUR and G. SCHINDLER (Biochem. Z., 1935, 281, 238—248; cf. A., 1934, 1314).—Results of experiments at 110° confirm those obtained at 80°. The unilateral equilibrium follows the mass action law, the reaction being of the first order. The val. for the heat of reaction deduced from the shift of the equilibrium with temp. change differs considerably from that deduced from calorimetric results, although there is qual. agreement.

W. McC.

Velocity of hydrolysis of cyclic acetals. II. R. LEUTNER (Monatsh., 1935, 66, 222—248; cf. A., 1932, 932).—The velocity of acid hydrolysis of the formal, acetal, and acetonal of $\alpha\gamma$ -butylene glycol, and the formal and acetal of pinacol have been measured. The relative ease of rupture of the 6-ring of the $\alpha\gamma$ -butylene glycol acetals of CH_2O , $MeCHO$, and $COMe_2$ is $1:4 \times 10^3:7 \times 10^6$. The relationship between hydrolysis and constitution is discussed.

T. G. P.

Aliphatic substitution and the Walden inversion. I. E. D. HUGHES, F. JULIUSBURGER, S. MASTERMAN, B. TOPLEY, and J. WEISS (J.C.S., 1935, 1525—1529).—The abs. rate in $COMe_2$ solution of the exchange of I between NaI and *sec*-octyl iodide, determined by means of the radioactive isotope of I, equals, within the limits of experimental error of the measurements of radioactivity (10%), the abs. rate of racemisation of *d-sec*-octyl iodide by NaI in $COMe_2$ solution. The result confirms that in this reaction inversion is directly caused by substitution.

J. G. A. G.

Kinetics of the interactions of sodium hydroxide with the bromoethanes in ethyl-alcoholic

solution. Mechanism of olefine formation in such systems. W. TAYLOR (J.C.S., 1935, 1514—1524; cf. this vol., 173).—Under the conditions of the kinetic experiments at 25° and 55°, the reactions with EtOH-NaOH are: (i) $CH_2Br.CBr_3$ gives $CHBr.CBr_3$, (ii) $CH_2Br.CHBr_2$ gives $CH_2.CBr_2$, (iii) $CMeBr_2$ yields NaOAc and 2.8% of bromo-olefine, (iv) $CHMeBr_2$ affords $MeCHO$ and a very small proportion of bromo-olefine, (v) $(CH_2Br)_2$ gives 79.5% of $CH_2.CHBr$ and 18.5% of $(-CH_2.OH)_2$, and (vi) EtBr yields EtOH and 1.3% of C_2H_4 . The reactions with measurable rate are bimol.; the velocity increases with dilution of NaOH, is independent of the concn. of the bromoethane, and is decreased by H_2O and large proportions of NaBr. There is a clear distinction between (a) reactions involving OH substitution of Br and (b) those involving complete or nearly complete conversion into olefine. In (a) two Br are displaced either simultaneously or consecutively at rates which are of the same order of magnitude, whilst in (b) one Br is displaced almost, if not quite, instantaneously and the second is displaced relatively slowly. Existing theories are criticised (A., 1933, 470; this vol., 452), and the data are interpreted by a mechanism involving a primary mutual attraction of OH' and an initially positively charged H, followed by simultaneous extension and rupture of the C-H and C-Br linkings of the two C of the ethane mol., whereby H_2O , Br', and olefine are formed. The consequences of the theory are discussed.

J. G. A. G.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. VII. *cyclopentanedicarboxylic esters*. Attempted check on the calculation of molecular dimensions. C. K. INGOLD and H. G. G. MOHRHENN (J.C.S., 1935, 1482—1486; cf. this vol., 1076).—From the velocity coeffs. at 20° of the first and second stages of the alkaline hydrolysis of Me_2 *cis*- and *trans*-1:2- and -1:3-*cyclopentanedicarboxylate*, the distances between the CO_2H have been deduced on certain assumptions. In general, the results conform more closely to the requirements of the mol. model when corr. for local dielectric effects in the aq. medium. The causes of the deviations are discussed.

J. G. A. G.

Constitution and reactivity. XIV. Kinetics of sulphonation with oleum and the properties of fuming sulphuric acid of different concentrations. K. LAUER and R. ODA (J. pr. Chem., 1935, [ii], 144, 32—40).—Vals. of q and $\alpha \times 10^{-10}$ (cf. A., 1933, 69) for the sulphonation of anthraquinone using H_2SO_4 with added SO_3 are determined and plotted against $[SO_3]$. The vals. of q and $\alpha \times 10^{-10}$ for sulphonation with SO_3 are 22,000 and 0.1, respectively. These are < the vals. for sulphonation with H_2SO_4 (cf. this vol., 863).

F. R. G.

Application of the law of mass action to the synthesis of β -glucosides.—See this vol., 1485.

Effect of substituents on organic reactions: a quantitative relationship. G. N. BURKHARDT (Nature, 1935, 136, 684).—Using the logarithms of the dissociation consts. of various *m*- and *p*-substituted BzOH as an arbitrary reference series, linear relationships are obtained when the logarithms of the velocity

coeffs. of a no. of side-chain reactions involving substances containing the same *m*- and *p*-substituents are plotted against them. Thus, a straight line is obtained for the alkaline hydrolysis of substituted EtOBz and substituted NH₂Bz, and the solvent hydrolysis of the benzyl chlorides, etc. The linear relationships are discussed in terms of the transition state conception of Evans and Polanyi. L. S. T.

Measurement of the velocity of rapid reactions. M. WYGAERTS and J. EECKHOUT (Natuurwetensch. Tijds., 1935, 17, 163—189).—The course of reactions in solution involving a change in absorption spectrum is followed by taking a photographic record of the galvanometer reading of a photo-electric cell registering the intensity of light of given λ transmitted by the solution. The decolorisation of malachite-green by a large excess of NaOH (such that [NaOH] is effectively const.) is unimol., with *k* 0.94 at 19.85° and 1.6 at 29.65°. The decolorisation of reddened phenolphthalein by a large excess of NaOH is reversible, the reaction in both directions being unimol., with *k*₁ 1.14×10^{-2} at 19.85° and 2.23×10^{-2} at 29.80°, and *k*₂ 7.1×10^{-5} at 19.85° and 3.87×10^{-4} at 29.80°. The absorption spectra of *m*-NO₂·C₆H₄·CH₂·NO₂ and its Na salt (I) have been determined. The action of HCl on excess of (I) in 70% aq. EtOH at 13.9° is a bimol. reversible reaction (*i.e.*, the velocity of both forward and back reactions \propto the concn. of each reactant); *k*₁ = 7.49, *k*₂ = 2.63. D. R. D.

Corrosion of iron and steel.—See B., 1935, 1048.

Atmospheric corrosion and tarnishing of tin.—See B., 1935, 996.

Kinetics of the oxidation of metal filaments. G. VALENSI (Compt. rend., 1935, 201, 602—604; cf. this vol., 1328).—A general expression is derived from diffusion considerations for the rate of oxidation of filaments of bivalent metals. The result accords with experimental vals. for Ni. H. J. E.

Kinetics of heterogeneous organic reactions: reaction between benzyl chloride and solid silver nitrate. M. V. NABAR and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 265—278).—The reaction, studied in the absence of solvents and diluents, is independent of the amount of CH₂PhCl (I), but \propto the surface of AgNO₃ present. Results, with particles of three different sizes, can be reproduced by the kinetic equation derived on the assumption that the rate of reaction depends only on the surface of AgNO₃. The velocity of the reaction is independent of the speed of shaking. H₂O inhibits the reaction; the effect of 0.18 wt.-% of (I) is marked, and this effect increases with the amount of H₂O added. N. M. B.

Rate of formation of fully-saturated glycerides during hydrogenation of different natural fats.—See B., 1935, 1053.

Catalytic effect of ozone in the oxidation of hydrocarbons. E. BRINER and J. CARCELLER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 85—86).—Oxidation of *n*-C₄H₁₀ by O₃ is greatly accelerated by small amounts of O₃ at \leq room temp. Products formed include aldehydes, acids, COMe₂, H₂, CO₂,

and peroxides. 1 part in 10,000 of O₃ in air causes knocking in an internal-combustion engine by promoting the formation of peroxides. S. J. G.

Decomposition of chloral catalysed by nitric oxide. F. H. VERHOEK (Trans. Faraday Soc., 1935, 31, 1521—1526; cf. A., 1934, 1314).—The thermal decomp. of both CCl₃·CHO and CHCl₃ vapour is catalysed by NO. The catalysed reaction is of the first order with CCl₃·CHO, and approx. so with CHCl₃. The mechanism is discussed. F. L. U.

Decomposition of acetaldehyde catalysed by nitrous oxide. F. H. VERHOEK (Trans. Faraday Soc., 1935, 31, 1527—1533; cf. preceding abstract).—Study of the thermal decomp. of MeCHO vapour in presence of N₂O indicates the occurrence of a reaction between the MeCHO and N₂O giving rise to a substance which acts as a catalyst or initiates a chain. In a clean SiO₂ bulb the catalysed reaction is of the first order with respect to MeCHO. F. L. U.

Decomposition of acetaldehyde catalysed by nitric oxide. F. H. VERHOEK (Trans. Faraday Soc., 1935, 31, 1533—1536; cf. preceding abstract).—The decomp. of MeCHO catalysed by NO at 480° is approx. 3/2 order with respect to MeCHO, and the rate \propto [NO] when NO is in excess. An explanation of the mechanism is offered. F. L. U.

Catalytic decomposition of hydrogen peroxide in presence of mixtures of salts of manganese and copper. M. BOBTELSKI and (MME.) L. BOBTELSKI-CHAJKIN (Compt. rend., 1935, 201, 604—606).—The unimol. velocity coeff. increases with increasing [Cu⁺⁺] to a max., and then diminishes. The max. val. increases with the [Mn⁺⁺]. Zn⁺⁺ and Cd⁺⁺ increase the catalytic activity of Cu⁺⁺-Mn⁺⁺ mixtures. A mechanism, involving intermediate compound formation between Mn⁺⁺ or Cu⁺⁺ and H₂O₂, is suggested. H. J. E.

Catalytic decomposition of nitroamide in acid and salt solutions. C. A. MARLIES and V. K. LA MER (J. Amer. Chem. Soc., 1935, 57, 1812—1820).—The rate of decomp. has been measured in aq. acid and salt solutions over a wide concn. range with an error of about 1%. A negative primary salt effect, which has been observed, is ascribed to the effect of the salt on the catalytic properties of H₂O. Acid catalysis has also been observed and a mechanism proposed. D₂O decreases the velocity of decomp., whilst HgCl₂ increases it. E. S. H.

Conditions of formation of the chloride of tervalent manganese in hydrochloric acid solutions, and its decomposition in presence of complex catalysts. M. BOBTELSKI and (MME.) R. COHEN (Compt. rend., 1935, 201, 662—664).—The catalytic activity of metals in the decomp. of MnCl₃ in presence of HCl was in the order Ag^I > Pt^{IV} > Pb^{II} > Cu^{II}. Increase in [HCl] in presence of Cu^{II}, Pb^{II}, or Pt^{IV} increases the rate of decomp. The temp. coeff. of the decomp. decreases with increasing [HCl]. In presence of Ag^I it is independent of [HCl], and approx. unity. H. J. E.

Catalytic polymerisation of gaseous olefines by liquid phosphoric acid.—See B., 1935, 1035.

Physical chemistry of amino-acids, peptides, and related substances. V. Influence of amino-acids, carbamide, and alcohol on the velocity constants of chemical reactions. D. STRAUP and E. J. COHN (J. Amer. Chem. Soc., 1935, 57, 1794—1800; cf. this vol., 695, 696).—The rate of reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with alkyl iodides is increased by EtOH, slightly increased by $\text{CO}(\text{NH}_2)_2$, and decreased by ions or amino-acids. The rate of reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{CH}_3\text{Br}\cdot\text{CO}_2'$ is increased by salts, NH_2 -acids, and $\text{CO}(\text{NH}_2)_2$, and but slightly influenced by EtOH. $\text{CO}(\text{NH}_2)_2$ and NH_2 -acids increase the dielectric const. of H_2O in proportion to their concn., but this factor does not entirely explain the influence on reaction rate. An extension of Kirkwood's equation for the activity coeffs. of the NH_2 -acids has been applied satisfactorily to the results.

E. S. H.

Catalytic decomposition of hydrogen peroxide on metals. J. WEISS (Trans. Faraday Soc., 1935, 31, 1547—1557; cf. A., 1935, 174).—The initial process in the catalytic decomp. of H_2O_2 by metals involves the transfer of an electron from the metal to the H_2O_2 , with the consequent formation of free radicals, thus: $\text{H}_2\text{O}_2 + e = \text{OH} + \text{OH}'$. This leads to the initiation of chain reactions, $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$ and $\text{O}_2' + \text{H}_2\text{O}_2 = \text{OH}' + \text{OH} + \text{O}_2$. The ease with which the primary electron transfer occurs depends on the electronic work function of the metal, and if this is decreased by cathodic polarisation catalytic decomp. becomes considerably greater, Hg and bright Pt, e.g., being effective catalysts under these conditions. The action of Ag, Pt, Au, Pd, and Zn on H_2O_2 has been studied in detail, and the observations support the theory, which also provides a simple explanation of the action of poisons such as H_2S and KCN.

F. L. U.

Mechanism of sulphur dioxide oxidation in presence of vanadium catalysts.—See B., 1935, 991.

Effect of the ferromagnetic transformation on the catalytic power of nickel for the reaction $2\text{CO} = \text{CO}_2 + \text{C}$. J. A. HEDVALL and F. SANDFORD (Z. physikal. Chem., 1935, B, 29, 455—463; cf. this vol., 153).—The catalysis by Ni of the above reaction in and near the Curie interval and the effect of impurities in Ni on the relation between its ferromagnetism and its catalysis of the reaction $\text{N}_2\text{O} = \text{N}_2 + 0.5\text{O}_2$ have been studied. The yield curves exhibit changes in direction corresponding with the characteristic temp. of ferromagnetic transformation of the catalysts.

R. C.

Active oxides. CXII. Interaction between solid substances. G. F. HÜTTIG [with T. MEYER, H. KITTEL, and S. CASSIRER] (Z. anorg. Chem., 1935, 224, 225—252; cf. this vol., 1204).—The catalytic activity towards N_2O decomp. of $\text{CuO}\text{--}\text{Fe}_2\text{O}_3$ and $\text{CuO}\text{--}\text{Cr}_2\text{O}_3$, the magnetic susceptibility, bulk d , and colour of $\text{Fe}_2\text{O}_3\text{--}\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--}\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2$, $\text{Fe}_2\text{O}_3\text{--}\text{TiO}_2$, $\text{Cr}_2\text{O}_3\text{--}\text{TiO}_2$, $\text{Cr}_2\text{O}_3\text{--}\text{Al}_2\text{O}_3$, and $\text{Cr}_2\text{O}_3\text{--}\text{SiO}_2$, and the rate of sorption of H_2O by $\text{MgO}\text{--}\text{Fe}_2\text{O}_3$, $\text{BeO}\text{--}\text{Fe}_2\text{O}_3$, $\text{ZnO}\text{--}\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--}\text{Fe}_2\text{O}_3$, $\text{ZnO}\text{--}\text{Cr}_2\text{O}_3$, and $\text{CuO}\text{--}\text{Al}_2\text{O}_3$ have been measured and are discussed. The relationship between H_2O sorption,

catalytic activity, and internal and surface migration of the lattice units of the catalyst are considered.

T. G. P.

[Catalytic] synthesis of methane.—See B., 1935, 1035.

Adsorption and oxidation of succinic acid on carbon. B. TAMAMUSHI and H. UMEZAWA (Z. Elektrochem., 1935, 41, 761—764).—The catalytic activity of different kinds of C in the oxidation of succinic acid by O_2 has been studied by gravimetric determination of fumaric acid, and compared with the adsorptive power of the C. The influence of the relatively greater adsorption of fumaric acid is discussed.

E. S. H.

Electrolytic preparation of deuterium from heavy water. F. NORLING (Physikal. Z., 1935, 36, 711—713).—The apparatus is described. A. J. M.

Concentrating the hydrogen isotope D by electrolysis of water. II. Production of heavy water and its apparatus. Y. OTA (Mem. Fac. Sci. Agric. Taihoku, 1935, 15, 165—170). T. G. P.

Hydrates of lithium perchlorate. K. N. MOCHALOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 21—25).— LiClO_4 was prepared electrolytically from aq. LiClO_3 (c.d. 0.2 amp. per sq. cm.; temp. $< 20^\circ$). $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ loses $2\text{H}_2\text{O}$ at $98\text{--}100^\circ$ and becomes anhyd. at $130\text{--}150^\circ$. CH. ABS. (e)

Electrolysis of aqueous solutions of alkali sulphates.—See B., 1935, 1000.

Electrochemical anodic behaviour of alloys. W. J. MÜLLER [with H. FREISSLER and E. PLETINGER] (Z. Elektrochem., 1935, 41, 774—778).—The anodic dissolution of Cu-Zn alloys in $N\text{--HCl}$ and $N\text{--H}_2\text{SO}_4$ has been studied by determining the loss of wt. of the anode and the amount of Cu dissolved from alloys of different compositions after the same time interval. No Cu was dissolved from alloys containing $< 40\%$ of Cu; with increasing Cu content the ratio of Cu to Zn in solution approaches more and more to that in the alloy. In HCl Cu enters solution as Cu^+ , in H_2SO_4 as Cu^{++} .

E. S. H.

Electrochemical behaviour of lead, lead-antimony, and lead-calcium alloys in storage cells.—See B., 1935, 1001.

Inorganic addition salts in the nickel-plating solution.—See B., 1935, 998.

Effect of oxidising agents on nickel deposition. II. Chromic acid. A. W. HOTHERSALL and R. A. F. HAMMOND (Trans. Faraday Soc., 1935, 31, 1574—1582; cf. A., 1930, 1134).—The effects of CrO_3 on cathode efficiency, cathode potential, rate of gas discharge, and appearance of deposits in the deposition of Ni from a NiSO_4 bath containing H_3BO_3 and KCl have been studied. The results suggest that at low $[\text{CrO}_3]$ initial depolarisation leads to pptn. of basic Ni compounds containing Cr, with resulting decrease of $[\text{Ni}^{++}]$, increased discharge of H^+ , and reduced cathode efficiency. At higher $[\text{CrO}_3]$ chemical interaction with the cathode metal leads to the formation of a selectively permeable film and consequent complete inhibition of Ni deposition.

F. L. U.

Concentrated copper cyanide plating baths.—See B., 1935, 997.

Copper plating of iron.—See B., 1935, 1050.

Electrodeposition of zinc from acid solutions.—See B., 1935, 1051.

Electrochemical purification of phosphoric acid.—See B., 1935, 1042.

Preparation of litharge by electrolysis.—See B., 1935, 1043.

Preparation of potassium persulphate by electrolysis.—See B., 1935, 1042.

Electrolytic reduction of nitro-compounds.—See B., 1935, 984.

Inversion of solutions of sucrose in contact with regions traversed by an electric current. P. FABRE (Compt. rend. Soc. Biol., 1935, 120, 179—181).—Sucrose solution in both compartments of a Daniell cell vessel is inverted by passing an electric current through the entire vessel. R. N. C.

Electrolytic preparation of nitrosonaphthols.—See B., 1935, 1036.

Photo-oxidation of hydrogen and deuterium iodides. G. A. COOK and J. R. BATES (J. Amer. Chem. Soc., 1935, 57, 1775—1778).—The reaction of HI or DI with O₂ at 0° under the influence of a low-voltage Hg-A lamp has been followed by pressure measurements and analysis of the products. The reaction between H and O₂ is a 3-body process. The results are: $k_{H+O_2+M}/k_{H+HI} = (2.11 \pm 0.29) \times 10^3$ c.c. per mol.; $k_{D+O_2+M}/k_{D+DI} = (3.98 \pm 0.75) \times 10^{-3}$ c.c. per mol.; $k_{H+O_2+O_2} \approx k_{D+O_2+O_2} \approx 1.2 \times 10^{14}$ cm.² mol.⁻² sec.⁻¹ E. S. H.

Use of the ortho-para-hydrogen conversion in the detection of free radicals produced in photodissociation. W. WEST (J. Amer. Chem. Soc., 1935, 57, 1931—1934).—Conversion is produced by MeI or COMe₂ vapour illuminated by radiation of frequency in their continuous absorption regions, but not by propaldehyde or C₆H₆. The results indicate the production of paramagnetic free radicals on illuminating MeI or COMe₂. E. S. H.

Photolysis of azomethane. G. S. FORBES, L. J. HEIDT, and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 1935—1938).—Quantum yields, ϕ , for the photolysis of Me₂N₂ at 181, 184, 377, and 665 mμ., using six monochromatic radiations, have been determined. ϕ approaches 1 as its upper limit for initial decomp. at low pressure; variation of temp. between 20° and 226° has no effect on ϕ ; with increasing pressure ϕ falls rapidly. In the region 366—335 mμ. approx., ϕ passes through a max., apparently corresponding with max. absorption by N.N. E. S. H.

Photographic detection of H-rays. M. BLAU and H. WAMBACHER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 285—301).—The effect of various baths in sensitising plates for the detection of H-particle tracks was examined. Optimum results were obtained with a mixture of pinakryptol and induline-scarlet. The action was not related to the desensitisation of this mixture for the action of light. The density of

grains in the H-particle track was of the same order as that in an α-particle track. H. J. E.

Simple method for determining the colour temperature of flashlights. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Z. wiss. Phot., 1935, 34, 237—240).—A colour chart (cf. Phot. Ind., 1930, 23, 629) was photographed by the flashlight on to panchromatic plates, and the result compared with sources of known colour temp. (C-filament, vac., gas-filled, and arc lamps). The val. for "Photoflux" flashlight [Al-Mg alloy (5—10% Mg) wire burning in pure O₂], as also for Mg or Al foil burning in O₂, was estimated to be about 4000° abs. J. L.

Case of negative photocatalysis. J. MILBAUER (Phot. Korr., 1935, 71, 94—95).—The action of photographic desensitisers on the photochemical decomp. of "Aktivin" (Na *p*-toluenesulphonchloroamide) in MeOH solution has been studied. Nile-blue, brilliant-green, Capri-blue, phenosafranine, fuchsin, and pinakryptol-green are negative catalysts. Malachite-green had no effect. Pinakryptol-yellow and methylene-blue are positive catalysts, even in the dark. J. L.

Free radicals in photodissociation of gaseous metal alkyls. N. PRILESHAEVA and A. TEREININ (Trans. Faraday Soc., 1935, 31, 1483—1487; cf. A., 1935, 1052).—The decomp. of COMe₂, HgMe₂, and PbEt₄ vapours at low pressure by ultra-violet light has been studied by photometric determination of the progressive thinning of films of Sb under attack by the free radicals produced. F. L. U.

Primary photochemical reactions. VII. Photochemical decomposition of isovaleraldehyde and di-*n*-propyl ketone. C. H. BAMFORD and R. G. W. NORRISH (J.C.S., 1935, 1504—1511).—The proportions of the products of decomp. in the full light of the Hg lamp correspond with the following primary processes: (i) Bu³CHO (I) → *iso*-C₄H₁₀ + CO (47%) and (I) → C₃H₆ + MeCHO (53%) and (ii) COPr^α₂ (II) → C₆H₁₄ + CO (37%) and (II) → C₂H₄ + COMePr (63%). The products containing :CO are further decomposed photochemically. Two types of primary photochemical change are distinguished in carbonyl compounds. In type (i) CO is eliminated and a saturated hydrocarbon is produced, and in type (ii) there is a rupture between the α- and β-C of the hydrocarbon chain, producing an olefine and a simpler CO-compound. Type (ii) occurs more readily with ketones than with aldehydes and is facilitated by increasing the length of the hydrocarbon chain. The mechanism of the processes is discussed. J. G. A. G.

Photochemical reaction of chlorophyll.—See this vol., 1510.

Decomposition of water by X-rays in presence of the iodide or bromide ion. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 596).—Br⁻ or I⁻ catalyses the decomp. of H₂O on irradiation with X-rays, no decomp. occurring in its absence. The concn. of the added ion remains unchanged. In presence of H₂SO₄ (*p*_H 3—4), H₂ and H₂O₂ are formed. In unbuffered solutions, or in presence of NaOH (*p*_H 11.0), the same amount of H₂ is formed, but H₂O₂ is replaced by its equiv. of O₂. The decomp. is

independent of $[\text{Br}']$ or $[\text{I}']$ from 1.0—0.01 millimole per litre. At higher $[\text{KI}]$ free I is formed. No effect was found with Cl' . H. J. E.

Oxidation of ferrocyanide, arsenite, and selenite ions by irradiation of their aqueous solutions with X-rays. H. FRICKE and E. J. HART (J. Chem. Physics, 1935, 3, 596).—The $[\text{Fe}(\text{CN})_6]^{4-}$ was oxidised to $[\text{Fe}(\text{CN})_6]^{3-}$, an equiv. amount of H_2 being liberated. The no. of equivs. oxidised was independent of concn. (0.1—100 millimoles per 1000 c.c.) and of p_{H} (2.0—11.0). AsO_3^{3-} and SeO_3^{2-} gave AsO_4^{3-} and SeO_4^{2-} together with an equiv. amount of H_2 . H. J. E.

Kinetic interpretation of the colouring of glass by X-rays. R. LIVINGSTON and C. E. NURNBERGER (J. Physical Chem., 1935, 39, 1011—1019).—The rate of colouring of Pyrex glass by irradiation with hard X-rays, and the distribution of relative absorption of the coloured glass as a function of λ for visible light, have been investigated. The analogous effects of Rn are discussed. E. S. H.

Ring deposits on glass by positive-ray bombardment. B. DASANNACHARYA, V. T. CHILPONKAR, and L. G. SAPRE (Nature, 1935, 136, 642).—Brown rings are formed. L. S. T.

Chemical action of penetrating radium radiations. XX. Action on aqueous solutions of glycerol, isobutyl and ethyl alcohols, and benzene. A. KAILAN (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 163—174; Chem. Zentr., 1935, i, 1968—1969).—Prolonged action of Ra radiation, filtered through 1 mm. of glass, on aq. glycerol and EtOH produced AcOH and some HCO_2H , + aldehyde. With aq. Bu^nOH , non-volatile acids resulted. The effect is ascribed to H_2O_2 produced from the H_2O by the action of the radiation. C_6H_6 was unaffected. J. S. A.

Preparation of deuterium.—See this vol., 1407.

Concentration of heavy isotopes in cellulose. K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 465—466).—Purified H_2O prepared by burning filter-paper, cotton-wool, cedar wood, and bamboo is 6.3, 5.7, 4.5, and 4.4 p.p.m., respectively, heavier than normal, owing to concn. of D. Purified H_2O from the skin, internal solid, and juice of a bamboo shoot is 4.4, 0.6, and 1.0 p.p.m., respectively, heavier than normal; the concn. is not due to the rapid growth, but is a general effect with carbohydrates. R. S. B.

Chemiluminescence of 3-aminophthalhydrazide. L. HARRIS and A. S. PARKER (J. Amer. Chem. Soc., 1935, 57, 1939—1942).—Under conditions of max. light intensity the quantum efficiency of the oxidation of the Na salt of 3-aminophthalhydrazide is about 0.3%. There is evidence of compound formation with H_2O_2 . E. S. H.

Oxidation of metals. II. Copper, brass, aluminium-brass, aluminium-bronze, magnesium, and some magnesium alloys. G. D. PRESTON and L. L. BIRCUMSHAW (Phil. Mag., 1935, [vii], 20, 706—720).—Investigations were made at temp. $\geq 400^\circ$, and the nature, crystal structure, and orientation of the oxide film were determined by

electron diffraction. The film on Cu, formed at room temp. and 100° in air, and at 183° in O_2 at atm. pressure, consists of ordinary cubic-structure Cu_2O , with a (111) plane parallel to the polished metal surface; there was no indication of CuO . A Cu—Zn brass containing 70% Cu oxidised at temp. $\geq 183^\circ$ acquires a Cu_2O film; at 400° the film is ZnO . Al brasses (22% Zn, 2% Al) show Cu_2O after oxidation at 183° for 10 min.; at 400° ZnO is present. Al_2O_3 was not found. Mg and Mg alloys, oxidised at 400° , acquire a film of cubic MgO . The orientation of oxide films on polished surfaces is discussed; it is probable that the plane in the oxide having the highest density of metal atoms per unit area tends to lie on the polished surface. N. M. B.

Influence of temperature on the formation of additive compounds. M. RAGNO and L. VADALÀ (Gazzetta, 1935, 65, 686—689; cf. this vol., 182).—From solutions of Cu salts in $\text{C}_5\text{H}_5\text{N}$, which have been kept at 70 — 80° for several hr., there crystallise out compounds which contain fewer mols. of $\text{C}_5\text{H}_5\text{N}$ per mol. of Cu salt than the corresponding compounds which are obtained at lower temp. O. J. W.

Reaction between calcium hydride and water. H. FLOOD (Kong. Norske Vid. Selsk. For., 1934, 7, 66—69; Chem. Zentr., 1935, i, 1516).—The primary reaction between CaH_2 and H_2O is to give CaO , but at low temp. < 2 mols. of H_2 per mol. of CaH_2 is evolved, owing to the low v.p. of $\text{Ca}(\text{OH})_2$. Above 350° reaction proceeds directly to CaO , and the drying effect of CaH_2 is most intensive. J. S. A.

Calcium chloroarsenate. C. M. SMITH (J. Washington Acad. Sci., 1935, 25, 435—436).—The compound $(\text{CaCl})_2\text{HAsO}_4 \cdot 2\text{H}_2\text{O}$ has been prepared by addition of $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ to aq. CaCl_2 . R. S.

Hydrates of monocalcium silicate. J. LEFOL (Compt. rend., 1935, 201, 669—672).—V.-p. and dehydration measurements proved the existence of the hydrates $\text{SiO}_2 \cdot 1.2\text{CaO} \cdot 2\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot 1.2\text{CaO} \cdot \text{H}_2\text{O}$. H. J. E.

Formation of barium aluminates from barium carbonate and alumina in the solid state. G. GRUBE and G. HEINTZ (Z. Elektrochem., 1935, 41, 797—804).—At 900 — 1050° the sole reaction product is $\text{BaO} \cdot \text{Al}_2\text{O}_3$, independently of which of the reagents is in excess. At higher temp. $2\text{BaO} \cdot \text{Al}_2\text{O}_3$ is formed; the equilibrium conditions have been determined. E. S. H.

Complex salts of mercury cyanide. R. UZEL (Lékárn., 1934, 14, 335—343; Chem. Zentr., 1935, i, 1353).—Salts of Cu, Ni, Zn, and Cd in aq. NH_3 solution react with $\text{Hg}(\text{CN})_2$ + excess of I' , Br' , CNS' , or N_3' to give complex salts of the general type, $[\text{M}(\text{NH}_3)_4][(\text{CN})_2\text{Hg} \leftarrow \frac{\text{X}}{\text{X}} \text{Hg}(\text{CN})_2]$. The following compounds were obtained: $[\text{Cu}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2\text{X}]_2$; $[\text{Cd}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2\text{X}]_2$; $[\text{Ni}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2\text{X}]_2$ ($\text{X} = \text{I}$, Br , CNS , or N_3); $[\text{Zn}(\text{NH}_3)_4][\text{Hg}(\text{CN})_2\text{Y}]_2$ ($\text{Y} = \text{I}$, Br , or CNS). J. S. A.

Ammonium mercury sulphites. Potentiometric investigations. G. SPACU and C. DRĂCULESCU (Z. anorg. Chem., 1935, 224, 273—279; cf. A., 1932, 1216).—Potentiometric titration of aq. HgCl_2

with aq. $(\text{NH}_4)_2\text{SO}_3$ confirms the existence of $[\text{HgCl}(\text{SO}_3)]\text{NH}_4$ and $[\text{Hg}(\text{SO}_3)_2](\text{NH}_4)_2$, which were isolated as stable, cryst. compounds. The substance $3\text{HgCl}_2 \cdot 2(\text{NH}_4)_2\text{SO}_3$, is probably a mixture.

T. G. P.

Alkali aluminium silicates. IX. Silicate component of ultramarine. E. GRUNER (Z. anorg. Chem., 1935, 224, 351—368; cf. this vol., 168).—Repeated fusion with KCN completely removes S from ultramarines (I). KCNS and K_2S_x are formed in the earlier, and KCNS and K_2S in the later, fusions. The residue has the composition KAlSiO_4 . The lattice of (I) with the ratio $\text{Al}_6 : \text{Si}_6$ remains unchanged, but that of (I) with higher proportions of Si is modified by the fusion. Jaeger's determinations of the dimensions of the unit cell have been confirmed and extended. A scheme showing relations between permutites, zeolites, nephelite, and kaolin is given.

F. L. U.

Purification of gallium by fractional crystallisation of the metal. J. I. HOFFMAN and B. F. SCRIBNER (J. Res. Nat. Bur. Stand., 1935, 15, 205—209).—If impure Ga is fractionally crystallised under aq. HCl, Ag, Hg, In, Pb, and Sn are conc. in the molten residue, Cu and Tl remain about equally divided between crystals and residue, Zn is dissolved by the HCl, whilst Sb, Bi, Cr, Co, Cb, Au, Fe, Mn, Mo, Ni, Os, Pd, Pt, Rd, Ru, and V concentrate in the crystals. It is impossible to separate Ga from $> 0.001\%$ Fe or Pt, from $> 0.01\%$ In or Pb, or from $> 0.02\%$ Sn by fractional crystallisation.

J. W. S.

Mixed polyhalides of titanium. G. P. LUTSCHINSKI [with A. I. LICHATSHEVA] (Z. anorg. Chem., 1935, 224, 420—426).—F.-p.-composition curves have been determined for mixtures of TiCl_4 and Br. The existence of compounds, TiCl_4Br (I) and TiCl_4Br_4 (II) is established. Eutectics are formed from TiCl_4 and (I), (I) and (II), and (II) and Br. Br is completely eliminated from (I) and (II) by the action of heat or of H_2O .

F. L. U.

Extraction of germanium and gallium from germanite. I. Removal of germanium by distillation of germanous sulphide. W. C. JOHNSON, L. S. FOSTER, and C. A. KRAUS. **II. Acid extraction of germanium.** L. S. FOSTER, W. C. JOHNSON, and C. A. KRAUS (J. Amer. Chem. Soc., 1935, 57, 1828—1831, 1831—1835).—I. Finely-ground germanite is heated in a stream of dry N_2 at 800° to remove As_2S_3 and S. NH_3 is passed over the residue at 825° , when GeS_2 is reduced to GeS , which distills and is collected. 99% of the original Ge is thus removed.

II. Ga is obtained from the residue of the above process by boiling with HCl, pptg. sulphides of heavy metals, and separating Ga and Al from large quantities of Fe and Zn by boiling the solution with NH_4HSO_3 , leaving Fe and Zn in solution. Al is separated as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ from a HCl-saturated $\text{Et}_2\text{O}-\text{H}_2\text{O}$ mixture in which Ga and traces of Fe remain dissolved. After removing the remaining Fe, Ga is pptd. as hydrated oxide; the metal is obtained by electrolysis of a solution of the oxide in aq. KOH.

E. S. H.

Allotropy of phosphoric oxide. A. N. CAMPBELL and A. J. R. CAMPBELL (Trans. Faraday Soc., 1935, 31, 1567—1574).—Amorphous P_2O_5 (I) has

$d_{400}^{20} 2.317$, and solubility in CHCl_3 (S) 0.099 g. per 100 g. Heating (I) for not too long at $350-600^\circ$ yields a cryst. variety, $d_{400}^{20} 2.195$, which has not been obtained pure, but is contaminated with a vitreous form which is the sole product when (I) is heated at 450° for 3 weeks. This latter is the stable form, and has $d_{400}^{20} 2.737$, S 0.0015 wt.-%.

F. L. U.

Formula of sodium antimonate. L. A. VASILEVA (Trans. Butlerov Inst. Chem. Tech., 1934, No. 2, 41—49).—Dissociation vals. agree with Tomula's results (A., 1922, ii, 74), showing the formula to be NaSbO_3 and not $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$.

CH. ABS. (e)

Reactions with oxygen. A. H. BELINFANTE (Chem. Weekblad, 1935, 32, 611—615).—Theoretical. The different types of reaction involving direct oxidation by O_2 are briefly reviewed.

D. R. D.

Reaction of sulphur with water at temperatures below 100° , and its geochemical significance. E. CHERBULIEZ and R. WEIBEL (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 87—88).—Appreciable quantities of H_2S and of $\text{S}_2\text{O}_3^{2-}$ were detected after boiling S with SO_2 buffered at p_{H} 7—6.1 for 24 hr.: $3\text{S} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{S} + \text{SO}_2$; $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$; $\text{H}_2\text{SO}_3 + \text{S} \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3$. The presence of H_2S and $\text{S}_2\text{O}_3^{2-}$ in mineral waters is explained in this way, these waters being buffered by H carbonates.

S. J. G.

Action of hydrogen sulphide on the chromates of hydrogen, ammonium, sodium, and potassium. M. A. HAMID, G. SINGH, and H. B. DUNNICLIFF (J. Indian Chem. Soc., 1935, 12, 595—600; cf. A., 1932, 133).—In the action of H_2S on solutions of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, of $\text{K}_2\text{Cr}_2\text{O}_7$, and of H_2CrO_4 the formation of SO_4^{2-} is favoured by increased temp. at the expense of $\text{S}_2\text{O}_3^{2-}$. Formation of SO_4^{2-} is suppressed by an alkaline medium. Analyses of the products of the reaction of H_2S with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and with $(\text{NH}_4)_2\text{CrO}_4$ solutions under varying conditions are recorded.

O. J. W.

Action of hydrogen sulphide on insoluble chromates. I. Lead chromate and silver chromate. H. B. DUNNICLIFF and B. PRAKASH (J. Indian Chem. Soc., 1935, 12, 505—513).—Treatment of a suspension of PbCrO_4 with H_2S leads to 90—95% attack with production of PbS , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{S}_2\text{O}_3)_3$ (partly co-ordinated), and $\text{Cr}(\text{OH})_3$, together with some S, probably due to oxidation of H_2S by atm. O_2 . The reaction occurs much more rapidly at higher temp., but with less tendency to form $\text{Cr}_2(\text{S}_2\text{O}_3)_3$. No H_2SO_3 or thionic acids are formed. Ag_2CrO_4 under similar conditions yields Ag_2S , $\text{Cr}_2(\text{SO}_4)_3$, $\text{Cr}_2(\text{SO}_3)_3$, $\text{Cr}_2(\text{S}_2\text{O}_3)_3$ and S.

J. W. S.

Preparation of phosphorescent substances. IX. X-Ray luminophores. N. F. SHIROV, T. E. GETMAN, and E. J. MATENKO (J. Appl. Chem. Russ., 1935, 8, 848—863).—The X-ray luminescence of the following rises in the order $\text{UO}_2\text{F}_4 \cdot 4\text{NaF} < \text{UO}_2\text{F}_2 \cdot 4\text{KF} < \text{UO}_2\text{F}_2 \cdot 4\text{NH}_4\text{F} < \text{BaPt}(\text{CN})_4 < \text{Zn}_2\text{SiO}_4$. Directions for the prep. of these substances are given, and the theoretical aspect of the problem of X-ray luminophores is discussed.

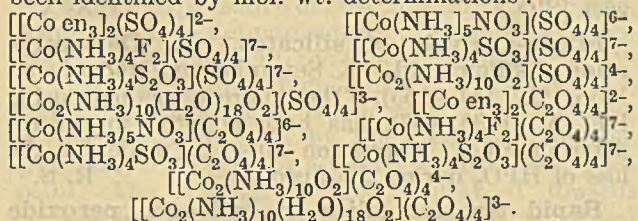
R. T.

Triple sulphates containing water. B. GOSNER and J. BESSLEIN (Zentr. Min., 1934, A, 358—364; Chem. Zentr., 1935, i, 1352).—A series of sulphates analogous to voltaite has been prepared, having the general formula $\text{Fe}^{+++}\text{M}^{++}\text{M}'(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, in which Fe is partly replaced by Al. The Zn K, Co NH_4 , Co Rb, and Mg Rb compounds are described. Mn forms with Li and Na compounds of type $\text{FeMn}_4\text{M}(\text{SO}_4)_6 \cdot 8\text{H}_2\text{O}$, either with or without partial replacement of Fe by Al. J. S. A.

Effect of dehydrated product on the course of dehydration. S. ŠKRAMOVSKÝ (Lékárn., 1934, 14, 317—322; Chem. Zentr., 1935, i, 1331).— $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$ dehydrate at $60\text{--}80^\circ$ to a product with $1.5\text{H}_2\text{O}$. Addition of dehydrated salt increases the rate of dehydration, and brings about initial formation of tetrahydrate, which then dehydrates further. J. S. A.

Complex ammines of tervalent metals. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 224, 280—282; cf. this vol., 1091).—Mol. wts. of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$, $[\text{Co}(\text{NH}_3)_4\text{S}_2\text{O}_3]^{+}$, $[\text{Co}(\text{NH}_3)_4\text{F}_2]^{+}$, $[\text{Co en}_3]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O} \cdot \text{Cl}]^{2+}$ have been determined by dialysis. The triethylenediamine cobaltic ion is dimeric; the remainder are normal. T. G. P.

Complex compounds of which the central ion is [itself] a complex cation. II. Complex sulphato- and oxalato-compounds with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 224, 283—288; cf. preceding abs.).—The following ions have been identified by mol. wt. determinations:



T. G. P.

Composition and properties of precipitated nickel and cobalt sulphides. I. A. W. MIDDLETON and A. M. WARD (J.C.S., 1935, 1459—1466).—The ppts. obtained from aq. solutions of the salts by means of H_2S in the absence of O_2 are probably $\text{Ni}(\text{SH})_2$, $\text{Co}(\text{SH})_2$, and $\text{Co}(\text{SH})_3$. In general, the ratios of combined S to metal in the ppts. dried in N_2 slightly exceed the vals. required by the formulæ NiS , CoS , and Co_2S_3 . The undried sulphides dissolve rapidly and extensively in $2N\text{-HCl}$ (but age to less sol. forms) and H_2S is evolved, but Co^{+++} changes into Co^{++} , leading to partial oxidation and lower solubility. With aq. and C_6H_6 solutions in presence of O_2 , the sulphide ppts. contain combined S exceeding the at. ratios corresponding with the simple formulæ and, in general, somewhat greater at. ratios of H and O. Drying removes H_2O and H_2S and may cause further oxidation. The portions of these sulphides sol. in acids afford SO_4^{--} , and only traces of H_2S are produced. The dry sulphides are slowly oxidised to sulphates in the air. J. G. A. G.

Bromo-salts of tervalent iridium. (MME.) M. DELÉPINE-TARD (Ann. Chim., 1935, [xi], 4, 282—291; cf. this vol., 868).—The following compounds are described: $\text{K}_2[\text{IrBr}_6] \cdot 4\text{H}_2\text{O}$; $\text{K}_2[\text{Ir}(\text{H}_2\text{O})\text{Br}_5] \cdot \text{H}_2\text{O}$; $\text{Rb}_3[\text{IrBr}_6] \cdot \text{H}_2\text{O}$; $\text{Rb}_2[\text{Ir}(\text{H}_2\text{O})\text{Br}_5]$; $\text{Cs}_3[\text{IrBr}_6] \cdot \text{H}_2\text{O}$; $\text{Cs}_5\text{Ir}_3\text{Br}_{14} \cdot 2\text{H}_2\text{O}$. F. L. U.

Double ammines of platinum. G. SPACU and V. ARMEANU (Bul. Soc. Științe Cluj, 1934, 7, 610—617; Chem. Zentr., 1935, i, 1354).—The following compounds are described: $[\text{Cu en}_2][\text{Pt}(\text{SCN})_6]$; $[\text{Co}(\text{NH}_3)_6][\text{Pt}(\text{SCN})_6]\text{Cl}$; $[\text{Co}(\text{NH}_3)_6]_2[\text{Pt}(\text{SeCN})_6] \cdot 6\text{H}_2\text{O}$; $[\text{Co en}_3]_2[\text{Pt}(\text{SeCN})_6]_3$; $[\text{Ni en}_3][\text{Pt}(\text{SeCN})_6]$. J. S. A.

Spectrum analysis. H. DINGLE (Nature, 1935, 136, 684—685).—Definitions are discussed. L. S. T.

Sensitivity of chemical analysis with X-rays. I. Emission methods. II. Absorption methods. L. MAZZA (Gazzetta, 1935, 65, 724—730, 730—734).—I. The use of X-ray emission spectra in chemical analysis is discussed with particular reference to the rare-earth elements. In the *K* spectra it is possible to detect 1 : 1000, in the *L* spectra 1 : 25,000 parts of an element in a mixture. With elements in the metallic state the sensitivity can be extended to 1 : 50,000.

II. In absorption methods the sensitivity is greatly dependent on the at. no. of the element which has to be detected. This practically limits the method to the detection of heavy elements in presence of lighter ones. O. J. W.

Rapid determination of water in small quantities of material. J. ERDÖS (Mikrochem., 1935, 18, 256—260).—The sample is distilled with xylene and the distillate centrifuged in a calibrated tube in which the H_2O is measured. The % of H_2O obtained after suitable corrections is < that obtained by the drying method. R. S.

Conductometric determination of water in acetone.—See B., 1935, 1036.

Determination of chloride with adsorption indicators. F. H. C. KELLY (J. Proc. Austral. Chem. Inst., 1935, 2, 250—254).—A review. The addition of 1% starch solution as protective colloid is advantageous. J. S. A.

Determination of the chlorate content of potassium and sodium chlorates.—See B., 1935, 990.

Determination of residual chlorine [in water].—See B., 1935, 1024.

α -Naphthoflavone as a reversible bromometric indicator. R. UZEL (Coll. Czech. Chem. Comm., 1935, 7, 380—387).—Colloidal α -naphthoflavone (I) forms reversibly an orange adsorption compound with free Br in solution. The indicator, 0.5—1 ml. of 0.1% (I) in EtOH or AcOH added to 50—100 ml. of solution, is used with KBrO_3 in determining, in HCl solution, As^{III} , Sb^{III} , Sb in tartar emetic, Sn^{II} , N_2H_4 , NH_2Ph , and NHPhAc after boiling with 20% aq. HCl, diluting and adding Br^+ . Fe^{II} , Ti^{I} , finely-divided Hg, Hg^{I} , PhOH, and salicylic acid

gave unsatisfactory results. When Br' is titrated with AgNO_3 in presence of 1—2 drops of 0.1N-KBrO₃ and 1 c.c. of 0.1% (I), the end-point is orange \rightarrow green. Small proportions of Cl' do not interfere.

J. G. A. G.

Micro-determination of iodine in common salt.—See B., 1935, 990.

Determination of fluorine in potable waters.—See B., 1935, 1024.

Colorimetric determination of dissolved oxygen [in water].—See B., 1935, 1072.

Determination of atmospheric ozone. Comparison of spectrographic and chemical methods. A. DAUVILLIER (Compt. rend., 1935, 201, 679—680).—The two methods gave approx. the same mean vals. (4.1, 3.3 mg. of O₃ per cu. m. of air, respectively).

H. J. E.

Determination of stibnite-sulphur in ores and minerals.—See B., 1935, 1049.

Volumetric determination of sulphate and barium ions. V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 164—167).—SO₄" is titrated with BaCl₂ in a buffered solution containing CrO₄". To determine Ba" an excess of standard H₂SO₄ is added before titrating with BaCl₂.

CH. ABS. (e)

Use of lead nitrate as precipitant in the titrimetric determination of certain ions. A. RINGBOM (Acta Acad. Aboensis, Math. Phys., 1934, 8, No. 5, 142 pp.).—The potential of a Pt electrode in a solution of Pb₂Fe(CN)₆ containing a small const. [Fe(CN)₆]" changes when an excess of Pb(NO₃)₂ is added. Using this electrode, SO₄" may be titrated in 0.025N-Pb(NO₃)₂ solutions in presence of moderate amounts of neutral salts. In more dil. solutions, or with large amounts of neutral salts, the end-point is improved by adding EtOH. Carbonate may be titrated with Pb(NO₃)₂ by adding excess of precipitant and titrating back, or by using hot solutions. SO₃" may be titrated at $p_H > 6$. CrO₄" cannot be titrated. Tungstate and molybdate can be titrated in presence of a moderate concn. of neutral salt. Pb(NO₃)₂ may be titrated with Na₂CO₃ (phenol-red indicator). Oxalate may be titrated at an initial p_H of 8—8.5 (phenol-red). For SO₄" the initial p_H should be 9—9.5 (bromocresol-purple). The same indicator is also used for SO₃" and CrO₄". With tungstate the initial p_H should be 8.5—9 (bromothymol- or bromocresol-blue). Phenol-red is suitable for molybdate.

CH. ABS. (e)

Detection of the use of azides in the preparation of electron tubes. H. FRITZ (Mikrochem., 1935, 18, 162—168; cf. this vol., 837).—The total N content of the mirror gives an indication of the amount of azide used. A further test is the appearance of a permanent brown coloration when the mirror is heated, owing to the presence of Ba etc. R. S.

Detection of very small amounts of phosphorus and phosphine. L. WOLF, W. DÜSING, and A. MARTOS (Mikrochem., 1935, 18, 185—192).—Gas containing P or PH₃ is passed through a capillary tube immersed in 1% AgNO₃ in aq. NH₃ and having the lower end turned up. The gas stream is adjusted

so as to impart an oscillatory motion to the liquid in the U, when a black ppt. is formed on the wall. 4×10^{-4} mg. P and 6×10^{-5} mg. PH₃ can be detected when a capillary of 0.83 mm. diameter is used.

R. S.

Elimination of phosphoric, oxalic, fluoride, silicate, and silicofluoride ions in group III. S. AUGUSTI (Annali Chim. Appl., 1935, 25, 448—451).—The method is based on the pptn. of these anions as Pb salts by treating with Pb(OAc)₂ in AcOH solution.

T. H. P.

Determination of arsenic and phosphoric acids and iron in presence of one another. G. BALĂNESCU and V. IONESCU (Bull. Soc. Chim. România, 1935, 17, 93—102).—The As is pptd. by H₂S and PO₄" obtained as molybdate, whilst Fe" is determined iodometrically after evaporation and treatment with HNO₃. As is obtained more accurately if titrated iodometrically with the Fe" and determined by difference.

R. S.

Step-photometric determination of silicic acid and its application to water and mineral water. R. STROHECKER, R. VAUBEL, and K. BREITWIESER (Z. anal. Chem., 1935, 103, 1—12).—50 c.c. of H₂O are treated with H₂SO₄ and 2 c.c. of 10% aq. (NH₄)₂MoO₄. The yellow NH₄ silicomolybdate (I) formed is determined by comparison with aq. picric acid (II) or aq. K₂CrO₄ (III) in filtered blue light using the step photometer. Fe and PO₄" must be removed by pptn. with Na₂HPO₄ + CaCl₂ + CaCO₃. Solutions of (I) with >10 mg. of Si per litre deviate from Bell's law. (II) and (III) behave similarly in the same region of colour intensity. At low [SiO₂], the intensity of Mo-blue formed by reduction of (I) is > corresponds with [SiO₂].

J. S. A.

Micro-analysis of silicates. I. Determination of silicic acid. K. SCHOKLITSCH (Mikrochem., 1935, 18, 144—153).—The indirect method, using HF (A., 1933, 687), has been adapted for micro-determinations. Correction must be made for the loss of HPO₃ during the fusion.

R. S.

Rapid test for silica in hydrogen peroxide solutions.—See B., 1935, 1043.

Sensitive test for non-metallic impurities in metals.—See B., 1935, 1051.

Micro-determination of hydrogen cyanide. M. T. FRANCOIS and M. N. LAFFITE (Bull. Soc. Chim. biol., 1935, 17, 1088—1096).—A method employing "picro-soda" paper for the determination of 2×10^{-6} — 1×10^{-5} g. HCN is described. EtOH, oil, and starch do not interfere.

A. L.

Dipicrylamine as a micro-reagent for potassium, rubidium, and caesium. C. J. VAN NIEUWENBURG and T. VAN DER HOECK (Mikrochem., 1935, 18, 175—178).—Cs can be distinguished from K and Rb by recrystallising the dipicrylamine in presence of glycerol. Photomicrographs are given.

R. S.

Gravimetric micro-determination of potassium in presence of sodium by chloroplatinic acid. P. WENGER, C. CIMERMAN, and C. J. RZYMOWSKA (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 89—93).—Details are given for the determination of K' in

presence of 50 times as much Na^+ by converting into perchlorates and pptg. as K_2PtCl_6 . S. J. G.

Triple nitrites of the rare earths and a new micro-test for caesium. H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 608—610).—By crystallising a mixture of aq. solutions of the rare-earth nitrate, NaNO_2 , and CsNO_3 , the following compounds have been prepared; $\text{Cs}_2\text{CaCe}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaLa}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaPr}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaNd}(\text{NO}_2)_6$, $\text{Cs}_2\text{NaSm}(\text{NO}_2)_6$, and $\text{Cs}_2\text{NaGd}(\text{NO}_2)_6$. A drop of a solution of $\text{Pr}(\text{NO}_3)_3$ (3 g.) and NaNO_2 (10 g.) in H_2O (110 g.) yields octahedral crystals with a drop of CsNO_3 solution. The test is not affected by presence of K or Rb and its limit of sensitivity is 4×10^{-8} g. Cs. J. W. S.

Determination of ammonium salts.—See B., 1935, 1043.

Electrolytic determination of silver. F. FRIEDRICH and S. RAPOPORT (Mikrochem., 1935, 18, 227—234).—Electrolysis is carried out in a micro-apparatus in presence of H_2SO_4 and tartaric acid, at 1.3—1.8 volts. R. S.

Electrolytic drop analysis. I. Theoretical principles. H. FRITZ (Mikrochem., 1935, 19, 6—16; cf. A., 1929, 1414).—(a) Relatively noble metals (e.g., Ag) in a drop of liquid may be detected by their deposition on a strip of base metal (e.g., Cu). By absorption of the drop in filter-paper, the baser metals may then be detected as usual. (b) Electrolysis of a drop absorbed in filter-paper and carried on an insulating support avoids interference due to dissolution of the electrodes. J. S. A.

Direct titration of barium salts with potassium chromate in pressure of rosolic acid as indicator. Application to determination of sulphates, especially of sulphur in pyrites and slags. A. V. VINOGRADOV (Ann. Chim. Analyt., 1935, [iii], 17, 285—288).—The use of rosolic acid (I) as indicator in the titration of Ba by the method of Jellinek (A., 1923, ii, 878) gives a clearly visible, sharp end-point. The solution is first neutralised towards (I), acidified with HCl, and finally exactly neutralised by boiling with CaCO_3 . SO_4^{--} is determined by adding BaCl_2 and titrating back the excess of Ba. Pyrites is oxidised by fusion with $\text{Na}_2\text{CO}_3 + \text{KClO}_3$, and SO_4^{--} is determined in the aq. extract. J. S. A.

Precipitation of barium sulphate in presence of chloride and bromide ions. N. A. RUDNEV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 143—156).—The effect of HCl or HBr on the wt. of BaSO_4 obtained in determining Ba^{++} or SO_4^{--} is explained. CH. ABS. (e)

Closed titration flask for use in the bromometric determination of magnesium with 8-hydroxyquinoline. Application to determination of magnesium in tissue and urine. D. M. GREENBERG, C. ANDERSON, and E. V. TUFTS (J. Biol. Chem., 1935, 111, 561—565).—Loss of Br in the determination of Mg (A., 1932, 764) is avoided by mixing the solutions in a filter flask provided with a funnel with a long stem which projects below the surface of the liquid. The side-arm is plugged with

glass wool saturated with 20% KI. For the determination of Mg in biological material dry ashing in a muffle and the removal of Fe by the Alten method (A., 1933, 1262) are recommended. H. D.

Determination of small quantities of magnesium sulphate. M. MÖLLER and G. SCHLEGEL (Mikrochem., 1935, 18, 159—161).—The method of repeated pptn. of MgSO_4 by $\text{Ba}(\text{OH})_2$ has been carried out in an atm. of H_2 using a special apparatus. R. S.

Indirect volumetric determination of zinc. G. SPACU and C. G. MACAROVICI (Bul. Soc. Ştiinţe Cluj, 1934, 8, 129—139; Chem. Zentr., 1935, i, 1422—1423).—Zn is pptd. as $[\text{Zn}(\text{CNS})_2(\text{C}_5\text{H}_5\text{N})_4]$ by addition of excess of 0.1N- $\text{NH}_4\text{CNS} + \text{C}_5\text{H}_5\text{N}$. An aliquot part of the filtered solution is neutralised (indicator: dinitrophenol), and excess of 0.1N- AgNO_3 is added. The excess of Ag is then titrated back with NH_4CNS , using diphenylcarbazone as indicator. J. S. A.

Micro-determination of zinc by anthranilic acid. C. CIMERMAN and P. WENGER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 94—98).—To 2 c.c. of solution at p_H 5.5—7 containing 1—3 mg. of Zn^{++} , freshly prepared Na anthranilate (I) is added dropwise, using 0.3 c.c. excess. After an interval the ppt. is collected, washed once with 1—2 c.c. of 0.1% (I) and 5 times with 1 c.c. of EtOH, dried at 110° , and weighed. An accuracy of $\pm 0.3\%$ is claimed. Details of a second method are also given. S. J. G.

Modification in the confirmatory test for zinc ion. M. W. KELLY and E. L. JOHNSON (J. Chem. Educ., 1935, 12, 481—483).— Zn^{++} (≤ 50 mg.) as the nitrate is fused to deflagration with NH_4NO_3 ; a rose-coloured residue, changing in colour to yellow on further heating, is obtained. L. S. T.

Iodometric determination of zinc by Lang's method. C. W. RAADSVELD (Chem. Weekblad, 1935, 32, 655—657).—The amount of I liberated when Zn^{++} reacts with $\text{Fe}(\text{CN})_6^{--}$ and I^- is not const. The method described by Lang (A., 1933, 799) is excellent for rough determinations, but is not sufficiently accurate for exact work. S. C.

Use of styryl dyes in quantitative micro-analysis. P. KRUMHOLZ and E. KRUMHOLZ (Mikrochem., 1935, 19, 47—54).—The styryl dyes formed by $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$ with quinaldines and benzthiazoles give in neutral or acid solution sensitive red to violet colorations with Zn, Au, Pd, Cu, and Mg; less sensitively with Ag, Sn, Co, Cd, and Fe. $p\text{-dimethylaminostyryl-}\beta\text{-naphthothiazole}$ will detect Zn at a concn. of 10^{-7} . J. S. A.

Micro-determination of cadmium by means of 8-hydroxyquinoline. P. WENGER, C. CIMERMAN, and M. WYSZEWIANSKA (Mikrochem., 1935, 18, 182—184, and Arch. Sci. Phys. nat., 1935, [v], 17, Suppl., 125—126).—8-Hydroxyquinoline is added to the Cd solution buffered at p_H 6—7 and the ppt. is washed, dried, and weighed, using the Emich micro-filter technique. The accuracy is 1 in 1000. R. S.

Volumetric determination of lead. S. N. ROY (J. Indian Chem. Soc., 1935, 12, 584—585).—Neutral solutions of Pb salts (free from other metallic ions) can

be titrated with standard K_2SO_4 solution, using fluorescein as external indicator. The method can also be applied to the determination of SO_4^{2-} . O. J. W.

Quantitative emission-spectrum analysis of lead and cadmium contained in zinc oxide.—See B., 1935, 1043.

Identification of the copper ore minerals by means of X-ray powder diffraction patterns. A. W. WALDO (Amer. Min., 1935, 20, 575—597).—X-Ray data for 48 minerals are indexed in a form which permits ready identification of the mineral from its X-ray diffraction lines. L. S. T.

Determination of mercury. S. AUGUSTI (Gazzetta, 1935, 65, 689—693).—To a solution of the Hg^{II} salt an ammoniacal solution of K_2CrO_4 is added, giving a ppt. of $(Hg_2N)_2CrO_4 \cdot 2H_2O$. When this is dissolved in a solution of KI or of $Na_2S_2O_3$, for every atom of Hg, 2 mols. of NaOH, which can be titrated with a standard acid solution, are liberated. The complete determination requires 40—50 min. O. J. W.

Determination of mercury in iodinated organic mercury compounds.—See B., 1935, 1068.

Microchemical contributions. XII. L. ROSENTHALER (Mikrochem., 1935, 19, 17—22; cf. A., 1934, 791).—Yellow, but not red, HgO reacts with NH_3 , aq. $NaHSO_3$, and aq. $KHSO_4$. Vanillin gives characteristic cryst. ppts. with $Ba(OH)_2$ and $MgSO_4 + NH_4Cl$. Phenols give sensitive, in some cases cryst., orange to red ppts. with p -diazonitroaniline. Phloroglucinol and pyrocatechol give characteristic ppts. with Zwicker's $Cu-C_6H_5N$ reagent. Prontosil gives characteristic ppts. with $[Co(NO_3)_4(NH_3)_2]K$, $AgNO_3$, $HgNO_3$, $Cu(OAc)_2$, and anthraquinone-1-sulphonic acid. J. S. A.

Volumetric determination of aluminium, $p_H > 10$. V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech., 1934, No. 1, 156—164).—Results in the determination of Al by titration with KOH with malachite-green as indicator depend on the temp., concn. of indicator, concn. of solutions, and absence of CO_2 . The method is untrustworthy.

CH. ABS. (e)

Quantitative separation of metals by hydrogen sulphide. VIII. Separation of aluminium from iron, nickel, and cobalt. H. KATô (J. Chem. Soc. Japan, 1935, 56, 210—212; cf. this vol., 719).— FeS , NiS , and CoS are pptd. with H_2S at a suitable p_H , basic Al acetate being pptd. from the filtrate by boiling with $NaOAc$. CH. ABS. (e)

Spectrophotometric determination of manganese in steel.—See B., 1935, 1047.

Mixed perchloric and sulphuric acids. III. Determination of chromium in chromic oxide. G. F. SMITH, L. D. McVICKERS, and V. R. SULLIVAN (J.S.C.I., 1935, 54, 369—372T; cf. A., 1934, 982).—The oxidation of Cr_2O_3 by $HClO_4$ alone is incomplete owing to the production of a small amount of H_2O_2 . Rapid cooling minimises this and quant. results may be obtained with a mixture of 1 vol. of aq. $HClO_4$ (72%) + 2 vols. of aq. H_2SO_4 (80%). R. S.

Conductometric titration of molybdate with silver nitrate. C. CÂNDEA and I. G. MURGULESCU

(Bull. Soc. Chim. România, 1935, 17, 103—105).— NH_3 must be removed by NaOH and the solution neutralised with HNO_3 before titration. Accurate results are obtained only when $[MoO_4^{2-}] > 0.002N$. R. S.

Use of induced precipitation for detection of small amounts of titanium and zirconium. F. FEIGL and E. RAJMANN (Mikrochem., 1935, 19, 60—63).—To a solution containing < 1 pt. of Ti in 50,000, a few drops of Zr solution are added, and Zr then pptd. with H_3AsO_4 . Ti is co-pptd. and may be detected with H_2O_2 in the ppt. after dissolution in H_2SO_4 . The sensitivity is lowered in presence of Fe, V, W, or Mo. Conversely, Ti may be added to a Zr solution, co-pptg. Zr, which is detected with azoarsinic acid. J. S. A.

Determination of vanadium in the field. V. A. SILBERMINTZ and K. P. FLORENZKI (Mikrochem., 1935, 18, 154—158).—A spot method depending on the oxidation of NH_2Ph is used. HCl and H_3PO_4 are added when Fe is present. R. S.

Relation between sensitivity and mol. wt. (Weighting effect.) P. KRUMHOLZ and H. WATZEK (Mikrochem., 1935, 19, 55—59).—The sensitivity of cyclic N bases as precipitants for $HBiI_4$ is raised by progressive weighting of the ring system, by replacement of S by Se, or by conversion into the corresponding ethiodide. J. S. A.

Micro-determination of bismuth as oxyiodide. F. HECHT and R. REISSNER (Mikrochem., 1935, 18, 283—288).—The method (A., 1928, 388) is inexact. R. S.

Micro-analytical determination of platinum metals in simple and complex salts. J. MEYER and K. HOEHNÉ (Mikrochem., 1935, 19, 64—71).—Pt may be determined by cautious ignition in air. Rh, Ir, Ru, and Pd salts may be ashed in air and finally reduced in H_2 . Only with Pd is cooling in CO_2 essential. Os salts must not be heated in air. Au invariably gives losses due to volatilisation of Au halides. The method is applicable only in the absence of other metals. J. S. A.

Water thermostat. (MME.) S. LALLEMAND (Bull. Soc. Chim. biol., 1935, 17, 1470—1471).—An arrangement for maintaining a water-bath at a temp. $<$ that of the room is described. A. L.

Temperature measurement with photo-electric cells. H. J. ZETZMANN (Arch. tech. Mess., 1934, 4, T, 116—117; Chem. Zentr., 1935, i, 1420).—Temp. and very rapid fluctuations of temp. above 550° may be measured by determining photo-electrically the intensity of some definite filtered spectral region of the emitted thermal radiation. J. S. A.

Errors in the measurement of temperatures with thermocouples.—See B., 1935, 1025.

Thermocouple vacuum calorimeter [for determining heats of adsorption]. W. E. GARNER and F. J. VEAL (J.C.S., 1935, 1436—1443).—The factors affecting the trustworthiness of several designs of thermocouple calorimeters for determining heats of adsorption of gases on oxides, whereby the adsorbent is placed in a glass vessel surrounded by a high vac., have been investigated. Total heats of slow and

rapid adsorption processes and differential heats of slow adsorption processes are determined accurately, but untrustworthy data for differential heats of rapid processes may be obtained owing to uneven distribution of gas throughout the adsorbent and low grain conductivity in the absence of sufficiently high mobility of the adsorbed mols. in the capillaries. J. G. A. G.

New optical method for the determination of elastic constants of crystals. C. SCHAEFER and L. BERGMANN (*Atti R. Accad. Lincei*, 1935, [vi], 21, 701—702).—Examples are given of the diffraction figures obtained when a beam of monochromatic light is passed through rapidly oscillating crystals of quartz and other substances. From a study of these figures the elastic const. of the crystal may be calc.

O. J. W.

Simple process for absolute calibration of photo-cells. H. THEISSING (*Physikal. Z.*, 1935, 36, 683—684).—The Hefner lamp, of which the spectral energy distribution closely follows Wien's law, is used to obtain a calibration curve.

A. J. M.

Standardisation of photo-electric cells for the measurement of visible light. H. H. POOLE and W. R. G. ATKINS (*Phil. Trans.*, 1935, A, 235, 1—27).—Representative types of vac. emission and rectifier photo-electric cells have been standardised in light from (a) open solid C arc, (b) vac. sub-standard filament lamp at 2360° abs., (c) artificial "mean noon sunlight" derived from the latter by interposing special filters. The cells were also compared in mixed daylight. Consts. relating to 19 such cells are recorded.

E. S. H.

Modified photographic method for substances of small rotatory dispersion. R. PADMANABHAN (*J. Indian Chem. Soc.*, 1935, 12, 559—565).—The usual method is unsatisfactory for substances of which the optical activity does not vary very much with λ , but by determining the rotatory dispersion of such a substance in a column which also contains another substance of normal dispersive power and high initial rotation, e.g., quartz plates, better results can be obtained. Measurements for β -pinene are recorded.

J. W. S.

Gaseous discharge tube designed as an intense source of continuous ultra-violet radiation. R. H. MUNCH (*J. Amer. Chem. Soc.*, 1935, 57, 1863—1865).—A low-voltage H_2 discharge tube, requiring no H_2O cooling, is described.

E. S. H.

Rapid measurement of optical absorption for small light intensities. M. VON ARDENNE and E. HAAS (*Z. physikal. Chem.*, 1935, 174, 115—121).—The current from a photo-electric cell creates a p.d. in a coupling resistance which is amplified to work a pointer galvanometer. By using a carrier frequency of ~ 20 hertz, produced by periodic cutting off of the incident light, it is possible to use an a.c. amplifier. Light intensities as low as 7×10^{-11} g.-cal. per sec. may be measured in 1 sec. with an accuracy of $\pm 1\%$. The method is suitable for measuring the absorption of light in living cells by the pigments involved in O transfer.

R. C.

New method of focussing in X-ray spectrography. V. KUNZL (*Compt. rend.*, 1935, 201, 656—658).

H. J. E.

Photographic measurement of intensities of spectral lines. E. W. MÜLLER (*Z. Physik*, 1935, 97, 97—106).—A subjective method applicable to comparison of heterochromatic lines is described.

A. B. D. C.

Compensating photo-electric colorimeter.—See B., 1935, 1001.

Variable layer photo-electric comparison photometer. New type of photo-electric colorimeter. A. GOUDSCHMIDT, jun., and W. H. SUMMERSON (*J. Biol. Chem.*, 1935, 111, 421—433).—The light beams, after passing through the tubes of the colorimeter, fall on two photo-electric cells, arranged to give a differential deflexion on a galvanometer, used as a null instrument. A sensitivity of about 0.5% is attained.

F. A. A.

[Colorimetric technique.] R. VLADESCO (*Compt. rend. Soc. Biol.*, 1935, 120, 221—223).—For colorimetric determinations in complex solutions, equal vols. of the unknown solution are introduced into both colorimeter vessels, a known vol. of the standard is added to one, and the concn. of the unknown determined by difference.

R. N. C.

Colour analysis and specification. J. RAZEK (*Paper Trade J.*, 1935, 101; T.A.P.P.I. Sect., 187—191).—A general outline of the spectrophotometric method of colour analysis is given, and the method of reduction to trilinear co-ordinates in accordance with the procedure suggested by the International Committee on Illumination is described. The significance of dominant λ , colorimetric purity, and relative brightness is discussed. In the case of white samples, it is possible from the co-ordinates to calculate the degree of whiteness in accordance with Judd's formula (B., 1935, 719).

H. A. H.

Errors in colorimetric determinations. R. DOLIQUE (*Bull. Soc. Chim. biol.*, 1935, 17, 1304—1317).—Errors in colorimetric determinations are attributed to the effects of eye-strain. These effects are reduced to a min. by systematic movements of the plungers alternating with periods of rest.

A. L.

Microscopical methods for determining refractive index by immersion. C. P. SAYLOR (*J. Res. Nat. Bur. Stand.*, 1935, 15, 277—294).—The sensitivity of the criterion of match, which limits the immersion method of determining n , has been studied as a function of the method, objective aperture, and size and shape of particle. Objectives of low numerical aperture lead to greater sensitivity. The effect of birefringence has also been studied.

J. W. S.

Mass spectrometer. S. H. BAUER (*J. Physical Chem.*, 1935, 39, 959—965).—The principles of a simple instrument are discussed.

E. S. H.

Measurement of dielectric constants. A. BÜCHNER (*Z. tech. Phys.*, 1935, 16, 10—12; *Chem. Zentr.*, 1935, i, 1828—1829).—A valve circuit for dielectric const. measurements which permits the simultaneous determination of dielectric losses is described.

J. S. A.

Simultaneous determination of dielectric constants and conductivity of conductors at high frequency (two-phase bridge). H. GROSS and I. HAÜSSER (Ann. Physik, 1935, [v], 24, 127—160).—Apparatus for a new bridge method which allows the determination at high frequency of the magnitude and angle of loss of a resistance without the use of compensating resistances is described. A. J. M.

Camera for electron diffraction. R. MORGAN and N. SMITH (Rev. Sci. Instr., 1935, [ii], 6, 316—319).—Full constructional details are given. C. W. G.

Transmission photographs of single crystals with fast electrons, and their use in structure determination. G. AMINOFF and B. BROOMÉ (Z. Krist., 1935, 91, 77—94).—Apparatus and technique for obtaining diffraction photographs with thin crystal flakes and also with thicker specimens are discussed. B. W. R.

Micro-cell for the measurement of electrolytic conductivities. A. FINK and P. GROSS (Mikrochem., 1935, 18, 169—174).—A cell having a vol. of 0.45—0.8 c.c. is described. The equiv. conductivity of DCl in D₂O is 250. R. S.

Applicability of conductometric methods with visual observation to titrations in presence of much indifferent electrolyte. G. JANDER and A. EBERT (Z. Elektrochem., 1935, 41, 790—794).—With good apparatus and technique, satisfactory results can be obtained when a 500-fold excess of foreign electrolyte is present. E. S. H.

Antimony electrode for p_H measurement. A. HOLMQUIST (Z. Elektrochem., 1935, 41, 807).—A claim for priority (cf. this vol., 1218). E. S. H.

[Antimony electrode for p_H measurement.] P. WULFF and W. KORDATZKI (Z. Elektrochem., 1935, 41, 807).—A reply (cf. preceding abstract). E. S. H.

Micro-analytical notes. I. Methods of dealing with small quantities of liquids and precipitates. B. L. CLARKE and H. W. HERMANOE (Mikrochem., 1935, 18, 289—298).—Various micro-pipettes, a steam-jacketed capsule, and a micro-distillation apparatus are described. The distillation flask is flat and contains sand to prevent frothing. Sulphides are best pptd. in sealed tubes under pressure by H₂S produced from AcSH. R. S.

Prevention of frothing in Arndt's determination of nitrogen. W. CLASSEN (Chem.-Ztg., 1935, 59, 857).—Froth produced on distilling nitrates according to Arndt's method may be removed by adding sulphate, e.g., 0.5% of MgSO₄ to MgCl₂ lye. Distillation is rapid and the flask is more easily cleaned. R. S. B.

Improved screw plunger for use with mercury piston micro-burettes. S. J. FOLLEY and E. A. ROWSELL (Mikrochem., 1935, 18, 303—304).—A cotton-wool gland is fitted. R. S.

Simple micro-burette without stopcocks. K. SCHWARZ (Mikrochem., 1935, 18, 309—311; cf. A., 1933, 586).—Further details are given. R. S.

Pregl micro-analysis. J. UNTERZAUCHER (Mikrochem., 1935, 18, 312—315).—A stopcock on the inlet tube of the Mariotte flask allows the experiment to be interrupted without interfering with the adjustment of the gas flow. Carius tubes can be opened with the blowpipe flame, thus avoiding contamination of the material by glass. R. S.

Analysis of small volumes of gas by means of the usual micro-analytical apparatus. W. F. BRUCE (Mikrochem., 1935, 18, 261—265).—The Pregl combustion train has been adapted to the analysis of small vols. of gas obtained from *B. aertrycke* in synthetic citrate medium. R. S.

Compact vacuum gauge for measuring pressures from 0.2 mm. to 0.0001 mm. of mercury. C. T. KNIPP (Trans. Illinois State Acad. Sci., 1935, 27, 127—128).—A small McLeod gauge, requiring 10 c.c. of Hg, and connected to the apparatus by a ground joint, is described. CH. ABS. (e)

Improved method of extraction. C. A. MARLIES and V. K. LAMER (J. Amer. Chem. Soc., 1935, 57, 2008).—Extraction of a H₂O-sol. substance, e.g., NH₂NO₂, by Et₂O is more complete and rapid if the H₂O is frozen in solid CO₂. R. S. C.

Dynamic methods for determination of Young's modulus. J. M. IDE (Rev. Sci. Instr., 1935, [ii], 6, 296—298).—The specimen is set in vibration by electric traction and the frequency determined by the use of a piezo-electric detector. C. W. G.

Hydrogenation apparatus for small quantities of material. J. ERDÖS (Mikrochem., 1935, 18, 305—308).—H₂ is admitted to the catalyst before addition of 0.5—1 c.c. of the solution. The vol. change is measured in a gas burette. R. S.

High-vacuum micro-desiccator. J. UNTERZAUCHER (Mikrochem., 1935, 18, 315—318).—The boat is contained in a stoppered vessel in the desiccator. Hygroscopic substances can be weighed without contact with the atm. R. S.

New methods of determining mol. wt. K. RAST (Chem.-Ztg., 1935, 59, 853—857).—A review, including micro-methods. R. S. B.

Camphor as cryoscopic solvent and mol. wt. determination by Rast's method. C. F. CAPELLO (Giorn. Farm. Chim., 1934, 83, 336—342, 345—347; Chem. Zentr., 1935, i, 1421).—The cryoscopic const. of camphor is taken as 400. J. S. A.

Micro-determination of mol. wt. M. AF HALLSTRÖM (Ann. Acad. Sci. fenn., 1934, 41, A, No. 6; Chem. Zentr., 1935, i, 1421).—Isotonic solutions of the substance under examination and of a reference substance are prepared by dropping solvent into an evacuated desiccator within which the two solutes are in similar open weighing bottles. The mol. wt. is calc. from the consens. of the solutions as determined from their increase in wt. J. S. A.

Apparatus for the determination of mol. wt. by the camphor method. C. TIEDCKE (Mikrochem., 1935, 18, 223—226).—The H₂SO₄ bath is enclosed by a glass cap carrying the thermometer, stirrer, and a hook for the m.p. tube. R. S.

Micro-filtration apparatus. H. YAGODA (Mikrochem., 1935, 18, 299—302).—The use of a micro-filter of the Buchner type for the detection of Fe etc. is described. R. S.

Fractional ultrafiltration. P. GRABAR (Bull. Soc. Chim. biol., 1935, 17, 1245—1303).—A review of recent work.

Fractional distillation of extremely small volumes of liquids. A. A. BENEDETTI-PICHLER and J. R. RACHELE (Mikrochem., 1935, 19, 1—5).—Apparatus is described for the evaporation of 5—15 cu. mm. of liquid below its b.p., condensation taking place on a cold point. J. S. A.

Sealing metals to glass. A. W. HULL (Physical Rev., 1934, [ii], 45, 285—286).—The differential thermal expansion between glass and metal has been measured for the common sealing materials and for some new alloys and glasses. A new alloy the expansion of which matches that of a particular glass from 0° to the softening point has been used to confirm the hypothesis that properly annealed seals will be strain-free to exactly the degree indicated by expansion data. L. S. T.

Adolf von Baeyer, 1835—1917. J. R. PARTINGTON (Nature, 1935, 136, 669—670).—Historical. L. S. T.

Geochemistry.

Helium content of the stratosphere. F. A. PANETH and E. GLÜCKAUF (Nature, 1935, 136, 717—718).—The % of He in the air of England remains practically const. ($5.27—5.35 \times 10^{-6}$ c.c. per c.c.) up to a height of 18 km., but at 21 km. an 8% increase has been observed. L. S. T.

Proportion of heavy water in the water of crystallisation of minerals. E. H. RIESENFELD and M. TOBIANK (Ber., 1935, 68, [B], 1962—1969; cf. A., 1934, 1327).—The enrichment in D₂O of the crystal water of rasorite, tincal, carnallite, polyhalite, and gypsum is < that recorded by other authors for natural waters of differing origin. Since similar results have been recorded by other workers, enrichment in D₂O by crystallisation of salts and minerals has never been observed. This is attributed to the rate of crystal formation being small in comparison with the rate of exchange reaction in the D₂O content of the aq. and cryst. phase. The solubility of hydrated salts in D₂O and that of salts containing D₂O of crystallisation in H₂O are therefore not consts. at const. temp., but depend on the amount of salt employed in determining the solubility and other factors. Both must lie between the solubility of hydrates in H₂O and that of D₂O-containing compounds in D₂O, both of which are true consts. H. W.

Occurrence of radium in north- and middle-German deep waters. O. HAHN and H. J. BORN (Naturwiss., 1935, 23, 739—740; cf. A., 1934, 505).—The high He content of sylvine indicates that it was deposited from H₂O more highly radioactive than sea-H₂O. The Ra content of H₂O from oil-borings and elsewhere in the neighbourhood of the north German salt deposits is > that of any previously investigated German H₂O. The Ra content increases with Ca content of the H₂O, and in the stronger Ra-containing H₂O, Li is present. A. J. M.

Chemico-physical analysis of waters of Lurisia and Mondovi. Presence of lithium in besimaudite, quartziferous porphyry, of the same locality. L. FRANCESCONI and R. BRUNA (Annali Chim. Appl., 1935, 25, 460—470).—These waters (cf. A., 1934, 273) are radio-active and contain P₂O₅ and Li₂O in appreciable amounts. T. H. P.

Travertine-depositing waters near Lexington, Virginia. E. STEIDTMANN (Science, 1935, 82, 333—334).—These waters are supersaturated with Ca(HCO₃)₂ throughout the year, the excess ranging from approx. 68 to 76 p.p.m. of CaCO₃. The largest excess appears in winter. The annual range of p_{H} , temp., free CO₂, and other constituents are recorded. The marked deposition of calcite (I) in the summer is due mainly to a rise in temp., but adjustment is also hastened by aeration and close contact of the H₂O with (I). Travertine grows from the base of the plants upwards by addition of (I) to (I), which may be a result of the catalytic action of (I) on unstable CaCO₃ solutions. L. S. T.

[Electrical conductivity of] salts dissolved in waters of the Autonomous Sandjak of Alexandria. V. FROLOW (Compt. rend., 1935, 201, 613—615).—Conductivity data are recorded. H. J. E.

Plate-like crystals of native silver from "Gottes Hülfe in der Not" mine, Kongsberg-fellet [Norway]. R. STØREN (Tids. Kjemi, 1935, 15, 124—126).—Their occurrence (in a cavity), form, and habit are described. The crystals contain > 3% Hg, whilst no trace of this has been detected in the ordinary ZnS and PbS ores of the mine. It is concluded that the crystals represent a primary deposition from magmatic H₂O. M. H. M. A.

Genetic significance of biotite-pyroxenite and hornblendite. D. L. REYNOLDS (Tsch. Min. Petr. Mitt., 1935, 46, 447—490).—The biotite-pyroxenite of the Newry igneous complex in Co. Down, Ireland, is believed to represent the parent magma from which the other rocks (monzonite, syenite, diorite, granodiorite) have originated by its action on the surrounding sedimentary rocks. Emanations rich in alkalis first gave rise to a feldspathisation of the sediments, which were then soaked with the highly fluid magma. Similar occurrences of biotite-pyroxenite or hornblendite in other regions are compared. L. J. S.

Petrochemistry of the Middle Bohemian pluton. A. ORLOV (Tsch. Min. Petr. Mitt., 1935, 46, 416—446).—43 analyses (8 new) are tabulated of rocks ranging from granite to gabbro from this

plutonic complex (the so-called Middle Bohemian granite massif). The relation of the intrusion to the tectonics of the district is discussed. Differentiation of the magma took place both before and after the intrusion. L. J. S.

Biogenic migration of rare elements. A. P. VINOGRADOV (Trans. Internat. Soc. Soil Sci., Sov. Sect., 1935, A, 64—69).—There appears to be a tendency towards the accumulation of elements of uneven at. no. in soil compared with the composition of the earth's crust. Elements which show greatest biogenic migration are those which most easily form sol. compounds. A. M.

Pyroxene group. A. N. WINCHELL (Amer. Min., 1935, 20, 562—568).—Variations in optical properties and composition, expressed as mol. %, are diagrammatically represented for the following series: clinoenstatite (I)—diopside (II), (II)—hedenbergite (III), (III)—clinohypersthene, MgSiO_3 — FeSiO_3 monoclinic pyroxenes, and clinoenstatite—(II)—(III). Minerals should no longer be regarded as compounds which can be expressed by simple formulæ, but as a series varying in composition through a considerable range. L. S. T.

Genesis of the ore at the Flathead Mine, N.W. Montana. P. J. SHENON (Econ. Geol., 1935, 30, 585—603).—The ore minerals are divided into hypogene and supergene sulphides and oxidation products. The former include pyrite, galena, antimonial matildite, and small amounts of enargite, and the latter, argentite, small amounts of covellite, and possibly marcasite. The associated gangue minerals are mainly quartz, barite, clay minerals, and alunite. The more common oxidation products are anglesite, melanterite, siderotil, malachite, and a yellow amorphous powder containing Pb, Sb, and Bi. Two stages of mineralisation are described, and the genesis of the deposit is discussed. L. S. T.

Red copper ore and plagioclinal hemihedry. R. SCHROEDER (Zentr. Min., 1934, A, 353—358; Chem. Zentr., 1935, i, 1354).—Crystals of red Cu ore from Cornwall exhibited plagioclinal hemihedry. Only right-handed forms were observed. J. S. A.

Copper ores of Kisenda (Belgian Congo). II. Presence of two varieties of chalcocite. III. Presence of a hypogene covellite and a supergene covellite. M. GYSIN (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 82—85, 116—119).—The varieties are described and explanations of their origin are offered. S. J. G.

Paragenesis of the Colorado copper sulphides, Cananea, Mexico. V. C. KELLEY (Econ. Geol., 1935, 30, 663—688).—The Colorado ore body is located within and along the contacts of a quartz porphyry stock which has been intruded into a series of massive, fine-grained, volcanic rocks. The early gangue minerals form an irregular, pegmatitic ring-dike and the subsequent sulphide mineralisation is localised within and along the pegmatite ring. The ore minerals consist chiefly of Cu sulphides, molybdenite, and sulpho-salts of Cu, mainly luzonite (I) and tennantite (II). They are of hypogene origin

with the exception of minor quantities of "sooty" chalcocite (III). Blue (III) and covellite (IV) replace an earlier chalcopyrite and bornite intergrowth, the latter being more susceptible to replacement. Deposition of (III) and (IV) has been followed by a later sulphide replacement, represented chiefly by (I) and (II). Alunite is abundant throughout the ore body, and its close association with (I) and (II) indicates that they were carried and deposited by acid solutions. L. S. T.

Grünerite from Rockport, Massachusetts, and a series of synthetic fluor-amphiboles. N. L. BOWEN and J. F. SCHAIRER (Amer. Min., 1935, 20, 543—551).—The occurrence of grünerite (I), d 3.597, α 1.686, β 1.709, γ 1.729 (all ± 0.002), as shells surrounding fayalite from Rockport is described. This (I) provides the nearest approach to pure $\text{Fe}_2\text{H}_2(\text{SiO}_3)_8$ yet encountered. The analysis is SiO_2 47.54, Al_2O_3 0.20, Fe_2O_3 0.71, FeO 47.25, MnO 2.14, MgO 0.04, CaO none, Na_2O 0.29, K_2O 0.11, H_2O 1.55, F 0.01, total 99.84%. Regarded as an end-member of the cummingtonite—grünerite series the properties of this (I) are compared with those of other members of the series. The optical properties of synthetic fluor-amphiboles, prepared from pyroxenes in closed tubes at atm. pressure in presence of NaF, are also compared with those of Mg—Fe amphiboles and pyroxenes. The amphibole obtained by this method is always more magnesian than the pyroxene from which it is produced, and in the typical discontinuous reaction series olivine, pyroxene, amphibole the general relation that each phase is more magnesian than the member of the preceding phase with which it is in equilibrium, appears to hold. L. S. T.

Occurrence of narsarsukite in Montana. W. A. P. GRAHAM (Amer. Min., 1935, 20, 598—601).—Optical and chemical data for narsarsukite occurring at East Butte, Sweet Grass Hills, Montana, associated with quartz veins cutting a green syenite are recorded and compared with similar data of the same mineral from the type locality in Greenland. L. S. T.

Study of opaque minerals by the method of imprints. Improvements in the technique of electrolytic attack. T. HILLER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 119—122).—A piece of gelatin paper is pressed on the polished surface of the grain by a metal spatula, plate of a press, etc., which is connected to the negative pole of an 8-volt battery. The positive pole is connected to a needle touching the free part of the grain. The various elements of the ore suffer anodic dissolution and are tested for in the gelatin by "developing" with suitable reagents. S. J. G.

Examination of linnaeites of N. Rhodesia and Katanga by the method of imprints. T. HILLER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 122—125).—The method described above is applied to the examination of certain linnaeites. S. J. G.

Stainierite. II. L. DE LEENHEER (Natuurwetensch. Tijds., 1935, 17, 148—156; cf. this vol., 725).—Further data are given. D. R. D.

Schoepite and becquerelite. V. BILLIET and W. F. DE JONG (*Natuurwetensch. Tijds.*, 1935, 17, 157—162).—Schoepite is $4\text{UO}_3 \cdot 9\text{H}_2\text{O}$ and has a 14.40, b 16.89, c 14.75 Å., and d 4.83. Becquerelite is $2\text{UO}_3 \cdot 3\text{H}_2\text{O}$ and has a 13.9, b 12.55, c 14.9 Å., and d 5.20. D. R. D.

Fluorescence experiments on natural sulphates. A. KÖHLER and H. LEITMEIER (*Zentr. Min.*, 1934, A, 364—375; *Chem. Zentr.*, 1935, i, 1354).—Data are given for barytes, celestine, anhydrite, anglesite, and other sulphates at room temp. and elevated temp. J. S. A.

Zaratite: synthetic zaratite. M. FENOGLIO (*Period. Min.*, 1934, 5, 265—274; *Chem. Zentr.*, 1934, i, 1851).—Material identical with zaratite in composition, properties, and crystal structure is obtained by the action of dil. aq. NiCl_2 on $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite). J. S. A.

Orientation of mica microliths in plagioclases from eruptive rocks. C. ANDREATTA (*Period. Min.*, 1934, 5, 217—235; *Chem. Zentr.*, 1935, i, 1851).—Tonalites, diorite, etc. frequently show partial conversion of plagioclase crystals into preferentially oriented mica microliths. J. S. A.

Natural mineral gel from Vashegy. L. VON ZOMBORY (*Földtani Közlöny*, 1933, 63, 219—220; *Chem. Zentr.*, 1935, i, 1851—1852).—A mineral gel consisting essentially of mixed Fe and Al sulphates + SiO_2 and P_2O_5 is described. J. S. A.

Composition of sky-blue diopside from 1906 Vesuvius eruption. S. RESTAINO (*Rend. Accad. Sci. Napoli*, 1934, [iv], 4, 32—35; *Chem. Zentr.*, 1935, i, 1852).—The diopside has less SiO_2 and more CaO than corresponds with $\text{CaMg}(\text{SiO}_3)_2$, + MnO , CuO , Fe_2O_3 , Al_2O_3 etc. J. S. A.

Minyulite, a new phosphate mineral from Dandaragan, W.A. E. S. SIMPSON and C. R. LE MESURIER (*J. Roy. Soc. W. Australia*, 1932—1933, 19, 13—16).—The formula is $\text{KAl}_2(\text{OH}, \text{F})(\text{PO}_4)_2 \cdot 3.5\text{H}_2\text{O}$. The occurrence and properties are described. CH. ABS. (e)

Rôle of certain riparian plants in the formation of argillaceous concretions. J. ROUSSEAU (*Natural. Canad.*, 1935, 62, 99—105). CH. ABS. (e)

Shungite. N. A. ORLOV, V. A. USPENSKI, and I. N. SHACHOVITZEV (*Khim. Tverd. Topl.*, 1934, 5, 601—619).—Shungite, a natural cryst. C of very low electrical resistance, contains H_2O 7.76, ash 1.09, C 98.11, H 0.43, O+S 1.03%. An ash analysis is given. CH. ABS. (e)

Igneous assimilation and associated contact metamorphism in the Virginia mining district, New Mexico. S. G. LASKY (*Amer. Min.*, 1935, 20, 552—561).—The rocks consist mainly of basalt of probably Comanche age intruded by late Cretaceous or early Tertiary porphyritic granodiorite (I). (I) generally has a dark border which contains much augite as well as a more calcic plagioclase and more magnetite than the main mass. The differences are attributed to partial assimilation of the adjacent basalt in accordance with Bowen's reaction principle. In addition, the basalt adjacent to the contact is metamorphosed to a rock mineralogically similar to the invading (I). L. S. T.

Some properties of opal. N. L. TALIAFERRO (*Amer. J. Sci.*, 1935, [v], 30, 450—474).—Vals. of d and n for opals and opaline cherts show ranges d 1.983—2.111, n 1.441—1.456, H_2O 4.75—2.70%, but they show no regular variation with H_2O ; when plotted, they lie scattered between the theoretical curves for SiO_2 glass + H_2O and cristobalite + H_2O . On slow dehydration at 120—350°, there is first an increase in d and n up to a transition point (1.6—2.8 mols. H_2O), after which they decrease, and in the completely dehydrated material d and n are < in the original material. X-Ray powder photographs show faint patterns of high-temp. β -cristobalite, but no actual crystals are present. L. J. S.

Conglomerates and grits of Kaldurga, Kadur district, Mysore. C. S. PICHAMUTHU (*Proc. Indian Acad. Sci.*, 1935, 2, B, 254—279).—Geological characteristics are described. F. O. H.

Chemical analyses of Finnish rocks. L. LOKKA (*Bull. Com. géol. Fin.*, 1934, No. 105; *Chem. Zentr.*, 1935, i, 1354).—A summary of published data. J. S. A.

Geology of St. Kilda. A. M. COCKBURN (*Trans. Roy. Soc. Edin.*, 1935, 58, 511—547).—The rocks, all of them of igneous origin, are described with chemical analyses of eucrite, gabbro, pitchstone, and basalt. L. J. S.

Geology of Raasay, Inner Hebrides. C. F. DAVIDSON (*Trans. Roy. Soc. Edin.*, 1935, 58, 375—407).—The igneous rocks of Tertiary age are described with chemical analyses of gabbroid teschenite, riebeckite-granophyre, peridotite, and andesitic pitchstone. L. J. S.

Rare elements in (A) coal ashes, (B) German brown coal ashes.—See B., 1935, 978.

Organic Chemistry.

Evaluation of the structural theory of organic chemistry. II. J. K. SENIOR (*J. Chem. Educ.*, 1935, 12, 465—472; cf. this vol., 1305).—A lecture. L. S. T.

Investigation of different types and isomerides of non-dissociated organic compounds with the help of the dialysis method. H. BRINTZINGER and H. G. BEIER (*Z. anorg. Chem.*, 1935, 224, 325—

328; cf. this vol., 1335).—Data obtained for 17 compounds shew that the diffusion velocity of non-ionised org. mols. depends on structure. T. G. P.

Specific refraction in predicting the composition of saturated synthetic hydrocarbon mixtures. H. I. WATERMAN and J. J. LEENDERTSE (*Rec. trav. chim.*, 1935, 54, 725—727).—The sp.

refraction gives vals. for the C : H ratio of the hydrogenated polymerides of unsaturated hydrocarbons of low mol. wt. in good agreement with analytical vals. (cf. B., 1932, 536). H. G. M.

Catalytic effect of ozone in the oxidation of hydrocarbons.—See this vol., 1466.

Influence of substituents on the addition reactivity of ethylene derivatives. III.—See this vol., 1465.

Addition of hydrogen sulphide to isoprene catalysed by ferrous sulphide. J. BÖESEKEN and N. v. D. LINDE (Rec. trav. chim., 1935, 54, 739—744).—Isoprene and H_2S when heated to 96° under pressure in presence of Fe_2O_3 or FeS yield a mixture, probably mainly β -thiol- β -methyl- Δ^2 -butene (I), b.p. $67^\circ/100$ mm. (red Hg salt; oxidised by I to a disulphide, b.p. $87^\circ/\text{high vac.}$), and, probably, β -dithiol- β -methylbutane, b.p. $135^\circ/20$ mm. (I) rapidly adsorbs SO when oxidised with AcO_2H . Further oxidation to H_2SO_4 also occurs (cf. A., 1934, 1307). H. G. M.

Dimerisation of Δ^2 -butadiene. S. LEBEDEV and S. SERGIENKO (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 79—82).—Thermal polymerisation of butadiene affords a monocyclic product, probably vinyl- Δ^1 -cyclohexene, which yields a trans-, m.p. 101.5 — 102.5° and a cis-tetrabromide, m.p. 74 — 75° , both of which can be reconverted into the original dimeride. No open-chain dimerides are formed, and there is no tendency to further polymerisation, which brings the probable mechanism of this reaction into line with the polymerisation of isoprene and diisoprenyl (cf. A., 1922, i, 1043). J. L. D.

Preparation of butadiene from *s*-dimethylethylene. B. A. KAZANSKI and I. A. RAFILZON (Sintet. Kauchuk, 1934, No. 1, 31—34).—3—4% of $\text{CHMe}:\text{CHMe}$ (I) is formed in the prep. of butadiene (II) from EtOH. Addition of Cl_2 to (I) affords $(\text{-CHMeCl})_2$ (III), removal of 2HCl from which yields (II); the latter process is best carried out by passing (III) over BaCl_2 at 360 — 400° [30—40% yield of (II)]. NiCl_2 and Al_2O_3 are much less efficient as catalysts. CH. ABS. (r)

Addition of methyl alcohol to dialkylacetylenes. G. F. HENNION and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 2006—2007).—Acetylenes and OH-compounds react to produce successively compounds of the types, $\text{CH}_2:\text{CH}:\text{OR}$ and $\text{CHMe}(\text{OR})_2$. Hg acetylides are not essential to the mechanism, since, in presence of a catalyst prepared from HgO , $\text{Et}_2\text{O}:\text{BF}_3$, $\text{CCl}_3:\text{CO}_2\text{H}$, and MeOH , Δ^2 -octene, b.p. 132 — 136° (from MeI and $\text{C}_5\text{H}_{11}:\text{C}:\text{CNa}$ in liquid NH_3), and MeOH give $\gamma\gamma$ -dimethoxyoctane, b.p. 90 — $92^\circ/26$ mm. (hydrolysed to $\text{COPr}^+\text{-C}_5\text{H}_{11}$), and $\text{OMe}:\text{CH}_2:\text{C}:\text{CMe}$ gives similarly $(\text{OMe})_2\text{CMe}:[\text{CH}_2]_2:\text{OMe}$, b.p. 67 — $69^\circ/30$ mm.

R. S. C.

Acetylene polymerides and their derivatives. XXII. α -Dialkylaminomethyl- β -vinylacetylenes. XXIII. δ -Cyano- Δ^2 -butadiene [Δ^2 -pentadienenitrile]. D. D. COFFMAN (J. Amer. Chem. Soc., 1935, 57, 1978—1980, 1981—1984; cf. A., 1934, 990).—XXII. $\text{CH}_2:\text{CH}:\text{C}:\text{CH}$ (I), paraformaldehyde, and the requisite *sec.*-amine in dioxan at 100 — 105°

give smoothly ϵ -dimethylamino- (II), b.p. 133 — $135^\circ/752$ mm., -diethylamino- (III), b.p. 166 — $167^\circ/766$ mm., -*N*-piperidino- (IV), b.p. 207 — $209^\circ/766$ mm., and -dihexylamino-pent- α -en- γ -inene, b.p. 138 — $140^\circ/0.5$ mm., which are stable and have characteristic odours. Hydrogenation of (III) and (IV) in EtOH (PtO_2) gives diethyl-*n*-amylamine and *N*-*n*-amylpiperidine, respectively. (II), (III), and (IV) add HCl in presence of aq. CuCl_2 at 60° [less readily than does (I)] to give γ -chloro- ϵ -dimethylamino-, - ϵ -diethylamino-, and - ϵ -*N*-piperidino- Δ^2 -pentadiene, which are fairly stable (do not give rubbery polymerides) and with naphthaquinone and $(\text{CH}:\text{CO})_2\text{O}$ give black, resinous additive compounds. (II) adds $p\text{-C}_6\text{H}_4\text{Me}:\text{SH}$ in ultra-violet light to give α -dimethylamino- ϵ -*p*-tolylthiol- Δ^2 -pentene, b.p. 156 — $158^\circ/0.5$ mm., adds MeOH in presence of NaOMe at 100° to give a substance, $\text{C}_8\text{H}_{15}\text{ON}$, b.p. 69 — $71^\circ/1$ mm. (destroyed by KMnO_4), and by exhaustive methylation ($\text{Ag}_2\text{O}:\text{H}_2\text{O}$ at 45°) gives a hydrocarbon, C_8H_4 , b.p. 80 — 90° , unstable to heat and O_2 . Physical data are given.

XXIII. $\text{CH}_2:\text{C}:\text{CH}:\text{CH}_2\text{Cl}$ and NaCN in hot MeOH react with shift of the ethylenic linking to give a poor yield of Δ^2 -pentadienenitrile (δ -cyano- Δ^2 -butadiene) (V), b.p. 49 — $53^\circ/30$ mm., and δ -methoxy- Δ^2 -pentenenitrile (VI), b.p. 65 — $67^\circ/7$ mm., $\beta\delta$ - or $\gamma\delta$ -dimethoxyvaleronitrile (VII), b.p. 70 — $73^\circ/1$ mm., and a substance, $\text{C}_5\text{H}_{12}\text{ON}_2$, b.p. 131 — $134^\circ/0.5$ mm. Structures are proved by the reactions described below. (V) with conc. $\text{HCl}:\text{Et}_2\text{O}$ at room temp. yields $\text{CH}_2:\text{CH}:\text{CH}:\text{CH}:\text{CO}_2\text{H}$, m.p. 71° (Et ester, b.p. 65 — $67^\circ/30$ mm.; polymerises slowly at 100° and does not add naphthaquinone), with H_2 - PtO_2 in Ac_2O gives *n*- $\text{C}_5\text{H}_{11}:\text{NH}_2$, with KMnO_4 - KOH gives $\text{H}_2\text{C}_2\text{O}_4$, and with $\text{HCl}:\text{EtOH}$ affords by 1:4-addition and hydrolysis Et δ -chloro- Δ^2 -pentenoate, b.p. 72 — $74^\circ/1$ mm., oxidised by KMnO_4 to $\text{CH}_2\text{Cl}:\text{CO}_2\text{H}$. (VI) and KMnO_4 give $\text{OMe}:\text{CH}_2:\text{CO}_2\text{H}$. (VII), obtained also in 23% yield from (VI) and $\text{NaOMe}:\text{MeOH}$ at 60° , with H_2SO_4 gives a dimethoxyvaleric acid, b.p. 119 — $122^\circ/1$ mm., hydrolysed by HBr to an unsaturated lactone, b.p. 83 — $85^\circ/3$ mm., 226 — $228^\circ/760$ mm. (solid polymeride formed at 150°), which is hydrogenated (PtO_2) in EtOH to δ -valerolactone [gives δ -hydroxyvaleric hydrazide, m.p. 105° (block)]. In light at 40 — 50° (V) gives a rubbery polymeride, resembling ω -polychloroprene. In 3 weeks at room temp. (V) gives 5% of an α -polymeride (VII), 14% of which is formed in 13 hr. at 100° with 42% of a dimeride. (VIII) can be compounded and partly vulcanised by heat. With hot NaOH (V) gives a brittle polymeride. Physical data are given.

R. S. C.

Kinetics of interactions of sodium hydroxide with bromoethanes.—See this vol., 1465.

Isolation of crotonyl [bromide] and methylvinylcarbinyl bromide [γ -bromo- Δ^2 -butene]. W. G. YOUNG and S. WINSTEIN (J. Amer. Chem. Soc., 1935, 57, 2013).— $\text{CHMe}:\text{CH}:\text{CH}_2\text{Br}$ or $\text{CH}_2:\text{CH}:\text{CHMe}:\text{OH}$ with HBr and PBr_3 gives mixtures of $\text{CHMe}:\text{CH}:\text{CH}_2\text{Br}$, b.p. $107^\circ/760$ mm., $49^\circ/93$ mm., and $\text{CH}_2:\text{CH}:\text{CHMeBr}$ (I), b.p. $86.5^\circ/760$ mm., which equilibrate in a few days at room temp., 1 hr. at 75° ,

and <5 min. at 100° to a mixture containing 14% of (I). Distillation/760 mm. of a mixture through a column gives pure (I). Physical data are given.

R. S. C.

Aliphatic substitution and Walden inversion. I.—See this vol., 1465.

Nitroso-compounds. III. Reactions of organo-metallic compounds with α -halogenonitroso-compounds. J. G. ASTON and D. F. MENARD.

IV. Reaction of ethyl nitrite with isopropyl and cyclohexyl ketones. J. G. ASTON and M. G. MAYBERRY (J. Amer. Chem. Soc., 1935, 57, 1920—1924, 1888—1891; cf. A., 1934, 868).—III. $\text{CMe}_2\text{Br}\cdot\text{NO}$ (I) (modified prep.; 90% pure) and $\text{CMe}_2\text{Cl}\cdot\text{NO}$ (II) react with organo-metallic compounds by loss of halogen hydride to give $\text{CH}_3\cdot\text{CMe}\cdot\text{NO}$ (III) [leading to $\text{CMe}_2\cdot\text{N}\cdot\text{OH}$ (IV)] or by addition at the NO. (I) and $\text{NH}_3\cdot\text{Et}_2\text{O}$ give only NH_4Br and (IV) [by way of (III)]. (II) and ZnMe_2 (1 mol.) give CH_4 (1 mol.), (IV), COMe_2 , and $\text{NHMe}\cdot\text{OH}$; the last two arise thus: (I) + $\text{ZnMe}_2 \rightarrow \text{CMe}_2\text{Cl}\cdot\text{NMe}\cdot\text{OZnMe} \rightarrow$

$\text{CH}_4 + \text{CH}_3\cdot\text{CMe}\cdot\text{NMe}\cdot\text{OZnCl} \xrightarrow{2\text{H}_2\text{O}} \text{COMe}_2 + \text{NHMe}\cdot\text{OH} + \text{ZnCl}\cdot\text{OH}$, although at least some loss of HCl occurs prior to addition. (I) and ZnEt_2 react similarly to the extent of about 70%, giving COMe_2 and $\text{NHMe}\cdot\text{OH}$, but the formation of C_2H_6 shows 30% of reaction thus: (I) + $\text{ZnEt}_2 \rightarrow \text{C}_2\text{H}_6 + \text{CMe}_2\text{Br}\cdot\text{NH}\cdot\text{OZnEt} \rightarrow \text{C}_2\text{H}_6 + \text{CMe}_2\cdot\text{N}\cdot\text{OZnBr} \rightarrow$ (IV). (I) and (II) react with MgEtBr (2 mols.) as with ZnEt_2 , giving C_2H_6 , C_2H_4 , COMe_2 , NH_2OH , and (IV), but formation of an excess of C_2H_6 shows also some reaction thus: (I) + $\text{MgEtBr} \rightarrow$ (III) + $\text{MgBr}_2 + \text{C}_2\text{H}_6$. (II) and MgMeCl (1 mol.) react by addition at the NO, giving $\text{NHMe}\cdot\text{OH}$. 2 mols. of MgMeCl give also replacement of the Cl, thus: (I) + $2\text{MgMeCl} \rightarrow \text{CHMeEt}\cdot\text{NMe}\cdot\text{OMgCl} \rightarrow \text{MgCl}\cdot\text{OH} + \text{CHMeEt}\cdot\text{NMe}\cdot\text{OH}$, the resultant *N-methyl-N-sec-butylhydroxylamine*, b.p. 85—93°/115 mm. (hydrochloride, hygroscopic, being identified by reduction by SnCl_2 to *N-methyl-sec-butylamine* (hydrochloride, m.p. 242—244°; oxalate, m.p. 109—110°; also obtained from $\text{CMeEt}\cdot\text{N}\cdot\text{OH}$ by reduction and methylation). (I) and MgMeCl react similarly, but lead also to a little *N-methyl-N-tert-butylhydroxylamine* [oxalate, m.p. 166—167° (decomp.)]. (I) and MgPhBr give 20% of C_6H_6 by loss of HBr .

IV. NO-OEt reacts with COPr^2 , or cyclohexyl ketone in presence of aq. or, better, dry HCl or AcCl at the $\alpha\text{-CH}_2$ or $\alpha\text{-CH}$ or both, but the relative amounts of the two reactions cannot be correlated with the structure of the second alkyl. The following are incidentally described: *1-nitrosocyclohexyl Me*, m.p. 114—115°, and *Et ketone*, m.p. 119.5—120°; *cyclohexyl α -oximinoethyl*, m.p. 78—78.2°, and *Bu³ α -oximino-isopropyl ketone*, m.p. 89.2—90°; *ethylisopropyl-*, m.p. 148.5—149°, and *propylisopropyl-glyoxime*, m.p. 140—140.3°.

R. S. C.

Chemical action of penetrating radium radiations. XX.—See this vol., 1469.

Reactivity of atoms and groups in organic compounds. XVI—XVIII.—See this vol., 1206.

Isomeric branched hexadecanols. W. M. Cox, jun., and E. E. REID (J. Amer. Chem. Soc., 1935,

57, 1801—1802).—All the isomeric C_{16} -alcohols, $\text{CHRR}'\cdot\text{CH}_2\cdot\text{OH}$, are prepared by reduction of the corresponding esters, prepared by the $\text{CH}_2(\text{CO}_2\text{Et})_2$ synthesis. The following are described, yields being stated in parentheses: *Et pentadecane- β -*, b.p. 185—187°/12 mm., γ -, b.p. 191—199°/15 mm., δ -, b.p. 181—183°/14 mm., ϵ -, b.p. 180—185°/15 mm., ζ -, b.p. 180—182°/14 mm., η -, b.p. 181—183°/14 mm., and *-o-carboxylate*, b.p. 182—183°/14 mm.; *cetyl alcohol*, m.p. 49.3°; *pentadecyl- β -*, m.p. 12—13°, b.p. 185—187°/15 mm. (66%), γ -, m.p. -0.2° , b.p. 186—188°/15 mm. (53%), δ -, m.p. 5.5° , b.p. 181—184°/15 mm. (32%), ϵ -, m.p. -14.5 to -14° , b.p. 181—183°/15 mm. (30%), ζ -, m.p. -9 to -8° , b.p. 181—182°/15 mm. (33%), η -, m.p. -30 to -26° , b.p. 181—183°/15 mm. (27%), and *-o-carbinol*, m.p. -25 to -18° , b.p. 181—182°/15 mm. (28%). *n* and *d* are given for the alcohols and their acetates.

R. S. C.

Velocity of hydrolysis of cyclic acetals.—See this vol., 1465.

Benzyl ethers of ethylene glycol and glycerol. S. DANILOV [with V. DRIABCHLITZIN and O. MANOCHINA] (Rev. gén. Mat. plast., 1934, 10, 364—367; Chem. Zentr., 1935, i, 1860).—Treatment of the Na_2 derivative of glycerol with CH_2PhCl affords *glyceryl benzyl*, b.p. 173—175°/9 mm., and *dibenzyl ether*, b.p. 214—216°/9 mm. These are also obtained from glycerol (46 g.), NaOH (60 g.), and CH_2PhCl (200 g.) at 130°. *Ethylene glycol mono-*, b.p. 134—135°/13.6 mm., and *di-*, b.p. 154°/2 mm. *-benzyl ethers* are prepared similarly.

H. N. R.

Synthesis of glycerides by means of triphenylmethyl compounds. I. Mono-acid diglycerides. P. E. VERKADE, J. VAN DER LEE, and (MISS) W. MEERBURG (Rec. trav. chim., 1935, 54, 716—724).—Glycerol $\alpha\text{-CPh}_3$ ether in quinoline and the requisite acid chloride in CHCl_3 yield the $\beta\gamma$ -distearate (I) and $\beta\gamma$ -dibenzoate in 82 and 84% yield, respectively (cf. A., 1933, 374). (I) with $\text{HBr}\cdot\text{Et}_2\text{O}$ affords $\alpha\gamma$ -distearin in 82% yield. Details are given for the determination of CPh_3 as $\text{CPh}_3\cdot\text{OH}$ in compounds which contain higher fatty acids.

H. G. M.

Preparation of *d*(-)-3-phosphoglyceric acid. See this vol., 1418.

Simplexes of lecithin with polysaccharides. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1935, 280, 413—415).—The prep. is described of sol. simplexes containing lecithin (I)—starch (II) [about 50 mols. (I) to 1 mol. (II)], of (I)—glycogen and of (I)—dextrin [about 4 mols. (I) to 1 mol. dextrin].

P. W. C.

Partial synthesis of ribose nucleotides. II. Muscle inosinic acid. P. A. LEVENE and R. S. TIFSON (J. Biol. Chem., 1935, 111, 313—323).—Inosine (modified prep. from adenosine; 100% yield), $[\alpha]_D^{25} -38.3^\circ$, with COMe_2 and ZnCl_2 gives the 2:3-isopropylidene derivative (I), m.p. 240—245° (decomp.) after softening at 225°, $[\alpha]_D^{25} -69.2^\circ$ in dry MeOH, $[\alpha]_D^{25} -88^\circ$ in $\text{C}_5\text{H}_5\text{N}$, the structure of which is proved by ready reaction of its 5-p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 185—186°, $[\alpha]_D^{25} +35.9^\circ$ in $\text{C}_5\text{H}_5\text{N}$, with NaI in COMe_2 . (I) and POCl_3 in $\text{C}_5\text{H}_5\text{N}$ at -40° to -10°

give *Ba* 2:3-isopropylideneinosine-5-phosphate, +3.5H₂O, hydrolysed by 0.05N-HCl to *Ba* inosine-5-phosphate, +7.5H₂O, $[\alpha]_D^{25} -36.8^\circ$ in 0.1N-HCl, identical with the salt of natural inosinic acid.

R. S. C.

Mechanism of reactions of diacyl peroxides with other organic substances and their thermal decomposition. P. H. HERMANS (Rec. trav. chim., 1935, 54, 760—767).—A review. Acyl peroxides when heated alone or with aromatic and aliphatic hydrocarbons (or their substituted derivatives) react according to one or more of the following schemes: $R\cdot CO\cdot O\cdot O\cdot CO\cdot R \rightarrow R\cdot R + 2CO_2$ (a) and $R\cdot CO_2R + CO_2$ (b), $Ph\cdot CO\cdot O\cdot O\cdot CO\cdot R \rightarrow R\cdot C_6H_4\cdot CO_2H + CO_2$ (c), $R\cdot CO\cdot O\cdot O\cdot CO\cdot R + R'\cdot H \rightarrow R'\cdot CO\cdot O\cdot O\cdot CO\cdot R + RH$ (d) and $R\cdot CO\cdot O\cdot O\cdot CO\cdot H$ (decomp. to $R\cdot CO_2H + CO_2$) + $R\cdot R'$ (e). Thermal decomp. is represented by (a) and (b). Purely aliphatic peroxides react mainly according to (a), but mixed aliphatic and aromatic peroxides react mainly according to (b) and (c), although, as with purely aromatic peroxides, all types of reaction are possible according to the conditions.

H. G. M.

Iodo-fatty acids. I. Additive products of lower unsaturated acids with hydriodic acid. E. MASUDA and K. NISHIDA (J. Pharm. Soc. Japan, 1934, 54, 1091—1100).—Addition of HI to $CH_2:CH\cdot CO_2H$ affords β -iodoacrylic acid (I), m.p. 147° , and $\beta\beta$ -diiodopropionic acid (II), m.p. 87° . Addition of HI to $Cl_2:CH\cdot CO_2H$ yields $\beta\beta$ -triiodopropionic acid (III), m.p. 131° , $\beta\beta$ -diiodoacrylic acid, m.p. 133° , and (II). Addition of HI to $Cl_2:CH\cdot CO_2H$ (IV) gives (III), whilst $CHI:CH\cdot CO_2H$ and HI afford no I₃-acid, but only (II). (II) may also be obtained by the reduction of (IV) with HI. (II) with 10% NaOH yields (I).

CH. ABS. (r)

Vinylacetic [Δ^2 -butenoic] acid. C. MANNICH (Arch. Pharm., 1935, 273, 415—417).—This acid is readily obtained in 65—75% yield from $CH_2:CH\cdot CH_2\cdot CN$ and conc. HCl at 100° (75 min.). With O₃ it gives only MeCHO, CO₂, and a little CH₂O and $CH_2(CO_2H)_2$, and with BzO₂H β -hydroxybutyrolactone. With SOCl₂ at 45° , followed by EtOH, or by way of the Ag salt and EtI it gives the *Et* ester, b.p. 118 — 120° , which with O₃ gives probably Et γ -formylglutaconate.

R. S. C.

Configurative relationship of acids of the isopropyl and isobutyl series to those of the normal series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1935, 111, 299—312).—Significant differences in $[M]_D^{25}$ between $Pr^a\cdot[CH_2]_m\cdot CHMe\cdot[CH_2]_n\cdot X$ and $Pr^b\cdot[CH_2]_m\cdot CHMe\cdot[CH_2]_n\cdot X$ exist only if $m=0$ or 1. *dl*- $CHMePr^b\cdot CO_2H$, b.p. $90^\circ/16$ mm., is resolved by quinine to give the *l*-form, $[\alpha]_D^{25} -18.9^\circ$. The *d*-acid, $[M]_D^{25} +6.7^\circ$, gives the *d*-*Et* ester, b.p. 146° , $[\alpha]_D^{25} +8.1^\circ$, and thence *d*- β -dimethylbutan- α -ol, b.p. 142° , $[\alpha]_D^{25} +1.9^\circ$ (acetate, b.p. 147° , $[\alpha]_D^{25} +2.7^\circ$), *d*- α -bromo- β -dimethylbutane, b.p. 140° , $[\alpha]_D^{25} +1.9^\circ$, *d*- β -dimethylvaleric acid, b.p. $109^\circ/14$ mm., $[\alpha]_D^{25} +1.3^\circ$ (*Et* ester, b.p. 165° , $[\alpha]_D^{25} +1.3^\circ$), β -dimethylpentan- α -ol, b.p. 164° , $[\alpha]_D^{25} +2.8^\circ$, *d*- α -bromo- γ -dimethylpentane, b.p. 162° , $[\alpha]_D^{25} +3.3^\circ$, and β -dimethylpentane, b.p. 90° , $[\alpha]_D^{25} +2.1^\circ$. $CHMePr^a\cdot[CH_2]_2\cdot Br$, $[\alpha]_D^{25} -4.7^\circ$, gives (Grignard) γ -dimethyl-*n*-hexoic

acid, b.p. $92^\circ/1$ mm., $[\alpha]_D^{25} -1.26^\circ$. 1- α -Dimethylvaleric acid (obtained by the cinchonine salt in COMe₂ at -10°), b.p. $117^\circ/17$ mm., $[\alpha]_D^{25} -13.8^\circ$, gives the *Et* ester, b.p. 164° , $[\alpha]_D^{25} +1.5^\circ$, 1- β -dimethylpentan- α -ol, b.p. 157° , $[\alpha]_D^{25} -1.1^\circ$, 1- α -bromo- β -dimethylpentane, b.p. $68^\circ/30$ mm., $[\alpha]_D^{25} -0.44^\circ$, and β -dimethylhexoic acid, b.p. $91^\circ/1$ mm., $[\alpha]_D^{25} -0.75^\circ$. $[\alpha]$ are for the homogeneous liquids, but are not necessarily max.

R. S. C.

Tetradesterostearic acid.—See this vol., 1407.

Fatty acids and glycerides of partly hydrogenated rape oil.—See B., 1935, 1054.

Polymerisation of fatty oils. IX. Hydrogenation of polymerised ethyl linolenate. X. Polymerisation of ethyl linoleate. A. STEIGER and J. VAN LOON (Rec. trav. chim., 1935, 54, 750—756, 756—759).—IX. Polymerisation of *Et* linolenate (I) at 300° in CO₂ is accompanied by the formation of a compound, b.p. 95 — 100° /high vac. (30.7%), incapable of polymerisation and hydrogenated (Pd, H₂, 1 atm., room temp.; Ni, H₂, 50 atm., 170°) to a monocyclic acid C₁₈H₃₄O₂, slowly oxidised by cold, alkaline KMnO₄. A little stearic acid is also formed, probably from unchanged (I), during hydrogenation. The main product from (I) is not completely hydrogenated by Pd (H₂, 1 atm., 15°) or by Ni (H₂, 100 atm., 170°). The resulting products have different I vals. and are oxidised by cold, alkaline KMnO₄ to products considered to consist of unsaturated compounds.

X. *Et* linoleate when heated (300° , 6—14 hr.) in CO₂ yields two main polymerisation products, b.p. $<100^\circ$ /high vac. and b.p. $>150^\circ$ /high vac. (some decomp.). The proportion of the latter increases with increase in the time of heating. The sap. and I vals., n_D^{20} , and mol. wt. of these fractions are given.

H. G. M.

Highly unsaturated acids in sardine oil. VII. Separation of highly unsaturated C₂₂-acids. VIII. Constitution of clupanodonic acid. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 433—440, 441—453).—VII. Fractionation of the highly unsaturated acids by pptn. as Na salts from COMe₂ affords clupanodonic acid, a more highly unsaturated fraction, chiefly docosahexaenoic acid, and a less unsaturated fraction containing cetoleic acid, C₂₂H₄₂O₂. Docosatetraenoic acid may be present.

VIII. Ozonolysis of amyl clupanodonate affords EtCHO, MeCHO, CO₂, ($\cdot CH_2\cdot CO_2H$)₂, amyl H succinate, and lower fatty acids. Ozonolysis of *di*-bromoclupanodonic acid affords a Br-compound converted by debromination and subsequent hydrogenation into C₆H₁₃·CO₂H. This procedure applied to tetrabromo- and hexabromo-clupanodonic acids affords deoico and myristic acids, respectively. On the above results clupanodonic acid is $\Delta^{7,11,15}$ -docosapentaenoic acid.

P. G. C.

Migration of allyl groups in the ethyl acetate series. E. BERGMANN and H. CORTE (J.C.S., 1935, 1363—1365).—*Et* sodioacetate with cinnamyl chloride in boiling C₆H₆ gives *Et* *dicinnamyl*-, b.p. $258^\circ/14$ mm., and *Et* *cinnamyl*-acetate (I), b.p. $200^\circ/14$ mm., which is hydrolysed (*Et*OH—10% KOH) to γ -benzylidenobutyric acid and

α -phenyl- Δ^6 -hexen- ϵ -one. Cinnamyl alcohol, Et β -ethoxycrotonate, and NH_4Cl at 150° give Et β -cinnamyl-oxy-crotonate (II); b.p. $162^\circ/12$ mm., and Et β -cinnamyl-oxy- α -cinnamylcrotonate (III), b.p. 200 — $210^\circ/5$ mm. (cf. A., 1919, i, 266). (II) with boiling EtOH-10% KOH gives cinnamyl isopropenyl ether, b.p. 120 — $122^\circ/12$ mm., and β -phenyl- β -vinylpropionic acid, b.p. $162^\circ/12$ mm., which involves a re-arrangement analogous to the changes in the Ph allyl ether series. (II) at 260° gives (I), the enolic form of which reacts with cinnamyl chloride to give (III).

J. L. D.

Detection of organic compounds with the help of spot reactions. X. F. FEIGL and O. FREUDEN (Mikrochem., 1935, 18, 272—276).— $\text{H}_2\text{C}_2\text{O}_4$ reacts directly with NHPh_2 to give aniline-blue, whilst the supposed intermediate HCO_2H does not. Insol. oxalates are treated with NHPh_2 and H_3PO_4 . The test is sp. and is affected only by conc. H_2SO_4 .

R. S.

New tetrahydroxyadipic acid. T. POSTERNAK (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 184—185; cf. this vol., 846).—By oxidation of *d*-allonolactone with HNO_3 , a tetrahydroxyadipic acid, m.p. 197 — 198° (monolactone, m.p. 196° ; Et₂ ester, m.p. 153 — 154°), has been obtained.

H. G. R.

Determination of ascorbic acid. A. L. BACHARACH and H. E. GLYNN (Nature, 1935, 136, 757).—*l*-Fructose and *l*-arabinose have no reducing action on 2 : 6-dichlorophenol-indophenol, the val. of which as a reagent for the determination of ascorbic acid is emphasised.

L. S. T.

Derivatives of glycuronic acid. VI. Preparation of methyl α -chloro- and α -bromo-triacetyl-glycuronate. Synthesis of β -glycuronides. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1935, 111, 347—353; cf. this vol., 1352).—Me β -tetraacetyl-glycuronate (modified prep. from glycuronolactone) and TiCl_4 in CHCl_3 at 40 — 45° afford Me α -triacetylchloroglycuronate, m.p. 99 — 100° , $[\alpha]_D^{25} +168.7^\circ$ in CHCl_3 , which with MeOH and Ag_2CO_3 gives the β -methylglucoside, m.p. 149 — 150° , $[\alpha]_D^{25} -28.9^\circ$ in CHCl_3 , stable to Fehling's solution and completely hydrolysed by 0.1N-HCl. Me α -tetraacetyl-glycuronate and HBr -AcOH give Me α -triacetyl-bromoglycuronate, m.p. 104 — 105° after sintering at 85° , which with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ and Ag_2CO_3 affords the *p*-nitrobenzyl- β -glucoside, deacetylated by $\text{Ba}(\text{OMe})_2$ to Me glycuronate *p*-nitrobenzylglucoside, m.p. 167 — 168° , $[\alpha]_D^{25} -63.2^\circ$ in H_2O .

R. S. C.

Catalytic decomposition of chloral and acetaldehyde.—See this vol., 1466.

Kinetics of thermal decomposition of acraldehyde.—See this vol., 1464.

Photochemical decomposition of isovaleraldehyde and di-*n*-propyl ketone.—See this vol., 1468.

Reaction of periodic acid with α -ketols, α -diketones, and α -ketonealdehydes. P. W. CLUTTERBUCK and F. REUTER (J.C.S., 1935, 1467—1469; cf. A., 1934, 1090).—Many α -ketols, -diketones, and -ketonealdehydes are oxidised with the theoretical amount of HIO_4 (cf. A., 1928, 269), the amount of

acid to be used being determined in a separate experiment. Acetoin and benzoin give $\text{MeCHO} + \text{AcOH}$ and $\text{PhCHO} + \text{BzOH}$, respectively. Ac_2 and Bz_2 give 2 mols. each of AcOH and BzOH . *p*-Toluoyl-phenylcarbinol (A., 1930, 475) gives $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ and PhCHO , which indicates that $\cdot\text{CH}\cdot\text{OH}$ gives rise to CHO , and $\cdot\text{CO}$ to CO_2H . 3 : 5-Dihydroxy-2-carboxybenzoyl Me ketone and -2-carboxyphenyl-acetylcarbinol with HIO_4 give AcOH and, respectively, 3 : 5-dihydroxyphthalic acid and 6-aldehydo-2 : 4-dihydroxybenzoic acid [dinitrophenylhydrazone + H_2O , m.p. 270° (decomp.)], thereby confirming the structures assigned to these compounds (A., 1933, 949). Benzofuroin (A., 1882, 499) gives 1 mol. each of PhCHO and furoic acid, and is therefore furoylphenylcarbinol.

J. L. D.

Preparation of *N*-carbethoxyketimines, $\text{CRR}'\text{N}\cdot\text{CO}_2\text{Et}$. J. HOCH (Compt. rend., 1935, 201, 560—562).—Et₂ acetals of ketones (1 mol.) with $\text{NH}_2\cdot\text{CO}_2\text{Et}$ (1.5 mols.) and a little $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 190° afford *N*-carbethoxyketimines, which are prepared (b.p. in parentheses) from the following ketones: COPr^a_2 (105 — $106^\circ/20$ mm.); COBu^a , (122 — $124^\circ/18$ mm.); Me nonyl ketone (170 — $172^\circ/15$ mm.); cyclohexanone ($138^\circ/51$ mm.); 2-methylcyclohexanone (144 — $145^\circ/17$ mm.); COPhMe (162 — $163^\circ/17$ mm.). COMe_2 affords isopropyl bisdiethylcarbamate, b.p. 145 — $155^\circ/15$ mm. The ketimines are decomposed instantly by dil. HCl . Et β -ethoxycrotonate with $\text{NH}_2\cdot\text{CO}_2\text{Et}$ gives Et *N*-carbethoxy- β -aminocrotonate, b.p. $133^\circ/17$ mm. The acetals of aldehydes similarly treated yield exclusively bisdiethylcarbamates.

J. L. D.

α -Xylomethylose and [its] derivatives. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1935, 111, 325—333).—5-Iodoisopropylidene-*d*-xylose (improved prep.) with H_2 -Raney Ni in MeOH - NaOH affords isopropylidene-*d*-xylomethylose (I) [$p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative, m.p. 41 — 42° , $[\alpha]_D^{25} -18.02^\circ$ in CHCl_3 , hydrolysed by hot KOH -aq. EtOH to (I)], hydrolysed by 1% H_2SO_4 at 100° (1 hr.) to *d*-xylomethylose, $[\alpha]_D^{25} +13.26^\circ$ in H_2O (cf. this vol., 609) [*p*-bromophenyl-osazone, cryst., $[\alpha]_D^{25} +64.7^\circ \rightarrow +29.4^\circ$ in 24 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (3 : 2); Ac_3 derivative, b.p. 105 — $106^\circ/0.3$ mm., $[\alpha]_D^{25} +60.87^\circ$ in CHCl_3 ; phenyl-osazone, m.p. 179 — 180° , $[\alpha]_D^{25} +66.6^\circ \rightarrow 0^\circ$ in 18 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (3 : 2)].

R. S. C.

Crystalline α -gulomethylose and [its] derivatives. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1935, 111, 335—346).—Partly a detailed account of work already reported (this vol., 734). *d*-Xylomethylose with aq. HCN - NH_3 gives *d*-ido-methylonolactone, a syrup, and *d*-gulomethylonolactone (I), $[\alpha]_D^{25} -68^\circ \rightarrow -63.8^\circ$ in H_2O . (I), MeI , and Ag_2O in COMe_2 give trimethylgulomethylono- γ -lactone, b.p. $96^\circ/0.3$ mm., oxidised by conc. HNO_3 at 95 — 100° to $i\text{-}[\text{CH}(\text{OMe})\cdot\text{CO}_2\text{H}]_2$, and with 2% Na - Hg in 20% H_2SO_4 at 0° giving *d*-gulomethylose, m.p. 130 — 131° , $[\alpha]_D^{25} -42.3^\circ \rightarrow -38.03^\circ$ in 30 min. in H_2O [*p*-bromophenylhydrazone, m.p. 135 — 136° , $[\alpha]_D^{25} -16.1^\circ \rightarrow +9.8^\circ$ in 2 weeks in EtOH, $-49.12^\circ \rightarrow +34.7^\circ$ in 2 weeks in $\text{C}_5\text{H}_5\text{N}$; phenyl-osazone, m.p. 180 — 183° , $[\alpha]_D^{25} 0^\circ \rightarrow +17.7^\circ$ in 1 hr. in $\text{C}_5\text{H}_5\text{N}$ -EtOH (2 : 3)].

R. S. C.

Manufacture of anhydrous glucose.—See B., 1935, 1064.

Test of von Fellenberg's titrimetric method for determination of sugar. T. VON FELLEBERG and P. DEMONT (Mitt. Lebensm. Hyg., 1935, 26, 168—182; cf. A., 1921, ii, 136).—The tables previously given are incorrect for lactose and maltose, since the specimens used were mixtures of the anhyd. substances and their monohydrates. Correct data are now given for the monohydrates and complete data for the calculation of mg. of glucose, invert sugar, sucrose, lactose hydrate, or maltose hydrate from c.c. of 0.1N-I used are tabulated. E. C. S.

Determination of glucose in presence of disaccharides with Barfoed's reagent. T. VON FELLEBERG (Mitt. Lebensm. Hyg., 1935, 26, 182—192).—The Cu_2O formed by reduction of Barfoed's reagent with glucose (I) is determined by the author's titrimetric method (cf. preceding abstract). The reagent is only slightly reduced by sucrose, maltose, and lactose. A table is given for calculating mg. of (I) from c.c. of 0.1N-I used. The method is applied to the examination of malt extract, starch syrup, and malt bonbons. E. C. S.

2:3:6-Trimethylglucose anhydride. K. FREUDENBERG and E. BRAUN (Ber., 1935, 68, [B], 1988).—Contrary to Hess *et al.* (this vol., 1109), the conversion of methylcellulose into 2:3:6-trimethylglucose anhydride (I) is reproducible provided the initial material is insol. in H_2O . (I) cannot be a derivative of idose, since it is hydrolysed to homogeneous 2:3:6-trimethylglucose. H. W.

Methylation of glucosphenylosazone and its formulation as a derivative of fructopyranose. (Mrs.) E. E. PERCIVAL and E. G. V. PERCIVAL (J.C.S., 1935, 1398—1402).—Glucosazone with Me_2SO_4 in COMe_2 -EtOH at 50° containing the theoretical amount of 30% NaOH gives 5-methylglucosazone (I), m.p. 116—117°, $[\alpha]_D^{20}$ -49° to -12° in EtOH, which with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ affords 5-methylglucosone, reconverted into the osazone with $\text{NHPh}\cdot\text{NH}_2$, and reduced (Zn-AcOH) to 5-methylfructose. (I) with 0.5% HCl-MeOH gradually forms a pyranoside (which supports the 5-Me structure), together with about 15% of furanoside, which forms rapidly and then remains const. in amount and is probably a result of a side reaction; fructose yields a furanoside exclusively and rapidly. (I) when boiled with MeOH-3\%HCl gives 5-methylmethylfructopyranoside, which when methylated with $\text{Me}_2\text{SO}_4\text{-NaOH}$ and then twice with $\text{MeI-Ag}_2\text{O}$ gives a *syrup*, b.p. $110^\circ/0.03$ mm., hydrolysed (3% HCl) to 1:3:4:5-tetramethylfructose, and is converted through its osone (as above) into 3:4:5-trimethylfructose, $[\alpha]_D^{20}$ -43° in MeOH, which with MeOH-HCl slowly affords a fructopyranoside (II), indicating substitution in position 5. (II) is further methylated and then hydrolysed to tetramethylfructopyranose, which shows that (I) probably contains a pyranose ring. J. L. D.

Crystalline structure of the sugars. II. Methylated sugars and the conformation of the pyranose ring. E. G. COX, T. H. GOODWIN, and (Miss) A. I. WAGSTAFF (J.C.S., 1935, 1495—1504;

cf. this vol., 1195).—The supposition that the C_5O ring of simple pyranose sugars is in a Sachse strainless form is without foundation, for it takes no account of the different radius and valency angle of O and assumes that the C valencies are directed towards the angles of a tetrahedron (cf. A., 1929, 383; this vol., 810). X-Ray evidence suggests that the C are nearly, although not quite, co-planar, and O is displaced (1—0.5 Å.) out of their plane. Single crystals of many of these sugars have a shortest axis of about 4.5 Å., which is possible only in a direction almost perpendicular to the ring plane; the more highly methylated sugars have shorter axes (cf. A., 1931, 1219), and the fact that configuration does not alter this val. greatly for the pyranose sugars (the furanose sugars also have as short or shorter axes) is additional evidence in favour of the "flat" structure for the ring. The assumption of a "flat" ring permits the ready interpretation of the formation of benzylidene and similar derivatives as compared with analogous reactions in compounds generally agreed to possess a Sachse configuration, e.g., cyclohexane derivatives, and in which there is at least as much strain as in the sugars. These considerations are applied in throwing light on the spatial configurations of several sugars. α - and β -Glucose are found to have been assigned correct stereochemical structures. Data as to cell dimensions and space-groups are recorded for many sugars. J. L. D.

Ketone sugar series. V. Validity of Hudson's rules of isorotation in the ketose group. Preparation of the true α -fructose<2:7>pentaacetate. E. PACSU and F. B. CRAMER (J. Amer. Chem. Soc., 1935, 57, 1944—1946; cf. this vol., 735).— β -Acetochlorofructose<2:6> (β -fructopyranosidyl chloride acetate) and NaOAc in boiling Ac_2O give 71.2% of β - and 28.8% of α -fructopyranose penta-acetate, m.p. 122—123°, $[\alpha]_D^{20}$ $+47.4^\circ$ in CHCl_3 (hydrolysed by 0.1N-NaOH to fructose), the first pair of true $\alpha\beta$ -ketose isomerides of undoubted structure. The $[\alpha]$ lead to a_{Ac} 32,850 and $b_{\text{fruct.ac.}}$ $-14,350$, and thence to $[\alpha]_D$ $+45.5^\circ$ for α -methylfructopyranose tetra-acetate [cf. 45.0° for Schlubach's product (A., 1928, 873)] and 51.3° for α -ethylfructopyranose tetra-acetate [cf. 51.6° for the author's product (*loc. cit.*)]. Hudson's rules, therefore, hold in this series. The following are calc.: a_{OMe} 30,850; a_{OEt} 33,650; a_{Cl} 44,750; a_{Br} 63,350; a_{OH} 17,750; all except a_{OH} are much $> A_x$ in the aldose series. $[\alpha]_D$ are predicted thus: acetates of α -fructopyranosidyl chloride $+82.0^\circ$, fluoride $+8.0^\circ$, and bromide $+119.2^\circ$; α -fructopyranose tetra-acetate $+9.2^\circ$.

R. S. C.

Colour reaction for fructose. S. SUGAHARA (J. Biochem. Japan, 1935, 22, 85—91).—Treatment of dil. aq. fructose (I) with $\text{H}_2\text{SO}_4\text{-Na}_2\text{WO}_4$ at slightly alkaline reactions produces a green ppt. At suitable concns. (e.g., 0.015%), (I) but not glucose (II) gives a positive reaction. Uric acid, $\text{CO}(\text{CH}_2\cdot\text{OH})_2$, and adrenaline react similarly to (I) even after addition of NaOH, when (I), (II), and arabinose give negative responses. The application of the reaction to deproteinised blood, uric acid-free urine, etc. is described. F. O. H.

Inversion of solutions of sucrose.—See this vol., 1468.

Test of Wein's gravimetric method for determination of maltose. C. ZACH (Mitt. Lebensm. Hyg., 1935, 26, 192—195; cf. Z. Anal. Chem., 1887, 26, 255).—The method is slightly modified to bring it into line with the invert-sugar determination. The mg. of Cu_2O corresponding with known wts. of maltose monohydrate are tabulated. E. C. S.

Comparative investigations on caramel and molasses colloids. A. JOSZT and S. MOLINSKI (Kolloid-Beih., 1935, 42, 367—383).—Three products of caramelisation of sucrose have been isolated by dialysis and their properties (solubility, composition, pentosan content, p_H , electrotitration behaviour, surface tension, viscosity, extinction coeff., colour, and ease of coagulation) determined. Points of similarity of these products with the colloids present in molasses are discussed. E. S. H.

Structure of heterosides based on their ultra-violet absorption spectra. (MME.) RAMART-LUCAS and J. RABATÉ (Bull. Soc. chim., 1935, [v], 2, 1596—1625).—Acetobromoglucose and phenols in quinoline with freshly prepared Ag_2O give the following: *phenol*-, m.p. 132—134°, $[\alpha]_D^{20}$ -60.8°, o-, m.p. 166°, $[\alpha]_D$ -68.3°, m-, m.p. 178°, $[\alpha]_D$ -67.9°, and *p-cresol*-, m.p. 177°, $[\alpha]_D$ -68.6°, *guaiacol*-, m.p. 152.5°, $[\alpha]_D$ -70.5°, and *resorcinol-glucoside*, m.p. 210°. Piceoside and Cl_2 in 5% Na_2CO_3 yield *chloropiceoside*, m.p. 209.5°, which with emulsin gives glucose and *chloropiceol*, 107.5°. Curves are given for the absorption spectra of these glucosides, together with the curves for β -methyl-, benzyl-, amygdonitrile-, phenylethyl-, salicyl-, and cinnamyl-glucoside, methylmannoside, aucuboside, amygdaloside, benzylgalactoside, betuloside, arbutoside, methylarbutoside, salicoside, coniferoside, helicoid, monotropitoid, lusitanicoside, geoside, populoside, and the corresponding alcohols and phenols. The results are discussed. F. R. G.

Enzymic synthesis of α -glucosides. I. VINTILESCU, C. N. IONESCU, and A. KIZYK (Bull. Soc. Chim. România, 1935, 17, 131—136).—In the presence of brewers' yeast extract trimethylene glycol (I) and glucose afford *trimethylene glycol- α -monoglucoside* (II), m.p. 96°, $[\alpha]_D^{20}$ +137.48° (? in H_2O), obtained pure by $\text{Ba}(\text{OH})_2$ -hydrolysis of its Ac_5 derivative, m.p. 84°, $[\alpha]_D^{20}$ +112.62° in 95% EtOH, the isolation of which from the substrate is described. The amount of (II) formed increases with increase in (I) concn. *Mannitol- α -monoglucoside*, m.p. 140°, $[\alpha]_D^{20}$ +88.44°, is similarly prepared. J. W. B.

Application of the law of mass action to the synthesis of β -glucosides. I. VINTILESCU, C. N. IONESCU, and A. KIZYK (Bull. Soc. Chim. România, 1935, 17, 136—150).—The supposed deviation of the emulsin (I)-catalysed synthesis of β -methylglucoside (II) from the mass action law is only apparent. It is not due to the deactivation of (I) by high $[\text{MeOH}]$, since the activity of (I) is unaltered by long contact with CHO-free MeOH at p_H 4.7. Moreover, after formation of (II) from glucose and (I) in 10—90%

MeOH solutions (Bourquelot *et al.*, A., 1913, i, 542, 781) has ceased, further addition of glucose affords more (II), showing that a true equilibrium has been reached. The real cause is the sp. action of (I) on β -glucose (III) and the decrease in the ratio (C_1) β -total glucose as the $[\text{MeOH}]$ increases (A., 1934, 927). The val. of $K_\beta = \frac{[(\text{III})][\text{MeOH}]}{[(\text{II})][\text{H}_2\text{O}]}$ is independent of $[\text{MeOH}]$ and is 0.149, the proportion of (III) being determined polarimetrically. The increase in $K_t = \frac{[\text{total glucose}][\text{MeOH}]}{[(\text{II})][\text{H}_2\text{O}]} = \frac{K_\beta}{C_1}$, observed with increasing $[\text{MeOH}]$ (Euler *et al.*, A., 1924, i, 1266) is due to diminution of C_1 consequent on the displacement of the equilibrium (III) $\rightleftharpoons \alpha$ -glucose towards the right. The strict application of the mass-action law is confirmed by the const. vals. of K_β for the β -glucosides of $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (0.380) and of mannitol (0.051). J. W. B.

Structure of cymarose. R. C. ELDERFIELD (J. Biol. Chem., 1935, 111, 527—535).—Partly a detailed account of work previously reported (this vol., 848). Cymarose (I) is proved to be 3-methyl-digitoxose. (I), Br, and $\text{Ba}(\text{OBz})_2$ in H_2O give *cymarolactone*, b.p. 110—111°/0.2 mm., $[\alpha]_D^{25}$ -25° in H_2O (stable), leading to *cymaronic acid phenylhydrazide*, m.p. 154°, $[\alpha]_D^{25}$ +2° in MeOH, and, by Ag_2O -MeI, 5-methylcymarol-1:4-lactone (II), b.p. 78—80°/0.2 mm., $[\alpha]_D^{25}$ -36° in CHCl_3 , which affords 5-methylcymaronic acid phenylhydrazide, m.p. 139°, $[\alpha]_D^{24}$ -6° in MeOH. *Methylcymaropyranoside* (mixture; prep. by 0.25% HCl-MeOH), b.p. 54—64°/0.2 mm., with MeI- Ag_2O gives *Me methylcymaropyranoside*, b.p. 45—48°/0.2 mm., which with 0.1N-HCl at 100° (10 min.) affords 4-methylcymarol-1:5-lactone (III), b.p. 88—90°/0.2 mm., $[\alpha]_D^{27}$ +30° in CHCl_3 (Ba salt), giving 4-methylcymaronic acid phenylhydrazide, m.p. 115—116°, $[\alpha]_D^{27}$ +17.5° in CHCl_3 . (III) and conc. HNO_3 at 90—94° lead to $\alpha\beta$ -dimethoxyglutardimethylamide, m.p. 173—174°, $[\alpha]_D^{28}$ -56° in H_2O . The known position of the Me in (III) proves that of the Me in (II). *Me dimethyl-digitoxoside*, b.p. 43—46°/0.2 mm., from digitoxose by 0.1N-HCl-EtOH at room temp. (1 hr.) and subsequent methylation (Purdie), is shown by changes of α during glucoside formation to be a mixture of furanose and pyranose forms. When hydrolysed and oxidised, it yields (II). R. S. C.

Hemicellulose from oat hulls. E. ANDERSON and P. W. KRZMARICH (J. Biol. Chem., 1935, 111, 549—552).—A mixture of hemicelluloses is obtained from oat husks by extraction with aq. NaOH after removal of starch with hot H_2O . Hydrolysis with dil. H_2SO_4 gives *d*-xylose, *l*-arabinose, and a compound of *d*-glycuronic acid containing 2 mols. of *d*-galactose. The unsaponifiable residue contains 47% of SiO_2 . H. D.

Behaviour of cellulose towards liquid chlorine, iodine, and iodine monochloride. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1935, 66, 249—254; cf. this vol., 478).—Cellulose (I) is not dissolved by liquid Cl_2 at up to 149°, nor by liquid I at 150°; each has, however, apparently a chemical action on (I). ICl at 90° dissolves (I), forming a *product* sol. in EtOH. E. W. W.

X-Ray examination of the transformation of sodium cellulose by the action of carbon disulphide. W. SCHRAMEK and F. KÜTTNER (Kolloid-Beih., 1935, 42, 331—366).—The action of CS_2 gives a sol. product only when the cryst. component of the fibre is Na-cellulose I; other Na-celluloses give insol. or partly sol. products. The CS_2 , after adsorption by the fibre, reacts to form $\text{SNa}\cdot\text{CS}\cdot\text{O}(\text{C}_6\text{H}_9\text{O}_4)(\text{C}_6\text{H}_{10}\text{O}_5)_n$. E. S. H.

Ammonia-cellulose. K. HESS and C. TROGUS (Ber., 1935, 68, [B], 1986—1988).—Condensation of dry NH_3 on cellulose at -77° to -80° and its subsequent removal by evaporation causes a profound alteration in the X-ray diagram of the material. The product is regarded as NH_3 -cellulose poor in NH_3 or as a third modification of cellulose provisionally named cellulose III. If it is treated with H_2O , MeOH , or aq. NH_3 , the original X-ray diagram is not restored. It does not appear to be the primary product of the reaction, since the diagram depends on the rate of evaporation of the NH_3 . H. W.

Mono- and tri-choline orthophosphates. E. L. JACKSON (J. Amer. Chem. Soc., 1935, 57, 1903—1905).—Choline chloride, H_3PO_4 , and P_2O_5 lead to *Ca choline diphosphate* (I), $\text{NMe}_3\langle\text{CH}_2\text{O}\cdot\text{P}(\text{O}_2\text{H})\rangle\text{O}$, free from choline, but containing 3—4% of dicholine phosphate, which was isolated therefrom as *aurichloride*, m.p. $271.5\text{--}272^\circ$ (corr.; decomp.). (I) is stable to N-HCl at 100° during 50 min. and leads to (impure) *choline phosphate aurichloride*, m.p. $174\text{--}176^\circ$ (corr.), and *platinichloride*, $+2\text{H}_2\text{O}$, m.p. $207\text{--}208^\circ$ (corr.; decomp.), hygroscopic. POCl_3 and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ in CCl_4 give a 60% yield of $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_3\text{PO}_4$, b.p. $180\text{--}182^\circ/2\text{--}3$ mm. (lit. $140^\circ/40$ mm), which under certain conditions with NMe_3 in EtOH gives *tri(choline chloride) phosphate*, $(\text{Cl}\{\text{NMe}_3\cdot[\text{CH}_2\text{O}]_3\text{PO}_4$, decomp. about 245° (*tri-aurichloride*, m.p. $216\text{--}230^\circ$), which at 90° (2 hr.) gives a substance (possibly a neurine derivative by intramol. change) with increased pharmacological activity without change of appearance or composition. R. S. C.

Interaction of amino-acids and salts.—See this vol., 1460.

Action of aromatic sulphonc and hydroxy-sulphonic acids on α - and β -amino-acids. II. G. MACHEK (Monatsh., 1935, 66, 345—356; cf. this vol., 970).—Hippuric acid (I) is largely unchanged when heated in boiling xylene with C_6H_6 and conc. H_2SO_4 , apparently owing to the sluggish interaction of the latter compounds with one another, since (I) and PhSO_3H readily give BzOH and *glycine benzenesulphonate*, m.p. $158\text{--}159^\circ$ (corr.). PhMe , *m*-xylene, H_2SO_4 , and (I) analogously give *glycine toluenesulphonate*, m.p. $200\text{--}201^\circ$ (corr.), and *m*-xylenesulphonate, m.p. $171.5\text{--}172.5^\circ$. *Glycine naphthalene-2-sulphonate*, m.p. $195\text{--}196^\circ$, is purified with difficulty when obtained from C_{10}H_8 and H_2SO_4 , but is readily isolated when $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ is used. *Glycine naphthalene-1-sulphonate* has m.p. $170\text{--}171^\circ$ (corr.) after softening at about 140° . PhOH and H_2SO_4 , $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, and $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, respectively, transform alanine into the corresponding

phenolsulphonate, m.p. $179.5\text{--}180.5^\circ$ (corr.), *toluenesulphonate*, m.p. $193.5\text{--}195^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. 227° after softening at 224° . Leucine yields a *toluenesulphonate*, m.p. $153\text{--}153.5^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. $202\text{--}203^\circ$ (corr.). The *phenolsulphonate*, m.p. $182\text{--}183^\circ$ (corr.), and *2-naphthalenesulphonate*, m.p. $157\text{--}158^\circ$ (corr.), of β -aminobutyric acid are described. H. W.

Creatinephosphoric acid. K. ZEILE (Z. physiol. Chem., 1935, 236, 263—272; cf. Fiske et al., A., 1929, 590).—When creatine is boiled with POCl_3 a cryst. Ca salt very similar to but isomeric with Ca salt of the natural acid is obtained. The synthetic acid is more slowly hydrolysed than is the natural, and its hydrolysis is not accelerated by molybdate. The titration curves of the acids are similar. Diphenoxyphosphoryl chloride (I) with $\text{CS}(\text{NH}_2)_2$ yields *diphenoxyphosphorylthiocarbamide*, m.p. 149° , which, when warmed with HgO , gives the Hg^{II} salt, m.p. 135° , of diphenoxyphosphorylcyanamide. Methylisothiocarbamide (II) with (I) gives the corresponding salt, m.p. 170° , of (II). W. McC.

Synthesis of alkylamino-acids corresponding with chitosamic acid. E. VOTOČEK and R. LUKES (Coll. Czech. Chem. Comm., 1935, 7, 424—429).—*d*-Glucosemethylamic acid, m.p. 230° (decomp.), $[\alpha]_D^{+4.0}$ to $+7.5^\circ$ in 2.5% HCl , is obtained by treatment of *d*-arabinose with aq. NH_2Me , HCN , and hydrolysis. Similarly, glucose affords *d*-glucoheptosemethylamic acid, m.p. $228\text{--}230^\circ$, $[\alpha]_D^{+18.2}$ to -35.9° in 2.5% HCl , converted by PhNCO into the carbamide derivative, $\text{C}_{15}\text{H}_{22}\text{O}_8\text{N}_2$, m.p. 210° . P. G. C.

Synthesis of homocystine. W. I. PATTERSON and V. DU VIGNEAUD (J. Biol. Chem., 1935, 111, 393—398).—A facile synthesis of homocystine is reported. $\text{CH}_2\text{Ph}\cdot\text{SNa}$ and $(\text{CH}_2\text{Cl})_2$ in MeOH give $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ (71—75% yield), which with $\text{CHNa}(\text{CO}_2\text{Et})_2$ and subsequent hydrolysis by KOH affords β -benzylthiolethylmalonic acid (75%), m.p. $114\text{--}117^\circ$. This acid, when brominated, allowed to react with conc. aq. NH_3 at room temp., and then boiled with HCl , yields *S*-benzylhomocystine, reduced by Na-liquid NH_3 to homocystine (I) (75% yield) with some $(\text{CH}_2\text{Ph})_2$ and PhMe , and by Na- EtOH to (I) (78%). $(\text{CH}_2\text{Ph})_2$ and PhMe are also produced in the reduction of $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NR}_2$ by Na-liquid NH_3 or H_2 -Pt. R. S. C.

Synthesis of crystalline cystinyldiglycine and benzylcystinyldiglycine and their isolation from glutathione. H. S. LORING and V. DU VIGNEAUD (J. Biol. Chem., 1935, 111, 385—392).—Dicarbobenzylcystinyldiglycine (I) (from dicarbobenzylcystine chloride and glycine), m.p. $182\text{--}183^\circ$ (corr.) (lit. $162\text{--}163^\circ$) [Et ester, m.p. 166° (corr.)], with Na in liquid NH_3 gives cryst. cystinyldiglycine (II), m.p. 210° (block), $[\alpha]_D^{27} -67.5^\circ$ in H_2O , which can be reconverted into (I) and leads to *S*-benzylcystinyldiglycine (III), m.p. $166\text{--}167^\circ$, also obtained from (I). Cryst. (II) and (III) were obtained by partial hydrolysis of glutathione. R. S. C.

Rotatory power of ricinoleamide. E. ANDRÉ and C. VERNIER (Ann. Off. nat. Combust. liq.,

1934, 9, 663—672; Chem. Zentr., 1935, i, 1532).—Ricinoleamides of varying properties are obtained by successive treatments of castor oil with EtOH-NH₃; the first reacting fraction yields an amide of m.p. 66.5—67°, $[\alpha]_D^{20} +2^\circ 35'$ to $+3^\circ 1'$ in CHCl₃, and the last reacting one of m.p. 63.5—64°, $[\alpha]_D^{20} +3^\circ 6'$ in CHCl₃. The oil thus contains two ricinoleic acids which may either be *d*- and *dl*-, or differ in the position of the double linking or OH. H. N. R.

Normal fatty acid amides of ethylenediamine. N. B. TUCKER (J. Amer. Chem. Soc., 1935, 57, 1989—1990).—Di-acet-, m.p. 173—173.5°, -propion-, m.p. 189°, -butyr-, m.p. 191—191.3°, *di-valer*-, m.p. 183°, -*hexo*-, m.p. 177—177.3°, -*hepto*-, m.p. 171.5°, -*octo*-, m.p. 169—169.5°, -*deco*-, m.p. 164°, -*undeco*-, m.p. 160.5°, -*dodeco*-, m.p. 159°, -*trideco*-, m.p. 156—156.4°, -*tetradeco*-, m.p. 154.5°, -*pentadeco*-, m.p. 153°, -*hexadeco*-, m.p. 148.5°, and -*heptadeco-ethylene-diamide*, m.p. 149.5—150°, are prepared by boiling (CH₂NH₂)₂ and the Et ester of the acid for 48 hr. Crystallographic data and solubilities are recorded for the first six compounds. R. S. C.

Chromium diguanide complexes. P. R. RAY and H. SAHA (J. Indian Chem. Soc., 1935, 12, 621).—Diguanide affords the triacidic, red base, [Cr(C₂H₆N₃)₃]H·OH, cryst., which gives cryst. salts. R. S. C.

Fulminic acid polymerisation.—See this vol., 1464.

Preparation of β-chlorovinylarsine sulphide. S. L. WARSCHAWSKI (J. Amer. Chem. Soc., 1935, 57, 2012—2013).—CHCl:CH·AsCl₂, b.p. 78°/12 mm., and excess of H₂S in EtOH give β-chlorovinylarsine sulphide, m.p. 114°, unstable to light, with only a faint odour (cf. A., 1925, i, 1470). R. S. C.

Wolfram's red salt and the possibility of tervalent platinum. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1244—1251; cf. Reihlen *et al.*, this vol., 182).—Pt etn₂Cl₂ (etn=NH₂Et) and NH₂Pr^a·H₂O yield the compound [Pt etn₂pn₂]Cl₂·2H₂O (pn=NH₂Pr^a), which with H₂O₂-HCl gives a reddish-brown compound, m.p. 187° (impure), considered to be an analogue of Wolfram's salt, [Pt etnCl]Cl₂·2H₂O (I). A similar red compound is obtained from the compound [Pt pn₄]Cl₂·2H₂O (II), derived from K₂PtCl₆ and NH₂Pr^a. [Pt etn₄]Cl₂·2H₂O (III), H₂O₂, and HCl yield according to conditions (I) and [Pt etn₄Cl₂]Cl₂ (IV), respectively. This is cream-white, readily reduced to (I), and with K[Pt(NH₃)Cl₃] gives yellow crystals, and with HAuCl₄ gives the salt [Pt etn₄Cl₂]AuCl₄, also obtained by treatment of (I) or (III) with HAuCl₄. The white compound [Pt pn₄Cl₂]Cl₂ (V) was similarly prepared, and became red when moistened and rubbed with steel. (I) is dehydrated to a yellow compound [rehydrated to the scarlet salt (I)] and reduced by NH₂Et, but not by C₂H₅N, to (III). With KBr and warm H₂O (I) yields the green compound [Pt etn₄Br]Br₂·2H₂O (VI), m.p. 182° (decomp.), which remained green on dehydration at 100° to the anhyd. salt. This turned reddish-chocolate when disturbed and then scarlet when moistened. With KNCS (I) gives the thiocyanate [Pt etn₄Cl](NCS)₂, which is unstable to boiling H₂O. (I) when boiled for a few

sec. with H₂O₂ yields [Pt etn₄OH]Cl₂·2H₂O (VII) (yellow), dehydrated to a yellow anhyd. salt, reconverted into (VII) in moist air. (VII) with HCl yields (I), and with HBr green needles, presumably (VI). (I) when boiled for a longer time with H₂O₂ gives [Pt etn₄(OH)₂]Cl₂, which with HCl yields (IV). A red colour was obtained when (III) and (V) or (II) and (V) were ground together between glass surfaces. H₂PtCl₆, HCl, and (I) yield [Pt etn₄Cl₂]PtCl₆·2H₂O and [Pt etn₂]PtCl₆. This when crystallised from HCl-H₂O yields the salt [Pt etn₄]PtCl₄ (VIII) and [Pt etn₄Cl₂]PtCl₆·2H₂O, and differs from the salt [Pt etn₄Cl₂]PtCl₄ (IX) prepared from (IV) and K₂PtCl₄. (I) and K₂PtCl₄ yield quantitatively the compound [Pt etn₄Cl]PtCl₄, but (I) when pptd. successively with 2 half-mol. proportions of K₂PtCl₄ yields (VIII) and (IX). Similarly (I) and 2 successive half-mol. proportions of K₂PdCl₄ give the salts [Pt etn₄]PdCl₄ (X) and [Pt etn₄Cl₂]PdCl₄ (XI), also prepared from (IV) and K₂PdCl₄. (I) and 1 mol. K₂PdCl₄ yields the salt [Pt etn₄Cl]PdCl₄, which can be separated by washing into (X) and (XI). The formulation of (I) as a double salt (Reihlen *et al.*, *loc. cit.*) does not accommodate all the above results, which support the view that (I) is a derivative of Pt^{III}. H. G. M.

Curves for use in colorimetric determination of carotene. W. S. FERGUSON (Analyst, 1935, 60, 680—683).—Curves are given connecting % carotene with Lovibond tintometer readings and with colorimeter readings using 1% aq. K₂Cr₂O₇ as standard. E. C. S.

Velocity of oxidation of sulphides and sulphoxides by peracetic acid.—See this vol., 1464.

Nitration. V. Nitration of monohalogenated derivatives of xylenes. P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 540—541).—The following have been obtained by direct nitration of the appropriate monohalogenoxylenes in Ac₂O with fuming HNO₃-nitrosulphonic acid mixture: 4-chloro-6-nitro-*m*-, 2-chloro-5-nitro-*p*-, (I), 4-bromo-6-nitro-*m*-, 2-bromo-5-nitro-*p*-, 4-iodo-6-nitro-*m*-, and 2-iodo-5-nitro-*p*-xylene (II). The reaction mixtures were refluxed on the water-bath for 4 hr. except that for (II), which was refluxed for about 2 hr. A little 3-chloro-*p*-toluic acid was isolated in the prep. of (I). H. G. M.

Hexabromomethylbenzene and hexamethylbenzenehexasulphonic acid. H. S. BACKER (Rec. trav. chim., 1935, 54, 745—749).—C₆Me₆ (improved prep.), Br, and ethylene bromide at the b.p. (20 hr.) give pure C₆(CH₂Br)₆ (I), m.p. 297°, which when heated with K₂SO₃·H₂O in an autoclave (210°, 14 hr.) gives hexamethylbenzene-*ω*-hexasulphonic acid, C₆(CH₂·SO₃H)₆·9H₂O [normal strychnine (+9H₂O), Th^I (+3H₂O), Ba (+9H₂O), brucine, and K salt (+3H₂O) (II)]. The crystal structure of (I) and (II) and the X-ray structure of (I) have been determined. H. G. M.

Uranium in organic synthesis. II. J. B. LAL (J. Indian Chem. Soc., 1935, 12, 616—621; cf. this vol., 1357).—CH₂PhCl and U with the ether, phenol, or hydrocarbon at 70—95° afford mixtures as follows: *o*- and *p*-OH·C₆H₄·CH₂Ph and the CH₂Ph ether, m.p. 365—367°, of the latter; *p*-C₆H₄Me·CH₂Ph,

dibenzyltoluene, b.p. 392—396°/760 mm., 280—285°/30 mm., and a substance, b.p. 280—300°; 1- and 2-C₁₀H₇·CH₂Ph; 5-, m.p. 110—111°, and β (3- or 4-)benzylacenaphthene, m.p. 47—49° (picrate, m.p. 100—101°); "α", m.p. 44—45°, and "β"-benzylidiphenyl, m.p. 51—56°. U cannot be used for condensation of CH₂PhCl with CH₂Ph·CN, the Ullmann reaction with picryl chloride or *p*-C₆H₄Cl·NO₂, or for reduction of COPh₂, PhNO₂, *p*-C₆H₄Me·NO₂, or picric acid in H₂O or aq. EtOH. R. S. C.

2-Nitrofluorene. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1935, [v], 2, 1703—1709).—2-Nitrofluorene (I) heated with PhCHO and piperidine at 160° yields 2-nitro-9-benzylidenefluorene (II), m.p. 155—156° [dibromide, m.p. 151—152° (decomp.)]. (I) with vanillin similarly gives 2-nitro-9-vanillylidene-fluorene, m.p. 173—175° (III) [Bz derivative (IV), m.p. 257—258°]. (I) and (III) in COMe, with 0.1N-NaOH give intense red colours, whilst (II) and (IV) give feeble red colours. F. R. G.

Dissociable organic oxides and the anthracene structure. Existence of a photo-oxide of anthracene: its thermal decomposition. C. DUFRAISSE and M. GÉRARD (Compt. rend., 1935, 201, 428—430; cf. this vol., 969).—Insolation of anthracene affords an oxide which decomposes explosively at about 120° without liberation of O₂ (cf. this vol., 1233). J. L. D.

Compound of phenol and aniline. P. LAURENT (Compt. rend., 1935, 201, 554—556).—Curves constructed to determine the relationship between the sp. inductive capacity and composition of solutions of varying proportions of PhOH and NH₂Ph in CCl₄, cyclohexane, and Et₂O indicate the formation of a substance, 2PhOH·NH₂Ph, which has m.p. 29.2°, and is decomposed rapidly in air. J. L. D.

Synthesis of thiocyno-carbamide derivatives. Z. HORII (J. Pharm. Soc. Japan, 1935, 55, 14—21).—*p*-NH₂·C₆H₄·CNS (I) reacts with HCl and KCNO, yielding *p*-thiocyanophenylcarbamide, m.p. 205°, which is also formed by the interaction of phenylcarbamide and KCNS in AcOH in the presence of Br. With COCl₂, (I) affords *s*-bis-*p*-thiocyanophenylcarbamide, m.p. 218°. (I) and PhNCO in C₆H₆ yield phenyl-*p*-thiocyanophenylcarbamide, m.p. 193°; (I) and *o*-C₆H₄Me·NCO similarly afford *p*-thiocyanophenyl-*o*-tolylcarbamide, m.p. 208—209°. *o*-Toluidine reacts with NaCNS in presence of Br, yielding *p*-thiocyano-*o*-toluidine (II), m.p. 69—79°. (II), with KCNO, yields *p*-thiocyano-*o*-tolylcarbamide, m.p. 176°, also formed from *o*-tolylcarbamide and NaCNS. (II) yields *s*-bis-*p*-thiocyano-*o*-tolylcarbamide, m.p. 208—209°, on treatment with COCl₂. (II) and *o*-C₆H₄Me·NCO afford *o*-tolyl-*p*-thiocyano-*o*-tolylcarbamide, m.p. 198°; phenyl-*p*-thiocyano-*o*-tolylcarbamide, m.p. 194—195°, is prepared similarly. CH. ABS. (r)

Influence of substituents on the solubility of salts (especially nitrates) of secondary aromatic bases. F. KONEK and H. RUPE (Math. nat. Anz. ung. Akad. Wiss., 1934, 51, 325—326; Chem. Zentr., 1935, i, 1535).—Of 9 substituted dibenzylamines, the *m*-Br-compound was distinguished by possessing a H₂O-sol. nitrate. H. N. R.

Action of perthiocyanic acid on amines. H. G. UNDERWOOD and F. B. DAINS (J. Amer. Chem. Soc., 1935, 57, 1768—1769).—The reaction of perthiocyanic acid with amines (2 mols.) at the lowest possible temp. (<100°) varies with the amine. The appropriate bases give *m*-tolyl-, m.p. 159°, *m*-chlorophenyl-, m.p. 164°, *p*-bromophenyl-, m.p. 169°, *α*β-di-*p*-bromophenyl-, m.p. 184°, *p*-iodophenyl-, m.p. 240°, *α*-naphthyl-, m.p. 235—236°, *m*-aminophenyl-, m.p. 226°, and 1-*p*-tolyl-1-methyl-dithiobiuret, m.p. 236°, *α*β-di-*p*-xenyl-, m.p. 228°, *α*β-dibenzyl-, m.p. 147—148°, *o*-phenylene-, m.p. 298—299°, and benzoxazole-thiocarbamide, m.p. 205°, and (from *o*-NH₂·C₆H₄·CO₂H or its Me ester) 4-keto-2-thio-tetrahydroquinoline, m.p. 285°. *p*-NO₂·C₆H₄·NH₂, 2 : 6 : 3-C₆H₄Br₂Me·NH₂, 2 : 5-C₆H₃Cl₂·NH₂, glycine, NHPH·CH₂·CO₂H, NHPHbz, and glutamic acid do not react. R. S. C.

Asymmetrical arylalkylcarbamides. Preparation, physical properties, and hypnotic effects. A. M. HJORT, E. J. DEBEER, J. S. BUCK, and W. S. IDE (J. Pharm. Exp. Ther., 1935, 55, 152—172).—Derivatives of the type NH₂·CO·NRR' are synthesised through the *sec*-amines, prepared by treating the primary amine with alkyl iodide and separation, by way of the NO-compound, by the Davis-Blanchard method (A., 1929, 918). The following are new: *n*-propyl-*m*-, b.p. 126° (28 mm.), *n*-amyl-*o*-, b.p. 139° (11 mm.), *n*-amyl-*p*-toluidine, b.p. 144° (12 mm.); ethyl-*m*-, b.p. 133—134° (12 mm.), and *p*-anisidine, b.p. 130° (12 mm.); methyl-*o*-, b.p. 120° (14 mm.), and *m*-, b.p. 139—143° (13 mm.), and ethyl-*m*-phenetidine, b.p. 142° (12 mm.); methyl-*o*-, m.p. 113°, and *m*-, m.p. 76°, ethyl-*o*-, m.p. 66°, and *m*-, m.p. 63—64°, *n*-propyl-*o*-, m.p. 80—81°, *m*-, m.p. 61—62°, and *p*-, m.p. 59—60°, *n*-butyl-*o*-, m.p. 71—72°, and *p*-, m.p. 36—37°, *n*-amyl-*o*- and *p*-tolyl-, methyl-*o*-, m.p. 107—108°, and *m*-, m.p. 109—110°, ethyl-*o*-, m.p. 98°, and *m*-anisyl-, m.p. 109—110°, methyl-*o*-, m.p. 104—105°, and *m*-, m.p. 113°, ethyl-*o*-, m.p. 80°, and *m*-phenethylcarbamide, m.p. 72°. The hypnotic potencies of the compounds, injected intraperitoneally into mice, increase with each addition of a CH₂ in the aliphatic portion; the heptane:H₂O distribution coeffs. run parallel with hypnotic potency and toxicity. H. D.

Reactions of unsaturated compounds. IV. Addition of aniline to olefines. W. J. HICKINBOTTOM (J.C.S., 1935, 1279—1282; cf. this vol., 205).—NH₂Ph (I), NH₂Ph·HBr, and CMe₂·CHMe when heated under seal at 230—250° (5.5—25 hr.) yield NHPH₂ (II), *p*-amino-*tert*-amylbenzene, *tert*-amylaniline, and β-anilino-γ-methylbutane (*p*-toluenesulphonyl derivative, m.p. 83—84°). By similar treatment (I), a NHPH₂ salt, and CHMe·CMeEt yield *p*-amino-*tert*-hexylbenzene, b.p. 135°/28 mm. (hydrochloride; sulphate; Ac, m.p. 102—103°, and *p*-toluenesulphonyl derivative, m.p. 119—120°), *tert*-hexylaniline (picrate, m.p. 132—133°), and some (II); (I), NH₂Ph·HCl (III), and CEt₂·CHMe yield (II), *p*-aminotriethylcarbinylbenzene, m.p. 56—58°, b.p. 144—145°/32 mm. (Ac derivative, m.p. 140—141°; hydrochloride), and γ-anilino-γ-ethyl-*n*-pentane, b.p. 131—132°/26 mm. (picrate, m.p. 129—130°; nitrosoamine, m.p. 49—

50°), also prepared from (I) and *tert*.-heptyl iodide, b.p. 64–66°/21 mm. (obtained from $\text{C}_6\text{H}_5\text{I}$ and dry HI). A trace of an unidentified amine was also formed. (I), (III), and octylene (obtained from *sec*.-octyl alcohol and H_2SO_4) when heated under seal at 210–240° (24 hr.) yield (II), an unidentified primary amine, and *sec*.-octylaniline, b.p. 288–289° (corr.)/751 mm., 150°/20 mm. (*p*-toluensulphonyl derivative, m.p. 59°), also prepared from (I) and *sec*.-octyl bromide. Similarly (I), (III), and $\text{CMe}_2\cdot\text{CMe}_2$ yield β -*p*-aminophenyl- β - γ -dimethylbutane, b.p. 138–139°/23 mm. (*Ac* derivative, m.p. 118°; *hydrochloride*), and an unidentified *sec*. amine. The relative yields of primary and *sec*. amines depend on the experimental conditions; excess of (I) and a small amount of (III) favour the formation of an alkylaniline.

H. G. M.

1-Chloro-3:4-dinitrobenzene series. III. A. MANGINI (Atti R. Accad. Lincei, 1935, [vi], 21, 759–763; cf. A., 1934, 177; this vol., 855).—Experiments on the reactivity of the 3- NO_2 -group of 1:3:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ with nitroanilines, toluidines, aminophenols, and aminobenzoic acids show: (1) that substitution takes place relatively easily with *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, but does not occur with the corresponding *o*-compounds; (2) that no reaction occurs with the three nitroanilines, even in $\text{C}_5\text{H}_{11}\cdot\text{OH}$ after prolonged boiling. The following were obtained: 5-chloro-2-nitro-3'-methyl-, m.p. 192–193° (decomp.), 5-chloro-2-nitro-3'-hydroxy-, m.p. 143–144° (decomp.), and 5-chloro-2-nitro-4'-hydroxydiphenylamine, m.p. 141–142°; 5-chloro-2-nitrodiphenylamine-3', m.p. 240.5–241°, and -4'-carboxylic acid, m.p. 270–272° (decomp.). T. H. P.

New derivatives of 2:2'-dinitrobenzidine. III. D. PONTE (Giorn. Farm. Chim., 1934, 83, 847–850; Chem. Zentr., 1935, i, 1863; cf. this vol., 613).—Partial reduction of 4:4'-di-iodo-2:2'-dinitrodiphenyl yields 4:4'-di-iodo-2-nitro-2'-aminodiphenyl, m.p. 155–156°, 4:4'-[2:2':7-7']Di-iodocarbazole, m.p. 265–266°, and a *di*-iododiphenyleneiodonium iodide are described.

H. N. R.

Diphenyl series. VI. Halogenation of 2:4'-diaminodiphenyl. V. BELLAVITA (Gazzetta, 1935, 65, 632–646).—2:4'-Diaminodiphenyl (I) (1 mol.) treated in AcOH with Cl_2 (1 mol.) yields the Ac_2 derivative, m.p. 200°, of 5-chloro-2:4'-diaminodiphenyl (*hydrochloride*, m.p. 255°), which is diazotised and converted through 3-chlorodiphenyl into *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$, and into 2:5:4'-trichlorodiphenyl, m.p. 67°. 4:2'-Dichloro-3-aminodiphenyl, m.p. 44°, obtained by reduction of the corresponding NO_2 -compound (A., 1933, 388), is similarly converted into 2:3':4'-trichlorodiphenyl, m.p. 54°. With Cl_2 (2 mols.) (I) gives the Ac_2 derivative, m.p. 224°, of 5:3'-dichloro-2:4'-diaminodiphenyl (II) [*hydrochloride*, m.p. 225° (decomp.)], which is converted into 3:3'-dichlorodiphenyl. 4:2'-Dichloro-3:5'-diaminodiphenyl (III), m.p. 105° (Ac_2 derivative, m.p. 124°), is obtained from the corresponding (NO_2)₂-compound. Either (II) or (III) can be converted into 2:5:3':4'-tetrachlorodiphenyl, m.p. 103°. 5:3'-Dichloro-2:4'-di-iododiphenyl, m.p. 104°, is obtained either from 4:2'-di-iodo-3:5'-di-

aminodiphenyl, or from (II) by diazotisation. With Br (1 mol.) in AcOH , (I) gives the Ac_2 derivative, m.p. 228°, of 5-bromo-2:4'-diaminodiphenyl [*hydrochloride*, m.p. 253–255° (decomp.)], which gives rise to 3-bromodiphenyl and to 2:5:4'-tribromodiphenyl, m.p. 76°. 4:2'-Dibromo-3-aminodiphenyl, m.p. 88° (Ac_2 derivative, m.p. 118°), obtained from the NO_2 -compound, yields 2:3':4'-tribromodiphenyl, m.p. 91°. With Br (2 mols.) (I) forms the Ac_2 derivative, m.p. 235°, of 5:3'-dibromo-2:4'-diaminodiphenyl (IV), m.p. 121°, which can be converted into 3:3'-dibromodiphenyl. 4:2'-Dichloro-3:5'-dibromodiphenyl, m.p. 100°, is obtained from either (III) or (IV). By diazotisation and treatment with KI , (IV) yields 5:3'-dibromo-2:4'-di-iododiphenyl, m.p. 113°.

E. W. W.

Condensations between maleic anhydride and phenylhydrazones. G. LA PAROLA (Gazzetta, 1935, 65, 624–627).—Maleic anhydride (I) condenses with phenylhydrazones in C_6H_6 at 70° to form *benzylidene*, m.p. 123–124°, *p*-toluylidene, m.p. 107°, *anisylidene*, m.p. 136°, and *salicylidene*, m.p. 126°, derivatives of maleic acid monophenylhydrazide, $\text{CHR}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. (I) does not react with $\text{CHPh}\cdot\text{N}\cdot\text{NPhMe}$.

E. W. W.

Stereoisomerism of azoxybenzene [derivatives]. V. E. MÜLLER and R. ILLGEN (Annalen, 1935, 521, 72–80; cf. A., 1933, 388).— $\text{CHPhMe}\cdot\text{CO}_2\text{H}$ and fuming HNO_3 under defined conditions give *o*- and *p*-nitrohydratropic acid (I), m.p. 87°. (I) is reduced by Zn dust in aq. $\text{NaHCO}_3\text{--NH}_4\text{Cl}$ to *p*-hydroxylaminoatropic acid (II), m.p. 155–158° after sintering at 95–96°, which with FeCl_3 yields the *p*-*NO*-acid (III), m.p. 93°. (II) and (III) in MeOH give *pp'*-di-(α -carboxyethyl)azoxybenzene (IV), m.p. 198°. Resolution of (I) by quinine gives the *d*- and *l*-forms, m.p. 88.5° and 86.5°, $[\alpha]_D^{25} +10.9^\circ$, -11.2° in MeOH , and thence the *d*- and *l*-forms of (II), m.p. 155–158°, $[\alpha]_D^{25} +9.6^\circ$ (V), -10.6° (VI) in MeOH , and of (III), m.p. 91°, and 92°, $[\alpha]_D^{25} +14.1^\circ$ (VII), -14° (VIII) in MeOH , respectively. (VI) and (VII) or (V) and (VIII) afford the *dl*-(+ -)-form of (IV), m.p. 198°. The *d*-(+)-form of (IV), m.p. 198°, $[\alpha]_D^{25} +14.3^\circ$ in MeOH , is obtained from (V) and (VII), in conformity with the *as*-structure of the N_2O group.

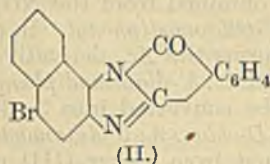
R. S. C.

New azo-derivatives of guaiacol. I. C. M. DANIEL and W. A. FLETCHER (Trans. Kansas Acad. Sci., 1934, 37, 119–122).—The following are described: 4-hydroxy-3:2'-dimethoxy-, m.p. 101.8°, 4-hydroxy-3-methoxy-2'-ethoxy-, m.p. 113.9°, 4-hydroxy-3-methoxy-4'-ethoxy-, m.p. 95.1°, and 4-hydroxy-3-methoxy-1':4'-dimethylazobenzene, m.p. 103.5°. *Na* salts of the above were prepared and also those of 4-hydroxy-3:3'-dimethoxy-, 4-hydroxy-3:4'-dimethoxy-, and 4-hydroxy-3-methoxy-3'-ethoxy-azobenzene, 4-hydroxy-3-methoxybenzeneazo- α -naphthylamine, 4-hydroxy-3-methoxybenzeneazo- β -naphthylamine, and 4-hydroxy-3-methoxybenzeneazo-4-naphthalenesulphonic acid.

CH. ABS. (p)

Chemistry of 2-arylozo- α -naphthylamine compounds compared with their 1-arylozo- β -naphthylamine isomerides. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 678–686).—

In 4-bromo-2-benzeneazo- α -naphthylamine (I) and its derivatives, the benzeneazo-grouping is unusually stable. The following are prepared: 4-bromo-2-p-toluene-, m.p. 170° (phthalimido-derivative, m.p. 220°), and -2-p-bromobenzene-, m.p. 149°, -azo- α -naphthylamine; diphenyl-pp'-bis-(4-bromo-2-azo- α -naphthylamine), m.p. 232°; 4-bromo-1-phthalimidonaphthalene, m.p. 220°. The phthalimido-derivative, m.p. 234°, from (I) is reduced (Zn in AcOH) to 1:2-o-benzoylene-5:4-($\alpha\beta$ -4'-bromonaphth)iminazole (II), m.p. 246°.



(I) forms Ni, m.p. 280°, and Cu, m.p. > 300°, co-ordination compounds; with PhCHO and MeCHO it yields 1-anilino-2-phenyl-4:5-($\alpha\beta$ -4'-bromonaphth)iminazole (III), m.p. 195°, and the -2-methyl analogue, m.p. 202°.

E. W. W.

Preparation of some diazo-thioethers of thio- β -naphthol. J. T. DUNN, jun., and W. A. FLETCHER (Trans. Kansas Acad. Sci., 1934, 37, 123—126).—Diazonium chlorides and thiophenols afford sulphides of the type Ar·N:N·S·Ar. The following are described: diazobenzene, m.p. 59.5—60.5°, m-diazotoluene, m.p. 59—61° (decomp.), β -diazonaphthalene, m.p. 101—102°, sulphodiazobenzene (Na salt, m.p. > 275°), and 4-sulpho-1-diazonaphthalene (Na salt, m.p. > 240°), 2-naphthyl sulphides; Na salt of p-sulphodiazobenzene p-tolyl sulphide, decomp. on warming.

CH. ABS. (r)

Acyl derivatives of o-anisidine. L. H. AMUNDSEN and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 2005—2006).—The following N-derivatives of o-anisidine are prepared. EtCO, m.p. 33.5—34.5°; PrⁿCO, m.p. 24.5—25.5°; BuⁿCO, m.p. 25.5—26.5°; isovaleryl, m.p. 49—49.5°; n-hexoyl, m.p. 33—33.5°; n-heptyl, m.p. 42—43°; CH₂PhCO, m.p. 82.5—83°; Ph·[CH₂]₂CO, m.p. 59.5—60°; m-C₆H₄Br·CO, m.p. 112.5—113°; p-OMe·C₆H₄·CO, m.p. 96.5—97.5°; Bz, m.p. 66—67° (lit. 59.5°); Ac, m.p. 85—85.5°; Bz₂, m.p. 149.5—150°; and (EtCO)₂, m.p. 62.5—63.5°. o-Benzmethylamidophenyl benzoate has m.p. 114—115°.

R. S. C.

Amidines of the type of holocaine and derivatives. E. BUREŠ and M. KUNDERA (Časopis českoslov. Lék., 1934, 14, 272—285; Chem. Zentr., 1935, i, 1368).—3:5-Dibromo-4-acetamidophenetole condenses (POCl₃) with p-phenetidine to yield N:3:5-dibromo-p-phenetyl-NH-p-phenetylacetamide (I), m.p. 131—132° (hydrochloride; sulphate; phosphate; tartrate; salicylate). (I) is also formed from acetyl- and 3:5-dibromo-p-phenetidine; with Ac₂O and EtOAc it yields 3:5-dibromoacetyl- and, with BzCl, 3:5-dibromobenzoyl-p-phenetidine. Di-p-phenetylacetamide, m.p. 116—117° (acetate; tartrate; salicylate, m.p. 176—178°), is formed in an analogous manner.

H. N. R.

Rearrangement of o-hydroxysulphones. V. F. GALBRAITH and S. SMILES (J.C.S., 1935, 1234—1238; cf. A., 1934, 647).—The rates of change of a series of o-hydroxysulphones to ether-sulphinic acids and the behaviour of some anthraquinonyl sulphones in the presence of alkali are in agreement with previous conclusions. 1-Anthraquinonyl 4-hydroxy-m-tolyl sul-

phide, m.p. 228° [obtained when anthraquinone-1-bromothiol (I) is heated (150°; 5—6 hr.) with excess of p-cresol (II) in PhCl], is oxidised by H₂O₂-AcOH at 100° to the sulphone, m.p. 220° (Me ether, m.p. 225°), converted by 2N-NaOH at 130° into 1-anthraquinonyl 3-sulphino-p-tolyl ether, m.p. 174°. 1-Anthraquinonyl 2-acetoxy-1-naphthyl sulphide, m.p. 208°, is oxidised by H₂O₂-AcOH at 100° to the sulphone, m.p. 264—265°, hydrolysed by hot H₂SO₄-EtOH to 1'-anthraquinonyl-2-hydroxy-1-naphthylsulphone, m.p. 210°, which rearranges in the presence of 2N-NaOH at the b.p. to 1-anthraquinonyl 1-sulphino-2-naphthyl ether, m.p. 160° (decomp.). This is converted by the usual method into 2- α -anthraquinonyloxy-1-naphthyl disulphide, m.p. 238°, and on oxidation with KMnO₄ followed by treatment with 20% H₂SO₄ at 100° yields 1-anthraquinonyl 2-naphthyl ether, m.p. 170° (lit. 180°), also obtained from 1-chloroanthraquinone and β -C₁₀H₇·OK when heated at 150° during 2 hr. 6-Bromo- β -naphthol and (I) when heated at 110° (4 hr.) yield 1-anthraquinonyl 6-bromo-2-hydroxy-1-naphthyl sulphide, m.p. 280—281°, the Ac derivative, m.p. 240°, of which is oxidised by H₂O₂-AcOH at 100° to 1'-anthraquinonyl-6-bromo-2-acetoxy-1-naphthyl sulphone, m.p. 223°. This is hydrolysed (H₂SO₄-EtOH) to the corresponding OH-sulphone, which on rearrangement yields 1-anthraquinonyl 1-sulphino-6-bromo-2-naphthyl ether, m.p. 170° (decomp.), reduced to 2- α -anthraquinonyloxy-6-bromo-1-naphthyl disulphide, m.p. 283—284°. Acid hydrolysis of 1-anthraquinonyl- β -acetoxyethylsulphone, m.p. 162—163° [obtained by oxidation of the corresponding sulphide (III) with H₂O₂-AcOH at 100°], yields 1-anthraquinonyl- β -hydroxyethylsulphone, m.p. 198°, which on rearrangement with NaOH-EtOH-H₂O at the b.p. yields a sulphinic acid (IV) which is methylated to methyl- β -1-anthraquinonyloxyethylsulphone, m.p. 145—146°. 1-Anthraquinonyl β -acetoxyethyl sulphoxide, m.p. 168° [also obtained by oxidation of (III)], is hydrolysed to 1-anthraquinonyl β -hydroxyethyl sulphoxide, m.p. 220°, which rearranges rapidly with NaOH-EtOH-H₂O at the b.p. yielding (IV) and di-(β -1-anthraquinonyloxyethyl) disulphide, m.p. 223°, also obtained by reduction of (IV). K 2-thiolbenzoate when heated with CH₂Cl·CH₂·OH at 100° (1 hr.) yields 2-carboxyphenyl β -hydroxyethyl sulphide, m.p. 127°, oxidised by H₂O₂-H₂O at 90° to the sulphoxide, m.p. 179°, further oxidised by H₂O₂-H₂O to the sulphone, m.p. 195°. The last two substances were recovered unchanged when heated (100°, 2 hr.) with N-NaOH. 2-Acetamido-2'-carboxydiphenylsulphone, m.p. 282°, and the corresponding amine were unaffected by 2N-NaOH at 100° during 3 hr. The following 4-hydroxy-m-tolyl sulphides were obtained by boiling the K salt of 4-hydroxy-m-tolylthiol with the appropriate bromo-compound in EtOH or EtOH-H₂O: 4-carboxy-2-nitrophenyl (V), m.p. 215° [Na salt; Ac derivative, m.p. 163°; the corresponding sulphone (VI), m.p. 265—266°]; 2-carboxy-4-nitrophenyl (VII), m.p. 237° [Ac derivative, m.p. 230—231°; gives the lactone, m.p. 178°, with hot Ac₂O; the corresponding sulphone (VIII), m.p. 245°]; 4-benzoyl-2-nitrophenyl, m.p. 165° [the corresponding sulphone (IX), m.p. 154°]; 2-benzoyl-4-nitrophenyl, m.p. 139° [prepared from 2-bromo-5-nitrobenzophenone, m.p. 122°; the corresponding

sulphone (X), m.p. 209°; 4-nitrophenyl [improved prep.; the corresponding sulphone, m.p. 162° (lit. 158°)]. Rearrangement of (VI) gives a *sulphinic acid*, converted without purification into 4-carboxy-2-nitrophenyl 3-methanesulphonyl-*p*-tolyl ether, m.p. 233°, and *di*-(*p*'-carboxy-*o*'-nitrophenoxym-tolyl) disulphide, m.p. 241°, by the usual methods, and degraded by successive treatment with HgCl₂ and HCl (cf. this vol., 485) to 4-carboxy-2-nitrophenyl *p*-tolyl ether, m.p. 212° (*lit* ester, m.p. 78°), identical with the ether synthesised from (II) and 4-bromo-3-nitrobenzoic acid. Similarly (VIII) yields a *sulphinic acid*, characterised as *di*-(*o*'-carboxy-*p*'-nitrophenoxym-tolyl) disulphide, m.p. 257°. This and the preceding disulphide are converted by warm NaOH-EtOH into (VII) and (V), respectively (cf. A., 1932, 735). By similar methods the crude *sulphinic acid* obtained by rearrangement of (X) yields 4-nitro-2-benzoylphenyl *p*-tolyl ether, m.p. 129°, also prepared from (II) and 2-bromo-5-nitrobenzophenone, and (IX) yields 2-nitro-4-benzoylphenyl *p*-tolyl ether, m.p. 100°, identical with that synthesised from (II) and 4-bromo-5-nitrobenzophenone.

H. G. M.

Rearrangement of *o*-aminophenyl ethers. III. 2-Acylamidodiphenyl ethers. K. C. ROBERTS and C. G. M. DE WORMS. **IV. *N*-Alkylphenoxazines.** K. C. ROBERTS and (Miss) H. B. CLARK (J.C.S., 1935, 1309—1312, 1312—1313; cf. this vol., 484).—III. The rates of rearrangement of some acylamidodiphenyl ethers, 1 : 3 : 6-NHY·C₆H₃R·O·C₆H₃(NO₂)₂, to 2-acyloxydiphenylamines (NO₂)₂C₆H₃·NH·C₆H₃R·OY (I) (R=H, Me, I, Br, Cl; Y=Ac, Bz, *o*- and *m*-NO₂·C₆H₄·CO, picryl; not all combinations of R and Y have been studied) are in general agreement with the mechanism previously proposed. Those of the acetamido-ethers, however, appear to be anomalous. 2' : 4'-Dinitro-2-hydroxydiphenylamine (II) [*o*-nitrobenzoate (III), m.p. 151°], picryl chloride, and NaOAc or NaOEt yield an unstable picrate, decomp. 140—145°, converted by warm C₅H₅N-H₂O into 2 : 4-dinitro-N-(2' : 4'-dinitrophenyl)-phenoxazine, decomp. 305—310°. 2' : 4'-Dinitro-2-aminodiphenyl ether (IV) with cold AcOH-Ac₂O-H₂O gives an *Ac* derivative, m.p. 146°, which is rearranged to (I) (R=H, Y=Ac), and with *o*-NO₂·C₆H₄·COCl (V), COMe₂, and anhyd. Na₂CO₃ gives the *o*-nitrobenzoyl derivative, m.p. 232°, which is rearranged to (III) in C₅H₅N. (IV) with excess of (V) yields (III). A similar rearrangement also occurs during picrylation. The *picryl* derivative, decomp. 245—250°, of (IV) is obtained when 2-hydroxyphenyl-picrylamine (VI) is treated with C₆H₃Cl(NO₂)₂ (VII), EtOH, and NaOAc, and is converted by C₅H₅N-H₂O (water-bath) into 1 : 3-dinitrophenoxazine. (VI), (VII), and NaOEt-EtOH yield 2-nitro-N-picrylphenoxazine, m.p. 225—230°. 4-Iodo-2' : 4'-dinitro-2-acetamidodiphenyl ether, m.p. 163°, is rearranged to 5-iodo-2' : 4'-dinitro-2-acetoxydiphenylamine, m.p. 200° [also obtained from the corresponding hydroxyamine (VIII)], and hydrolysed, with rearrangement, to (VIII). Similarly 4-iodo-2' : 4'-dinitro-2-(*o*-nitrobenzamido)diphenyl ether, m.p. 194° [also obtained from (VIII) and excess of (V)], is rearranged slowly to the *o*-nitrobenzoate, m.p. 174°, of (VIII). The *Ac*, m.p. 171°, and *Bz* derivatives, m.p. 176°, of 4-bromo-2' : 4'-dinitro-2-

aminodiphenyl ether (IX) are rearranged respectively to the *Ac*, m.p. 205°, and *Bz* derivatives, m.p. 172°, of 5-bromo-2' : 4'-dinitro-2-hydroxydiphenylamine (X) (*p*-toluenesulphonate, m.p. 211°), and are hydrolysed, with rearrangement, to (X). The *o*-, m.p. 178° [also obtained from (X) and excess of (V)], and *m*-nitrobenzoyl derivatives, m.p. 189°, of (IX) are rearranged respectively to the *o*- (XI), m.p. 202°, and *m*-nitrobenzoates, m.p. 183°, of (X). The foregoing derivatives of (X) were also obtained directly from (X). The *Ac*, m.p. 160°, *o*-, m.p. 200° [also obtained from 5-chloro-2' : 4'-dinitro-2-hydroxydiphenylamine (XII) and excess of (V)], and *m*-nitrobenzoyl derivatives, m.p. 197°, of 4-chloro-2' : 4'-dinitro-2-aminodiphenyl ether are rearranged respectively to the *Ac*, m.p. 207°, *o*- (XIII), m.p. 196°, and *m*-nitrobenzoyl derivatives, m.p. 184°, of (XII). (XI) and (XIII) were not rearranged under any conditions. Attempts to prepare *o*-nitrobenzoyl derivatives of 2' : 4'-dinitro-2-hydroxy-5-carboxydiphenylamine and the isomeric 2-amino-4-carboxydiphenyl ether or of their dinitrophenyl esters were unsuccessful.

IV. *N*-Methyl-*p*-toluenesulphon-*o*-anisidide. m.p. 100° (obtained from *p*-toluenesulphon-*o*-anisidide), is hydrolysed by heating under seal with fuming HCl at 170° (5 hr.) to *o*-methylaminophenol, which with (VII), NaOEt, and EtOH yields 2' : 4'-dinitro-2-hydroxy-*N*-methylidiphenylamine (XIV), m.p. 160°, and 2' : 4'-dinitro-2-methylaminodiphenyl ether, m.p. 182°, converted by C₅H₅N-H₂O-alkali, or by NaOH-EtOH-H₂O, at 100° into 3-nitro-6-methylphenoxazine, m.p. 182—183° [also obtained from warm alkaline solutions of (XIV)]. (II), (VII), and NaOEt in EtOH yield ON-*bis*-2 : 4-dinitrophenyl-*o*-aminophenol, m.p. 176°, converted by C₅H₅N-NaOH-H₂O into 3(?)*nitro*-6-dinitrophenylphenoxazine, m.p. 230—233° (decomp.), unaffected by boiling alkali. (IV) would not condense with (VII) under conditions which precluded rearrangement of the ether.

H. G. M.

β-Substituted ethylamines. II. Catalytic hydrogenation of oximes. O. SCHALES (Ber., 1935, 68, [B], 1943—1945).—The production of *sec.* amines during the catalytic hydrogenation of oximes is ascribed to the intermediate formation of aldimine (I) which condenses with the primary amine. The occurrence of (I) in appreciable amount is avoided by slowly adding the oxime in AcOH to the Adams catalyst in AcOH-H₂SO₄. Under these conditions β-*p*-methoxyphenylethylamine and homopiperonylamine are obtained in 80% and 84% yield, respectively, from the appropriate oxime.

H. W.

Action of dicyanogen on phenols. G. HAHN and W. LEOPOLD (Ber., 1935, 68, [B], 1974—1986).—Contrary to Machek (A., 1932, 1245; 1933, 709), the action of C₂N₂ on phenols invariably involves addition of the phenolic OH to the triple linking of C₂N₂. Nuclear cyanisation is never observed. The primary products are so unstable that isomerisation cannot be attempted. Passage of C₂N₂ into aq. pyrocatechol (I) causes separation of an unstable oil almost instantaneously transformed by dil. HCl into *di*-*o*-hydroxyphenyl *di*-imino-oxalate (II) [C(NH)·O·C₆H₄·OH]₂, decomp. 220°, which passes when heated into pyrocatechyl carbonate, m.p.

120°, thus excluding the possibility of the presence of Machek's "3-cyanopyrocatechol." The constitution of (II) follows from its hydrolysis by boiling HCl-EtOH to (I) and $(\cdot\text{CO}\cdot\text{NH}_2)_2$, its solubility in NaOH, and its ability to yield a Ac_2 and a Bz_2 , m.p. 129—130°, derivative. Treatment of (II) with CH_2N_2 in COMe_2 affords *di-o-anisyl di-imino-oxalate*, m.p. 164°, which is insol. in alkali and transformed by 4*N*-NaOH into guaiacol and $(\cdot\text{CO}\cdot\text{NH}_2)_2$. The constitution $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\text{C}(\text{CN})\cdot\text{NH}_2$ is assigned to the oil. If C_2N_2 is passed into (I) in H_2O containing H_3BO_3 (I) is pptd. without intermediate production of oil. In presence of NaH_2PO_4 the compound $[\text{C}(\text{NH}_2)(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2$, m.p. 144° (decomp.), is produced, the constitution of which is established by the formation of a Me_2 ether, m.p. 129—130°, a Ac_4 derivative, m.p. 105°, and by its hydrolysis to (I), NH_4Cl , and $\text{H}_2\text{C}_2\text{O}_4$. The dependence of the course of the reaction on the p_{H} of the solution is discussed. The constitution $[\text{C}_6\text{H}_4\langle\text{O}\rangle\text{C}(\text{NH}_2)]_2$ is assigned to the product, decomp. 139°, obtained when the reaction is conducted in MeOH. It is insol. in dil. NaOH and unaffected by CH_2N_2 . Warm AcCl causes resinification. It is hydrolysed to (I), $\text{H}_2\text{C}_2\text{O}_4$, $(\cdot\text{CO}\cdot\text{NH}_2)_2$, and occasionally *o*-hydroxyphenyl oxalate.

H. W.

New method for fission of methylenedioxy-groups. L. HELFER and M. MOTTIER (Rev. Marques Parfum. Savonn., 1934, 12, 362—364; Chem. Zentr., 1935, i, 1862).—Safrole gives a blue colour with NaNH_2 , which disappears on heating, with production of tar and evolution of NH_3 . The reaction is moderated by using an indifferent solvent, propenylpyrocatechol (methylated to *isoeugenol* and *isochavibetol*) being formed; *isosafole* is broken down similarly. Pyrocatechol methylene ether and dihydrosafrole similarly undergo fission to pyrocatechol and *n*-propylpyrocatechol, respectively.

H. N. R.

Synthesis of bis-2:2'-(1:3-diphenylinden-3-ol). Rubrene problem. J. C. ECK and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 1898—1900).—*Bis*-2:2'-(1:3-diphenylinden-3-ol) (I) differs from dihydroxydihydorubrene. *Bis*-2:2'-(1:3-indandione) exists largely in the dienolic form, since with MgPhBr it gives 65% of *bis*-2:2'-(1-phenylindan-3-on-1-ol), forms, m.p. 345° (block) and 358° (block), respectively, dehydrated by KHSO_4 at 250° to *bis*-2:2'-(1-phenylinden-3-one), m.p. 213—214°. With LiPh this gives (I), forms, m.p. 273° (block), unstable, and m.p. 293° (block), stable, respectively, oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ to *o*- $\text{C}_6\text{H}_4\text{Bz}_2$ (88% yield). (I) and $\text{HCl}\cdot\text{Et}_2\text{O}$ give *bis*-2:2'-(3-chloro-1:3-diphenylindenyl), m.p. 245—247° (block), which does not give rubrene with Ag. (I) sublimes at 280°/0.3 mm. and could not be converted into an oxide.

R. S. C.

Synthesis of bis-2:2'-(1:3-diphenylinden-3-ol). C. F. KOELSCH and H. J. RICHTER (J. Amer. Chem. Soc., 1935, 57, 2010).—Diphenylmethylene-succinic acid [from $(\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, COPh_2 , and NaOEt] with H_2SO_4 gives 3-phenylindenone-2-acetic acid, m.p. 166—167°, which with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and NaOAc yields 2'-(3'-phenylindenone)methylenephthalide, m.p. 173.5—174°, converted by NaOMe into 2-3'-phenyl-

indenone-2'-hydrindane-1:3-dione, m.p. 190.5—191.5°. This with MgPhBr yields successively 1-hydroxy-1'-keto-1:3:3'-triphenyl-2:2'-di-indenyl, m.p. 244—245°, *bis*-2:2'-(1:3-diphenylinden-3-ol), m.p. 292°, and *bis*-2:2'-(1-chloro-1:3-diphenylindene), m.p. 237—242° (unreactive to Zn and Hg, but giving a Na derivative with 40% Na-Hg), identical with the products of Eck and Marvel (preceding abstract).

R. S. C.

Synthesis of pharmacologically important amines. X. Catalytic hydrogenation of ω -nitrostyrenes to β -arylethylamines. K. KINDLER and E. BRANDT (Arch. Pharm., 1935, 273, 478—483; cf. A., 1934, 669).—Owing to compound-formation with H_2SO_4 the appropriate ω -nitrostyrenes are readily hydrogenated in $\text{AcOH}\cdot\text{H}_2\text{SO}_4$ to good yields of tyramine, mescaline, homo-veratrylamine, piperonylamine, and -myristicylamine.

R. S. C.

Synthesis of substances related to sterols.

IV. Derivatives of chrysene (contd.). H. J. LEWIS, G. R. RAMAGE, and R. ROBINSON (J.C.S., 1935, 1412—1414).— $\beta\gamma$ -Dianisyladipic acid-b, m.p. 180° (*Me* ester, m.p. 67°, isolated from the Et_2O -sol. portion of the reduction products of *Me* 4-methoxycinnamate; A., 1933, 828), is cyclised by AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ to 2:11-diketo-5:14-dimethoxy-, m.p. 220°, reduced ($\text{Zn}\cdot\text{Hg}$ -conc. HCl) to 5:14-dimethoxy-1:2:9:10:11:18-hexahydrochrysene-b, m.p. 140—141°. Reduction ($\text{Al}\cdot\text{Hg}$ in Et_2O) of *Me* 3-methoxycinnamate affords mainly *Me* β -3-methoxyphenylpropionate, b.p. 146°/12 mm., and some *Me* $\beta\gamma$ -di-3-methoxyphenyladipate-a, m.p. 139.5°, hydrolysed to the acid, m.p. 247—248°, cyclised (90% H_2SO_4 at 100°) to 2:11-diketo-6:15-dimethoxy-, m.p. about 350°, reduced to 6:15-dimethoxy-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 159°. Condensation of piperonal with MeOAc and Na affords *Me* 3:4-methylenedioxy-cinnamate, m.p. 133—134° [probably not identical with the ester, m.p. 68—69°, of Feuerstein *et al.* (A., 1901, i, 465)], reduction of which gives only *Me* β -3:4-methylenedioxyphenylpropionate, b.p. 165—170°/13 mm., m.p. 34—35°. Similar reduction of *Me* 3:4-dimethoxycinnamate gives *Me* β -3:4-dimethoxyphenylpropionate, b.p. 175—180°/12 mm., m.p. 37°, and the *Me* ester, m.p. 184°, of $\beta\gamma$ -di-3:4-dimethoxyphenyladipic acid-a, m.p. 255°, cyclised to the 2:11-diketo-compound, m.p. 330° (decomp.), reduced to 5:6:13:14-tetramethoxy-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 204°. *cis*-Diketohexahydrochrysene with MgMeI in C_6H_6 and aërial oxidation of the product affords 2:11-dimethylchrysene, m.p. 237° [compound with 1:3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 222°; styphnate, m.p. 207° (decomp.)].

J. W. B.

cycloHexyl sulphite. W. VOSS and W. WACHS (Ber., 1935, 68, [B], 1939—1941).—Contrary to Carré *et al.* (this vol., 480) repetition of the action of SOCl_2 on cyclohexanol as described by Voss *et al.* (A., 1931, 462) affords cyclohexyl sulphite, b.p. 173—173.5°/14.5 mm., the identity of which is confirmed by analysis, determination of mol. wt., quant. hydrolysis, mol. refraction, and viscosity. Carré's results are unexplained.

H. W.

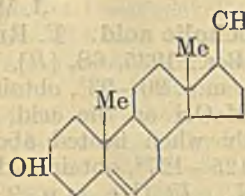
Synthesis of ephedrine derivatives. V. BRUCKNER and A. KRÁMLI (Arch. Pharm., 1935, 273, 372—384).—Hydrochlorides of β -hydroxylamino- α -aryl-*n*-propyl acetates (I) with aldehydes and alkali give nitrones before migration of acyl occurs (method A). Sometimes the acyl is removed by hydrolysis, giving the OH-nitrone, which is also obtained by hydrolysis of the β -*N*-acylhydroxylamino- α -aryl-*n*-propyl alcohols with dil. H_2SO_4 and subsequent condensation with the aldehyde and Na_2CO_3 (method B). Nitrones are thus obtained by the methods given in parentheses from β -hydroxylamino- α -3:4-dimethoxyphenyl-*n*-propyl alcohol and PhCHO , m.p. 160° (A and B), *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. $148\text{--}150^\circ$ (A and B), *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 174° (B) [Ac derivative, m.p. 196° (A)], and 3:4- $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CHO}$, m.p. $148\text{--}150^\circ$ (A), and from β -hydroxylamino- α -3:4-methylenedioxyphenyl-*n*-propyl alcohol and PhCHO , m.p. 149° (B) [Ac derivative, m.p. $158\text{--}159^\circ$ (B)], *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. $117\text{--}118^\circ$ (B) [Ac derivative, m.p. 146° (decomp.) (A)], *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 171° (B) [Ac derivative, m.p. 196° (A)], and piperonal [Ac derivative, m.p. $158\text{--}160^\circ$ (A)]. Reduction by Cu-Zn and AcOH affords 3:4-dimethoxy-*N*-benzyl-, m.p. $102\text{--}103.5^\circ$, and -homoveratryl-, m.p. $125\text{--}127^\circ$, and 3:4-methylenedioxy-*N*-benzyl-, m.p. $117.5\text{--}119.5^\circ$, and -homopiperonyl-norephedrine, m.p. $123.5\text{--}125^\circ$.

R. S. C.

Halogen derivatives of novocaine. II. 4-Bromo-2-aminobenzoylethylaminoethanol. J. FREJKA and F. VYMETAL (Coll. Czech. Chem. Comm., 1935, 7, 436—443).—2:4- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$, prepared from *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{COMe}$ or from *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ (the intermediate steps are described), is converted into β -chloroethyl 4-bromo-2-aminobenzoate, m.p. $80\text{--}81^\circ$, which, with NH_4Et , affords 4-bromo-2-aminobenzoylethylaminoethanol; the hydrochloride, m.p. 160° , has local anæsthetic action.

P. G. C.

Structure of sitosterol. M. VANGHELOVICI and B. N. ANGELESCU (Bull. Soc. Chim. România, 1935, 17, 177—190).—When heated with citraconic anhydride cholesterol (I) and sitosterol (II) (following formula suggested) afford, respectively, *cholesteryl*,



m.p. 195° (Br-derivative, m.p. 162°), and *sitosteryl*, m.p. 169° , citraconate. The following reactions, similar in both series, show the identity of the structures of ring II in (I) and (II). With conc. HNO_3 sitosteryl chloride affords *nitrodehydro-sitosteryl chloride*, m.p. 118° , reduced (Zn-AcOH) to *chlorositostan-6-one* (III), $\text{C}_{29}\text{H}_{49}\text{OCl}$ (oxime, m.p. 180° ; semicarbazone, m.p. 207° ; *p*-nitrophenylhydrazone, m.p. 188°), reduced by Na-Hg in boiling EtOH to *sitostan-6-one*, m.p. 77° (oxime, m.p. 173°). Oxidation of (III) with fuming $\text{HNO}_3\text{--AcOH}$ affords a dibasic acid, $\text{C}_{24}\text{H}_{49}\text{O}_4\text{Cl}$, m.p. 277° . Reduction (Clemmensen) of (III) affords a *chlorositostane*, m.p.

108° . Reduction of chlorocholestan-6-one (oxime, m.p. 178° ; semicarbazone, m.p. 155° ; *p*-nitrophenylhydrazone, m.p. 207°) with Na-Hg-EtOH affords *ischolestan-6-one*, m.p. 97° (oxime, m.p. 157°), probably stereoisomeric with the known derivative, m.p. 98° (Windaus, A., 1920, i, 434), and by Clemmensen reduction gives an *ischolesteryl chloride*, m.p. 110° . The presence of the suggested side-chain in (II) is indicated by the production (in small yields) of COMe_2 and a solid ketone (menthol odour), which is not methylheptanone, by oxidation of sitosteryl acetate with $\text{CrO}_3\text{--AcOH}$.

J. W. B.

Polyterpenoid nature of the sterols. F. S. SPRING (Chem. and Ind., 1935, 972—973).—A scheme is proposed whereby the cholestane skeleton is built up from six isoprene units by cyclisation and loss of three C. The ergosterol and stigmasteryl structures are derived by use of one or two C, respectively, of another isoprene unit. Sterols with 30—32 C may thus be expected in nature.

R. S. C.

Relationship between cholesterol and carotene structures. W. H. D. BRYANT (Chem. and Ind., 1935, 907).—Formation of cholesterol by ring-closure is more probable from α - or β -carotene than from squalene (cf. Robinson, this vol., 209).

F. R. G.

Sterol group. XXI. Lumisterol. I. M. HEILBRON, F. S. SPRING, and P. A. STEWART (J.C.S., 1935, 1221—1223).— BzO_2H titration and hydrogenation of lumisterol (I) confirm that it is tetracyclic with three ethylenic linkings. (I) with BzO_2H in CHCl_3 at 0° yields *lumistadienetriol monobenzoate* (II), m.p. $185\text{--}186^\circ$, $[\alpha]_D^{25} -68.0^\circ$ in CHCl_3 (gives carmine coloration, which changes to brown and then to green, with SbCl_3), hydrolysed by MeOH--KOH to *lumistadienetriol* (III), m.p. $180\text{--}181^\circ$, $[\alpha]_D^{25} -8.7^\circ$ in CHCl_3 (Ac_2 derivative, m.p. $128\text{--}130^\circ$, $[\alpha]_D^{25} -48.4^\circ$ in COMe_2 , extremely sol. in the common org. solvents). (I) is dehydrated by POCl_3 and $\text{C}_6\text{H}_5\text{N}$ giving *lumistatetraene*, m.p. $88\text{--}90^\circ$, $[\alpha]_D^{25} +298.9^\circ$ in CHCl_3 (coloration, changing from crimson, through purple, to green, with SbCl_3 in CHCl_3), which is not identical with Rygh's ergostatetraene (A., 1930, 203). This proves that other changes apart from possible epimerisation occur in the photochemical transformation of ergosterol (IV) into (I). Titration of (II) with BzO_2H and (III) with $\text{Pb}(\text{OAc})_4$ indicates that (II) is not and (III) is an α -glycol. By analogy with similar known reactions with (IV) it is concluded that (I) contains a $\Delta^{5:6}$ -ethenoid linking. Lumisteryl acetate is dehydrogenated by $\text{Hg}(\text{OAc})_2$ in AcOH to *dehydro-lumisteryl acetate*, m.p. $142\text{--}143^\circ$, $[\alpha]_D^{25} +126.4^\circ$ in CHCl_3 (cf. A., 1928, 424).

H. G. M.

Actiniasterol.—See this vol., 1398.

Colour standard for cholesterol determinations.—See this vol., 1552.

Physiologically active crystalline esters of vitamin-A.—See this vol., 1545.

Optically active diphenylhydroxyethylamines and isohydrobenzoins. VII. The 1:2-cyclohexanediols and related compounds. N. A. B. WILSON and J. READ (J.C.S., 1935, 1269—1273).—

Methods for the separation of *cis*- (I) and *dl-trans*-1:2-cyclohexanediol (II) are described. The following derivatives of (II) have been prepared by adding the appropriate acid chloride to (II) in C_5H_5N : *monobenzoate* (III), m.p. 92—93°, b.p. 200—205°/35 mm.; *dibenzoate*, m.p. 93°; *di-m*- m.p. 141—142°, and *di-p-nitrobenzoate*, m.p. 149—150°; *bis-3:5-dinitrobenzoate*, m.p. 179°. 1-(3':5'-*Dinitrobenzoate*)-2-benzoate prepared from (III) exists in two forms, m.p. 105° and 132.5°, respectively: 1-*p*-, m.p. 131°, and 1-*m-nitrobenzoate*-2-benzoate, m.p. 102°, were similarly prepared. The mono- and the di-*d*-camphor-10-sulphonate could not be recrystallised. The following derivatives of (I) were similarly prepared: *mono*-, b.p. 139—140°/0.5 mm. and *di-benzoate*, m.p. 63—64°, obtained as a mixture together with an unsaturated hydrocarbon; *di-p-nitrobenzoate*, m.p. 128—128.5°; *bis-3:5-dinitrobenzoate*, m.p. 169°; 1-(3':5'-*dinitrobenzoate*)-, m.p. 102°, 1-*p-nitrobenzoate*-, m.p. 82°, and 1-*m-nitrobenzoate*-2-benzoate, m.p. 96—97°. Both the *cis*- and the *dl-trans*-diols give an absorption edge in the ultra-violet region, the former being the less transparent. The *trans*-monobenzoate is more rapidly esterified than the *cis*-isomeride (cf. this vol., 88). (II) with *l*-menthoxyacetyl chloride and C_5H_5N yields *d*-, m.p. 126—127°, $[\alpha]_D -32.7^\circ$ in EtOH, and *l-trans*-1:2-cyclohexane *mono-l-menthoxyacetate*, m.p. 64°, $[\alpha]_D -91.7^\circ$ in EtOH, hydrolysed, respectively, to the *d*- and *l-trans*-diol, m.p. 113—114°, $[\alpha]_D \pm 46.5^\circ$ (cf. A., 1922, i, 651). *l-trans*-1:2-cyclohexanediol *di-p-nitrobenzoate* has m.p. 126.5°, $[\alpha]_D -25.5^\circ$ in $CHCl_3$, and the corresponding *bis-3:5-dinitrobenzoate* has m.p. 160°, $[\alpha]_D -83.0^\circ$ in $CHCl_3$ (the corresponding *d-bis-ester* has m.p. 160°, $[\alpha]_D +83.9^\circ$ in $CHCl_3$). 1:2-cyclohexanedione (IV) shows an absorption band with head at about 2650 Å.; the mol. extinction coeff. is about 2700, corresponding with a marked proportion of the enol form (cf. A., 1934, 414). (IV) with $MgMeI$ in Et_2O yields *dl*-1-methylcyclohexane-1-ol-2-one, b.p. 91—95°/30 mm. (*semicarbazone*, m.p. 202°; *p-nitrobenzoate*, m.p. 125—126°; 3:5-dinitrobenzoate, m.p. 158°; the *l*-menthoxyacetate and *d*-camphor-10-sulphonate were syrups), reduced by $Na-EtOH$ to *dl*-1-methylcyclohexane-1:2-diol, m.p. 84° (*bis-3:5-dinitrobenzoate*, m.p. 189°; acetone compound derived from the *cis*-diol had b.p. 72—73°/20 mm.).

2-Aminocyclohexanol (V) is most readily obtained by shaking 2-chlorocyclohexanol with conc. NH_3-H_2O , and with $MeI-NaOMe-MeOH$ yields *dl*-cyclohexan-1-ol-2-trimethylammonium iodide, m.p. 214°. The *d*-aminoalcohol (A., 1933, 156) when similarly treated yields the *d*-iodide, m.p. 217°, $[\alpha]_D +25.8^\circ$ in H_2O . Neither deamination nor exhaustive methylation indicated whether (V) has the *cis*- or the *trans*-configuration; when boiled with Ag_2O-H_2O both the *dl*- and the *l*-quaternary NH_4 iodide give a mixture of (II) (inactive) and 2-dimethylaminocyclohexanol which when heated yields cyclohexene oxide (VI) and $NHMe_2$. Deamination of (V) in the presence of H_2SO_4 gave some (VI) in addition to cyclopentyl-formaldehyde (cf. A., 1934, 892). Attempts to prepare a stereoisomeride of (V) were unsuccessful. cyclohexanone when treated below 5° with amyl nitrite and conc. HCl yields oximinocyclohexanone

nitrite, decomp. 190°, decomposed on attempted reduction (catalytic, or $Na-EtOH$). Crude 1:2-cyclohexanediol monobenzoate is oxidised by $K_2Cr_2O_7-H_2SO_4-H_2O$ to 1:2-cyclohexanolone benzoate, m.p. 85—86° (cf. A., 1913, i, 1201) (*oxime*, m.p. 120°). 1:2-cyclohexanoloneoxime, m.p. 109°, when reduced by $Na-EtOH$ yields only the known form of (V).
H. G. M.

Nitrones. A new transposition reaction. I. V. BELLAVITA (Gazzetta, 1935, 65, 755—765).—*N*-Phenyl-*o*-, *m*-, and *p*- (II) -nitrobenzaldoximes are converted by KCN in $MeOH$ into *Me o*- (III), *m*-, and *p-nitrobenzoate-N-phenylimides*, m.p. 74.5°, 76.5°, and 47°, respectively, the transposition $CHR:NPh:O \rightarrow [OH:CR:NPh] \rightarrow OMe:CR:NPh$ having occurred. In the formation of (III) from (I), an intermediate substance, m.p. 103—105°, is isolated by adding H_2O ; with $MeOH$ and KCN it gives (III). When (II) is treated with KCN in $EtOH$, *Et p-nitrobenzoate-N-phenylimide*, m.p. 46°, is formed. On hydrolysis, the imides give either the anilide of the acid, or aniline and the ester (or acid).

E. W. W.

β -Alkoxyethyl *p*-aminobenzoates. H. V. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1935, 57, 1862—1863).—The appropriate ethers, $OH-[CH_2]_n-OR$, afford β -propoxy-, b.p. 181.6—182.6°, -isopropoxy-, b.p. 172—172.8°, -isobutoxy-, b.p. 184.8—185.6°, -sec-butoxy-, b.p. 183.5—184.5°, and tert-butoxy-ethyl *p*-nitrobenzoate, b.p. 174.8—175.8°, hydrogenated (PtO_2 ; 45 lb. per sq. in.) in $EtOH$ in good yield to the corresponding *p-aminobenzoates*, m.p. 44.5° (138.4°), m.p. 95.4° (156°), an oil, b.p. 176.5—177.5°/0.7 mm. (150.3°), an oil, b.p. 177—178°/0.7 mm. (132.5°), and m.p. 77.4°, b.p. 173.5—174.5°/0.3 mm. (140°), respectively, figures in parentheses being the m.p. of the *picramides*. β -Methoxy-, -ethoxy-, and -*n*-butoxy-ethyl *p*-aminobenzoate have m.p. 75.9° (132°), 79.2° (136.7°), and 34° (123.1°), respectively.

R. S. C.

Resolution of *r*-mandelic acid with (–)-ephedrine. R. ROGER (J.C.S., 1935, 1544).—A method of resolution using only (–)-ephedrine is described.

J. W. B.

Nor- and bisnor-lithocholic acid. F. REINDEL and K. NIEDERLÄNDER (Ber., 1935, 68, [B], 1969—1973).—*Me lithocholate* (I), m.p. 90—93°, obtained by the action of HCl and $MeOH$ on the acid, passes slowly when kept, rapidly when heated above its m.p., into the form, m.p. 125—127°, obtained directly from the acid and CH_2N_2 . *Et* (II), m.p. 92—93°, and CH_2Ph , m.p. 145—148°, *lithocholate* are obtained by means of HCl . *Et 3-acetyl-lithocholate*, m.p. 90—91°, is derived from (II) and boiling Ac_2O ; treatment of 3-acetyl-lithocholic acid with HCl and $EtOH$ involves loss of Ac . (I) and $MgMeI$ in Et_2O afford *norepicopropane-3:24-diol*, $C_{26}H_{46}O_2$, m.p. 141—142° (also $+1H_2O$). The corresponding *acetate*, m.p. 79—80°, is oxidised by $CrO_3 (=6O)$ in $AcOH$ at 100° to *acetylnorlithocholic acid*, m.p. 175—176° (also obtained in poorer yield by similar oxidation of *diphenylcholane-3:24-diol diacetate*), hydrolysed to *norlithocholic [α -3-hydroxynorcholanic] acid*, m.p. 170—171°, and, after re-solidification, m.p. 181—182°.

which is oxidised by CrO_3 in cold AcOH to *dehydro-norlithocholic* [*3-ketonorcholanic*] acid, m.p. 179—180° [*Me* ester, m.p. 90°; *semicarbazone*, m.p. 208—210° (decomp.)]. *Me norlithocholate*, m.p. 99—100° (corresponding *Et* ester, m.p. 83—85°), is converted by MgMeI into *bisnorepicopropane-3:23-diol*, m.p. 196—197° (also +0.5 H_2O) the *acetate*, m.p. 105—106°, of which is oxidised and then hydrolysed to *bisnorlithocholic* [α -3-hydroxybisorcholanic] acid, m.p. 210—212° (*acetate*, m.p. 200—202°; *Me* ester, m.p. 148—150°). H. W.

Synthesis of substances related to sterols. V. Condensation of phenylsuccinic anhydride with veratrole under the influence of aluminium chloride. R. ROBINSON and P. C. YOUNG (J.C.S., 1935, 1414—1416).—The above condensation in PhNO_2 affords β -*veratroyl- α -phenylpropionic acid* (I), m.p. 142—143° (NO_2 -derivative, m.p. 176—179°), the *Me* ester, m.p. 100—100.5°, of which is identical with the product obtained by condensation of β -carbomethoxy- β -phenylpropionyl chloride and veratrole with AlCl_3 in CS_2 . Reduction (Zn-Hg-conc. HCl) of (I) affords some 1-keto-6:7-dimethoxy-2-phenyl-1:2:3:4-tetrahydronaphthalene (II), m.p. 140—141°, and α -phenyl- γ -*veratrylbutyric acid*, m.p. 83°, cyclised by 80% H_2SO_4 to (II). With Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 (II) affords *Et 6:7-dimethoxy-2-phenyl-3:4-dihydronaphthyl-1-acetate*, m.p. 159—161.5°. J. W. B.

Synthesis of substances related to sterols. VI. R. ROBINSON and J. WALKER (J.C.S., 1935, 1530—1533).—Reduction of *Et 3:4-dihydro-1-naphthylacetate* (improved prep.) with Na in boiling EtOH gives β -1:2:3:4-tetrahydro-1-naphthylethyl alcohol, b.p. 158—160°/11 mm. (solidifies, but could not be crystallised). Condensation of the Grignard compound of β -1-naphthylethyl bromide (improved prep. of alcohol) and *Et 2-methylcyclopentanone-2-carboxylate* (improved prep.; with Me_2SO_4 *Et cyclopentanonecarboxylate* gives 27% of the *O-Me* ether) affords some α -di-1-naphthylbutane, and the crude *OH-ester*, which, after hydrolysis and re-esterification with CH_2N_2 , affords pure *Me 2- β -1'-naphthylethyl-1-methylcyclopentan-2-ol-1-carboxylate*, b.p. 206—214°/0.4 mm. (*methylamide*, m.p. 100°), dehydration-cyclisation of which could not be effected. Methylation of 2-hydroxymethylenecyclohexanone by the method of Bishop *et al.* (A., 1895, i, 62) effects *C-methylation* and hydrolysis to 2-methylcyclohexanone, but with Me_2SO_4 -aq. KOH is obtained the *O-Me ether*, b.p. 75—80°/13 mm., condensed with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}\cdot\text{NaOEt}\cdot\text{EtOH}$ to an intermediate, hydrolysed by boiling $\text{NaOEt}\cdot\text{EtOH}$ to 6-hydroxy-1:2:3:4-tetrahydronaphthalene-7-carboxylic acid, m.p. 178°. J. W. B.

8-Methylhydrindane derivatives and cis- and trans-2-methylcyclopentane-1-carboxylic-2-acetic acid. C. K. CHUANG, C. M. MA, and Y. L. TIEN (Ber., 1935, 68, [B], 1946—1952).—In connexion with a possible synthesis of sterol hydrocarbons, the following experiments are described. 2-Acetyl-1-methyl- Δ^1 -cyclopentene, b.p. 71°/11 mm., from 1-methyl- Δ^1 -cyclopentene and AcCl in presence of SnCl_4 , condenses readily with $\text{CHNa}(\text{CO}_2\text{Et})_2$ to *Et 2:4-*

diketo-8-methylhydrindane-1-carboxylate, b.p. 160—170°/3 mm., [*monosemicarbazone*, m.p. 208—209° (decomp.)], hydrolysed by boiling 5*N*- HCl to 2:4-diketo-8-methylhydrindane (I), m.p. 90—92° (*dioxime*, m.p. 137—138°), which is freely sol. in NaOH and Na_2CO_3 , and gives a brown colour with FeCl_3 and condenses with CH_2O to *methylenedi-2:4-diketo-8-methylhydrindane*, m.p. 123—124°. Reduction of (I) by Hg-Zn and conc. HCl at 170° affords 8-methylhydrindane, b.p. 80—82°/50 mm., which could not be dehydrogenated to C_{10}H_8 by Se at 280—300°. Oxidation of (I) with NaOBr smoothly yields *cis-2-methylcyclopentane-1-carboxylic-2-acetic acid* (II), m.p. 165—166° (*Ag salt*), transformed by the successive action of PCl_5 and NH_2Ph in Et_2O into the *dianilide*, m.p. 202—204°, and by boiling Ac_2O into the *anhydride* (III), m.p. 93—94°, reconverted by boiling H_2O or dil. acid into the *cis-acid*. Treatment of (II) with conc. HCl at 200° affords *trans-2-methylcyclopentane-1-carboxylic-2-acetic acid*, m.p. 101—102° (*dianilide*, m.p. 156—157°), which with boiling Ac_2O gives (III), which does not pass into an equilibrium mixture at 240° or 300°. H. W.

Multiplanar cyclohexane rings. R. D. DESAI and R. F. HUNTER (Nature, 1935, 136, 608—609).—Evidence that there are only two stereoisomerides of 4-methylcyclohexane-1-carboxylic-1-acetic acid is presented (cf. this vol., 1236). The carboxy-3:3-dimethylcyclohexane-1-acetic acid obtained from 3:3-dimethylcyclohexanone could not be isolated in more than one form. L. S. T.

Synthesis of phenanthrene and hydrophenanthrene derivatives. I. Bougault reaction. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1935, 57, 1851—1854).— $\text{Ph}[\text{CH}_2]_3\text{CO}_2\text{Et}$ and $\text{Et}_2\text{C}_2\text{O}_4$ with KOEt or NaOEt give *Et α -keto- β -carbomethoxy- δ -phenylvalerate*, converted by H_2SO_4 at 25° into 3:4-dihydronaphthalene-1:2-dicarboxylic anhydride, b.p. 227—230°/23 mm., m.p. 126—127°, triboluminescent, which with S at 240—250° gives a 76% yield of 1:2- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$ (I), b.p. 211—214°/11 mm., m.p. 164—165° (cf. A., 1925, i, 402). β - $\text{C}_{10}\text{H}_7\cdot\text{OMe}$ (I), and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ give a *lactone*, m.p. 238—239°, isomerised by AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ at 100° to a *naphthaloylnaphthol*, m.p. 264—265°. *Et γ -1-naphthylbutyrate*, b.p. 210—211°, treated as above affords a *keto-ester*, sulphonated by conc. H_2SO_4 , but with 80% H_2SO_4 at 100° cyclised to 3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride (II), m.p. 263.5—264.5°, which with S at 320—325° gives *phenanthrene-1:2-dicarboxylic anhydride* (III), m.p. 311—312°. *Et γ -2-naphthylbutyrate*, b.p. 227—228°/25 mm., affords similarly 1:2-dihydrophenanthrene-3:4-dicarboxylic anhydride, m.p. 151—152°. (II) and (III) are oestrogenic to mice. R. S. C.

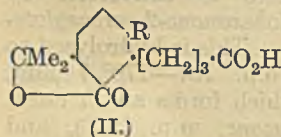
Intermediates for the synthesis of phenanthrene. R. GHOSE (Sci. and Cult., 1935, 1, 299).—*Et cyclohexanone-2-carboxylate* is converted by $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ into *Et₂ cyclohexanone-2-carboxylate-2-acetate*, b.p. 161—162°/5 mm. This is hydrolysed to *cyclohexanone-2-acetic acid*, b.p. 167—170°/7 mm. (*semicarbazone*, m.p. 200°), which forms an *Et* ester, b.p. 130°/10 mm. (*semicarbazone*, m.p. 196°), and when treated with Na-Hg and with dil. H_2SO_4 yields

hexahydro- α -coumaranone, b.p. 137°/15 mm. When either this or Δ^1 -cyclohexenyl-1-acetic acid is condensed with C_6H_6 ($AlCl_3$), 2-phenylcyclohexyl-1-acetic acid, m.p. 69–70°, b.p. 195–200°/8 mm. (chloride, b.p. 168–171°/7 mm.; amide, m.p. 196–197°), is formed. E. W. W.

Diphenyl series. III. [Synthesis of] phenanthrene [derivatives]. N. N. CHATTERJEE (J. Indian Chem. Soc., 1935, 12, 591–594; cf. this vol., 1361).—Et cyclohexanone-2-carboxylate, NaOEt, and CH_2Cl-CO_2Et give *Et*₂ cyclohexanone-2-carboxylate-2-acetate (I), b.p. 168–175°/11 mm., hydrolysed by conc. HCl to cyclohexanone-2-acetic acid, b.p. 163°/4 mm., the *Et* ester, b.p. 122°/5 mm., of which with MgPhBr affords *Et* 2-hydroxy-2-cyclohexylphenylacetate, b.p. 170–180°/8 mm. (corresponding acid, m.p. 129°). With S this yields *Et* diphenyl-2-acetate, b.p. 165–175°/8 mm., which, when hydrolysed by KOH and heated with conc. H_2SO_4 at 100°, gives 9-hydroxyphenanthrene, m.p. 153° (picrate, m.p. 185°). (I) and MgPhBr give *Et* 2-hydroxy-1-carbethoxy-2-cyclohexylphenylacetate (II), b.p. 180–190°/9 mm., and the lactone, m.p. 97°, of 2-hydroxy-1-carbethoxy-2-cyclohexylphenylacetic acid [also obtained by keeping (II) over H_2SO_4 ; with hot KOH–EtOH gives the 1-carboxy-lactone, m.p. 141°]. R. S. C.

Stereoisomerism of 2 : 2'-disubstituted derivatives of diphenyl. III. A. CORBELLINI and C. VIGANÒ (Gazzetta, 1935, 65, 735–743).—Et H diphenate, Mg, and EtBr give 2- α -hydroxy- α -ethyl-n-propyldiphenyl-2'-carboxylic acid (I), m.p. 92–93° (by pptn.) or 111° (from light petroleum) (Na salt), converted by Ac_2O into the corresponding lactone (II), m.p. 104°; 2 : 2'-di- α -hydroxy- α -ethyl-n-propyldiphenyl, m.p. 98–99°, is also formed. The substances previously regarded as (I) and (II) (A., 1933, 64) are a mixture of cis- and trans-, and either cis- or trans-2- α -ethylidene-n-propyldiphenyl-2'-carboxylic acid (III), respectively. (III) is obtained from (II) and HCl in EtOH; with I in $CHCl_3$ it gives 2- β -iodo- α -hydroxy- α -ethyl-n-propyldiphenyl-2'-carboxylic acid lactone, m.p. 111° (decomp.); a similar Br-compound is formed. Et H diphenate, Mg, and Pr^iBr yield 2- α -hydroxy- α -n-propyl-n-butyldiphenyl-2'-carboxylic acid, m.p. 149° (lactone, m.p. 92°, hydrolysed to the acid, m.p. 158°). CH_2PhCl yields 2-(α -hydroxy- β -phenyl- α -benzylethyl)diphenyl-2'-carboxylic acid, m.p. (from lactone, m.p. 146°) 172°. Pr^iBr , Bu^iBr , Bu^sBr , o - and p - C_6H_4MeI , 1- $C_{10}H_7Br$, and 2- $C_{10}H_7I$ give similar products, which are, however, not purified. E. W. W.

Picrotoxin. XII. Degradation of picrotic acid, $C_{15}H_{18}O_4$, to the dibasic acids, $C_{14}H_{14}O_6$ and $C_{12}H_{10}O_6$. P. HORMANN [with K. THELO] (Arch. Pharm., 1935, 273, 433–446; cf. A., 1922, i, 161).—Previous evidence and the reactions described below indicate that picrotic acid (I) is (II; R=Me). Dry distillation of the base, $C_{14}H_{17}O_2 \cdot NMe_3 \cdot OH$, obtained by Hofmann degradation of (I), yields AcOH and an aldehyde, $C_{12}H_{12}O_3$, oxidised by aq. NH_3 – Ag_2O to an acid, $C_{12}H_{12}O_4$. Dry distillation of picrotin ketone (III) gives a residue, which on KOH-fusion affords



2 : 3- $C_6H_3Me_2 \cdot CO_2H$ and another acid. Picrotindicarboxylic acid with red P and I gives 64% of (I) and 30% of (II) (phenylhydrazones, m.p. 185°). (I) and 38% KOH at 280° give an acid, $C_{13}H_{14}(CO_2H)_2$, m.p. 138° (Ag_2 salt). (I) and $KMnO_4$ (30) give γ -4-carboxydimethylphthalide-3-n-butyric acid (II; R= CO_2H), m.p. 183°, affording at 300–330° H_2O , CO_2 , and an α -tetralone derivative (IV), $C_{14}H_{14}O_3$, m.p. 147°, b.p. 228°/12 mm. [semicarbazone, m.p. 322° (decomp.); phenylhydrazones, m.p. 184°; oxime, m.p. 185° (decomp.)]. (IV) and hot HNO_3 (d 1.37) yield β -4-carboxydimethylphthalide-3-propionic acid (V), $+H_2O$, m.p. 235° (decomp.) (Ag_2 salt), and dimethylphthalide-3 : 4-dicarboxylic acid (VI), $+H_2O$, decomp. (slow heating) 293° or (rapid heating) 209–210° (with formation of the anhydride, m.p. 293°) (Ag_2 salt). (V) at 240–270°/12 mm. affords the 1-hydrindone derivative, $C_{13}H_{12}O_3$, m.p. 187° [phenylhydrazones, m.p. 210°; semicarbazones, m.p. 350° (decomp.)], oxidised by HNO_3 to (VI). R. S. C.

Synthesis of substances related to sterols. VII. W. S. RAPSON, R. ROBINSON, and (in part) R. HIRT (J.C.S., 1935, 1533–1543).—Four lines of synthesis are developed. (A) Reduction of Et 2-methylcyclopentanone-2-carboxylate with Na–Hg (CO_2 stream) is incomplete, but dehydration of the OH-ester with P_2O_5 in boiling C_6H_6 and fractionation affords *Et* 1-methyl- Δ^2 -cyclopentene-1-carboxylate (I), b.p. 70–71°/13 mm. (free acid, b.p. 110°/14 mm.), reduced (Bouveault) to 1-methyl- Δ^2 -cyclopentenylmethyl alcohol (II), b.p. 162–165°/760 mm. (p-nitrobenzoate, m.p. 67°), converted by PCl_5 in ligroin at –5° into the impure chloride, b.p. 40–56°/18 mm., which failed to give the required condensation product with $CHAcNa \cdot CO_2Et$. Dehydration of (II) with $KHSO_4$ affords a hydrocarbon (probably a dihydro-toluene), b.p. 112–113°/760 mm. m -OH- $C_6H_4 \cdot CHO$ is readily reduced electrolytically to the alcohol, converted by Me_2SO_4 (*in situ*) into 3 : 3'-dimethoxyhydrobenzoin $\alpha \alpha'$ - Me_2 ether, m.p. 112–113°, and m -OMe- $C_6H_4 \cdot CH_2 \cdot OH$ (III). (III) is converted through the chloride, nitrile, and ester into β -m-methoxyphenylethyl alcohol, the iodide of which condenses with $CHAcK \cdot CO_2Et$ in PhMe to give *Et* β -m-methoxyphenylethylacetate, b.p. 180°/2 mm., hydrolysed (cold aq. NaOH followed by hot 10% HCl) to γ -m-methoxyphenylpropyl Me ketone, b.p. 168°/19 mm. (semicarbazones, m.p. 109°), condensation of which with (I) was unsuccessful. (B) cyclopentanone cyanohydrin with $SOCl_2$ – C_5H_5N affords 1-cyano- Δ^1 -cyclopentene, b.p. 69°/15 mm. Et trans-cyclopentane-1-carboxylate-2-cyanoacetate (Cook *et al.*, A., 1934, 1002) condenses with $CH_2Ph \cdot CH_2Br$ –K–PhMe to give *Et* α -cyano- α -(trans-2-carbethoxycyclopentyl)- γ -phenylbutyrate, b.p. 195–200°/1 mm., hydrolysed (conc. HCl, then 25% KOH–EtOH) to α -cyano- α -(trans-2-carboxycyclopentyl)- γ -phenylbutyric acid, m.p. 210° (decomp.), converted by boiling H_2SO_4 –AcOH into α -(trans-2-carboxycyclopentyl)- γ -phenylbutyric acid (IV), m.p. 160–161°, the trans-anhydride, m.p. 112°, of which is converted at 250° into the cis-anhydride, hydrolysed to the corresponding cis-acid, m.p. 133°. When heated with aq. H_2SO_4 at 100° (IV) gives 1-keto-2-(trans-2'-carboxycyclopentyl)-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 164–165° (Me ester, m.p. 45°),

but with boiling Ac_2O - NaOAc , the corresponding *cis*-compound, m.p. 155–156°, is obtained. These with SOCl_2 afford, respectively, 1-hydroxy-2-(trans-2'-carboxycyclopentyl)- (V), m.p. 162°, and 1-hydroxy-2-(*cis*-2'-carboxycyclopentyl)-3 : 4-dihydronaphthalene lactone, m.p. 66° (cryst. data by CROWFOOT). (V) is reduced by H_2 -1% Pd- SrCO_3 in EtOAc to 2-(2'-trans-carboxycyclopentyl)-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 107°. *Et cyclopentanone-2-carboxylate* with PCl_5 in ligroin (b.p. 40–60°) affords *Et 2-chloro- Δ^1 -cyclopentene-1-carboxylate*, b.p. 95–98°/12 mm. (acid, m.p. 115–116°). (c) *m-Benzoyloxybenzaldehyde*, m.p. 54° (CH_2PhCl - NaOEt on the OH-compound), with $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and Ac_2O at 100° affords *m-methoxy-(?benzyloxy)benzylidenephénylisooxazolone*, m.p. 129°, hydrolysed to the phenylpyruvic acid, converted by H_2O_2 - NaOH into *m-benzoyloxyphenylacetic acid*, m.p. 126°. The Na salt of this with 6-nitro-3-methoxybenzaldehyde and Ac_2O affords *2-nitro-5-methoxy- α -(m-benzoyloxyphenyl)cinnamic acid*, m.p. 148°, reduced (FeSO_4 -aq. NH_3) to the 2- NH_2 -acid, m.p. 137°. 2-Nitro-, m.p. 148°, and 2-amino-5-methoxy- α -(m-methoxyphenyl)cinnamic acid (VI), m.p. 185°, are similarly prepared. Diazotisation of (VI) effects cyclisation to a mixture of 2 : 5-, m.p. 191° (56%), and 2 : 7-dimethoxyphenanthrene-9-carboxylic acid, m.p. 265° (44%), decarboxylated, respectively, to 2 : 5-, m.p. 117° (picrate, m.p. 154–156°), and 2 : 7-dimethoxyphenanthrene (Fieser, A., 1929, 1171) (picrate, m.p. 144°). 2 : 5-Dihydroxyphenanthrene (Ac_2 derivative, m.p. 144°) has m.p. 180°. With dil. HCl the reaction product from the prep. of β -2-hydroxy-1-naphthylethyl Me ketone (A., 1934, 1356) affords 2-methyl-5 : 6-(1 : 2-naphtha)- γ -pyran, m.p. 44–45°. (d) Condensation of *Et cyclopentanonecarboxylate* with $n\text{-C}_8\text{H}_{17}\text{Br}$ and K in xylene affords *Et 2-n-octylcyclopentanone-2-carboxylate*, b.p. 157–165°/1 mm. (semicarbazone, m.p. 117°), hydrolysed by $\text{Ba}(\text{OH})_2$ to α -n-octyladipic acid, m.p. 74°, converted by distillation at 760 mm. into 2-n-octylcyclopentanone, b.p. 135–138°/11 mm. (semicarbazone, m.p. 183°), reduced (Na - EtOH) to 2-n-octylcyclopentanol, b.p. 140°/8 mm., the bromide, b.p. 135–140°/8 mm., of which loses HBr in attempted condensations to give *n-octyl- Δ^1 -cyclopentene* (VII), b.p. 125–128°/12 mm. (also obtained from $\text{C}_8\text{H}_{17}\text{MgBr}$ and cyclopentanone). Condensation of (VII) with β -carbomethoxypropionyl chloride and AlCl_3 in CS_2 at $<0^\circ$ and heating the product with NPhMe_2 at 180° affords 2-(β -carbomethoxypropionyl)-1-n-octyl- Δ^1 -cyclopentene, b.p. 173–177°/1 mm. When refluxed with AcCl , cyclopentanone-2- β -propionic acid (VIII) gives the *enolic lactone*, b.p. 116–117°/17 mm., which could not be reduced, but cyclopentanol-2- β -propionic acid lactone, b.p. 138–139°/18 mm., is obtained by reduction (Na - EtOH) of (VIII) and distillation of the OH-acid. With PCl_5 at 130–140° it gives the 2- Cl -derivative, b.p. 126–127°/15 mm., converted by NPhEt_2 into *Et Δ^1 -cyclopentene-1-propionate*. γ -Phenylpropyl Me ketone (new prep.) is converted by 85% H_2SO_4 at 0° into 1-methyl-3 : 4-dihydronaphthalene, b.p. 107–108°/14 mm. J. W. B.

Action of trimethylene bromide on ethyl acetonedicarboxylate : new synthesis of ethyl

cyclohexane-2 : 6-dicarboxylate. P. C. GUHA and N. K. SESHADRIENGAR (Current Sci., 1935, 4, 158).— $[\text{CH}_2]_3\text{Br}_2$ (I) and the Na derivative of $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (II) in C_6H_6 at 140–150° form $\text{Et}_2\beta\zeta$ -dehydrohexan- ζ -ol- β -one- $\alpha\gamma$ -dicarboxylate (J.C.S., 1887, 51, 739) and a phloroglucinol lactone (J.C.S., 1897, 71, 1110), but (I) with the Mg derivative of (II) gives Et_2 cyclohexanone-2 : 6-dicarboxylate. E. W. W.

Mechanism of polymerisation reactions. IV. α -Phenylbutadiene. E. BERGMANN (J.C.S., 1935, 1359–1360).—*Et sodiopropene- $\alpha\gamma$ -tricarboxylate* in boiling C_6H_6 with $\text{CHBrPh}\cdot\text{CO}_2\text{Et}$, followed by hydrolysis (18% MeOH - KOH) and decarboxylation at 130° gives δ -phenyl-n-butane- $\alpha\gamma\delta$ -tricarboxylic acid, m.p. 163–165° (decomp.), which is different from the acid (I) obtained by oxidising the dimeride of α -phenylbutadiene, as is the $\alpha\beta\delta$ -tricarboxylic acid (cf. this vol., 976). (I) is identical with δ -phenyl-n-butane- $\alpha\beta\gamma$ -tricarboxylic acid (this vol., 977), so that the dimeride is 2-benzoyl-1-styryl- Δ^3 -cyclopentene and implies that dimerisation is effected by 1 : 4-addition (cf. simple ethylenes) followed by cyclisation as a result of the activation of a further H atom by the newly formed conjugated system (cf. A., 1929, 674; 1931, 1031; 1932, 856). $\text{CHNa}(\text{CO}_2\text{Et})_2$ with Et_2 fumarate and subsequent treatment of the Na derivative with CH_2PhCl gives *Et δ -phenyl-n-butane- $\alpha\beta\gamma$ -tricarboxylate*, a mixture of diastereoisomerides, b.p. 220–230°/19 mm. and 230–240°/9 mm.; the former is hydrolysed to (I) and the latter to an acid, m.p. 168° (lit., 165°). J. L. D.

Substitution-syntheses of mellitic acid and replaceability of chlorine in the benzene nucleus. F. FEIST (Ber., 1935, 68, [B], 1941–1943).—Rosenmund's method (A., 1920, i, 44) for the replacement of Cl by CO_2H can be applied only with difficulty to PhCl and is inapplicable to polychlorobenzenes. The presence of negative substituents, however, enables it to proceed. Thus $\text{C}_6\text{Cl}_4(\text{CO}_2\text{K})_2$ is transformed by KCN - CuCN - H_2O at 180–200° into mellitic acid in 60% yield. H. W.

Reduction reactions and oxidation reactions. [Aromatic aldehydes and Fehling's solution.] V. PAOLINI (Gazzetta, 1935, 65, 630–632).— PhCHO , anisaldehyde, and cuminaldehyde do not reduce Fehling's solution, but, by action of the alkali it contains, undergo the Cannizzaro reaction. Salicylaldehyde and vanillin are unaffected. E. W. W.

Perkin reaction. III. Condensation of acid chlorides with benzaldehyde. H. KATOH (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, A, 257–265).—In presence of NEt_3 , PhCHO reacts with the following acid chlorides (products and % yields of theory in parentheses): AcCl ($\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, 11.86), $\text{Pr}^\circ\text{COCl}$ ($\text{CHPh}\cdot\text{C}^\circ\text{Et}\cdot\text{CO}_2\text{H}$, 6.63), $\text{CH}_2\text{Ph}\cdot\text{COCl}$ ($\text{CHPh}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, 43.78 of combined *cis*- and *trans*-forms), $\text{CMe}_2\cdot\text{CH}\cdot\text{COCl}$ (α -isopropenylcinnamic acid, 6.2). Lævulic acid gives α -benzylidenelævulic acid and $\text{CMePh}\cdot\text{CH}\cdot\text{COCl}$ does not react. Bases other than NEt_3 give lower yields. P. G. C.

New derivatives of dehydrodivanillin and the catalytic reduction of nitrostyrenes. K. MAURER and B. SCHIEDT (J. pr. Chem., 1935, [ii], 144, 41—

48).—Divanillin with Ac_2O and a little H_2SO_4 yields the *hexa-acetate*, m.p. 160° , and with Me_2SO_4 in NaOH gives *diveratraldehyde*, m.p. 138° , (*dioxime*, m.p. 184°), which with MeNO_2 and KOH in MeOH yields *bis-(3:4-dimethoxy- ω -nitrostyrene)*, m.p. 206° , hydrogenated [$\text{Pd}(\text{OAc})_2$] to *dihomoveratrylamine*, an oil (*Ac*₂ derivative, m.p. 78°). 3:4-Methylenedioxy- ω -nitrostyrene, 3:4-dimethoxynitrostyrene, and β -nitro- α -methoxy- α -3:4-dimethoxyphenylethane similarly give homopiperonylamine ($\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ derivative, m.p. 131°), homoveratrylamine, and α -methoxyhomoveratrylamine (cf. Kindler *et al.*, this vol., 1362).

F. R. G.

Chemical reactivity and Raman spectra of the eugenols, vanillins, and safoles, and of piperonal, estragol, and anethole.—See this vol., 1446.

Isomerides and derivatives of hexetone. R. WEGLER and W. FRANK (Arch. Pharm., 1935, 273, 408—414).—The *d*- and *l*-forms of hexetone (3-methyl-5-isopropyl- Δ^2 -cyclohexenone) (I) have the same cardiac activity as *dl*-(I) (*phenylhydrazone-p-sulphonic acid*, m.p. 228° , gives only oily alkaloidal salts). $\text{CHPhMe}\cdot\text{NH}_2$ is readily resolved by the *H* tartrate, the *l*-salt crystallising from MeOH and the *d*-salt being purified by crystallising the salt from the mother-liquors from H_2O . (I) is resolved by α -phenylethylsemicarbazide to give forms, $[\alpha]_D^{20} -37.8^\circ$ and $+37^\circ$, respectively. (I) and Grignard reagents give hydrocarbons. (I) and H_2 -Pd-black in MeOH give the saturated ketone, but with Pt-black the CO is also reduced to $\text{CH}\cdot\text{OH}$, or in AcOH slowly to CH_2 . (I) and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ give a Schiff's base, b.p. $125^\circ/13$ — 14 mm., stable to H_2 -Pd-C, but reduced by H_2 -Pt-C to 3-methyl-5-isopropylcyclohexyl- β -hydroxyethylamine, b.p. $151^\circ/15$ — 16 mm. (I) and $\text{HCO}\cdot\text{NH}_2$ give a base, hydrolysed by conc. HCl to 3-methyl-5-isopropyl- Δ^2 -cyclohexenylamine, b.p. $90^\circ/12$ mm. [oxalate; resolved by $(\cdot\text{CHPh}\cdot\text{CO}_2\text{H})_2$], which with pyridine-3-carboxyl chloride gives the *amide*, b.p. $230^\circ/14$ mm.

R. S. C.

p-Bromophenacyl formate, a solid derivative of formic acid. C. D. HURD and R. E. CHRIST (J. Amer. Chem. Soc., 1935, 57, 2007).—Contrary to Judefind *et al.* (A., 1920, i, 480) this compound, m.p. 140° , is readily prepared.

R. S. C.

Beckmann change. III. Rearrangement of ketoxime hydrochlorides. A. W. CHAPMAN (J.C.S., 1935, 1223—1229; cf. A., 1934, 1312).—The velocity of the rearrangement to NHPhBz (I) of $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ (II) in $(\cdot\text{CH}_2\text{Cl})_2$ in the presence of HCl at 100° is small at first, but increases with increasing time to a val. which is nearly const. for the last two thirds of the reaction. The time required for a given amount of change depends on the $[\text{HCl}]$. The initial slow period also occurs when the hydrochloride of (II) is used, but is reduced by the addition of (I) and completely abolished by addition of a small amount of $\text{CClPh}\cdot\text{NPh}$ (III) (A., 1931, 843). The change is inhibited by partial replacement of the $(\cdot\text{CH}_2\text{Cl})_2$ by EtOH , which prevents the formation of (III). The presence of HCl is essential to the progress of the change. The rearrangement does not take place

in Et_2O in presence of HCl , except when some (III) is also present.

(II) and (III) in Et_2O with $\text{NaOEt}\cdot\text{EtOH}$ yield *benzophenoneoxime O- α -phenyliminobenzyl ether* (IV), m.p. 72 — 76° , and 5—10% of *benzophenoneoxime N- α -phenyliminobenzyl ether*, m.p. 178 — 179° , which yields (I) with conc. HCl , and (I) and (III) with $\text{Et}_2\text{O}\cdot\text{HCl}$, but no benzoyl-*s*-diphenylbenzamidine (V) with $\text{Et}_2\text{O}\cdot\text{H}_2\text{SO}_4$. The constitution of (IV) is confirmed by the oxidation by $\text{KMnO}_4\cdot\text{AcOH}$ to $\text{CPh}_2\cdot\text{N}\cdot\text{OBz}$. (IV) yields (I) with conc. HCl , and (I) and (III) with $\text{Et}_2\text{O}\cdot\text{HCl}$, and (V) with $\text{Et}_2\text{O}\cdot\text{H}_2\text{SO}_4$. The dry hydrochloride of (II) when heated above 130° yields (I) and *s*-diphenylbenzamidine. (II) when heated at 100° with picric acid and MeNO_2 in a sealed tube gave some (I), but no benz-*N*-picrylanilide, which would have been expected had the change occurred through *N*-phenylbenzimidopicyrlyl ether.

The following mechanism of the Beckmann change accounts for the foregoing observations. (a) A primary slow rearrangement of (II) brought about by acids alone; (b) a much more rapid change beginning as soon as a trace of (I) is formed by (a) and proceeding as follows. (I) and HCl yield (III) which condenses with (II) giving (IV), which with HCl forms the salt $\text{CPh}_2\cdot\text{N}\cdot\text{O}\cdot\text{CPh}\cdot\text{NHPh}\cdot\text{Cl}$. This, by analogy with the picryl ethers, rearranges to $\text{NPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{CPh}\cdot\text{NHPh}\cdot\text{Cl}$ which may rearrange further to (V) or be split by HCl to (I) and (III). The (III) thus formed can transform further quantities of (II). Attempts to prepare di-(α -phenyliminobenzyl) ether by interaction of (III) and dry Ag_2O failed, the only isolable products being (I) and (V).

H. G. M.

Preparation of o-nitrophenyl aryl ketones. M. BOËTIUS and H. RÖMISCH (Ber., 1935, 68, [B], 1924—1932).—*o*-Nitrophenyl aryl ketones can be obtained by the Friedel-Crafts method if FeCl_3 in mol. proportion is substituted for AlCl_3 . $\text{C}_2\text{H}_5\text{Cl}_4$ at 30 — 40° is the most suitable solvent, but smaller yields can be obtained in PhNO_2 , CHCl_3 , and C_6H_6 ; CS_2 and CCl_4 are unsuitable. In addition to the ketones, larger amounts of black, amorphous products are obtained separable into portions sol. and insol. in Na_2CO_3 , but from which a homogeneous material could not be obtained by reduction, acetylation, or benzylation. Distillation of them with Zn dust affords acridine. $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ condenses with C_6H_6 in presence of $\text{C}_2\text{H}_5\text{Cl}_4$ and FeCl_3 to *o*-nitrobenzophenone (I), m.p. 105° (yield 20%). With mixtures of FeCl_3 and AlCl_3 containing 10% of the latter, (I) is not produced. The following *o*-nitrophenyl aryl ketones are described; *p*-tolyl, m.p. 155° (yield 17—14.6%); *m*-xyl, m.p. 81.5° (yield 19.7—22.6%); *p*-xyl, m.p. 94° (yield 41.6—47.4%); *mesityl*, m.p. 146° (yield 6.9%); *p*-methoxyphenyl, m.p. 105° (yield 1.4%). (II) is reduced by Sn and conc. HCl to *o*-aminophenyl *p*-xyl ketone, m.p. 88 — 90° after softening at 76 — 78° .

H. W.

Synthesis of substances related to the sterols. II. General method for the synthesis of substituted cyclohexenones. W. S. RAPSON and R. ROBINSON. III. Synthesis of certain ketohydro-

phenanthrene derivatives. R. ROBINSON and E. SCHLITTLER (J.C.S., 1935, 1285—1288, 1288—1291).—II. cyclohexenones are obtained by dehydration of diketones, e.g., $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3 \rightarrow$

$\text{CH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$. Sodicyclohexanone (I) (from cyclohexanone, NaNH_2 , and Et_2O) and $\text{CHPh} \cdot \text{CH} \cdot \text{COMe}$ (II) in Et_2O yield 2-keto-4-phenyl- $\Delta^{1:9}$ -octalin, m.p. 91—92°, b.p. 175—185°/1 mm., hydrogenated ($\text{Pd} \cdot \text{SrCO}_3$) to 2-keto-4-phenyldecalin, m.p. 82—83° (2:4-dinitrophenylhydrazon, m.p. 180°). Similarly (I) and acetylcyclohexene (III) yield 9-keto- $\Delta^{10:11}$ -dodecahydrophenanthrene, m.p. 89°, b.p. 150—155°/1 mm. The Na derivative (IV) of 1-keto-2-methyl-1:2:3:4-tetrahydronaphthalene, (II), and C_6H_5 yield 3-keto-1-phenyl-11-methyl-2:3:4:9:10:11-hexahydrophenanthrene, m.p. 135°, b.p. 235—240°/1 mm. 1-Keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (V) (improved prep.) when refluxed with NaNH_2 and Et_2O in a current of H_2 and then treated with (III) yields 2-keto-10-methoxy-2:3:4:5:6:7:8:14:15:16-decahydrochrysene, m.p. 228—229°, hydrogenated ($\text{Pd} \cdot \text{SrCO}_3$) to a saturated alcohol, $\text{C}_{19}\text{H}_{26}\text{O}_2$, m.p. 151°. 1-Acetylcyclopentene, b.p. 75—78°/22 mm. (semicarbazone, m.p. 210—211°; obtained not quite pure by heating the product obtained from the interaction at -10° of cyclopentene, anhyd. SnCl_4 , CS_2 , and AcCl , with NPhMe_2 at 180° during 3 hr), with the Na derivative of (V) and Et_2O yields 3-keto-7-methoxy-1:2:3:9:10:11-hexahydro-1:2-cyclopentenophenanthrene, m.p. 196—197°, hydrogenated ($\text{Pd} \cdot \text{SrCO}_3$) in MeOH to a tetrahydro-derivative, $\text{C}_{18}\text{H}_{24}\text{O}_2$, m.p. 167—168°. An attempt to condense (IV) and (III) gave two forms (cis- and trans-), m.p. 205—206° and 126—127°, of a dimeride (VI),

$\text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{CHAc}) \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CH}_2\text{CH}_2) \cdot \text{CH}_2$, of (III). On oxidation by the Kuhn-Roth micro-method (VI) gave 1 mol. of AcOH .

III. 5-Keto-8-m-methoxyphenyloctoic acid, m.p. 69—70°, obtained by the method of G. M. Robinson (A., 1930, 742) from γ -m-methoxyphenylbutyryl chloride and Et sodio- α -acetylglutarate, is converted into the Me ester, which is cyclised by $\text{NaOEt} \cdot \text{Et}_2\text{O}$ to β -m-methoxyphenylethylcyclohexane-2:6-dione, m.p. about 150° (has pseudo-acidic character, but gives negative Fe^{III} reaction in EtOH). This is dehydrated by P_2O_5 in C_6H_6 to 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene, m.p. 75—76°, b.p. 165—169°/0.23 mm. [2:4-dinitrophenylhydrazon, m.p. 256° (decomp.), sinters at 253—254°], which has no oestrogenic properties, and absorbs 6H_2 with an active Pt catalyst but only 2H_2 with a Pd-black- BaSO_4 catalyst. It is reduced by Na-EtOH to 1-hydroxy-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene (p-nitrobenzoate, m.p. 140°, sinters at 125°). An improved prep. of γ -m-methoxyphenylbutyric acid (VII) (A., 1932, 1122) is described. Et β -m-methoxyphenylpropionate, b.p. 145—146°/10.5 mm., is reduced by Na-EtOH to γ -m-methoxyphenylpropyl alcohol (cf. this vol., 752), converted through the corresponding chloride into the iodide, b.p. 152—162°/11 mm., which with $\text{KCN} \cdot \text{H}_2\text{O} \cdot \text{EtOH}$

gives some γ -m-methoxyphenylbutyramide, m.p. 96—97°, and the corresponding butyronitrile, b.p. 164—170°/11 mm., hydrolysed by $\text{KOH} \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ to (VII), m.p. 49—50°. Dehydration of 1-allyl-2-methylcyclohexanol by P_2O_5 yields a dicyclic hydrocarbon, $\text{C}_{10}\text{H}_{16}$, b.p. 169—170°, which absorbs 1 mol. of Br in cold CHCl_3 . H. G. M.

Vat dyes of the benzanthrone series. XI. Formation and separation of isomeric dichlorobenzanthrones. XII. Constitution of the dichlorobenzanthrones. T. MAKI and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1935, 38, 487—489B, 489—493B; cf. A., 1933, 611).—XI. Benzanthrone (I) when treated with AcOH , Cl_2 , and Fe at 100° (68 min.) gives a 94% yield of a mixture of two dichlorobenzanthrones, (II), m.p. 273.5—274.5° (corr.), and (III), m.p. 228° (corr.), separated by means of EtOH and AcOH . A eutectic, m.p. 203.5—204.5° (corr.), of (II) and (III) is also obtained.

XII. Oxidation of 13-chlorobenzanthrone (IV) with $\text{CrO}_3 \cdot \text{AcOH} \cdot \text{H}_2\text{O}$ yields anthraquinone-1-carboxylic acid. Similarly, oxidation of (II) and (III) yields 6- and 8-chloroanthraquinone-1-carboxylic acid, respectively. The above eutectic gave only a mixture of these acids. Since dichlorination of (I) proceeds through (IV), (II) and (III) are 6:13- and 8:13-dichlorobenzanthrone, respectively. The fusion diagram of (II) and (III) is given. H. G. M.

Synthesis of benzoin. 2':4':6'-Trimethylbenzoin. R. C. FUSON, H. H. WEINSTOCK, jun., and G. E. ULLYOT (J. Amer. Chem. Soc., 1935, 57, 1803—1804).—Benzoin is obtained from α -ketoaldehydes, aromatic hydrocarbons, and AlCl_3 . 2':4':6'-Trimethylbenzoin [thus prepared from mesitylglyoxal (I) and C_6H_6 at 10°], m.p. 102° (urethane, m.p. 158.5—159°), is oxidised by air to $\text{PhCO} \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Me}_3$ (II), and with more (I) in C_6H_6 at 50° gives (II) and $[\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO} \cdot \text{CH}(\text{OH})]_2$ (cf. A., 1934, 525). $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO} \cdot \text{CH}_2\text{Bz}$ and SeO_2 in hot dioxan give mesityl Ph triketone (III), m.p. 90—91°, and other products including a substance, m.p. 169—170°. (III) gives 3:2':4':6'-trimethylbenzoyl-2-phenylquinazoline, m.p. 134—134.5°, and with 10% NaOH yields (II), $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO}_2\text{H}$, and CO_2 .

R. S. C.

(A) Structures of bimolecular reduction products of dibenzoyl ethylene. R. E. LUTZ and F. S. PALMER. (B) Reduction of unsaturated 1:4-diketones with zinc combinations. Formation of the cyclic bimolecular products. R. E. LUTZ, L. LOVE, jun., and F. S. PALMER. (C) Catalytic hydrogenation of unsaturated 1:4-diketones. R. E. LUTZ and F. S. PALMER (J. Amer. Chem. Soc., 1935, 57, 1947—1952, 1953—1957, 1957—1961).—(A) Reduction of $(\text{CHBz})_2$ with Zn-AcOH or other reducing agents gives bimol. products, including meso-“bisdibenzoyl ethane-A” (meso- γ - δ -dibenzoyl- α - ζ -diphenyl-n-hexa- α - ζ -dione) (I) and its less stable dl-B-isomeride (II), and three stereoisomeric 2:3:4-tribenzoyl-1-phenylcyclopentan-1-ols [-A (III), -B (IV), and -C (V)], termed “cyclobisdibenzoyl ethanes,” the structures of which are proved by the following reactions. (I), m.p. 202°, obtained from $(\text{CH}_2\text{Bz})_2$, $(\text{CHBz})_2$, and NaOEt (62% yield), from (III) and

cold NaOEt, or (IV) and 1 drop of C_5H_5N in hot EtOH, is stable in boiling PhCl or EtOH and distils unchanged at 240–250°/vac. (II), m.p. 168°, best prepared from (III) and hot C_5H_5N -EtOH or by heating (III) at 200° [gives also $(CHBz)_2$ and $(CH_2Bz)_2$ in equal amount], is also obtained from (V) and C_5H_5N -EtOH, showing that (III) and (V) are stereoisomeric at C3 and 4. Since (I) is the *meso*-form, (IV) has the *cis*-configuration at C3 and 4, and (III) and (V) the *trans*. (II) at 230–240° gives (I), $(CH_2Bz)_2$, and $(CHBz)_2$, and with cold NaOEt yields (I) only. (I) or (II) with H_2SO_4 - Ac_2O affords 3:3'-bis-(2:5-diphenylfuran) (VI), $\left[\begin{array}{c} \text{CPh:CH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CPh:C} \end{array} \right]_2$, m.p. 195–196°, also obtained by AcCl with some 2:5-diphenyl-3:4-diphenacylfuran (VII), m.p. 165°. (VI) with HNO_3 -AcOH at 30–35° gives "bis-1:2-dibenzoylthylene" ($\gamma\delta$ -dibenzoyl- $\alpha\alpha'$ -diphenylhexadiene- $\alpha\alpha'$ -dione), m.p. 214–218°, hydrogenated (Pt) in EtOAc to a little (I) and other products, and reduced by $Na_2S_2O_4$ to much (I) and by Zn-AcOH to substances, m.p. 160–165° and 199–200°, respectively. (VII) and HNO_3 -AcOH give *cis*- $\gamma\delta$ -dibenzoyl- $\alpha\alpha'$ -diphenyl- Δ^7 -hexene- $\alpha\alpha'$ -dione, m.p. 183–184°, reduced by $Na_2S_2O_4$ in 70% EtOH to a mixture of (I) and (IV). (III), (IV), or (V) with Ac_2O - H_2SO_4 at 90° gives 2:3:4-tribenzoyl-1-phenyl- Δ^1 -cyclopentene (VIII), m.p. 182°, which with O_3 in $CHCl_3$ yields a 1:2-peroxide, m.p. 132–133° (decomp.), which, when heated slowly to 140°, gives (VIII), or rapidly BzOH and a substance, m.p. 217–219°, and which regenerates (VIII) with KI-EtOH and is hydrolysed by 70% EtOH to 2:3:4-tribenzoyl-1-phenylcyclopentane 1:2-oxide, m.p. 117–119°. This oxide is unchanged by H_2SO_4 - Ac_2O , but with cold NaOMe gives slowly a little BzOH and much $\alpha\beta\gamma$ -tribenzoylpropane (β -phenacyl- $\alpha\delta$ -diphenyl-n-butyl- $\alpha\delta$ -dione) (IX), m.p. 122°, which is obtained in 50–60% yield from $(CHBz)_2$ and $CHBz:CBz:ONa$ in cold EtOH or from $(CHBz)_2$ and $COPhMe$. (IX) is dehydrated by Ac_2O - H_2SO_4 to 3-phenacyl-2:5-diphenylfuran. The compound (A., 1891, 680), obtained from tricarballic chloride and previously called (IX), is α - or β -phenacyl- $\gamma\gamma$ -diphenylbutyro- γ -lactone, since it gives only a mono-phenylhydrazone and with $KMnO_4$ affords equal amounts of BzOH and $COPh_2$.

(B) Zn reduction of *trans*- $(CHBz)_2$ (X) gives large yields of bimol. products, that of *cis*- $(CHBz)_2$ (XI) only small yields thereof, whilst only unimol. products result by Zn-AcOH (room temp.) reduction of *cis*- and *trans*- $(CH:CO:C_6H_4Cl-p)_2$, *trans*- $(p-C_6H_4Me:CO:CH)_2$, *trans*- $(C_6H_5Me_3:CO:CH)_2$, *cis*- $(CBrBz)_2$, *cis*- $CHBz:CPhBz$ (XII), *cis*- $CBrBz:CPhBz$ (XIII), $CH_2Bz:CHXBz$ (XIV), or *dl*- or *meso*- $(CHXBz)_2$ (X=Cl or Br). Formation of the bimol. products probably involves conjugated reduction. $ZnBr_2$ often has a catalytic effect. (X) and hot Zn-AcOH or sol. reducing agents give $(CH_2Bz)_2$, but slower reduction or, best, Zn-AcOH- C_6H_6 at 30–35° gives much (III), m.p. 161°, whereas under these conditions (XI) gives only $(CH_2Bz)_2$. (XIII) with Zn-AcOH gives mainly 2:3:5-triphenylfuran (XV). (XII) with Zn-AcOH gives a little (XIV) with much $CH_2Bz:CHPhBz$ (XVI). (XVI) is stable to Zn-AcOH, so that reduction of (XII) probably proceeds by way of

$OH:CPh:CH:CPh:CPh:OH$. If, however, $ZnBr_2$ is added, (XII) gives only (XV). Reduction of (XIII) thus undoubtedly proceeds by way of $OH:CPh:C:CPhBz$ and (XIII). *dl*- and *meso*- $(CHBrBz)_2$, but not $(CHClBz)_2$ or (XIV), with $Zn-COMe_2$ give much (III). (X) reacts with $Zn-COMe_2$ only if $ZnBr_2$ is added, but $CHBz:CBrBz$ and (XIV; X=Br) are not affected, so that reduction of $(CHBrBz)_2$ probably proceeds by way of (X). This is in harmony with the production of very little (III) if the concn. of (X) is kept low. (XI) with $Zn-ZnBr_2-COMe_2$ gives mainly unimol. products. $Na_2S_2O_4$ in 60–65% EtOH with (X) gives mainly $(CH_2Bz)_2$, but deteriorated samples give bimol. products and the additive compound (XVI), $CH_2Bz:CHBz:SO_3Na$, m.p. 255–262° (converted by hot conc. HCl into 2:5-diphenylfuran), whilst in one case mainly (II) was formed. $NaHSO_3$ in 90% EtOH converts (X) into much (III) and some (IV), (V), $(CH_2Bz)_2$, and (XVI). (IV), m.p. 202–203°, or (V), m.p. 204–205°, with NaOMe gives (I).

(c) Catalytic hydrogenation with PtO_2 of (X) in EtOAc or dioxan, or with Raney Ni in decahydronaphthalene or 95% EtOH, gives mostly $(CH_2Bz)_2$, but with PtO_2 in other solvents much (III) and sometimes (I) and (II) are formed. Acid increases the amount of $(CH_2Bz)_2$ formed in EtOH. Hydrogenation of (X) probably proceeds by a conjugate mechanism, but is unique in that (XI) gives 45–50% of $(CH_2Bz)_2$ and other similar ketones give mostly or only unimol. products. M.p. in (A), (B), and (C) are corr.

R. S. C.

Testicular hormone. L. RUZICKA (J. Amer. Chem. Soc., 1935, 57, 2011–2012).—Androstene-3:17-dione, androstane-3:17-dione and -diol are more active than androsterone. Androsten-3-ol-17-one with Na-EtOH gives *androstene-3:17-diol* (I), m.p. 175–178° (corr.), the dibromide of which by partial oxidation and debromination gives *androstene-3-one-17-ol*, identical with testosterone, also obtained from (I) by partial hydrolysis of the diacetate and oxidation of the acetate dibromide.

R. S. C.

Constitution and preparation of the testicular hormone. E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1935, 57, 2012).—Concerning priority.

R. S. C.

Dideuterocholestanone.—See this vol., 1408.

Two modifications of 4:2':3':4':6'-pentamethoxychalkone. G. MARTINEZ (Rend. Semin. Fac. Sci. Univ. Cagliari, 3, 147; Chem. Zentr., 1935, i, 1537).—Crystallographic examination shows the stable form, m.p. 111–112°, to be monoclinic ($a:b:c=1.267:1:0.83412$) and the labile form triclinic ($a:b:c=0.5660:1:0.7514$).

H. N. R.

Mechanism of additions to double linkings. II. **Steric course of two diene syntheses.** A. WASSERMANN (J.C.S., 1935, 1511–1514; cf. this vol., 938).—The additive products of cyclopentadiene with benzoquinone or maleic anhydride exist in geometrically isomeric forms ("endo-" and "exo-"), the rates of formation of which differ. The dipole induction energy is greater for orientations of the reacting mols. which might lead to the *endo*-additive

product than for orientations suitable for *exo*-addition. The activation energy of the latter process is greater.

H. J. E.

Reaction between 2 : 3-dimethyl-1 : 4-naphthaquinone and magnesium phenyl bromide. I. (MISS) H. M. CRAWFORD (J. Amer. Chem. Soc., 1935, 57, 2000—2004).—2 : 3-Dimethyl-1 : 4-naphthaquinone (I) reacts with MgPhBr by reduction and 1 : 2- and 1 : 4-addition to give mono- and di-additive products. (I) (348 g.; 1.87 mols.) and MgPhBr (3.5 mols.) give (I) + its *quinhydrone*, m.p. 136—140° (dissociated in C_6H_6), 65 g., 1 : 4-dihydroxy-1 : 2-diphenyl-2 : 3-dimethyl-1 : 2-dihydronaphthalene (II), m.p. 208—209° (2 active H) 40 g., 1-hydroxy-1-phenyl-4-keto-2 : 3-dimethyl-1 : 4-dihydronaphthalene (III), m.p. 197—197.5° (1 active H) 20 g., 2-phenyl-2 : 3-dimethyl-2 : 3-dihydro-1 : 4-naphthaquinone (IV), m.p. 123°, 2.4 g., and a compound (V), m.p. 137—138°, 14 g. When (I) (55.8 g., 0.3 mol.) and MgPhBr (0.55 mol.) react and the mixture is decomposed by AcCl, there are formed (I) 7.5 g., the Ac derivative, m.p. 153—157°, of (III) [also obtained from (III)] 0.22 g., 1 : 4-diacetoxy-2 : 3-dimethylnaphthalene, m.p. 189°, 7.9 g., and a substance (VI), $C_{24}H_{20}O$, m.p. 183°, b.p. 250—270°/15 mm., 1.1 g. With $K_2Cr_2O_7$, (IV) gives CPhMe, (III) gives o - C_6H_4 Bz- CO_2H , and (II) gives both products. (II) is stable to $KMnO_4$ in $COMe_2$ and to hot 20% H_2SO_4 , but with PBr_3 in $CHBr_3$, $ZnCl_2$ and HCl in hot C_6H_6 , or I in AcOH yields (VI). (VI) is stable to hot HBr, $K_2Cr_2O_7$, and $MgMeI$. The Grignard reaction leads occasionally to small amounts of compounds, $C_{24}H_{22}O_2$, m.p. 203—204° [additive compound with 2 mols. of (I)=(V)], and $C_{24}H_{20}O$, m.p. 124° (no active H; with $K_2Cr_2O_7$, gives CPhMe and o - C_6H_4 Bz- CO_2H).
R. S. C.

Constitution of perezone. F. KÖGL and A. G. BOER (Rec. trav. chim., 1935, 54, 779—794; cf. Fichter *et al.*, A., 1913, i, 279).—Perezone (I), m.p. 102—103° (cf. lit.), $[\alpha]_D^{20}$ —17.0° in Et_2O {m.p. and $[\alpha]$ are depressed when (I) is sublimed owing to facile racemisation; Ag salt; Me ether, b.p. 128—133°/0.002 mm.}, is shown, from the known results and those which follow, to be 2-hydroxy-3-methyl-6-(α -dimethyl- Δ^8 -hexenyl)benzoquinone. (I), has 1 active H (Zerevitinov) and when boiled with Ac_2O , NaOAc, and Zn yields triacetyl-leucoperezone (II), $C_{21}H_{28}O_6$, b.p. 176—178°/0.2 mm., $[\alpha]_D^{20}$ —30.7° in EtOH, whilst when treated successively with $Na_2S_2O_4$ and Me_2SO_4 -KOH-MeOH it yields trimethyl-leucoperezone, b.p. 110°/0.01 mm. Hydroxyperezone (III) prepared by the method of Fichter (*loc. cit.*) is impure and contains some hydroxyperezone hydrate, m.p. 139° [contains 3 active H (Zerevitinov)], H_2O having been added across the ethylenic linking in the side-chain. An Et_2O solution of (I) when hydrogenated (Adams-Schriner) and then shaken with air yields dihydro-perezone (IV), m.p. 95°, but if treated with CH_2N_2 immediately after hydrogenation yields dihydro-perezone Me_1 ether, b.p. 150°/0.01 mm. (IV) when heated (water-bath) with NH_2Ph and EtOH affords anilino-dihydro-perezone, $C_{21}H_{27}O_3N$, m.p. 139°, which when heated (water-bath) with H_2SO_4 -AcOH yields hydroxy-dihydro-perezone, m.p. 143—144°, $[\alpha]_D^{20}$ —30° in Et_2O . This when boiled with Ac_2O , NaOAc, and a little Zn

yields the Ac_4 derivative, m.p. 134°, $[\alpha]_D^{20}$ —46.6° in $COMe_2$, of hydroxydihydroleucoperezone (V), and when treated successively with $Na_2S_2O_4$ and Me_2SO_4 -KOH-MeOH yields the Me_4 ether, b.p. 120°/0.01 mm., $[\alpha]_D^{20}$ —31.7° in EtOH, of (V). Perezinone (A., 1885, 777) prepared from (III) has 1 active H (Zerevitinov), and is considered to be 2-hydroxy-3 : 8-dimethyl-5-isopropenyl-5 : 6 : 7 : 8-tetrahydro-1 : 4-naphthaquinone. (I) and (IV) do not undergo a similar reaction, as they do not contain respectively the suitably situated OH or the ethylenic linking. Oxidation of (I) and (II) by H_2O_2 affords AcOH and an unsaturated C_9 carboxylic acid, hydrogenated to a nonoic acid, also obtained by oxidation of (IV) and shown, when completely racemised, to be α -dimethyl-heptioic acid (VI) (A., 1929, 296). This acid was synthesised from isohexyl bromide and $CHMeNa(CO_2Et)_2$ through Et_3 methylisohexylmalonate, b.p. 145°/14 mm., hydrolysed to the acid, m.p. 114—115°, which by loss of CO_2 affords (VI). This is resolved by means of the cinchonidine salt, from which the l-acid, $[\alpha]_D^{20}$ —17.5° (l-amide, m.p. 75—77°, $[\alpha]_D^{20}$ —18.1° in EtOH), is obtained. (II) on ozonolysis gives $COMe_2$ but no other volatile aldehydes or ketones, showing the presence of $COMe_2$ in (II). Distillation of (I) with Zn yields a hydrocarbon which is oxidised to p - $C_6H_4(CO_2H)_2$ by H_2SO_4 - CrO_3 - H_2O , showing that the side-chains in (I) are in the *p*-positions.
H. G. M.

Lichen acids. VI. Constituents of Ramalina scopulorum. F. H. CURD and A. ROBERTSON (J.C.S., 1935, 1379—1381).—From *R. scopulorum*, d-usnic acid and Zöpf's scopularic acid (I) have been isolated; the latter is identical with stictic acid (II) (Asahina *et al.*, A., 1933, 1050). The dianil, m.p. 234°, of (II) may be obtained from (II) and from (I), and differs from the monoanil and distictic acid anilide. (II) and KOH yield stictinic acid, m.p. 223—224°, by opening of the lactone ring, and (II) is methylated by MeI - Ag_2CO_3 to a Me ether, m.p. 174°, and by MeI - Ag_2O to an isomeric Me ether, m.p. 242—243°.
F. R. S.

Condensation of balata bromide with phenols and phenolic ethers. T. HARDIE and J. MAIR (J.C.S., 1935, 1242—1244).—Balata bromide when heated at 100—120° for 2.5 hr. with anhyd. $FeCl_3$ and PhOH affords *p*-dihydroxydiphenylhydrobalata, $[C_5H_8(C_6H_4 \cdot OH)_2]_n$, m.p. 195—200° (shrinks at 130°; di-*p*-nitrobenzoate, m.p. 87—90°), oxidised by $KMnO_4$ in $COMe_2$ to complex resin acids and *p*-OH- C_6H_4 - CO_2H . This shows that condensation has occurred in the *p*-position. Similar compounds are obtained from *o*-cresol (m.p. 193—195°; di-*p*-nitrobenzoate, m.p. 190—192°), *m*-cresol [m.p. 165—169° (shrinks at 140°); di-*p*-nitrobenzoate, m.p. 146—148°], *p*-cresol (m.p. 167—169°; shows a colour change when its acid suspension is made alkaline; di-*p*-nitrobenzoate, m.p. 143—145°), resorcinol [(I), m.p. 220°; tetra-*p*-nitrobenzoate, m.p. 195—200°], α - $C_{10}H_7 \cdot OH$ (m.p. 190—195°; di-*p*-nitrobenzoate, m.p. 150—152°), anisole (m.p. 105—110°; gives fluorescent solution in EtOAc), phenetole (m.p. 125—130°; has fluorescent properties). *p*-Dimethoxy-, m.p. 195—197°, and *p*-diethoxy-diphenylhydrogutta-percha, m.p. 205—207°, are obtained from gutta-percha bromide by similar methods; both

give fluorescent solutions in EtOAc. (I) and the corresponding compounds of gutta-percha and caoutchouc show marked indicator properties, considered to be due to the presence of the compound obtained when resorcinol is heated at 110° with FeCl₃, although the indicator properties of this compound are less well-defined. None of the foregoing condensation products gives a depression of the f.p. of C₆H₆, and mol. wt. determinations (Rast) give variable results (cf. A., 1929, 321). H. G. M.

Jute lignin. VIII. Methylation of lignin.
IX. Acetylation of lignin. P. B. SARKAR (J. Indian Chem. Soc., 1935, 12, 542—546, 547—551).—VIII. Jute lignin (I) carefully isolated at a low temp. (cf. A., 1934, 1355) is insol. in alkali, gives 2.78% CH₂O, and has an OMe val. of 19.18% (cf. this vol., 978) [corresponding with 5 · OMe in (I) if its mol. wt. is 830], also obtained after (I) has been boiled with 28% H₂SO₄. These results show that the CH₂O₂ and · OMe have not been affected during isolation of (I) and that the · OMe is entirely present in ether form. After methylation of (I) an OMe val. of 34.51% is obtained corresponding with the presence of 5 free · OH in (I) in addition to 5 · OMe. In OMe determination (Zeisel) MeI first appears at the same temp. from (I) as from vanillin and vanillic acid, but at a lower temp. from methylated lignin. It is inferred that (I) contains OMe attached to the C₆H₆ nucleus and that the OH (subsequently methylated) are in the side-chain. Oxidation of methylated (I) by 5*N*-HNO₃ gave no anisic acid. (I) when boiled with 28% H₂SO₄ and subsequently methylated does not reduce Fehling's solution, although it will do so if the methylation is omitted. This confirms the view (cf. A., 1934, 1355) that the reducing action of ordinary lignin is due to 2 *o*-OH attached to the C₆ ring and formed by the hydrolysis of the CH₂O₂ when lignin is isolated in the ordinary way. It therefore contains no · CHO.

IX. Two successive treatments with Ac₂O-C₅H₅N of (I) isolated as described above gave a product (II) the AcOH content (26.45%) of which is in good agreement with that (28.85%) required for 5 · OH. Reducing lignin (III) [obtained when (I) is boiled with HCl or 28% H₂SO₄] when acetylated gives a product which has a higher AcOH content than (II) and does not reduce AgNO₃-NH₃-H₂O, in agreement with the view that the reducing action, when shown, is due to the presence of 2 *o*-OH (see above). Moreover (III), COMe₂, and P₂O₅ give a non-reducing compound insol. in alkalis (cf. Böeseken *et al.*, A., 1932, 860). The · OMe and CH₂O₂ in (I) are unaffected by acetylation. (I) is not hydrogenated (Pd), and therefore contains no ethylenic linking (cf. this vol., 214). The amounts of ICl and IBr absorbed by (I) are comparable with those absorbed by many saturated C₆H₆ compounds, and are not evidence for an ethylenic linking. Raw jute and HCl-lignin give CHI₃ with NaOH-I. The foregoing quant. results are considered to support the val. of 830 for the mol. wt. of (I).

H. G. M.

Lignin. X. Lignin ethyl ether and thioglycollic acid. G. A. BERG and B. HOLMBERG (Svensk Kem. Tidskr., 1935, 47, 257—265).—When lignin from pinewood is extracted by means of EtOH-HCl,

lignin Et ether (I) is obtained, which is supposed to react as ROEt + SH·CH₂·CO₂H (II) = RS·CH₂·CO₂H + EtOH. By heating with (II) CH₂Ph·OEt yields CH₂Ph·S·CH₂·CO₂H, CHPhMe·OEt yields *S*-α-phenyl-ethylthioglycollic acid, m.p. 63—65°, CH₂Ph·CH₂·OEt does not react, CHPh₂·OEt yields *S*-benzhydrylthioglycollic acid, m.p. 129—130°, CPh₃·OEt yields *S*-triphenylmethylthioglycollic acid, m.p. 163—165° (Et ester, m.p. 94—95°), (I) yields a brown powder containing > 1 mol. of (II); also H₂O [not replaced by (II)] is eliminated. (I) with (II) in the presence of HCl yields an amorphous compound, C₄₀H_{41.5}O_{9.4}(S·CH₂·CO₂H)_{5.3}. E. P.

Cerin and friedelin. II. Functional derivatives. N. L. DRAKE and S. A. SHRADER (J. Amer. Chem. Soc., 1935, 57, 1854—1856; cf. this vol., 1373).—The following derivatives confirm identification of friedelin as a ketone and cerin (modified prep.), m.p. 250—256° (acetate, m.p. 259—261°) as a OH-ketone. *Friedelin oxime*, m.p. 290—294° (hydrolysed by H₃PO₄-C₅H₁₁·OH; *acetate*, m.p. 237—239°; rearranged by PCl₅ in CHCl₃ to an unreactive substance, m.p. 316—318°), 2:4-dinitro-, m.p. 297—299° (decomp.), and *p*-nitro-phenylhydrazones, m.p. 277—279° (decomp.). *Cerin Me ether*, m.p. 265—270°, [α]_D²⁵₄₆₁ -58.9° in CHCl₃ [*oxime*, m.p. 258—262°; 2:4-dinitro-phenylhydrazones, m.p. 284—285° (decomp.)], 2:4-dinitrophenylhydrazones, m.p. 253—255° (decomp.), *oxime*, m.p. 266—272°, H₂-derivative, *cerinol*, m.p. 293—295°, [α]_D²⁵₄₆₁ +9.4° (Ac₂ derivative, m.p. 267—269°).

R. S. C.

Determination of urushiol in lacquer. VII. Structure of the substance produced from urushiol by oxidation or polymerisation. S. HIRANO (J. Soc. Chem. Ind., Japan, 1935, 38, 445—447b).—A structure derived from 2:5:8:11-tetrahydroxy-3:4:9:10-perylenediquinone is proposed for the polymerisation and oxidation product of urushiol (cf. Majima, "Untersuchungen über den Japanlack," 1924, 108). H. G. M.

Toad poisons. VII. Bufo arenarum, Bufo regularis, and Xenopus laevis. H. JENSEN (J. Amer. Chem. Soc., 1935, 57, 1765—1768; cf. A., 1934, 412).—The secretion of *B. arenarum* yields arenobufagin (I), arenobufotoxin, bufotionine, and adrenaline (II); that of *B. regularis* yields regularobufagin (III), C₂₅H₃₄O₆, m.p. 235—236°, *regularobufotoxin*, C₃₉H₆₀O₁₁N₄, m.p. 205° after softening at 190°, (II), and regularobufotenine, C₁₁H₁₂O₂N₂ [flavinate, m.p. 264° (decomp.)], picrate, +H₂O, m.p. 203—204°; identical with that obtained from *B. valliceps* (A., 1934, 1232)]; that of *X. laevis* yields cholesterol, fatty acids, and bufotenidine, C₁₃H₁₈ON₂ (flavinate, +H₂O, m.p. 200°; picrate, m.p. 197°; *hydriodide*, m.p. 208—209°). (I) with hot *N*-NaOH-EtOH gives AcOH and *arenobufaginic acid*, C₂₃H₃₄O₆, m.p. 220—235°, and with CrO₃ *arenobufagone*, C₂₅H₃₂O₆, m.p. 219—220°, but its *Ac* derivative (prep. by hot Ac₂O), m.p. 162—163°, is stable to CrO₃. (III) gives similarly *regularobufagone*, C₂₅H₃₂O₆, m.p. 210—211°, and with alkali *regularobufaginic acid*, C₂₃H₃₄O₆, decomp. from 125°, and AcOH, but with Ac₂O loses AcOH to give a substance, C₂₅H₃₂O₅, m.p. 224—225°, which does not give a ketone with CrO₃. (I) and (III) are thus *Ac* deriv-

atives of a doubly unsaturated lactone, $C_{23}H_{39}O_2(OH)_3$, of which one OH (that accessible to Ac_2O) is *sec.* and one is *tert.* and carries the Ac. Both probably have sterol structure. R. S. C.

Bongkreki acid.—See this vol., 1540.

Constitution of cuscutelein.—See this vol., 1550.

Bitter principle from *Andrographis paniculata*.—See this vol., 1549.

Isolation of pyrethrin.—See this vol., 1550.

Derivatives of vitamin-E.—See this vol., 1546.

Volatile terpenes as acid hydrolysis products of saponins. K. LEUPIN (Schweiz. Apoth.-Ztg., 1934, 72, 755—756; Chem. Zentr., 1935, i, 2018—2019).—Steam-distillation of *Tilia* saponin and Merck's *Sapindus* saponin affords volatile terpenes as hydrolysis products; these were identified by their odour and by various colour reactions. A little $PrCO_2H$ (?) was present in the distillate. H. N. R.

Anomalous mutarotation of salts of Reyckler's acid. III. Reduction of ketimines of *d*-camphor-10-sulphonic acid. Formation of *sultams*. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1896—1898; cf. this vol., 1246).—*d*-Camphoranil-10-sulphonic acid with H_2 -PtO₂ in MeOH gives α - (I), m.p. 300—302° (block), $[\alpha] -88.5^\circ$, and β -2-anilino-camphor-10-sulphonic acid (II), m.p. 350—351°, $[\alpha] +8.5^\circ$ in $CHCl_3$ -MeOH. With $PhSO_2Cl$ or Ac_2O at 100° (I) gives the *sultam* (III), m.p. 172—173°, but the isomeric *sultam*, m.p. 137—138°, $[\alpha] +140.5^\circ$ in $CHCl_3$, is obtained from (II) only by $PhSO_2Cl$ - C_5H_5N at 100°. Both are hydrolysed by conc. HCl, the second more easily, to regenerate the parent acids. R. S. C.

Neutral salt action in non-aqueous solution.—See this vol., 1461.

Constitution of cedrene. R. ROBINSON and J. WALKER (Chem. and Ind., 1935, 906—907, 946—947).—Contrary to Treibs (this vol., 983) and Short (*ibid.*, 1376) the most probable structure of cedrene is as annexed. F. R. G.

Reactions of β -ketonic esters containing the furan nucleus. A. MIRONESCO and G. IOANID (Bull. Soc. Chim. România, 1935, 17, 107—129).—Condensation of the Mg compound of CH_2Cl - CO_2Et with furoyl chloride in Et_2O affords Et furoylacetate (I) [*amide* (II), m.p. 159°], also obtained (70% yield) by hydrolysis ($NaOEt$ - NH_4Cl -20% aq. NH_3 at 40°) of Et furoylacetylacetate, b.p. 167°/17 mm., obtained by condensation of CH_2Ac - CO_2Et and C_4H_3O - $COCl$ with Na in Et_2O . By the action of the appropriate alkyl halide on the Na derivative of (I) are obtained Et α -furoyl-propionate, b.p. 143°/11 mm. (*amide*, m.p. 183°), -isobutyrate, (III) b.p. 150°/20 mm. (*amide*, m.p. 164°), -butyrate, b.p. 148°/14 mm. (*amide*, m.p. 188°), - α -ethylbutyrate (IV), b.p. 177/25 mm. (*amide*, m.p. 164°), and - α -methylbutyrate (*amide*, m.p. 164°), and, with $(\cdot CH_2Br)_2$, Et 2-furoylcyclopropane-1-carboxylate (V), b.p. 148—149°/16 mm. [*amide*, m.p. 162°, prepared from (II)]. By hydrolysis

(HCl) of these esters or amides are obtained furoyl Et (VI) (*semicarbazone*, m.p. 189°), Pr^a , b.p. 96°/20 mm. (*semicarbazone*, m.p. 90°), Pr^b , b.p. 67°/33 mm., Bu^b , b.p. 96°/16 mm. (*semicarbazone*, m.p. 174°), α -ethyl-n-propyl, b.p. 97°/17 mm. (*semicarbazone*, m.p. 162°), and cyclopropyl, b.p. 75°/23 mm. (*semicarbazone*, m.p. 167°), *ketone*. With $MgRX$ compounds of the type C_4H_3O - CO - CHR - CO_2Et ($R=H$ or alkyl) regenerate the parent β -keto-ester when the product is hydrolysed, but (V) affords Et 1-(α -hydroxy- α -ethylfurfuryl)- (Bz derivative, b.p. 161°/12 mm.) and 1-(α -hydroxy- α -phenylfurfuryl)-, b.p. 180°/18 mm., -cyclopropane-1-carboxylate. With $MgEtBr$ (III) affords Et β -hydroxy- β -furyl- α -dimethyl-n-valerate, b.p. 160°/16 mm., together with unchanged (III), Pr^aCO_2Et , (VI), and the alcohol obtained from (VI) and $MgEtBr$. With $MgPhBr$ the ester group of (III) is attacked to give 2-furyl (β -hydroxy- β -diphenyl- α -dimethyl)ethyl *ketone*, b.p. 181°/12 mm. With $MgEtBr$ or $MgPhBr$ (IV) undergoes scission to give, respectively, 2-furyl-diethyl-, b.p. 84°/17 mm., and -diphenyl-, m.p. 90°, -carbinol. J. W. B.

Synthesis of hexahydro- α -coumaranone. R. GHOSH (J. Indian Chem. Soc., 1935, 12, 601—603).—Et cyclohexanone-2-carboxylate, Na, and CH_2Cl - CO_2Et in C_6H_6 give Et₂ cyclohexanone-2-carboxylate-2-acetate, b.p. 161—162°/5 mm., hydrolysed by hot 25% HCl to cyclohexanone-2-acetic acid, b.p. 169—170°/7 mm. [*semicarbazone*, m.p. 199—200°; Et ester, b.p. 130°/10 mm. (*semicarbazone*, m.p. 196°)], which is reduced by 30% Na-Hg to hexahydrocoumaranone, identical with that obtained from Δ^1 -cyclohexeneacetic acid. R. S. C.

Synthesis of coumarins from phenols and β -ketonic esters. III. Use of various condensing agents. D. CHAKRAVARTI (J. Indian Chem. Soc., 1935, 12, 536—539).—Except in the case of β - $C_{10}H_7$ -OH and CH_2Ac - CO_2Et (I) which give a coumarin and a chromone (A., 1932, 858), a phenol and a β -ketonic acid, when they condense, give a coumarin whatever the condensing agent used. Thus 7-hydroxy-4-methylcoumarin is formed from resorcinol and (I) when H_3PO_4 , $NaOAc$, $NaOEt$, or B_2O_3 is used, the best yield being with H_3PO_4 . Other examples are given. Et 5-hydroxy-4:7-dimethylcoumarin-3-acetate, m.p. 198—200°, is obtained from orcinol, CO_2Et - $CHAc$ - CH_2 - CO_2Et (II), and H_2SO_4 , P_2O_5 , or H_3PO_4 , and Et 7:8-dihydroxy-4-methylcoumarin-3-acetate, m.p. 186°, is obtained from pyrogallol, (II), and H_2SO_4 . H_3PO_4 is a better condensing agent for Pechmann's and for Bülow's reactions than is the usual agent. H. G. M.

Synthesis of coumarins from phenols and β -ketonic esters. IV. Coumarins from 4-chloro- and 2-nitro-resorcinol. D. CHAKRAVARTI and B. GHOSH (J. Indian Chem. Soc., 1935, 12, 622—626; cf. A., 1932, 1257).—4-Chlororesorcinol readily gives coumarins by H_2SO_4 or P_2O_5 . 2-Nitroresorcinol gives 60 and 15% yields of coumarins with CH_2Ac - CO_2Et and $CHMeAc$ - CO_2Et , respectively, with H_2SO_4 , but does not condense with the Et-, Pr^a -, or Pr^b -substituted esters; P_2O_5 gives intractable resins. The following coumarin derivatives are described: 6-Cl-7-OH-, m.p. 271° (Ac derivative,

m.p. 166°); 6-*Cl*-7-*OH*-4-*Me*-, m.p. 280° (*Ac* derivative, m.p. 168°); 8-*NO*₂-7-*OH*-4-*Me*-, m.p. 256° (decomp.) [*Ac* derivative, m.p. 198° (lit. 165°)]; 8-*NO*₂-7-*OH*-3:4-*Me*₂-, m.p. 260° (decomp.) (*Ac* derivative, m.p. 246°); 6-*Cl*-7-*OH*-3:4-*Me*₂-, m.p. 248° (*Ac* derivative, m.p. 170—171°); 6-*Cl*-7-*OH*-4-*Me*-3-*Et*-, m.p. 257—258° (*Ac* derivative, m.p. 145°); 6-*Cl*-7-*OH*-4-*Me*-3-*Pr*ⁿ-, m.p. 230° (*Ac* derivative, m.p. 135°); 6-*Cl*-7-*OH*-4-*Me*-3-*Bu*ⁿ-, m.p. 199°; 6-*Cl*-7-*OH*-3-*CH*₂*Ph*-4-*Me*-, m.p. 249°; 3:6-*Cl*₂-7-*OH*-4-*Me*-, m.p. 254° (*Ac* derivative, m.p. 192°); 6-*Cl*-7-*OH*-4-*Ph*-, m.p. 258—260°; 6-chloro-7-hydroxycoumarin-4-acetic acid, m.p. 210°, and *Et* 6-chloro-7-hydroxy-4-methylcoumarin-3-acetate, m.p. 174°

R. S. C.

Triarylpyrylium borofluorides. W. C. DOVEY and R. ROBINSON (J.C.S., 1935, 1389—1390).—COPhMe and BF₃ give 2:4:6-triphenylpyrylium borofluoride, m.p. 225—226°, also obtained in better yield from COPhMe and Ph styryl ketone; *p*-methoxyphenyl *p*-methoxystyryl ketone, *p*-methoxyacetophenone, and BF₃ afford 2:4:6-tri-*p*-methoxyphenylpyrylium borofluoride, m.p. 345—347°. F. R. S.

Constitution of the dihydroxy-derivative of diphenylene oxide obtained from resorcinol. K. HATA, K. TATEMATSU, and B. KUBOTA (Bull. Chem. Soc. Japan, 1935, 10, 425—432).—A substance (this vol., 220) obtained by passing resorcinol vapour over W₂O₃ at 500—550° is now proved to be 2:7-dihydroxydiphenylene oxide (I). *p*-Iodo-*m*-nitroanisole gives (Ullmann) 2:2'-dinitro-4:4'-dimethoxydiphenyl, m.p. 136—137°, reduced to 2:2'-diamino-4:4'-dimethoxydiphenyl, m.p. 110.5—111.0°; diazotisation and treatment with CuSO₄ solution affords 2:7-dimethoxydiphenylene oxide (II), m.p. 150°, together with 2:7-dimethoxyphenazone, m.p. 97°. Demethylation of (II) with HI gives (I), m.p. 241—241.5°. The absorption curves of diphenylene oxide, 2-hydroxydiphenylene oxide, and (I) are given.

P. G. C.

Bases prepared from pyrogallol ethers. (MME.) Y. DE LESTRANGE (Bull. Soc. chim., 1935, [v], 2, 1678—1684).—1:2:3-C₆H₃(OH)₃ heated with Et₂SO₄ and 10% Na₂CO₃ gives a mixture separated by fractionation into 1:2-dihydroxy-3- (I), m.p. 95.5° (*Ac* derivative, m.p. 75°), 1:3-dihydroxy-2- (II), m.p. 102° (*Ac* derivative, m.p. 77°), 2-hydroxy-1:3-di- (III), m.p. 90°, 3-hydroxy-1:2-di- (IV), b.p. 120°/11 mm., -ethoxybenzene. (I) and (II) with glyceryl α,β-dichlorohydrin give, respectively, a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-hydroxymethylbenzdioxan (V), b.p. 190—193°/13 mm., and 2:6-bis-γ-chloro-β-hydroxypropoxyphenol. (V) with SOCl₂ in C₅H₅N yields a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-chloromethylbenzdioxan, b.p. 173°/13 mm., which when heated in a sealed tube with NHEt₃ gives a mixture of 8-ethoxy-2- or -3- and 8-ethoxy-3- or -2-diethylaminomethylbenzdioxan, b.p. 188—190°/14 mm. (hydrochlorides, m.p. 228° and 140°). Similarly are prepared: mixtures of 8-methoxy-2- and -3-hydroxy-, b.p. 193°/12 mm., and -chloro-, b.p. 167°/10 mm., -diethylamino-methylbenzdioxan, b.p. 172—175°/10 mm. (hydrochlorides, m.p. 197° and ?). (III) and (IV) with epichlorohydrin give 2-epoxy-1:3-, b.p.

172°/12 mm., and 3-epoxy-1:2-diethoxybenzene, b.p. 172°/12 mm. These when heated (sealed) with NHEt₃ give 2-γ-diethylamino-β-hydroxypropoxy-1:3-, b.p. 198°/13 mm. (hydrochloride, m.p. 112—113°), and 3-γ-diethylamino-β-hydroxypropoxy-1:2-diethoxybenzene, b.p. 198°/13 mm. (hydrochloride, m.p. 78—80°). (III) and (IV) heated with NEt₂·CH₂·CH₂Cl and Na in EtOH yield, respectively, 2-diethylaminoethoxy-1:3-, m.p. 134—135°, and 3-diethylaminoethoxy-1:2-diethoxybenzene hydrochloride, m.p. 112—113° (free base, b.p. 180°/14 mm.). The colours given by (I), (II), (III), and (IV) with FeCl₃, NiSO₄, CoSO₄ and diazotised bases are described. F. R. G.

Pyrolysis. Elimination of two hydroxyl groups from a glycol. A. SCHÖMBERG and R. MICHAELIS (J.C.S., 1935, 1403—1404).—1:4-Bis(diphenylmethylene-Δ^{2:5}-cyclohexadiene with HNO₃ gives ωωω'ω'-tetraphenyl-*p*-xylylene glycol, a reaction analogous to the conversion of chromanorufen (I) into 5:12-dihydroxychromanorufan (II) (cf. Liebermann *et al.*, A., 1934, 531), which is easily reconverted by heat or AcOH into (I). (II) and NPhMe₂ give 5:12-bis-*p*-dimethylaminophenylchromanorufan, decomp. 340°, not obtained directly from (I).

F. R. S.

Bromonitrothiophen. V. S. BABASIAN (J. Amer. Chem. Soc., 1935, 57, 1763—1764).—2-Bromothiophen with HNO₃-AcOH in Ac₂O gives 2-bromo(?-5)-nitrothiophen, m.p. 45—46°, b.p. 235—237°/750 mm. Other nitrating agents cause oxidation; *e.g.*, pure HNO₃ gives H₂SO₄.

R. S. C.

[3-Aminopyridine.] A. BINZ and O. VON SCHICKH (Ber., 1935, 68, [B], 1989; cf. this vol., 498).—A correction.

H. W.

Synthesis of β-bromonicotdiethylamide. T. UGAI and S. IZUMI (J. Pharm. Soc. Japan, 1935, 55, 13—14).—3-Bromoquinoline (modified prep.) is oxidised (KMnO₄) to 5-bromopyridine-2:3-dicarboxylic acid, m.p. 165° [anhydride (I), m.p. 134—136°]. (I) and NHEt₃ yield β-bromonicotdiethylamide, b.p. 160°/4 mm., which is without action on the extirpated frog's heart.

CH. ABS. (r)

Synthesis of pyridine derivatives of barbituric acid. C. S. KUHN and G. H. RICHTER (J. Amer. Chem. Soc., 1935, 57, 1927—1929).—β-Picolyl bromide [from β-picoline and Br (2 mols.) in conc. HCl at 150°] with Et₂ alkylmalonates (I) give esters, which with CO(NH₂)₂ and NaOEt at 100° yield 5-β-picolyl-5-ethyl-, m.p. 213—214°, -*n*-propyl-, m.p. 250° (decomp.), -*n*-butyl-, m.p. 218—219°, and -isoamyl-barbituric acid, m.p. 229—230°. 2-Bromopyridine does not react with (I).

R. S. C.

2-Pyridylethylmalonic acid. L. A. WALTER and S. M. McELVAIN (J. Amer. Chem. Soc., 1935, 57, 1891—1892).—CETNa(CO₂Et)₂ and 2-bromopyridine in EtOH give 2-ethoxypyridine (I), b.p. 66°/25 mm., 160—161°/760 mm. [HgCl₂-derivative, m.p. 152—153° (lit. 141°); hydrochloride, m.p. 90—91°]; without EtOH there are formed a little (I), CET₂(CO₂Et)₂, Et α-2-pyridylbutyrate, b.p. 97—98°/2 mm., and Et₂-2-pyridylethylmalonate (19%), b.p. 136—137°/2 mm. The last ester does not give a barbituric acid derivative, as it is extremely easily cleaved. With

$\text{CO}(\text{NH}_2)_2$ it yields α -2-pyridylbutyramide, m.p. 125—126°.

R. S. C.

Arylated pyridines. IX. W. DILTHEY and H. DIERICH (J. pr. Chem., 1935, [ii], 144, 1—31; cf. A., 1926, 1254).—2:4:6-Triphenylpyrylium perchlorate (A., 1916, i, 829) heated with NH_2Ph or its appropriate derivative yields the following perchlorates; 1:2:4:6-tetraphenylpyridinium, m.p. 260°; 1-p-tolyl-, m.p. 243—244° [compound with $\text{NH}_2\text{OH} (+\text{H}_2\text{O})$, m.p. 163°]; 1-o-tolyl-, m.p. 254—255°; p-phenetyl-, m.p. 274°; o-anisyl-, m.p. 242—243°; p-anisyl-, m.p. 243° (iodide, m.p. 309—310°, compound with NH_2OH , m.p. 145—146°); 1-p-hydroxyphenyl-pyridinium (I), m.p. 245° [chloride, m.p. 380—381°; bromide, m.p. 382—383°; periodide, iodide, m.p. 340°; nitrate, m.p. 323—324° (decomp.); perhydroxide, m.p. 201° (decomp.); picrate, m.p. 214—215°; Ac derivative, m.p. 288° (periodide, m.p. 185°)]. (I) with KOH in MeOH yields a red base, m.p. 197—198°, $[\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{CPh}:\text{CH}:\text{CPh}:\text{CH}:\text{CPh}:\text{CPh}]$
 $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{N}(\text{C}_6\text{H}_4\text{OH})\text{CPh} \end{array} \text{CH} \text{OH}^-$ (anhydro-base; perchlorate, m.p. 225°, picrate, m.p. 240°; nitrate, m.p. 222—223°; chloride, m.p. 214—215°; bromide, m.p. 225—228°; iodide, m.p. 229°).

F. R. G.

Indoles and isatogens. XIX. Transformation of o-aminated tolans or stilbenes into derivatives of indole or indoline. P. RUGGLI and O. SCHMID (Helv. Chim. Acta, 1935, 18, 1215—1228).—A further example of the formation of an indoline under the action of picric acid is recorded. Acetylation of 4:6-diamino-1:3-distyrylbenzene (I) appears to yield an Ac_4 derivative, m.p. 198.5—199°, as well as the Ac_1 and Ac_2 [picrate, m.p. 232° (decomp.)] derivatives. Treatment of (I) with picric acid in boiling EtOH affords resinous matter and 6-amino-2-phenyl-5-styrylindoline (II), m.p. 210—211° [picrate; oxalate, m.p. 272°; yellow-orange monohydrochloride, and (?) higher hydrochlorides], in 23% yield. The presence of 1NH_2 in (II) is established by the isolation of 6-benzylideneamino-2-phenyl-5-styrylindoline (III), m.p. 143° (corresponding o-chlorobenzylidene compound m.p. 173°), from which (II) is regenerated by AcOH. Cautious treatment of (II) with warm Ac_2O gives the Ac_2 derivative (IV), m.p. 242° (picrate, decomp. 272°; hydrochloride, m.p. 232—242°), whereas more drastic treatment appears to yield a Ac_3 compound. With $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ a di-p-toluenesulphonyl derivative, m.p. 250—251°, results. Attempts to prepare monoacyl compounds directly or by partial hydrolysis of diacyl compounds were unsuccessful. Cautious treatment of (II) with HNO_2 gives a compound, $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}_3$, the formation of which involves extensive decomp. Evidence against the possibility that (II) is an indole derivative is afforded by its strong basicity, the non-incidence of the pine-shaving reaction, and its inability to react with NaOEt and amyl nitrite. It is hydrogenated (Pd) to 6-amino-2-phenyl-5- β -phenylethylindoline, m.p. 163° (CHPh, m.p. 118°, and Ac, m.p. 220°, derivatives). [Under these conditions 2-phenylindole (V) is not hydrogenated to 2-phenylindoline (VI).] Stronger evidence is based on the production of (IV), since (V) is unchanged by boiling Ac_2O , whereas (VI) immediately affords

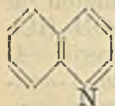
an Ac derivative, m.p. 129°. Further (V) does not react with EtI, whereas (VI) gives a cryst. ethiodide. (III) is converted into 6-benzylideneamino-2-phenyl-5-styryl-1-ethylindoline ethiodide, decomp. 251°, converted by dil. HCl into 6-amino-2-phenyl-5-styryl-1-ethylindoline ethiodide, m.p. 218°. Ring formation is not observed with the following substances: o-aminotolan, m.p. 89° (picrate, m.p. 85—90°, decomp. 95°), obtained by reduction of o-nitrotolan with SnCl_2 in HCl-AcOH at 40°; o-aminostilbene; cis- and trans-2:2'-diaminostilbene; Et o-aminocinnamate (picrate, decomp. 145°) obtained by reduction of $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ by SnCl_2 in AcOH-HCl, whereas H_2 and Ni afford dihydrocarbostyryl; 4-nitro-6-amino-1:3-distyrylbenzene; 6-amino-4-acetamido-1:3-distyrylbenzene, m.p. 218° [picrate, m.p. 225° (decomp.)]; corresponding Ac_2 derivative, m.p. 284°; 2:4:6-triamino-1:3-distyrylbenzene; 4:6-diamino-3-styryl-1-o'-aminostyrylbenzene. Catalytic reduction of 2:4-dinitrostilbene leads to 2:4-diaminostilbene, m.p. 115°, which gives an orange monopicrate, decomp. 134°, and red dipicrate, decomp. 160°, which are interconvertible and from which the original material is regenerated. Isomerisation in PhNO_2 at 140° gives a picrate, decomp. 250°, from which (II) and a substance $\text{C}_{15}\text{H}_{12}\text{N}_2$, m.p. 152°, are isolated.

H. W.

Indoles and isatogens. XX. Aminated double stilbenes. P. RUGGLI and O. SCHMID (Helv. Chim. Acta, 1935, 18, 1229—1239).—The following observations were made during attempts to extend the indole synthesis of Thiele and Dimroth to benzodipyrroles. Brown resins are obtained when 4:6-diamino-1:3-distyrylbenzene is heated with its hydrochloride (I) or $\text{NH}_2\text{Ph}\cdot\text{HCl}$. When heated with anhyd. Na_2CO_3 (I) yields small amounts of a substance, $\text{C}_{10}\text{H}_{13}\text{N}$, m.p. 218° (Ac, m.p. 178°, and CHPh, m.p. 174°, derivatives). The poor yields of o-nitrostilbene (II) from $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III) and PhCHO are not due to lack of reactivity of CH_2 , but to concurrent decarboxylation of (III) to $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$. $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ afford (II) in 10% yield. Catalytic hydrogenation of (II) readily involves the ethylenic linking, and reduction is best effected by SnCl_2 . 4:6-Diamino-1:3-di-m'-aminostyrylbenzene, m.p. 190—191°, is obtained by hydrogenation (Ni) of the $(\text{NO}_2)_4$ -compound (improved prep.). $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (improved prep. by hydrogenation of $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$) is converted by Ac_2O into $o\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 71°, which condenses with 4:6-dinitro-m-xylene in presence of piperidine at 130—120° to 4:6-dinitro-1-o'-acetamidostyryl-3-methylbenzene, m.p. 256°; the latter is hydrolysed by HCl in boiling AcOH to 4:6-dinitro-1-o'-aminostyryl-2-methylbenzene, m.p. 183°, catalytically reduced to 4:6:2'-triamino-3-methylstilbene, m.p. 152°, which gives a little indole when heated with its hydrochloride. 4:6-Dinitro-3-styryl-1-o'-acetamidostyrylbenzene, m.p. 267°, is hydrolysed to 4:6-dinitro-3-styryl-1-o'-aminostyrylbenzene, m.p. 193°, catalytically reduced to 4:6-diamino-3-styryl-1-o'-aminostyrylbenzene, m.p. 145°, which gives a little indole when heated with its hydrochloride. 4:6-Dinitro-3-m'-nitrostyryl-1-o'-acetamidostyrylbenzene, m.p. 270°, gives 4:6-dinitro-3-m'-

nitrostyryl-1-o''-aminostyrylbenzene, m.p. 249—250°, which could not be reduced satisfactorily to the tetra-amine. H. W.

Dipole moments and structures of some quinoline derivatives, and the orientation of Claus and Hofmann's α -nitroisoquinoline. (Mrs.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 1470—1475).—Calculation of dipole moments from measurement of mol. polarisations and refractivities at infinite dilutions of quinoline, 2- and 6-methyl-, 2:4-dimethyl-, 5-, 6-, and 8-nitro-quinoline, and *p*-toluquinoline, indicates that in quinoline derivatives, except α -Me compounds, the mobilities of the linkages are so diminished by ring fusion that the skeleton is best formulated as (I). The nitration product, m.p. 110°, of solid isoquinolinium nitrate or sulphate (Claus and Hofmann, A., 1893, i, 366) is most probably the 5-compound. F. R. S.



(I)

4-Hydroxy-2-methylquinoline and its derivatives. M. MAUREN (Ann. Chim., 1935, [xi], 4, 301—363).—The following derivatives of 4-hydroxy-2-methylquinoline are described: *sulphate*; 3-*tolueneazo*-derivative, m.p. 210°; *methosulphate*, m.p. 126°; *ethosulphate*, m.p. 120°; *phthalidene* derivative, m.p. >300°; *Ac*, m.p. 134°, and *Bz* derivative; *methiodide cyanine*, m.p. about 230°; *ethiodide*, m.p. 205° (4-dimethylaminobenzylidene, m.p. 230°, *vanillylidene*, m.p. 205°, *anisylidene*, m.p. 218—222°, and *cinnamylidene* derivative, m.p. 215°); *methiodide* (4-dimethylaminobenzylidene, m.p. 230°, and *vanillylidene* derivative, m.p. 165°); 4-*ethoxy*-2-methylquinoline, m.p. 37—40° (*hydrochloride*, m.p. 170°; *ethiodide*, m.p. 205°); *ethylquinolone*, m.p. 180—183°. 4-Methoxyquinoline (*ethobromide*, m.p. 201°) heated with Me_2SO_4 gives a 4-methoxy-2-methylquinoline *methosulphate*, (I), m.p. 201° [*methochloride*, m.p. 200°; *cyanine*, m.p. 245° (*hydroxide*, m.p. 165°)], which gives a violet colour with alkalis. Prolonged heating of methylquinolone with Me_2SO_4 in EtOH yields a second form of 4-methoxy-2-methylquinoline *methosulphate*, m.p. 201° (no colour with alkali). Two forms of the *methiodide* (II) (*cyanine*, m.p. about 235°) were also prepared and probable structures for these isomerides are given. (II) with the appropriate aldehydes or nitrosoamines yields the following derivatives: *anisylidene*, m.p. about 220°; *vanillylidene*, m.p. about 220°; *piperonylidene*, m.p. 220°; 4-dimethylaminophenylazomethine, m.p. 170°; 4-diethylaminophenylazomethine, m.p. 175°. (I) and HCl with the appropriate aldehyde yield the *vanillylidene*, m.p. 220°, and *piperonylidene*, m.p. 220°, *methochlorides*. F. R. G.

Attempts to find new antimalarials. XIV. Derivatives of 8-methylquinoline. W. O. KERMACK and T. W. WIGHT (J.C.S., 1935, 1421—1426).—6-Methoxy-8-methylquinoline (*hydrobromide*, m.p. 268°) is brominated to the 5-*Br*-compound (I), m.p. 116—117°. 4-Bromo-6-nitro-*m-cresol*, m.p. 146°, separated from a bromination mixture, is methylated to the -*m-tolyl Me ether*, m.p. 110—111°, reduced to 4-bromo-5-methoxy-*o-toluidine*, m.p. 79—80°. The base is converted (Skraup) into (I) and by diazotisation and CuBr into 4:6-dibromo-*m-tolyl Me ether*. A similar series of reactions on 6-bromo-4-nitro-*m-cresol* gives

6-bromo-4-nitro-*m-tolyl Me ether*, m.p. 113—115°, 2-bromo-5-methoxy-*p-toluidine*, m.p. 71—73°, and its *Ac* derivative, m.p. 130—133°. From a mixture of bromo-6-nitro-*m-cresols*, 7-bromo-6-methoxy-8-methylquinoline, m.p. 134—135°, is obtained. Bromination in $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ of 6-nitro-8-methylquinoline gives the 3-*Br*-compound, m.p. 188—189°. 8-Bromo-methylquinoline and H_2SO_4 yield 8-quinolylmethyl alcohol, m.p. 75—76°, and 5-nitro-8-quinolylmethyl alcohol, m.p. 148—149°, similarly obtained, with $\text{C}_5\text{H}_{11}\text{N}$ affords 5-nitro-8-piperidinomethylquinoline (*hydrobromide*, m.p. 248—249°).

o-Nitrobenzylethylamine and $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}\cdot\text{HCl}$ (II) condense to β -(*o*-nitrobenzylethylamino)triethylamino (*picrate*, m.p. 167—168°), reduced to the -amino-compound (*picrate*, m.p. 134°). (II) and the appropriate amine yield β -(benzylethylamino)triethylamine (*picrate*, m.p. 150—152°) and the -*p*-nitrobenzyl compound (*picrate*, m.p. 195—197°), β -diethylamino-ethyl-propylamine (*monopicrate*, m.p. 133—135°), -*n*-butylamine (*dipicrate*, m.p. 234°), and -isobutylamine (*dipicrate*, m.p. 141°), which with $\text{C}_5\text{H}_{11}\text{N}$ give β -piperidino-ethylpropylamine (*dipicrate*, m.p. 169°), -*n*-butylamine (*dipicrate*, m.p. 191—192°), -isobutylamine (*dipicrate*, m.p. 167—168°), -ethylmethylamine (*dipicrate*, m.p. 174°), and -diethylamine (*dipicrate*, m.p. 154°). $\text{C}_2\text{H}_4\text{Br}_2$ and NH_2Me afford *s*-dimethylethylenediamine (*picrate*, m.p. 160°). Condensation of 8-bromomethylquinoline with the appropriate amine gives the following: 8-(β -diethylamino-ethylmethylaminomethyl)-quinoline (*trihydrobromide*, m.p. 215—216°), -diethylaminomethyl)-(*trihydrobromide*, m.p. 218—219°, *picrate*, m.p. 131—132°) -ethylpropylaminomethyl) (*monopicrate*, m.p. 113—115°, *dipicrate*, m.p. 163—164°), -ethyl-*n*-butylaminomethyl) (*dipicrate*, m.p. 178—180°), and -ethylisobutylaminomethyl) (*dipicrate*, m.p. 169—171°); 8-(β -piperidino-ethylpropyl-aminomethyl)quinoline (*trihydrobromide*, m.p. 210°), -ethyl-*n*-butylamino- (*trihydrobromide*, m.p. 211—212°), -ethylisobutylamino- (*dipicrate*, m.p. 210—211°), -ethylmethylamino- (*dipicrate*, m.p. 205—206°) and -diethylamino- (*trihydrobromide*, m.p. 222°) and *s*-bis-(8-quinolylmethyl)dimethylethylenediamine *dihydrobromide*, m.p. 232°. Bis-(8-quinolylmethyl)- β -diethylaminoethylamine, m.p. 97—98°, 8-(β -diethylaminoethylaminomethyl)quinoline *trihydrobromide*, m.p. 223—224°, 1- β -bis-(8'-quinolylmethyl)aminoethylpiperidine, m.p. 97—98°, and 1:4-bis-(8'-quinolylmethyl)piperazine (+0.5 H_2O), m.p. 153—154°, are also described. F. R. S.

Dyes derived from acridic acid. M. P. GUPTA and S. DUTT (J. Indian Chem. Soc., 1935, 12, 581—584).—Acridic acid (quinoline-2:3-dicarboxylic acid) gives *dyes* of phthalein type with PhOH , m.p. 184°, resorcinol, m.p. 203° (*Br*₄-derivative, m.p. >290°), phloroglucinol, quinol, and orcinol, m.p. >280°, *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 280—285°, *m*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 168°, *m*- $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 120°, and *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 295°. They are more absorptive than the corresponding dyes from quinoline-2:3:4-tricarboxylic acid. R. S. C.

Phenanthridine series. IV. Synthesis of plasmquin-like derivatives. L. P. WALLS (J.C.S.,

1935, 1405—1410).—Phenanthridones have been prepared by oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7\text{--AcOH}$) of 9-methylphenanthridines and by the action of NaN_3 on a substituted fluorenone in H_2SO_4 , a method which gives a mixture of isomerides. The following have been obtained by the oxidation method: 9- and 9- ω -chloro-, 3-nitro-, m.p. $> 360^\circ$, and 3-bromo-phenanthridone, decomp. 302° (from 3-bromo-9-methylphenanthridine, m.p. $129.5\text{--}130^\circ$), which is converted by POBr_3 into 3:9-dibromophenanthridine, m.p. $170\text{--}171^\circ$. The following have been prepared from fluorenones: phenanthridone, 2(or 7)-nitro-, decomp. about 340° , 2(or 7)-chloro-7(or 2)-nitro-, m.p. 340° , 2:7-dinitro-, m.p. $> 340^\circ$, and 2(or 7)-amino-phenanthridone, m.p. about 285° (by reduction and also directly from the fluorenone). The mixture of OH-compounds, from the NH_2 -derivatives, may be separated by crystallisation to give 2-hydroxy-, m.p. $341\text{--}343^\circ$, -acetoxy-, m.p. $273\text{--}274^\circ$ (decomp.), and -methoxy-phenanthridone, m.p. 251° , and 9-chloro-2-methoxyphenanthridine, m.p. 137.5° , 7-hydroxy-, m.p. $320\text{--}322^\circ$ (decomp.), -acetoxy-, m.p. $261\text{--}264^\circ$ (decomp.), and -methoxy-phenanthridone, m.p. $271\text{--}272^\circ$, and 9-chloro-2-methoxyphenanthridine, m.p. 107° . $\text{NEt}_2\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{AcCO}_2\text{Et}$ give δ -amino- α -diethylaminopentane (I) (dipicrate, m.p. $134\text{--}135^\circ$), which with 9-chlorophenanthridine condenses to α -diethylamino- α -methylbutylamino-9-phenanthridine, isolated as the dipicrate, m.p. $196\text{--}197^\circ$, and converted into the sulphate. 3:9-Dibromophenanthridine with $\text{NEt}_2\text{CH}_2\text{CH}_2\text{NH}_2$ followed by HCl yield 3-bromo-9- β -diethylaminoethylaminophenanthridine dihydrochloride (dipicrate, decomp. about 156°) and with (I) affords 3-bromo-9- δ -diethylamino- α -methylbutylaminophenanthridine dihydrochloride (dipicrate, decomp. $217\text{--}218^\circ$). 9-Chloro-2-methoxyphenanthridine with $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ gives 9- β -diethylaminoethylamino-2-methoxyphenanthridine dihydrochloride [dipicrate, m.p. 207° (decomp.)], and with (I) the 9- δ -diethylamino- α -methylbutylamino-dihydrochloride (dipicrate, decomp. $192\text{--}193^\circ$). Although these nuclear-substituted meso-aminophenanthridines resemble quinoline and acridine antimalarials in type they possess no therapeutic val. F. R. S.

Manufacture of acridinium compounds.—See B., 1935, 1069.

Synthesis of glyoxaline derivatives. R. WEIDENHAGEN and R. HERRMANN (Ber., 1935, 68, [B], 1953—1961).—The synthesis of glyoxalines is more readily effected from $\alpha\beta$ -hydroxyketones or $\alpha\beta$ -hydroxyaldehydes than from $\alpha\beta$ -diketones. Treatment of these with Cu--NH_3 solution readily yields the ketones which in presence of an aldehyde are immediately condensed to the glyoxaline, usually pptd. at the Cu salt. The carbinols may be replaced by their acetates and sometimes by the corresponding Cl-compounds. The yields may attain 90%. Thus are obtained: 4(5)-phenylglyoxaline, m.p. $129\text{--}130^\circ$, from CH_2BzOH , CH_2O , $\text{Cu}(\text{OAc})_2$, and NH_3 ; 4(5)-phenyl-2-methylglyoxaline, m.p. $161\text{--}162^\circ$; 4(5)-phenyl-2-ethylglyoxaline, m.p. 133° (Cu salt); 4(5)-phenyl-2-isopropylglyoxaline, m.p. 180° (Cu salt); 2:4(5)-diphenylglyoxaline, m.p. 193° (Cu salt; hydrochloride monohydrate, m.p. 273°); 4(5)-2'-hydroxy-

phenylglyoxaline, m.p. 181° (Cu salt), from 2: ω -dihydroxyacetophenone, m.p. 65° ; 4(5)-2'-hydroxy-5'-methylphenylglyoxaline, m.p. $136\text{--}137^\circ$ (Cu salt), from 2-hydroxy-5-methylbenzoylcarbinol, m.p. $76\text{--}77^\circ$; 4(5)-p-methoxyphenylglyoxaline, m.p. 137° ; 4(5)-p-acetamidophenylglyoxaline, m.p. $250\text{--}251^\circ$ (Cu salt); 4(5)-p-aminophenylglyoxaline ($+0.5\text{H}_2\text{O}$), m.p. 97° (Cu salt); 4(5)-p-carboxyphenylglyoxaline, m.p. 308° [Cu salt; hydrochloride ($+1\text{H}_2\text{O}$), m.p. 338°]; 4(5)-methylglyoxaline from acetol acetate or COMeCH_2Cl ; 2:4(5)-dimethylglyoxaline; 4(5)-hydroxymethylglyoxaline from $\text{CO}(\text{CH}_2\text{OH})_2$; glyoxaline. H. W.

Acetanilidoalkylbarbituric acids [alkyl-5-barbiturylacetanilides]. J. A. TIMM (J. Amer. Chem. Soc., 1935, 57, 1943—1944).— $\text{NHPhCOCH}_2\text{Cl}$ (I) and 5-alkylbarbituric acids with NaOAc and KI (not NaOAc alone) in aq. EtOH give 5-ethyl-, m.p. $243\text{--}247^\circ$ (decomp.), -n-butyl-, m.p. $250\text{--}256^\circ$ (decomp.), -isobutyl-, m.p. $250\text{--}255^\circ$ (decomp.), -isomethyl-, m.p. $245\text{--}250^\circ$ (decomp.), and -allyl-5-barbiturylacetanilide, $\text{CO} < \begin{smallmatrix} \text{NHCO} \\ \text{NHCO} \end{smallmatrix} > \text{CRCH}_2\text{CO-NHPh}$, m.p. $237\text{--}242^\circ$ (decomp.). (I) and $\text{CNaEt}(\text{CO}_2\text{Et})_2$ in EtOH at 100° give only N,N' -diphenyldiketopiperazine and (?) $\text{OEtCH}_2\text{CO-NHPh}$. R. S. C.

Sulphur-containing barbiturate hypnotics. D. L. TABERN and E. H. VOLWILER (J. Amer. Chem. Soc., 1935, 57, 1961—1963).—Contrary to Johnson et al. (A., 1911, i, 502) Et_2 alkylmalonates, $\text{CS}(\text{NH}_2)_2$, and NaOEt--EtOH at $100\text{--}120^\circ$ give 5-ethyl-5-isopropyl-, m.p. 192° , -n-butyl-, m.p. $144\text{--}145^\circ$, -sec-butyl-, m.p. $163\text{--}165^\circ$, -allyl-, m.p. $172\text{--}173^\circ$, - β -methylallyl-, m.p. $160\text{--}161^\circ$, -isomethyl-, m.p. $167\text{--}169^\circ$, - α -methylbutyl-, m.p. $158\text{--}159^\circ$, -n-hexyl-, m.p. $136\text{--}137^\circ$, - β -ethylbutyl-, m.p. $137\text{--}138^\circ$, and - γ -chloro- Δ^8 -butenyl-, m.p. $128\text{--}130^\circ$, 5-cyclohexyl-5-ethyl-, m.p. $205\text{--}207^\circ$, 5-phenyl-5-ethyl-, m.p. $215\text{--}217^\circ$, 5-methyl-5- β -methylallyl-, m.p. $128\text{--}130^\circ$, 5:5-diallyl-, m.p. 134° , 5-allyl-5- β -methylallyl-, m.p. $180\text{--}182^\circ$, 5-sec-butyl-5-allyl-, m.p. $142\text{--}143^\circ$, 5- α -methylbutyl-5-allyl-, m.p. $127\text{--}129^\circ$, and 5-benzyl-5-allyl-2-thiobarbituric acid, m.p. $140\text{--}150^\circ$. When injected intravenously into rabbits, many of these are powerful hypnotics of very brief action with low toxicity. R. S. C.

5:5-Diphenylbarbituric acid, 5-phenyl-5-cyclohexylbarbituric acid, and 5-phenyl-5-cyclohexenylbarbituric acid. H. J. MORSMAN (Helv. Chim. Acta, 1935, 18, 1254—1264).— $\text{CPh}_2(\text{COCl})_2$ (I) in Et_2O is transformed by NH_3 into diphenylmalon-diamide, m.p. $243\text{--}244^\circ$ (corr.), which with COCl_2 in PhMe at 150° or with $(\text{COCl})_2$ in boiling C_6H_6 affords 5:5-diphenylbarbituric acid (II), m.p. $298\text{--}299^\circ$, also obtained from (I) and $\text{CO}(\text{NH}_2)_2$ at 100° or in boiling xylene. (II) is best prepared by the addition of 20% oleum to alloxan monohydrate in C_6H_6 at 20° , heating the mixture at $70\text{--}75^\circ$, and removing by-products by the successive action of dil. NaOH and KMnO_4 in alkaline solution. Treatment of (II) with excess of CH_2N_2 in Et_2O gives 5:5-diphenyl-1:3-dimethylbarbituric acid, m.p. $206\text{--}207^\circ$ (corr.), also obtained from (I) and $\text{CO}(\text{NHMe})_2$ in boiling xylene. 5-Phenylbarbituric acid is obtained from $\text{CHPh}(\text{CO-NH}_2)_2$ and $(\text{COCl})_2$ in C_6H_6 at 80° .

CHPh(CO₂Me)₂, cyclohexenyl bromide, and KOMe in C₆H₆ afford *Me₂ phenylcyclohexenylmalonate* (III), m.p. 79—80° (*by-product*, m.p. 204—205°), transformed by boiling KOH—MeOH into *phenylcyclohexenylacetic acid*, m.p. 123—123.5° (corresponding *amide*, m.p. 167—168°). (III) and CO(NH₂)₂ in MeOH containing NaOMe at 105—108° give *5-phenyl-5-cyclohexenylbarbituric acid* (IV), m.p. 209—210°, also obtained from K 5-phenylbarbiturate and cyclohexenyl bromide in dioxan. Hydrogenation of (III) by PtO₂ in MeOH affords *Me₂ phenylcyclohexylmalonate*, m.p. 89—90°, whereas interaction of CHPh(CO₂Et)₂ and cyclohexyl bromide yields unchanged material, CH₂Ph·CO₂Et, and (IV). Similar hydrogenation of (IV) gives *phenylcyclohexylbarbituric acid*, m.p. 256° (corr.). (II) is only a feeble narcotic. H. W.

Formation of "triacylacetic ester." II. F. SEIDEL, W. THIER, A. UBER, and J. DITTMER (Ber., 1935, 68, [B], 1913—1924; cf. A., 1932, 931).—Evidence of the formation of CAc₃·CO₂Et by the action of AcCl on Et sodioacetoacetate has been based on the formation of "Et 4-acetyl-3:5-dimethylpyrazole-4-carboxylate" (I) when the product is treated with N₂H₄. Since the substance when heated above its m.p. passes into β-5-hydroxy-3-methyl-4-pyrazolylcrotonolactone, m.p. 246°, and is hydrolysed by alkali to β-5-hydroxy-3-methyl-4-pyrazolylcrotonic acid, m.p. 154° (decomp.), it is now recognised as Et β-5-hydroxy-3-methyl-4-pyrazolylcrotonate (II). It arises from CHAc₂·CO₂Et, which loses Ac under the influence of N₂H₄; excess of N₂H₄ reacts with CH₂Ac·CO₂Et thus produced, yielding 3-methylpyrazol-5-one, which condenses with residual CH₂Ac·CO₂Et to (II). During unsuccessful attempts to prepare (I) synthetically, the following observations have been made. Et 3:5-dimethylpyrazole-4-carboxylate is converted by AcCl in C₅H₅N into *Et 1-acetyl-3:5-dimethylpyrazole-4-carboxylate*, m.p. 69°, in which the position of Ac is established by decarboxylation of the corresponding *acid*, m.p. 164°, to *1-acetyl-3:5-dimethylpyrazole*, b.p. 70°/12 mm., also obtained from 3:5-dimethylpyrrole (III) and AcCl in C₅H₅N or from NH₂·NHAc and CH₂Ac₂ in boiling EtOH. *1-Benzoyl-3:5-dimethylpyrazole*, b.p. 158°/12 mm., is derived from (III) and BzCl in C₅H₅N or from CH₂Ac₂ and NH₂·NHBz in boiling EtOH. N₂H₄·H₂O and CHAc₃ in H₂O afford *4-acetyl-3:5-dimethylpyrazole*, m.p. 128° [*monohydrate*, m.p. 121° (decomp.)], which with AcCl in C₅H₅N at 0° gives *1:4-diacetyl-3:5-dimethylpyrazole*, m.p. 50°. 3-Methylpyrazol-5-one, m.p. 270°, is obtained from N₂H₄·H₂O and Et isodehydracetate in boiling MeOH. *1-Phenyl-3-methylpyrazol-5-one*, CH₂Ac·CO₂Et, and NaOH in H₂O at 15—20° yield *Et β-5-hydroxy-1-phenyl-3-methyl-4-pyrazolylcrotonate*, m.p. 88°, which loses EtOH at 70° and forms *β-5-hydroxy-1-phenyl-3-methyl-4-pyrazolylcrotonolactone*, m.p. 132°. *β-5-Hydroxy-1-benzoyl-3-methyl-4-pyrazolylcrotonolactone* has m.p. 181°. H. W.

Piperazine. VI. Alkylation by means of aldehydes. W. T. FORSEE, jun., and C. B. POLLARD. VII. Procaine analogues. I. D. E. ADELSON, L. G. MACDOWELL, and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1788—1789, 1988—1989; cf. this

vol., 1253).—VI. Piperazine (I) and its *N*-Ph derivative are alkylated by CH₂O or MeCHO in Zn—HCl. H₂O-insol. aliphatic aldehydes rapidly effect alkylation in hot HCO₂H, but aromatic aldehydes require several days. The following derivatives of (I) are thus obtained: *N-Ph-N'-Me*, b.p. 109—100°/5 mm., *N-Ph-N'-Et*, b.p. 144—145°/10 mm., *NN'-Me₂*, b.p. 130—135° [*dihydrochloride*, m.p. 263° (decomp.)], *NN'-Et₂*, b.p. 174—177°, *NN'-Bu₂*, b.p. 195—195.5°/12 mm., *NN'-(CH₂Ph)₂*, m.p. 92—93° (also obtained from CH₂PhCl), and *NN'-di-p-methylbenzyl*, m.p. 101—102°.

VII. Anhyd. (I) and (CH₂)₂O in hot MeOH give a 98% yield of *NN'*-di-β-hydroxyethylpiperazine, m.p. 135—135.5°, the *di-p-nitrobenzoate*, m.p. 158—158.5°, of which is reduced (Fe) to the *di-p-amino-benzoate*, m.p. 203—204° (*tetrahydrochloride*, cryst., hygroscopic). R. S. C.

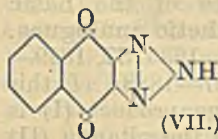
Naphthopyrazoles (benzindazoles). V. VESELY, A. MEDVEDEVA, and E. MÜLLER (Chem. Listy, 1935, 29, 259—263).—2:1-C₁₀H₆Me·NO₂ in C₂H₂Cl₄ and Cl₂ in presence of FeCl₃ at 40—50° yield *8-chloro-1-nitro-2-methylnaphthalene*, m.p. 114°, reduced by Fe in AcOH to *8-chloro-1-amino-2-methylnaphthalene*, m.p. 89° [*N-Ac derivative* (I), m.p. 214—215°], which, when diazotised and treated with NaOH, affords *8'-chloronaphtho-1':2':3:4-pyrazole*, m.p. 159° (*1-Ac derivative*, m.p. 196°), also obtained by treating (I) with HNO₂ in AcOH, and boiling a C₆H₆ solution of the *N*-NO-derivative so obtained. *4'-Nitro-*, m.p. 304—305° (*1-Ac derivative*, m.p. 196—197°), and *5'-bromo-naphtho-1':2':3:4-pyrazole*, m.p. 249—250° (*1-Ac derivative*, m.p. 168°), were prepared analogously. *1-Nitrosoacetamido-2-methylnaphthalene*, m.p. 82° (decomp.), affords *naphtho-1':2':3:4-pyrazole*, m.p. 158° (*picrate*, m.p. 193°; *1-Ac derivative*, m.p. 108—109°), when boiled in C₆H₆ for 4 hr., whilst *2-nitrosoacetamido-1-methylnaphthalene*, m.p. 91°, yields *naphtho-1':2':4:3-pyrazole*, m.p. 231° (*picrate*, m.p. 217—218°; *1-Ac derivative*, m.p. 116.5°), when similarly treated. R. T.

Comparison of heterocyclic ring systems with benzene. V. Benzotriazole (azimidobenzene) series. VI. Quinones of the quinoline and isoquinoline series. VII. Isologues of anthraquinone containing one and two triazole rings. L. F. FIESER and E. L. MARTIN (J. Amer. Chem. Soc., 1935, 57, 1835—1839, 1840—1844, 1844—1849; cf. this vol., 1377).—V. E₀, 0.672 volt, for K benzotriazole-4:5-quinone-7-sulphonate indicates that the aromaticity of the triazole ring is intermediate between that of thiophen and C₆H₆. Benzotriazole-quinones are difficult to prepare. *p*-NHAc·C₆H₄·OAc and HNO₃ (*d* 1.5) at 0—5° give *3-nitro-4-acetamidophenyl acetate*, m.p. 144—145°, hydrogenated (PtO₂) in hot EtOH to a little *2:2'-diacetamido-5:5'-acetoxyhydrazobenzene* (corresponding azo-compound, decomp. 280—285°) and 75% of *2-acetamido-5-acetoxyaniline* (I), m.p. 178—179°, which yields *3:4-diacetamidophenol*, m.p. 214—215° (lit. 205—207°), and its acetate, m.p. 187—188° (lit. 184—185°). (I) and HNO₂ give *5-acetoxy-1-acetylbenzotriazole*, m.p. 125—126°, hydrolysed by HCl to *5-hydroxybenzotriazole*, m.p. 234—235° (decomp.) [lit. 228° (decomp.)];

53% over-all yield from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$; hydrochloride, decomp. about 225° ; 4-p-, m.p. $224\text{--}225^\circ$, and 4-o-toluenazo-, m.p. $243\text{--}244^\circ$ (decomp.), NO_2 -, m.p. $262\text{--}263^\circ$ (lit. 236°), and NO - (II) -derivatives]. 4-Amino-5-hydroxybenztriazole, m.p. $216\text{--}217^\circ$ (decomp.), best (83%) obtained from (II) and aq. $\text{Na}_2\text{S}_2\text{O}_4$ (dihydrochloride, decomp. 225°), in dil. solution gives a quinone, which, however, cannot be isolated. (II) and NaHSO_3 , followed by H_2SO_4 at 40° , gives 4-amino-5-hydroxybenztriazole-7-sulphonic acid, cryst., which with $\text{Br}\cdot\text{H}_2\text{O}$ readily gives a quinone, which could not be isolated; the resultant solution, however, with SO_2 yields *K* 4:5-dihydroxybenztriazole-7-sulphonate, cryst. $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ with $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ in C_6H_6 yields $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, m.p. $92\text{--}93^\circ$, hydrogenated (PtO_2) in hot EtOH to $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ (III), m.p. $132\text{--}133^\circ$, a little 2:2'-diacetamidazo benzene, m.p. $270\text{--}271^\circ$, and 2-methylbenzimidazole. (III) leads to benztriazole, m.p. $98\text{--}99^\circ$ ($>90\%$ yield in each step; *Ac* derivative, m.p. $50\text{--}51^\circ$). Electrolytic reduction in conc. H_2SO_4 of 4-nitrobenztriazole and its 1-Me derivative, m.p. $181\text{--}182^\circ$ (lit. 173°), gives 4-amino-7-hydroxybenztriazole, decomp. about $225\text{--}230^\circ$, and -1-methyltriazole (sulphate; *Bz*₂ derivative, m.p. $262\text{--}263^\circ$), which do not give quinones, but similar reduction of 7-nitro-1-methylbenztriazole was unsuccessful.

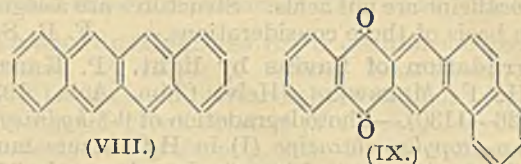
VI. The aromaticity of the quinoline and isoquinoline rings, as indicated by the E_0 of quinones, is about equal, but $<$ that of triazole or thiophen rings. The general validity of connecting E_0 and aromaticity of fused rings is discussed. Caution is necessary in interpreting the results. 5(?8)-Hydroxyisoquinoline (IV) (from the $\alpha\text{-SO}_3\text{H}$) gives a PhN_2 -compound, reduced by SnCl_2 to 8(?5)-amino-5(?8)-hydroxyisoquinoline dihydrochloride (V), cryst. Electrolytic reduction in H_2SO_4 of 5(?8)-nitroisoquinoline, m.p. $104\text{--}108^\circ$, gives 5(?8)-amino-8(?5)-hydroxyisoquinoline (VI) (sulphate; dihydrochloride; *Bz*₂ derivative, m.p. $223\text{--}224^\circ$), which with FeCl_3 gives 5:8-dihydroxyisoquinoline hydrochloride, darkens at about 260° , also obtained similarly from (V) and from (IV) by Fe-reduction of the NO -derivative. The Ac_2 derivative, m.p. $208\text{--}209^\circ$, of (VI) is partly hydrolysed by cold 0.4% NaOH and then couples affording 5(?8)-acetamido-8(?5)-hydroxy-7(?6)-p-sulphobenzeneazoisquinoline, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 7(?6)-amino-5(?8)-acetamido-8(?5)-hydroxyisoquinoline dihydrochloride, which with FeCl_3 affords 5(?8)-acetamidoisoquinoline-7:8(?5:6)-quinone hydrochloride.

VII. *lin*-Naphthatriazole-8:9-quinone (VII) is strongly acidic; its E_0 differs from that of its 1-Me derivative and (VII) may thus be as shown.



Naphthacene and "2:3-phthaloylphenanthrene" are probably (VIII) and (IX), respectively, on the theory that max. aromaticity must be achieved. Inability to give the vat test is connected with low E_0 rather than with absence of a true quinone ring, as in (IX). 3-Chloro-2-acetamidonaphthaquinone and NH_3 in boiling PhNO_2 give 3-amino-2-acetamido-1:4-naphthaquinone, m.p. $233\text{--}234^\circ$, which does not give a triazole owing to its sparing solubility. Reduction by

$\text{Na}_2\text{S}_2\text{O}_4$ to the corresponding $(\text{OH})_2$ -compound [*Ac*₂ derivative, m.p. 255° (decomp.)] allows reaction to form



(VII), decomp. $240\text{--}245^\circ$ (*N*-Me derivative, m.p. $248\text{--}250^\circ$). The Ac_2 derivative, m.p. $253\text{--}254^\circ$, of 3:6-dichloro-2:5-diaminoquinone (improved prep.; 75% yield) with $\text{NH}_3\text{--EtOH}$ gives 3:6-diamino-2:5-diacetamidobenzoquinone, converted (only in hot AcOH) into colourless bistriazolo-p-benzoquinone (X) (*Na* salt, $+\text{H}_2\text{O}$). The prep. of *K* 2:3-dihydroxynaphthalene-6-sulphonate, 2:3- $\text{C}_{10}\text{H}_6(\text{OH})_2$, and $-\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ is improved. Hydrogenation (PtO_2) of 2:5- $\text{C}_6\text{H}_3(\text{NHAc})_2\cdot\text{NO}_2$ in hot EtOH affords 2:5-diacetamidoaniline, m.p. $236\text{--}237^\circ$ (lit. $231\text{--}232^\circ$), converted into 5-aminobenztriazole and thence by way of the PhN_2 -compound into 4:5-diaminobenztriazole, the *Ac* derivative of which with HNO_2 gives 1:2:3:4-bistriazolobenzene, which did not yield a quinone. R. S. C.

Condensation of 4-aminotetrazole with carbonyl compounds. E. BUREŠ and F. BARŠI (Časopis českoslov. Lék., 1934, 14, 345–352; Chem. Zentr., 1935, i, 1867).—4-Aminotetrazole (I) and MeCHO yield 4-amino-1-methylmethenyltetrazole, $\text{C}(\text{NH}_2)\cdot\text{N}=\text{N}>\text{N:CMe}$, m.p. $164\text{--}165^\circ$. (I), with PhCHO and with cinnamaldehyde, similarly affords 4-amino-1-benzenyl-, m.p. 120° (decomp.) and -1-styrylcarbylamino-, m.p. $162\text{--}163^\circ$, -tetrazole, respectively; the last-named, with Br in CHCl_3 , yields 4-amino-1-dibromostyrylcarbylamino-tetrazole, m.p. $174\text{--}175^\circ$. (I) condenses with COMe_2 to yield 4-dimethylmethenyltetrazole, m.p. $187\text{--}188^\circ$. Aminoguanidine carbonate has m.p. 173° . H. N. R.

Rearrangement of allyl ethers in the purine series, with some remarks on the hydrogenation of allyl ethers. E. BERGMANN and H. HEIMHOLD (J.C.S., 1935, 1365–1367).—2:6-Dichloro-7-methylpurine (I) and Na allyloxide yield 2:6-diallyloxy-7-methylpurine, m.p. $111\text{--}112^\circ$, which on hydrogenation gives heteroxanthine, and on heating is isomerised to 1:3-diallyl-7-methylxanthine, m.p. $277\text{--}278^\circ$. (I) and Na in Δ^8 -hexen-8-ol, after heating, form 1:3-di-(α -methyl- Δ^8 -pentenyl)-7-methylxanthine, b.p. $215\text{--}225^\circ/12\text{ mm.}$, from which the products of ozonolysis are EtCO_2H and EtCHO . Ph allyl ether gives on hydrogenation PhOPr but 2:6-dipropoxy-7-methylpurine, m.p. 92° , is not affected by $\text{Pd}\text{--H}_2$. The isomerisation is due to migration of the allyl group from O to N. F. R. S.

Constitution of the purine nucleosides. III. Potentiometric determination of the dissociation constants of methylated xanthines. A. G. OGSTON (J.C.S., 1935, 1376–1379).—Measurements of dissociation consts. indicate that 3-, 7-, 9-methyl-, 1:3-, 1:7-, and 1:9-dimethyl-xanthines, and xanthosine

are "zwitterions," xanthine, 1-methyl- and 3:7-dimethylxanthines are normal acids, whilst caffeine and isocaffeine are not acids. Structures are assigned on the basis of these considerations. F. R. S.

Degradation of flavins by light. P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1935, 18, 1126—1130).—Photodegradation of 9- β -hydroxy- β -methyl-n-propylisalloxazine (I) in H₂O occurs much more slowly than that of lactoflavin, whereas in 75% MeOH the difference in the rates is less marked. Preliminary dehydrogenation of β -OH is not therefore essential to degradation, which can be initiated in some other unknown manner. NH₂·CH₂·CO₂Et is converted by MgMeI into aminotrimethylcarbinol, b.p. 53—57°/15 mm., which condenses with o-C₆H₄Cl·NO₂ in boiling C₅H₅N to o-nitro- β -hydroxy- β -methyl-n-propylaniline (I), m.p. 83°. (I) is hydrogenated (Pd-C in abs. EtOH) and the product is condensed with alloxan to (I), decomp. 285°. H. W.

Modified flavin synthesis. P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1935, 18, 1130—1134).—3:4-C₆H₃Me₂·NH₂ and l-arabinose in boiling MeOH-H₂O give 3:4-dimethylphenyl-l-arabamine, C₆H₃Me₂·NH·CH₂·[CH·OH]₃·CH₂·OH, m.p. 123°, which couples with p-NO₂·C₆H₄·N₂Cl in aq. acid solution to 6(?)·p-nitrobenzeneazo-3:4-dimethylphenyl-l-arabamine, reduced (Zn dust and AcOH or H₂-Ni-MeOH) to 9-l-1'-arabityl-6:7-dimethylisalloxazine, m.p. 299°. Similarly, 3:4-dimethylphenyl-d-ribamine, m.p. 143°, is converted into 9-d-1'-ribityl-6:7-dimethylisalloxazine, m.p. 280°. H. W.

Methylalloxazines. P. KARRER and C. MUSANTE (Helv. Chim. Acta, 1935, 18, 1134—1140).—The fluorescence colours of solutions of alloxazines in MeOH induced by ultra-violet light depend greatly on substituents in the mol. Introduction of Me progressively displaces the fluorescence from violet through blue, greenish-blue, and yellow to yellow-violet, whereby Me *ortho* to the azine ring has greater displacing influence than at 6 or 7. Ph behaves similarly. 6-Nitro-2:4:5-trimethylaniline is reduced (Pt in EtOH) to the corresponding diamine, which condenses with alloxan (I) to 5:7:8(? 5:6:8)-trimethylalloxazine, decomp. >290°. 2-Nitro-3:4:5-trimethylaniline similarly affords 6:7:8(? 5:6:7)-trimethylalloxazine, whilst 5:6-dinitro-1:2:3:4-tetramethylbenzene, m.p. 171°, is transformed into 5:6:7:8-tetramethylalloxazine, 2-Chloro-3-nitro-toluene and NH₂·CH₂·CH₂·OH in boiling C₅H₅N afford non-cryst. 3-nitro-2- β -hydroxyethylaminotoluene, reduced and then condensed with (I) to 8-methyl-9- β -hydroxyethylisalloxazine, m.p. 294°, degraded by sunlight to 8-methylalloxazine, 2:3-Diaminotoluene and (I) give 8(? 5)-methylalloxazine. H. W.

Synthetic flavins. P. KARRER, H. SALOMON, K. SCHÖPP, and F. BENZ (Helv. Chim. Acta, 1935, 18, 1143—1146).—Condensation of d-deoxyribose with 4-amino-5-carbethoxyamino-o-xylene in MeOH at 100° in presence of H₂/25 atm. and Ni affords 2-carbethoxyamino-4:5-dimethylphenyl-d-deoxyribamine, CO₂Et·NH·C₆H₃Me₂·NH·[CH₂]₂·[CH·OH]₂·CH₂·OH, m.p. 115°, [α]_D²⁰ +21°±2° in H₂O, which is transformed by alloxan into 6:7-dimethyl-9-d-1'-deoxyribityliso-

alloxazine, m.p. 283°, [α]_D²⁰ -78°±8° in 0.05N-NaOH. Similarly, d-ribose and o-NH₂·C₆H₄·NH·CO₂Et yield 2-carbethoxyaminophenyl-d-ribamine, m.p. 158°, [α]_D²⁰ ±0° in H₂O, hydrolysed and condensed to 9-d-1'-ribitylisoalloxazine, m.p. 283° (tetra-acetate, m.p. 237°). 2-Carbethoxyamino-5-methylphenyl-d-ribamine, m.p. 150°, [α]_D²⁰ -14.2°±2°, affords 7-methyl-9-d-1'-ribitylisoalloxazine, m.p. 285—286° (tetra-acetate, m.p. 215°).

H. W.

Optical activity of lactoflavin.—See this vol., 1521.

Formation of porphyrins from pyrrole and aldehydes. P. ROTHMUND (J. Amer. Chem. Soc., 1935, 57, 2010—2011).—Pyrrole and dry CH₂O or MeCHO in MeOH-Et₂O with or without catalysts give cryst. porphyrins. R. S. C.

Optical absorption of porphyrins.—See this vol., 1444.

Photochemical reaction of chlorophyll. E. BAUR (Helv. Chim. Acta, 1935, 18, 1157—1160).—A film of chlorophyll (I) in collodion when exposed to sunlight under air-free H₂O through which CO₂ is passed rapidly becomes yellow without apparent production of CH₂O. Similar films containing also methylene-blue (II) when exposed under H₂O through which O₂-free N₂ and CO₂, respectively, are passing slowly exhibit incomplete bleaching of (I) with pronounced formation of CH₂O, which is therefore produced from (I) and not from CO₂; the change cannot be accomplished from (I) without aid. (II) does not function as photosensitiser, but as redox agent, since it can be qualitatively replaced by Fe²⁺, Fe³⁺, or O. The course of the change is discussed. H. W.

Magnetic behaviour of porphyrin and porphyrindin.—See this vol., 1453.

Thiocarbonylsalicylamide (4-keto-2-thioketo-3:4-dihydro-1:3-benzoxazine). I. T. UGAI and M. HAYASHI (J. Pharm. Soc. Japan, 1935, 55, 8—12).—Salicylic acid and allylthiocarbimide yield thiocarbonylsalicylamide (I), C₈H₅O₂NS, m.p. 253°. Methylation of (I) with CH₃N₂ affords a substance, C₉H₇O₂NS, m.p. 163°, whilst with alkaline H₂O₂ (I) yields a substance, C₈H₅ON, m.p. 227°. Methylation of carbonylsalicylamide yields a substance, C₉H₇O₂N, m.p. 149°. CH. ABS. (r)

Crystalline vitamin-B₁. X. Sulphite cleavage. III. Basic product. E. R. BUCHMAN, R. R. WILLIAMS, and J. C. KERESZTESY. XI. Presence of quaternary nitrogen. R. R. WILLIAMS and A. E. RUEHLE. XII. Sulphur-containing moiety. H. T. CLARKE and S. GURIN. XIII. Ultra-violet absorption of some derivatives of the basic cleavage product and their synthetic analogues. A. E. RUEHLE (J. Amer. Chem. Soc., 1935, 57, 1849—1851, 1856—1860, 1876—1881, 1887—1888; cf. this vol., 1385).—X. The basic cleavage product (I) is probably C₄H₄NS·CH₂·CH₂·OH and the vitamin (II) a quaternary salt thereof. (I) [picrolonate, m.p. 184° (decomp.); platinichloride, m.p. 181° (decomp.); picrate, m.p. 162—163°; aurichloride, an oil; p-nitrobenzoate, m.p. 131°; methiodide (IV), cryst., very sensitive to alkalis (gives S'')] does not give the pine-

splinter reaction nor a colour with $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$, is stable to hot 20% NaOH, and does not give CHI_3 with NaOH-I. With HCl at 145° it affords the substance (III), $\text{C}_6\text{H}_5\text{NSCl}$ (hydrochloride), closely resembling it in ultra-violet absorption. With HNO_3 at 40° it gives Windaus' acid (V), $\text{C}_5\text{H}_5\text{O}_2\text{NS}$, decomp. $200\text{--}250^\circ$ (Me ester, m.p. 74°).

XI. Electrometric titration shows that (II) and (IV) have two basic centres, one very weak, the other not quite as strong as a true quaternary salt; two equivs. of alkali are required for complete liberation of these bases; after liberation of the strong basic centre slow rearrangement occurs to a much weaker base. (I) behaves as an ordinary weak base. 4-Methylthiazole ethiodide (VI) exactly resembles (II) and (IV), but 2:4-dimethylthiazole ethiodide behaves as a true quaternary salt. Previous speculation as to the nature of (II) is thus confirmed.

XII. (I), (III), and (V) are synthesised. The neutralisation of an extra mol. of alkali by (II) and (IV) is due to reversible opening of the thiazole ring; (VI) is similarly cleaved by alkali and its alkaline solution with air or I gives $\beta\text{-N-formethylaminoallyl disulphide}$, $[\text{HCO}\cdot\text{NEt}\cdot\text{CMe}\cdot\text{CHS}]_2$, m.p. $101\text{--}102^\circ$. The sulphite cleavage of (II) is a peculiarity due to the pyrimidine portion, since synthetic thiazolium salts are not thus cleaved. (I) is readily oxidised by $\text{Br}\cdot\text{H}_2\text{O}$ and reacts relatively slowly with $\text{Pb}(\text{ONa})_2$; with (II) the relative rates of reaction are reversed. Synthetic thiazoles and thiazolium salts show similar behaviour. The hydrochloride of (II) gives a resinous additive product with KI_2 , whence it is recovered by $\text{H}_2\text{O}\text{--Et}_2\text{O}$ with unimpaired activity. 4-Methylthiazole (VII) [modified prep. from $\text{HCS}\cdot\text{NH}_2$ and $\text{CH}_2\text{Cl}\cdot\text{COMe}$ (VIII)] [platinichloride, $\text{B}_2\text{H}_2\text{PtCl}_4$, m.p. 198°] gives (VI), m.p. $144\text{--}5^\circ$. 2:4-Dimethylthiazole (IX) (modified prep.) gives the ethiodide, m.p. 212° (decomp.). $\text{CHClAc}\cdot\text{CO}_2\text{Et}$ and $\text{HCS}\cdot\text{NH}_2$ in Et_2O at $0\text{--}5^\circ$ give Et 4-methylthiazole-5-carboxylate, m.p. 28° , b.p. $140^\circ/12\text{ mm.}$, which with NaOH-EtOH yields the corresponding acid, sublimes at 255° (Me ester, m.p. 75°), identical with (V). $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ and $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{Br}$ in EtOH give Et α -(β -ethoxyethyl)acetoacetate, b.p. $85\text{--}90^\circ/10\text{ mm.}$, which with SOCl_2 affords the α -Cl-ester, b.p. $115\text{--}118^\circ/12\text{ mm.}$ This with hot 15% H_2SO_4 and AcOH (1:1) gives Me α -chloro- γ -ethoxypropyl ketone, b.p. $72\text{--}73^\circ/12\text{ mm.}$, converted by $\text{HCS}\cdot\text{NH}_2$ into 4-methyl-5- β -ethoxyethylthiazole, b.p. 235° (decomp.) [platinichlorides, $\text{B}_2\text{H}_2\text{PtCl}_4$, m.p. $154\text{--}155^\circ$ (decomp.), and $\text{B}_2\text{H}_2\text{PtCl}_4$, m.p. $144\text{--}145^\circ$; picrate, m.p. 112°]. Conc HCl at 150° thence affords 4-methyl-5- β -chloroethylthiazole hydrochloride, m.p. $127\text{--}128^\circ$ (corresponding picrate, m.p. 139°), identical with (III), hydrolysed by H_2O at 150° to 4-methyl-5- β -hydroxyethylthiazole (hydrochloride; picrate, m.p. $162\text{--}163^\circ$), identical with (I). NPh- CSMe and (VIII) in EtOH give 3-phenyl-2:4-dimethylthiazolium platinichloride, m.p. 245° (decomp. from 240°), iodide, m.p. 210° , and chloride, an oil. (VIII) and $\text{HCS}\cdot\text{NPh}$ at 50° give 3-phenyl-4-methylthiazolium iodide, m.p. 241° .

XIII. The absorption spectra of (I), (VII), (IX), and 2-hydroxy-4-methylthiazole are very similar, as are those of (IV) and (VI). The identities of synthetic

and natural (I), (III), and (V) are confirmed by absorption spectra. (V) closely resembles (I), showing the small effect of replacement of OH by Cl. R. S. C.

Thiazole derivatives from ω -chloroacetylpyrocatechol. Z. HORII (J. Pharm. Soc. Japan, 1935, 55, 21—32).— ω -Chloroacetylpyrocatechol (I) and $\text{CS}(\text{NH}_2)_2$ (II) give 2-amino-4-(3':4'-dihydroxyphenyl)-thiazole hydrochloride, m.p. $235\text{--}236^\circ$. 2-Acetamido-, m.p. 268° , and 2-allylamino-, m.p. $208\text{--}209^\circ$, 4-(3':4'-dihydroxyphenyl)thiazole are similarly prepared from appropriately substituted (II). (I) and diphenylthiocarbamide afford 2-anilo-3-phenyl-4-(3':4'-dihydroxyphenyl)-2:3-thiazoline, m.p. $252\text{--}253^\circ$. The following are obtained from the appropriate disubstituted (II) and (I): 2-o-tolylimino-3-o-tolyl-, m.p. 130° ; 2-m-tolylimino-3-m-tolyl-, m.p. $226\text{--}227^\circ$; 2-p-tolylimino-3-p-tolyl-, m.p. 280° ; and 2-p-hydroxyanilo-3-p-hydroxyphenyl- (hydrochloride, m.p. $198\text{--}200^\circ$), 4-(3':4'-dihydroxyphenyl)-2:3-thiazoline. CH. ABS. (r)

Derivatives of o-thioldiphenylamine. W. J. EVANS and S. SMILES (J.C.S., 1935, 1263—1265).—2-o-Nitrophenyl-1-methylbenzthiazolium iodide (I) (this vol., 485) when boiled with $\text{CH}(\text{OEt})_3$, Ac_2O , and $\text{C}_5\text{H}_5\text{N}$ yields 2-2'-di-o-nitrophenylthiocarbonyl iodide, m.p. 269° (decomp.), whereby its structure as the salt of a pseudo-base is confirmed. 2-Nitro-2'-benzamidodiphenyl sulphide when boiled with COMe_2 and NaOH-EtOH is rearranged to a thiol, which with HI affords 1-phenyl-2-o-nitrophenylthiazolinium iodide, m.p. 195° . The thiol is regenerated by NaOH- H_2O and is methylated in alkaline solution (cf. *ibid.*, 615). Similarly 2-nitro-2'-cinnamidodiphenyl sulphide, m.p. 132° , is rearranged to a thiol, which on methylation yields 2-cinnamo-o-nitrophenylamidodiphenyl Me sulphide, m.p. $170\text{--}171^\circ$ (decomp. by warm HI into MeSH), and with HI yields 2-o-nitrophenyl-1-styrylthiazolinium iodide, m.p. 225° (decomp.). Rearrangement of 4-chloro-2-nitro-2'-acetamidodiphenyl sulphide (II) yields a thiol, which is rapidly converted into bis-2-aceto-p-chloro-o-nitrophenylamidodiphenyl disulphide, m.p. $187\text{--}188^\circ$, and when boiled with COMe_2 , EtOH, and NaOH yields 3-chlorothioldiphenylamine, m.p. 199° (also formed during the original rearrangement). 2:4-Dinitro-2'-acetamidodiphenyl sulphide (III) when boiled with COMe_2 and EtOH-NaOH yields 3-nitro-N-acetylthioldiphenylamine (IV), m.p. 146° , hydrolysed by EtOH-NaOH to 3-nitrothioldiphenylamine, which is also obtained when 4-nitrodiphenylamine-2-sulphinic acid (V) (corresponding methylsulphone, m.p. $170\text{--}171^\circ$) is reduced by HI in warm H_2O containing H_2SO_3 . This proves that (IV) is formed from the corresponding thiol and not from (III) before rearrangement. No stable thiazolinium salts analogous to (I) were obtained from the thiols derived from (II) and (III). The following substances are obtained when (V) is warmed with the appropriate aldehyde or ketone: 5-nitro-2-phenylbenzthiazoline S-dioxide, m.p. 147° , and its 1-methyl (VI), m.p. 150° , 1:1-dimethyl, m.p. 200° , and 1-p-hydroxyphenyl, m.p. 220° (decomp.), derivatives. Attempts to convert (VI) by oxidation in acid media into salts analogous to (I) failed. H. G. M.

Dithiazine rings. H. G. UNDERWOOD and F. B. DAINS (J. Amer. Chem. Soc., 1935, 57, 1769—1771).—Methylene halides and thiocarbamides give occasionally methylene ethers, $S\langle\begin{smallmatrix} CH_2 \\ C(NR) \end{smallmatrix}\rangle NPh$, but usually

1:3:5-dithiazans, $S\langle\begin{smallmatrix} CHR' & S \\ C(NR) & NH \end{smallmatrix}\rangle C:NR$, the stab-

ility of which is greatly increased if R is aromatic. CH_2I_2 and $CS(NH_2)_2$ (I) in hot EtOH give 4:6-di-imino-1:3:5-dithiazan, m.p. 202—209°, unstable (hydriodide, cryst., stable), hitherto (J.C.S., 1916, 109, 1255) assumed to be $CH_2[S\langle C(NH) \cdot NH_2 \rangle]_2$. (I) and $CHPhCl_2$ (II) at 150° give 4:6-di-imino-2-phenyl-1:3:5-dithiazan, unstable to 0.1N-alkali (hydrochloride, m.p. 236°). $NH_2 \cdot CS \cdot NHPh$ (III) and CH_2Br_2 at 120—130° give 4:6-dianilo-1:3:5-dithiazan, m.p. 107° (hydrobromide, m.p. 268°; with 15% KOH gives H_2S , $PhNCS$, and NH_2Ph ; 5- or 6-Bz derivative, m.p. 120—121°), the hydriodide, m.p. 263°, being similarly obtained with CH_2I_2 ; the structure of this base is proved by its prep. also from CH_2Br_2 and s-diphenyldithiobiuret (IV). $NH_2 \cdot CS \cdot NH \cdot C_6H_4Me$ (V) at 130° gives 4:6-di-p-, m.p. 175° (hydrobromide, m.p. 283°), and -o-tolylimino-1:3:5-dithiazan, m.p. 174° (hydrobromide, m.p. 236°). (III) with $CHMeBr_2$ at 160° gives 4:6-dianilo-2-methyl-1:3:5-dithiazan, m.p. 181° (hydrobromide, m.p. 248°), and with (II) at 110—150° gives 4:6-dianilo-2-phenyl-1:3:5-dithiazan, m.p. 145° (hydrochloride, m.p. 232°), also obtained from (IV) at 150°. (V) yields similarly 4:6-di-p-tolylimino-2-phenyl-1:3:5-dithiazan hydrochloride, m.p. 222°. $CS(NHPh)_2$ and CH_2I_2 in EtOH give an impure base and $NHPh \cdot CS \cdot OEt$ (cf. lit.). $CS(NH \cdot C_6H_4Me-p)_2$ and CH_2I_2 in hot $COMe_2$ give $C_6H_4Me \cdot NH_2$, $C_6H_4Me \cdot NCS$, and the ether, $C_{16}H_{16}N_2S$, m.p. 151°. $NPh \cdot C(SMe) \cdot NH \cdot CS \cdot NHPh$ (VI) gives similarly the 4-thiolmethylenether, $C_{16}H_{15}N_2S_2$, m.p. 125° (hydriodide, m.p. 275°), and $PhNCS$, but (II) gives triphenyl- and tritolyl-guanidine. (IV) with CH_2I_2 gives a dithiazan, but with CH_2Br_2 and $NH_3 \cdot EtOH \cdot H_2O$ it gives 2-anilotetrahydrothiazole-3-thioformanil, m.p. 165°, hydrolysed by $KOH \cdot EtOH$ to 2-anilinothiazolidine. (VI) and $CH_2Cl \cdot CO_2Et$ in EtOH give 3-phenyl-4-thiazolidone-2-thiolmethyl-ψ-thiocarbamide, m.p. 127°, the $:CHPh$ derivative, m.p. 157°, of which is hydrolysed to 5-benzylidene-3-phenylthiazolidone. Phenylmethylthiobiuret and $CH_2Cl \cdot CO_2Et$ or $CH_3Cl \cdot COCl \cdot C_6H_5N$ in $COMe_2$ afford phenylmethylthiazolidone-2-thiocarbamide, m.p. 222° ($:CHPh$ derivative, m.p. 274°, hydrolysed as above).

R. S. C.
Thiohydrazides as reagents for aldehydes. H. WUYTS and H. WACHSMUTH (J. Pharm. Chim., 1935, [viii], 22, 289—305; cf. A., 1934, 537).—The appropriate aldehyde and thioacylhydrazine in EtOH with a little HCl give the following substituted 2:3-dihydro-1:3:4-thiadiazoles (thiodiazolines): 3:5-diphenyl-2-styryl-, m.p. 127.5—128°; 3:5-diphenyl-2-p-anisyl-, m.p. 130.5—131°; 3:5-diphenyl-2-piperonyl-, m.p. 154—154.5°; 3:5-diphenyl-2-(1-furyl)-, m.p. 111—111.5°; 5-phenyl-3-p-bromophenyl-, m.p. 112.5—113.5°; 5-phenyl-3-p-bromophenyl-2-methyl-, m.p. 93.5—94°; 2:5-diphenyl-3-p-bromophenyl-, m.p. 142.5—143.5°; 5-phenyl-3-p-bromophenyl-2-styryl-,

m.p. 114—114.5°; 5-phenyl-3-p-bromophenyl-2-p-anisyl-, m.p. 132.5—133°; 5-phenyl-3-p-bromophenyl-2-piperonyl-, m.p. 138—139°; 3-phenyl-5-α-naphthyl-, m.p. 71—71.5°; 3-phenyl-2-styryl-5-α-naphthyl-, m.p. 52—53.5°; 3:5-diphenyl-2-(2-hydroxyphenyl)-, m.p. 51—52.5°; 3:5-diphenyl-2-(4-hydroxy-3-methoxyphenyl)-, m.p. 132.5—133°; 5-phenyl-3-p-bromophenyl-2-(2-hydroxyphenyl)-, m.p. 159.5—161°; 5-phenyl-3-p-bromophenyl-2-(4-hydroxy-3-methoxyphenyl)-, m.p. 152.5—153°; 3-phenyl-2-(2-hydroxyphenyl)-5-α-naphthyl-, m.p. 72—73.5°; 3-phenyl-2-(4-hydroxy-3-methoxyphenyl)-5-α-naphthyl-, m.p. 156.5—157°.

F. R. G.

Fluorescent dehydrogenation product from vitamin-B₁.—See this vol., 1286.

Ergometrine. H. W. DUDLEY (Proc. Roy. Soc., 1935, B, 118, 478—484, and J. Amer. Chem. Soc., 1935, 57, 2009—2010).—Ergometrine, $C_{19}H_{23}O_2N_3$, m.p. 160—161°, $[\alpha]_D^{25} + 40.25^\circ$ in EtOH, is identical with "ergotocine" of Kharasch and Legault (this vol., 872, 995) and with "ergobasine" of Stoll and Burkhardt (*ibid.*, 995). The hydrochloride, m.p. 245—246° (decomp.), $[\alpha]_D + 63^\circ$ in H_2O , and hydrobromide, m.p. 236—237° (decomp.), oxalate, m.p. 193° (decomp.), $[\alpha]_D + 55.4^\circ$ in H_2O , and interconvertible yellow, hydrated, m.p. 148° (decomp.), and red pierates, anhyd., m.p. 188—189° (decomp.), are described.

H. G. R.

Spectrographic absorption of ergometrine in relation to the B.P. colour test. N. L. ALLPORT and S. K. CREWS (Quart. J. Pharm., 1935, 8, 447—452).—Ergometrine (I), m.p. 164°, giving a colour test with p-NMe₂·C₆H₄·CHO (II) (B., 1932, 1135) equiv. to that produced by 1.78 times its wt. of ergotocine (III) base, has an extinction coeff., $E_{1\%}^{1\text{cm.}}$ 1.85 at 316 mμ. In aq. tartaric acid solution, both (I) and (III) have a max. absorption band at 316 mμ, whilst the colours due to (II) are spectroscopically identical.

F. O. H.

Ergostetrine. M. R. THOMPSON (J. Amer. Pharm. Assoc., 1935, 24, 748—753).—The prep. of the pure alkaloid, m.p. 160—162.5° (decomp.), $[\alpha]_D^{30} + 50^\circ \pm 10^\circ$ in EtOH, colour reactions, and pharmacological properties are described. The identity of ergostetrine with ergometrine, ergotocine, and ergobasine is suggested.

H. G. R.

Optical rotation study of the new orally effective principle of ergot. E. C. KLEIDERER (J. Amer. Chem. Soc., 1935, 57, 2007—2008).—The $[\alpha]_D$ of ergotocine in H_2O remains const. (+76.1°), but in MeOH changes gradually (from +40.2° to 61.8° in 95.5 hr.); that of its maleate changes both in H_2O (+46.2° to +53.7° in 48 hr.) and MeOH (+37.9° to +24.6° in 48 hr.). Only slight decrease in pharmacological activity accompanies this change in $[\alpha]$.

R. S. C.

Ergot alkaloids. VI. Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1935, 111, 455—465; cf. this vol., 1137).—Formula (I) for lysergic acid is discussed. Dihydrolysergic acid and KOH in H_2 at 295—300° give ? 2-methyl-3-ethylindole (picrate, m.p. 148—150°), a base (? a methyl-ethyleneindole), b.p. 145—150°/0.2 mm., m.p. 68°

(picrate, decomp. 195–200°), EtCO_2H , ? AcOH , a base (I) (picrate, m.p. 165–170°), an acid, m.p. 270° [probably gives (I) by decarboxylation], and NH_2Me (0.96 mol.). α -Dihydrolysergol with MeI-MeOH at 30° gives a methiodide, m.p. 237°, with the properties of an onium salt.

R. S. C.

Dehydrogenation of nicotine in toluene as a solvent. A. A. MORTON and D. HORVITZ (J. Amer. Chem. Soc., 1935, 57, 1860–1861).—Nicotine and S, best in PhMe , give H_2S (69%), thidinicotyryne (18%), and nicotyryne (2.5%).

R. S. C.

Oxidation products of vasicine with hydrogen peroxide. T. P. GHOSE, S. KRISHNA, K. S. NARANG, and J. N. RAY (Current Sci., 1935, 4, 158–159).—Contrary to the view of Morris, Hanford, and Adams (this vol., 873) that the product, m.p. 168°, obtained by the authors (A., 1933, 77) from H_2O_2 and vasicine, is a mixture, it gives const. analytical vals., and has a homogeneous appearance under the microscope. It is now regarded as 4-hydroxy-2:3:2':3'-bis- α -hydroxytrimethylene-4:4'-bisdihydroquinazoly.

E. W. W.

Cotarnine series. IV. 5-Bromonarcotine, 5-bromocotarnine, 5-bromohydrocotarnine, and 5-bromonarceine and their derivatives. B. B. DEY and T. K. SRINIVASAN (J. Indian Chem. Soc., 1935, 12, 526–536).—Narcotine when treated with HBr , H_2O , Br, and subsequently with H_2S yields 5-bromonarcotine (I), m.p. 176°, $[\alpha]_D^{20} -95^\circ$ in CHCl_3 (hydrochloride + H_2O , m.p. 120°; hydrobromide + H_2O , m.p. 168°; platinichloride; picrate, m.p. 197°; and methiodide, m.p. 220°), which with $\text{HBr-Br-H}_2\text{O}$ yields a perbromide hydrobromide, m.p. 220° (decomp.), from which (I) is regenerated by H_2S . (I) is oxidised by $\text{HNO}_3\text{-H}_2\text{O}$ to 5-bromocotarnine (II), m.p. 135° [hydrochloride, m.p. 170° (decomp.); picrate, m.p. 171°; platinichloride; Bz derivative, m.p. 103°; oxime, m.p. 138°; oxime hydrochloride, m.p. 169°; and perbromide hydrobromide, m.p. 200° (decomp.)] (cf. Wright, J.C.S., 1877, 32, 525; Small, "Chemistry of the Opium Alkaloids," 1932, pp. 68, 70, and 98), also obtained, but less conveniently, by bromination of cotarnine. (II) with PhNCO and C_6H_6 yields phenyl-5-bromocotarnomethylcarbamide, m.p. 160° (oxime, m.p. 168–169°), and when heated with MeNO_2 at the b.p. yields anhydrobromocotarninonitromethane, m.p. 148° (hydrochloride, m.p. 166°). (II) when heated with excess of Ac_2O at the b.p. yields N-acetyl-5-bromocotarnidineacetic acid, m.p. 211° (Ag salt). (II) and MeI when heated under pressure yield 5-bromocotarnomethine methiodide, m.p. 179°, which when steam-distilled with NaOH yields 5-bromocotarnone, m.p. 104°, oxidised by KMnO_4 , K_2CO_3 , COMe_2 , and H_2O to 5-bromocotarnolactone, m.p. 172°, further oxidised to 5-bromocotarnic acid [2-methoxy-3:4-methylenedioxy-5-bromophthalic acid], m.p. 185° (anhydride, m.p. 225°). This establishes the constitution of (II). (II) is reduced by Na-Hg-N-HCl to 5-bromohydrocotarnine, m.p. 80° (hydrobromide, m.p. 242°), the perbromide hydrobromide, m.p. 166° (decomp.), of

which does not yield any (II) (contrast Wright, loc. cit.). (I) and $\text{Me-p-toluenesulphonate}$ when heated at 100° (45 min.), then at 110–120° (30 min.), and subsequently treated with NaOH and steam yields 5-bromonarceine, m.p. 193° [hydrochloride, m.p. 241°; hydrobromide, m.p. 225°; picrate, m.p. 153°; platinichloride, m.p. 198° (decomp.); Me ester, m.p. 114°]. H. G. M.

Cotarnine series. V. Condensation of cotarnine with aromatic nitroaldehydes. B. B. DEY and (Miss) P. L. KANTAM (J. Indian Chem. Soc., 1935, 12, 604–607).—Cotarnine and $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in EtOH give 1- o -nitrobenzoyl-5- α -hydroxy- o -nitrobenzylhydrocotarnine (I), m.p. 153° [hydrochloride, m.p. 172° (decomp.); hydrobromide + H_2O , m.p. 177° (decomp.); nitrate, m.p. 181° (decomp.); sulphate, m.p. 191–192° (decomp.); picrate, m.p. 175–176°], reduced by SnCl_2 to the corresponding $(\text{NH}_2)_2$ -base m.p. 122° (Ac_2 derivative, m.p. 126°). 1-m-Nitrobenzoyl-5- α -hydroxy-m-nitrobenzyl-, m.p. 146° [hydrochloride, m.p. 188° (decomp.); corresponding $(\text{NH}_2)_2$ -compound, m.p. 113°], 1-2'-nitro-4':5'-dimethoxybenzoyl-5- α -hydroxy-2'-nitro-4':5'-dimethoxybenzyl-, m.p. 168° [hydrochloride, m.p. 193° (decomp.)], and 1-6'-nitropiperonyl-5- α -hydroxy-6'-nitro-3':4'-methylenedioxybenzyl-hydrocotarnine, m.p. 168° [hydrobromide, m.p. 180° (decomp.)], are similarly obtained. 5-Bromocotarnine, however, condenses with only 1 mol. of aldehyde to give 5-bromo-1- o -nitrobenzoyl-, m.p. 120° after sintering [hydrobromide, m.p. 162° (decomp.)], and -6-nitropiperonyl-hydrocotarnine, m.p. 125° (hydrobromide, m.p. 172°), thus confirming Robinson's formulation (A., 1924, i, 666) of (I) etc. The "1-cotarnino- o -nitrophenyl ketone" of Ahluwalia et al. (A., 1933, 960) was (I).

R. S. C.

Condensation of cotarnine and o -nitrobenzaldehyde. K. N. KAUL and G. S. AHLUWALIA (J. Indian Chem. Soc., 1935, 12, 610).—The compound formulated as "1-cotarnino- o -nitrophenyl ketone" (A., 1933, 960) is 5- o -nitrobenzoyl-1- α -hydroxy- o -nitrobenzylhydrocotarnine.

R. S. C.

Corynantheine. RAYMOND-HAMET (J. Pharm. Chim., 1935, [viii], 22, 306–325; cf. this vol., 894).—Corynantheine hydrochloride hydrolysed with KOH in EtOH gives corynantheic acid, $\text{C}_{19}\text{H}_{22}\text{N}_2(\text{OMe})\cdot\text{CO}_2\text{H}$, $[\alpha]_D^{20} +7.53^\circ$ in $\text{C}_5\text{H}_5\text{N}$.

F. R. G.

Quinoidine. Occurrence of epiquinine and epiquinidine in cinchona bark. W. DIRSCHERL and H. THRON (Annalen, 1935, 521, 48–71).—A C_6H_6 extract of quinoidine (I), the syrupy residue of cinchona bark alkaloids after removal of the quinine (II) etc., deposits 4–5% of (II), and then yields with $\text{KMnO}_4\text{-CrO}_3$ 44% of quinic acid, absorbs 0.66 mol. of H_2 when hydrogenated, and by the $\text{Hg}(\text{OAc})_2$ method yields 65% of vinyl bases. With H_2SO_4 these last give amorphous quinoidotoxin, $[\alpha]_D^{21} +16.6^\circ$ in N-HCl [yielding quinotoxin oxalate, m.p. 166–167°, $[\alpha]_D^{20}$ (anhyd.) $+25^\circ$ in EtOH-CHCl_3 (1:2)], and thence its Bz and oximinobenzoyl derivatives, benzoylquinoidinonitrile, meroquinoidine, acetylmerquinine, meroquinine Et ester, and β -collidine. The presence of epiquinine and epiquinidine in the bark, thus indicated, is confirmed by their direct isolation as benzoyl-d-tartrates, m.p. 160°, $[\alpha]_D^{21} -26.3^\circ$ in EtOH ,

and m.p. 166—167°, $[\alpha]_D^{25} +1.9^\circ$, respectively, and by partial benzoylation of (I). *Benzoylquinotoxin* has m.p. 113—114°, $[\alpha]_D^{25} +36^\circ$ in EtOH. Toxins, if present at all, constitute < 10% of (I). R. S. C.

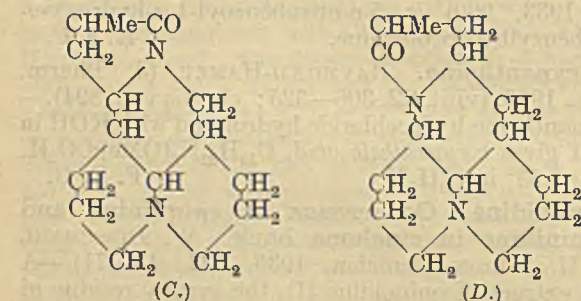
Constitution of matrine. XVII. H. KONDO, E. OCHIAI, and K. TSUDA (Ber., 1935, 68, [B], 1899—1904; cf. this vol., 766).—Catalytic dehydrogenation (Pd-asbestos at 270—280°) of the base, $C_{14}H_{26}N_2$, obtained by reduction of decarbonylmethylmatrinane affords the base, $C_{14}H_{20}N_2$, identical with that obtained by catalytic dehydrogenation of matrine. Oxidation with $KMnO_4$ of the methohydroxide of this base affords Pr^aCO_2H , showing the presence of a Pr^a side-chain. Control experiments with matrine methohydroxide do not give Pr^aCO_2H , so that the Pr^a chain is obtained by degradation of the lactam ring which in matrine has the structure

$C_{10}H_{17}N \left\{ \begin{array}{l} \cdot N \cdot CO \cdot CHMe \\ \cdot CH - CH_2 \end{array} \right.$ or $C_{10}H_{17}N \left\{ \begin{array}{l} \cdot N \cdot CO - CH_2 \\ \cdot CH \cdot CH_2 \cdot CH_2 \end{array} \right.$, probably the former. Dihydro- α -matrinidine (I) is therefore $C_{10}H_{17}N \left\{ \begin{array}{l} -NH \\ -CHMe \end{array} \right.$; considered in conjunction

with the production of pyridine-2:3-dicarboxylic acid by oxidation of the compound, $C_{12}H_{14}N_2$, obtained by degradation of (I) with CNBr and sub-

sequent oxidation, the structure A or B can be assigned to (I). Dehydro- α -matrinidine therefore has a 2-methylpyridine nucleus; in confirmation, it condenses with PhCHO in presence of $ZnCl_2$ at 230—250° to benzylidene-

dehydro- α -matrinidine, m.p. 106—107°, hydrogenated (PtO_2) to the benzyl compound (platinichloride, decomp. 190°). If it be assumed that displacement of a ring does not take place during the formation of α -matrinidine the constitution of matrine (II) may be represented by C or D.



(II) and lupanine are not stereoisomerides. On oxidation lupanine methohydroxide gives glutaric acid, which is formed with certainty from its α -piperidone ring since it could not be obtained from sparteine but is derived from tetrahydrocytisine. H. W.

Curare alkaloids. I. Tubocurarine. H. KING (J.C.S., 1935, 1381—1389; cf. this vol., 655, 1138).—*d*-Tubocurarine chloride (+5H₂O), m.p. 274—275°, $[\alpha]_{5461}^{20} +235^\circ$ in H₂O, is methylated to *O*-methyltubocurarine iodide (+3H₂O), m.p. 267°, $[\alpha]_{5461}^{20} +178.2^\circ$ in H₂O. Hofmann degradation of the iodide yields *O*-methyltubocurarinemethine methiodide A (+2.5H₂O), m.p. 234°, and B (+2.5H₂O), m.p. 230° (A and B are

optically inactive), and *d*- (+5H₂O), m.p. 190°, $[\alpha]_{5461}^{20} +105^\circ$ in MeOH, and *l*-*O*-methyltubocurarinemethine methiodide (+5H₂O), m.p. 171—172°, $[\alpha]_{5461}^{20} -57^\circ$ in MeOH; at the second stage of degradation, a N-free substance, m.p. 198—199°, is obtained. Similar methylation and degradation of *d*-bebeerine yields a series of substances identical with those obtained from tubocurarine: *O*-methylbebeerinemethine methiodide A and -B, and *d*-*O*-methylbebeerinemethine methiodide (a monomethiodide, $C_{41}H_{49}O_6N_2I \cdot H_2O$, has also been separated, m.p. 261°, $[\alpha]_{5461}^{20} +63^\circ$ in *N*-HCl), and at the second stage, *O*-methylbebeerilene, m.p. 198—199°. Probable structures are given and discussed for tubocurarine and its derivatives. F. R. S.

Alkaloids of *Cytisus caucasicus*.—See this vol., 1549.

Preparation of asymmetric secondary arylarsinic acids. G. K. KAMAI (Trans. Kirov. Inst. Chem. Tech. Kazan, 1935, No. 3, 49—53).—Bart's method (A., 1922, i, 1201) is superior to that of Blicke and Smith (A., 1930, 99), whose phenyl-*p*-tolylarsinic acid (I) probably contained unoxidised tetra-arylsarsine oxide. Pure (I) has m.p. 159—160°; its prep. from PhAsO and *p*-C₆H₄Me·N₂Cl, from *p*-C₆H₄Me·AsO and PhN₂Cl, and from MgPhBr and *p*-C₆H₄Me·AsO is described. Diazotised *p*-nitroaniline and PhAsO yield phenyl-*p*-nitrophenylarsinic acid, m.p. 181° (NH₄, Ba, Na, NH₂Ph, m.p. 162—166°, and *p*-C₆H₄Me·NH₂, m.p. 78—79°, salts). CH. ABS. (7)

Preparation of 3-nitro-4-hydroxyphenylarsinic acid from *p*-chloroaniline. V. A. ISMAILSKI and A. M. SIMONOV (J. Pharm. Chim., 1935, 22, [viii], 337—357).—*p*-Chlorophenylarsinic acid with KNO₃-conc. H₂SO₄ at 100° (cf. A., 1929, 584) gives 4-chloro-3-nitrophenylarsinic acid (I), which is converted by 40% alkali at 85° into 3-nitro-4-hydroxyphenylarsinic acid, also obtained by hydrolysis (25% NaOH at 100°) of 2-nitrodiphenylamine-4-arsinic acid, prepared by boiling the Na salt of (I) in H₂O with NH₂Ph. J. L. D.

Stereochemistry of tervalent arsenic. II. Preparation of *o*-, *m*-, and *p*-phenylmethylarsinobenzoic acids and their attempted resolution into optically active components. G. KAMAI (Ber., 1935, 68, [B], 1893—1898; cf. this vol., 875).—Attempts to resolve the acids into their optically active components were unsuccessful. AsPhMeI is converted by Mg and *p*-C₆H₄MeBr into phenyl-*p*-tolylmethylarsine, b.p. 166—167°/8 mm. (compound, m.p. 59—60°, with CuBr), oxidised by $KMnO_4$ in H₂O to phenyl-*p*-carboxyphenylmethylarsine oxide hydrochloride (I), m.p. 150—152° (decomp.), which with H₂S affords phenyl-*p*-carboxyphenylmethylarsine sulphide, m.p. 159—160°. (I) is transformed by SO₂ in presence of I into *p*-phenylmethylarsinobenzoic acid, AsPhMe·C₆H₄·CO₂H, m.p. 149—151° (NH₄, Ba, strychnine, m.p. 183—185°, $[\alpha]_D^{20} -16.05^\circ$ in CHCl₃, quinine, m.p. 210—211°, $[\alpha]_D^{20} -56.91^\circ$ in CHCl₃, and non-cryst. brucine and cinchonine salts). The following compounds are obtained similarly: phenyl-*m*-tolylmethylarsine, b.p. 165—166°/9 mm., (non-

cryst. compound with CuBr), *phenyl-m-carboxyphenylmethylarsine oxide hydrochloride*, m.p. 148—150° (decomp.) (compound with HgCl₂), *phenyl-m-carboxyphenylmethylarsine sulphide*, m.p. 134—135°, and *m-phenylmethylarsinobenzoic acid*, m.p. 92—93° (quinine, m.p. 169—170°, $[\alpha]_D^{25}$ —83.01°, and strychnine, m.p. 138—139°, $[\alpha]_D^{25}$ —19.8°, salts): *phenyl-o-tolylmethylarsine*, b.p. 162—163°/? pressure, *phenyl-o-carboxyphenylmethylarsine oxide*, m.p. 226—227°, *phenyl-o-carboxyphenylmethylarsine sulphide*, m.p. 164—165°, and *o-phenylmethylarsinobenzoic acid*, m.p. 232—233°. H. W.

Heterocyclic compounds containing arsenic in the ring. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1935, 12, 627—628).—C₆H₆, CHCl:CH·AsCl₂, and AlCl₃ give 1-chloroarsindole (I). PhAsCl₂, C₂H₂, and AlCl₃ give β-chlorovinylphenylchloroarsine and di-(β-chlorovinyl)phenylarsine, the former with AlCl₃ yielding (I). Et o-aminocinnamate gives (Bart) cinnamic acid-o-arsinic acid, converted by HBr into o-α-bromo-β-carboxyethylphenylarsinic acid, which with alkali yields o-vinylphenylarsinic acid. With SO₂-HCl this gives o-vinylphenyldichloroarsine, whence (I) is obtained. Compounds of the types (CHPh:CH)₂Hg, CHPh:CH·HgCl, and (CHPh:CH)₃As, have been obtained. R. S. C.

Reactions of bismuthiol. J. V. DUBSKÝ and A. OKÁČ (Chem. Obzor, 1934, 9, 171—173; Chem. Zentr., 1935, i, 1707; cf. A., 1934, 1193).—Dithiolthiodiazole (bismuthiol) (I) yields red needles with Bi salts. Analogues of (I) which cannot undergo tautomeric change do not give the colour reaction. H. N. R.

Reactions of bismuth with organic hydrosulphides. I. J. V. DUBSKÝ, A. OKÁČ, and J. TRTÍLEK (Chem. Obzor, 1934, 9, 173—174; Chem. Zentr., 1935, i, 1707—1708; cf. preceding abstract).—Compounds of the type Bi(Bis)₃ and Bi(Bis)X [(Bis) = bismuthiol residue] can be isolated from the intensely coloured Bi salts of bismuthiol (I). The importance of the secondary valencies of the S atoms is shown by replacement of SH by OH, when the reaction no longer takes place. The colour reactions of many analogues of (I) with metallic salts are described. H. N. R.

Mercuration of ethylenes and reaction of methoxy-mercurials. G. F. WRIGHT (J. Amer. Chem. Soc., 1935, 57, 1993—2000).—The reaction of Hg(OAc)₂, MeOH, and ethylenes is in the main bimol. It is accelerated by NO₃⁺ or NaOMe, is slow in H₂O, faster in higher alcohols, and fastest in MeOH. These and other considerations indicate reaction thus: Hg(OAc)₂ + R'OH ⇌ AcOH + OR'·Hg·OAc (I); (I) + CHR:CHR' ⇌ OR'·CHR·CHR'·Hg·OAc (II). The facile decomp. of (II) by various reagents and the determination of Hg⁺⁺ in presence of org. mercurials by KCNS are described. *trans*-CHPh:CH·CO₂Me (III) gives 88% of Me α-chloromercuri-β-methoxy-β-phenylpropionate, m.p. 134°. The *cis*-cinnamate gives the *isomeric*, m.p. 141°, but both, when distilled at 25 mm., give (III), decomp. temp. being *trans*-170° and *cis*-157°, and both with Na₂S₂O₃ yield OMe·CHPh·CH₂·CO₂H (also obtained similarly from anhydro-α-hydroxymercuri-β-methoxy-β-phenyl-

propionic acid). *iso*Stilbene gives α-chloromercuri-β-methoxy-α-β-diphenylethane, m.p. 143°, but *trans*-stilbene does not react; this mercurial with a variety of reagents gives a mixture of isomeric stilbenes. Styrene affords α-acetoxymmercuri-β-methoxy-β-phenylethane, m.p. 64—65°, stable to Ac₂O at 25° and boiling C₅H₁₁·OH, but reconverted into styrene by boiling Ac₂O and other reagents. α-Benzoyloxy-, m.p. 80° (stable in hot PhMe), and α-bromo-mercuri-β-methoxy-β-phenylethane (IV), m.p. 63°, are prepared; the latter affords OMe·CHPh·CH₂Br and thence CH₂:CPh·OMe. Styrene and Hg(OAc)₂ in dioxan give a gummy intermediate product, which with MeOH in ligroin gives (IV). CH₂Ph·CH:CH₂ gives β-chloromercuri-α-methoxy-α-phenylpropane, m.p. 95—95.5° (with products which, when brominated and hydrolysed, give CPhEt), converted by Br and hydrolysis into CHMeBr·CHPh·OMe, b.p. 122—125°, and CHMe:CPh·OMe, b.p. 96—97°/19 mm. cycloHexene yields a labile form, m.p. 114—115°, of 1-chloromercuri-α-methoxycyclohexane, converted slowly in hot EtOH into a stable form, m.p. 86°; evidence of the formation of an intermediate compound is given. 1-Lactomercuri-2-methoxycyclohexane, m.p. 144° (decomp.), is described. Phenylbutadiene affords diacetylmercuridimethoxyphenylbutane, m.p. 142—145°, and chloromercurimethoxyphenylbutene, m.p. 89° (corresponding Br-compound, m.p. 76°), which with O₃ in CHCl₃ gives PhCHO and, when further mercurated, forms dichloromercuridimethoxyphenylbutane, m.p. 180°, obtained more readily from the (HgOAc)₂-compound. R. S. C.

Decomposition voltage of Grignard reagents in dry ether. E. Q. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2005).—Differences in the decomp. voltage produced by substitution show an alternating effect, diminishing in intensity as the substituent becomes more remote from the Mg. R. S. C.

Reaction between mercury diaryls and diaryl-selenium dihalides. H. M. LEICESTER (J. Amer. Chem. Soc., 1935, 57, 1901—1902).—In CS₂ or cold COMe₂ reaction occurs thus: HgAr₂ + SeAr₂X₂ → HgArX + RX + SeR₂. In hot COMe₂ or at 140—150° without a solvent, a second reaction follows, thus: HgArCl + SeAr₂Cl₂ → SeAr₂Cl·HgCl₂. SeAr₂Br₂ in COMe₂ leads also to CH₂Br·COMe. R. S. C.

Denaturation and structure of seed-globulins.—See this vol., 1433.

Combination of bivalent manganese with certain proteins, amino-acids, etc.—See this vol., 1460.

New absorption apparatus for micro-carbon-hydrogen determination. A. FRIEDRICH (Mikrochem., 1935, 19, 23—37). J. S. A.

Volumetric modification of the Pregl halogen micro-combustion method for organic iodine. P. L. KIRK and K. DOD (Mikrochem., 1935, 18, 179—181).—I obtained by the Pregl halogen combustion method is oxidised to IO₃⁺ by Br. When the colour is uniformly brown, the excess of Br is removed by boiling and KI added to the acidified solution. The I liberated is equiv. to 6 times that originally present. R. S.

Methods of chemical analysis by hydrogenation. H. TER MEULEN (Bull. Soc. chim., 1935, [v], 2, 1692—1694).—Methods are described for overcoming the difficulties observed by Gauthier (this vol., 506) in the determination of org. S, O, and N by hydrogenation in presence of a catalyst. J. W. S.

Determination of deuterium in organic compounds.—See this vol., 1408.

Micro-volumetric determination of methoxyl. D. T. GIBSON and T. H. CAULFIELD (J.C.S., 1935, 1419—1420).—Contrary to Vieböck and Brecher (A., 1931, 246), the determination cannot be satisfactorily carried out on 1—5 mg. of material because the "blank" correction is significant and is increased by time, temp., and dilution. Improvements in technique are described. J. L. D.

Biochemical detection of organic compounds.—See this vol., 1416.

Structure and oxidation of nitrogenous substances. C. N. ACHARYA (Nature, 1935, 136, 644).—When N compounds are oxidised by a mixture of $\text{CrO}_3 + \text{H}_2\text{SO}_4$, full recovery of N is obtained in the form of NH_3 and NO_3^- when the N are attached to different C. When two or more N are attached to the same C, however, a definite amount is lost either as N_2 or N_2O . The proportions of NH_3 recovered from typical groups are: $\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot$, 2/3 of total N; $\cdot\text{N}:\text{CH}\cdot\text{N}\cdot$, 4/5; guanidine group, 4/11, and creatine group, 2/3. NH_2OH derivatives are almost quantitatively oxidised to NO_3^- , whilst in N_2H_4 derivatives the N is almost completely lost as gas. Cl⁻ present as impurity and as hydrochlorides of bases tends to increase the ratio $\text{NO}_3^- : \text{NH}_3$ and should be removed by Ag_2SO_4 . L. S. T.

Colour reactions for tartaric, citric, and aconitic acids. O. FÜRTH and H. HERRMANN (Biochem. Z., 1935, 280, 448—457).—With Ac_2O and $\text{C}_5\text{H}_5\text{N}$ tartaric acid gives an emerald-green, citric acid a carmine-red, and aconitic acid a violet colour whereas many of the aliphatic dibasic acids give no or only a brown colour. The reaction is very sensitive and using the fluorescence in ultra-violet light can detect 10^{-6} g. of these acids.

P. W. C.

Determination of diacetyl and acetyl-methylcarbinol. C. R. BARNICOAT (Analyst, 1935, 60, 653—662).— Ac_2 is separated by distillation in CO_2 , and converted into Ni dimethylglyoxime, which is

dissolved in CHCl_3 and determined colorimetrically. $\text{CHMeAc}\cdot\text{OH}$ (I) is determined by oxidation to Ac_2 during distillation, the Ac_2 originally present being subtracted from the total determined. The results are slightly low owing to escape of Ac_2 in the CO_2 . The detection of added Ac_2 is difficult, but addition may be inferred from the ratio of Ac_2 to $\text{Ac}_2 + (\text{I})$. E. C. S.

Micro-detection of liquid amines, especially methylamine in presence of ammonia. A. VON WACEK and H. LÖFFLER (Mikrochem., 1935, 18, 277—282; cf. A., 1934, 1278).—Methods of distinguishing between NH_3 and NH_2Me are discussed and photomicrographs are given of the products obtained with 1 : 2 : 4- and 1 : 4 : 8- $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\cdot\text{OH}$, and 1 : 2 : 4 : 5- $\text{C}_{10}\text{H}_4(\text{NO}_2)_3\cdot\text{OH}$. R. S.

Microscopy of the amino-acids and their compounds. I. Phosphotungstates and phosphomolybdates. B. BULLOCK and P. L. KIRK. II. Picrates and flavianates. B. L. CROSBY and P. L. KIRK (Mikrochem., 1935, 18, 129—136, 137—143).—Photomicrographs of the above salts of a no. of NH_2 -acids are given, together with *n* vals. of the flavianates. R. S.

Determination of creatinephosphoric acid.—See this vol., 1521.

[Analytical reactions of vanillin, phenols, and "prontosil"].—See this vol., 1474.

Volumetric determination of camphor by the hydroxylamine method. R. VANDONI and G. DESSEIGNE (Bull. Soc. chim., 1935, [v], 2, 1685—1691).—Camphor, fenchone, menthone, carvone, and camphenilone are converted by $\text{NH}_2\text{OH}\cdot\text{HCl}$ into their oximes and the liberated HCl is titrated with $\text{N}\cdot\text{Na}_2\text{CO}_3$ (bromophenol-blue indicator). Experimental error is <1%. F. R. G.

Determination of pyridine in presence of nicotine. R. L. FRATKIN, L. P. JURAVLEVA, and A. G. BLANKSCHTEIN (Sborn. Robot Chim. Otdela, 1935, 88—106).—The $\text{C}_5\text{H}_5\text{N}$ is distilled off in presence of excess of AcOH . The residue is made alkaline and the nicotine distilled in steam and determined as silicotungstate. The acid $\text{C}_5\text{H}_5\text{N}$ distillate is made alkaline, redistilled into dil. H_2SO_4 , pptd. with NH_4CNS and CuSO_4 , and the solution titrated with standard AgNO_3 . The method is more accurate than that of Mach and Sindlinger (A., 1924, ii, 357). T. H. P.

Biochemistry.

Cerebral blood in conscious and narcotised men. D. LASZLO, H. URBAN, and E. WEISSENBERG (Arch. exp. Path. Pharm., 1935, 179, 266—272).—The difference in O_2 content of arterial and venous blood of the brain supply in man varies considerably, the average being 3.7 vol.-% (during Et_2O narcosis 2.23%). The difference in CO_2 content also diminishes (average vals. 4.6 and 3.9%, respectively), giving R.Q. of 1.3 before and 1.7 during narcosis. The effect is due to inhibition of metabolic oxidation and subsequent accumulation of acidic products. F. O. H.

Colloid osmotic pressure of the blood of sea-fish. P. MEYER (Compt. rend. Soc. Biol., 1935, 120, 303—305).—Vals. are given for the colloid osmotic pressure of the blood of a no. of fish. Those of teleosts are of the same order as for terrestrial mammals, whilst those of selachians are of the order of 3—6 cm. of H_2O . Results for teleosts do not support Krogh's hypothesis. R. N. C.

Study by micro-incineration of the red corpuscles of the teleostean fish, *Cichlasoma*

fascetum. A. POLICARD and P. ROJAS (Compt. rend. Soc. Biol., 1935, 120, 366—367).—The nuclei on incineration yield a fine white ash. The peripheral zone of the cytoplasm yields a coarse yellow ash, less abundant than that from amphibia, which contains Fe, whilst the inner region yields no ash. The colour and character of the ash vary with the Fe content. R. N. C.

Thickness of the wall of the red blood-corpuscle. J. F. DANIELLI (J. Gen. Physiol., 1935, 19, 19—22).—Max. vals. for the dielectric consts. of lipid substances in unimol. films are calc. from surface potential measurements. These are in accordance with the val. 3 assumed by Fricke for the erythrocyte cell-wall. F. A. A.

Hæmatopoietic action of phosphoric acid compounds of creatine and creatinine. V. SUZUKI, W. NAKAHARA, and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 1—9).—The compound obtained by the interaction of creatine or creatinine with P_2O_5 and HPO_3 administered *per os* to normal rabbits in 30 mg. daily doses gave a marked increase in the erythrocyte count. A. L.

Hæmoglobin metabolism and its disorders. L. HEILMEYER (Zentr. inn. Med., 1934, 55, 818—828; Chem. Zentr., 1935, i, 1731—1732).—Porphyrin eliminated during hæmatoporphyrinuria is not a decomp. product of hæmoglobin (I), but results from defective synthesis. The decomp. of blood-pigment follows the stages, bilirubin \rightarrow urobilin and stereobilin. Urobilinogen is identical with mesobilirubinogen. A secondary decomp. of (I) leads to formation of uroerythrin and urochrome B. A. G. P.

Hæmoglobin studies. I. In rachitic chickens : effect of ultra-violet irradiation. G. H. MAUGHAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 389—390).—Hæmoglobin is low in the blood of rachitic chickens, but on ultra-violet irradiation increases to vals. > those of normal controls. R. N. C.

Escape of hæmoglobin from the red cell during hæmolysis. E. PONDER and D. MARSLAND (J. Gen. Physiol., 1935, 19, 35—44).—Cinematograph films of red blood-corpuscles losing hæmoglobin under the influence of saponin (I) show that the permeability is a function of the concn. of (I). In lysis by hypotonic solutions the permeability is nearly independent of the tonicity. F. A. A.

Volumetric determination of hæmoglobin. S. RUSZNYAK and E. B. HATZ (Biochem. Z., 1935, 280, 242—247).—Defibrinated blood (1—2 c.c.) is saturated with CO (excess removed in N_2) and the bound CO is liberated by the action of 32% aq. $K_3Fe(CN)_6$ containing lactic acid. The liberated CO is then determined by Winkler's method (B., 1934, 557). W. McC.

New hæmatological stain. I. Constituents and methods of use. D. M. KINGSLEY (Stain Tech., 1935, 10, 127—133).—A two-solution stain for general hæmatological use is described. When mixed it is stable for 8 months and may be used for blood-smears, fixed and frozen sections, and touch preps. H. G. R.

Absorption of carbon monoxide with reduced hæmatin and pyridine-hæmochromogen. L. E. CLIFCORN, V. W. MELOCHE, and C. A. ELYEHJEM (J. Biol. Chem., 1935, 111, 399—409).—The relative rates of absorption of CO by alkaline (I) and acid reduced hæmatin (II), and by pyridine-hæmochromogen (III) at 25° have been determined. (I) absorbs faster than (II). Excess of C_5H_5N expels CO from CO-(III). K for the system $CO-(III) \rightarrow CO+(III)$ in a solution containing no excess of C_5H_5N is 1.24×10^{-4} . J. N. A.

Effect of varying concentrations of oxyhæmoglobin on its light absorption. G. B. RAY and H. A. BLAIR (J. Biol. Chem., 1935, 111, 371—378).—Oxyhæmoglobin in all concns. at λ 540 and 560 $m\mu$ obeys Beer's and Lambert's laws, p_H and salts in solution having no effect. At λ 650 $m\mu$ Beer's law is not obeyed, the absorption diverging from the calc. val. at 4 g. per 100 c.c., indicating that mol. changes are taking place. J. N. A.

Modifications of blood composition under the influence of general application of short waves. A. COMPÈRE (Compt. rend. Soc. Biol., 1935, 120, 237—240).—Short-wave application in the dog causes diminution of the alkaline reserve and p_H of the blood, and increase of non-protein-N and total protein. Total fixed bases, mineral acids, and protein acidity are scarcely modified. Corpuscular vol. is generally diminished. R. N. C.

Regulation of protein disequilibrium of blood-serum under the influence of injections of serin : experiments on man. G. LEFROU and P. BONNET (Compt. rend. Soc. Biol., 1935, 120, 424—427).—Serin (I) injected into lepers exhibits feeble anaphylactic properties. Serum-globulin and total albumin are decreased, whilst (I) and the (I)-globulin ratio are increased. (I) injections hence exert a regulating effect on protein disequilibrium. R. N. C.

Application of the differential determination of albumoses, polypeptides, and amino-acids, using ninhydrin, to blood. E. CHERBULEZ and A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 150—152).—After pptn. with various reagents the various fractions are determined with ninhydrin (A., 1933, 1181). H. G. R.

Determination of the amino-acids of blood-serum with tyrosinase. A. MIRIMANOFF and E. PERROTTET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 163—172).—The ninhydrin and tyrosinase methods are compared. The former is more rapid, but the latter can be carried out without clarification. H. G. R.

Modified Nessler's reagent for micro-determination of urea in tungstic acid blood-filtrate. J. F. BARRETT (Biochem. J., 1935, 29, 2442—2445).—Addition of NaOCl to Nessler's reagent prevents its reduction by glucose, creatinine, etc., and allows direct colorimetric determination of urea in blood-filtrates. F. A. A.

Effect of thyroidectomy on the lipin, fatty acid, cholesterol, and protein content of blood-serum. C. I. PARHON and I. ORNSTEIN (Bull. Soc. Chim. biol., 1935, 17, 1119—1123).—Thyroidectomy in

rabbits resulted in increases in total lipins, fatty acids, and cholesterol of the blood-serum. Little change was observed in the protein content. A. L.

Determination of blood-sugar. I. Deproteinisation with cadmium hydroxide. II. Iodometric micro-determination of blood-sugar. C. DUMAZERT (Bull. Soc. Chim. biol., 1935, 17, 1163—1170, 1171—1177; cf. this vol., 642).—I. A micro-method employing deproteinisation with $\text{Cd}(\text{OH})_2$, followed by oxidation (Hagedorn-Jensen), for the determination of blood-sugar is described. 0.1 c.c. of blood is used and the error is 1—2%. By this method, glucose in the blood-corpuscles of diabetics is > that in the plasma.

II. Deproteinisation with $\text{Hg}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$, followed by iodometric determination of the aldoses (A., 1934, 992) is employed. 1 c.c. of blood is used and the error is 3%. A. L.

Modifications of the glycerol content of the blood in glycolysis *in vitro*. M. POLONOVSKI, H. WAREMBOURG, and P. LAMOUR (Compt. rend. Soc. Biol., 1935, 120, 191—192).—Glycerol (I) and glycerophosphoric acid increase in blood during glycolysis *in vitro* at 37°. (I) falls after reaching 50% of the calc. val., so that a (I)-destroying reaction begins in the later stages of glycolysis. (I) variations are not \propto the hydrolysis of blood-lipins; they are almost wholly responsible for the increase of the residual chromic index, which is not affected by non-protein-N variations. R. N. C.

Significance of phosphoric esters in the course of blood-glycolysis. II. Degradation of hexose monophosphate in hæmolysed blood. Z. DISCHE (Biochem. Z., 1935, 280, 248—264; cf. this vol., 104).—The degradation is preceded by a phosphorylation, $\frac{1}{2}$ two thirds of the phosphoric acid which esterifies the monophosphate (I) being transferred from adenosinetriphosphoric acid. Decrease in the rate of trans-esterification \propto the decrease in the concn. of (I). The aldo-form of (I) is probably only indirectly involved, serving to provide nascent keto-form which is phosphorylated much more rapidly than is the ordinary keto-form. There is no evidence of direct conversion of (I) into 1 mol. of triose ester and 1 mol. of triose. W. McC.

Gravimetric determination of fat and cholesterol in blood. G. GORBACH and R. KADNER (Mikrochem., 1935, 18, 266—271).—The sample is extracted with ligroin in the micro-extractor (A., 1933, 139). Cholesterol in the extract is pptd. by digitonin and the fat obtained by difference. R. S.

Sulphur content of pancreatic blood and of thoracic lymph. VI. Glucose injection in vagotomised dogs. S. KUMAMI (J. Biochem. Japan, 1935, 22, 163—179).—The S content of the thoracic lymph of vagotomised dogs varies considerably from hr. to hr., the average tendency being a gradual diminution. That of blood from the pancreatic vein is not changed by injection of glucose, whereas that of thoracic lymph slowly falls and then returns to normal levels. The difference between these results and those in normal dogs is due to the influence

of vagotomy on insulin secretion (cf. A., 1934, 1379; this vol., 378). F. O. H.

Level of carbonyl compounds in human blood. R. E. JOHNSON, A. P. MEIKLEJOHN, R. PASSMORE, and R. H. S. THOMPSON (Biochem. J., 1935, 29, 2506—2509).—The amounts of total HSO_3^- -binding substances in human blood fall within the limits 1.96—4.00 with an average of 2.81, expressed as mg. of AcCO_2H per 100 g. of blood. The HSO_3^- -binding capacity of blood from various cases suffering from mental and physical diseases showed no appreciable difference from that of normal blood. The latter may contain some CO-compound other than AcCO_2H , COMe_2 , or $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$. J. N. A.

Blood-iodine values. H. DOERING (Biochem. Z., 1935, 280, 442—447).—The low blood-I vals. obtained by the Fellenberg method are correct, and there is no volatile I fraction which is lost on ashing in an open crucible. The high vals. obtained by ashing in a closed system are incorrect, and are due either to traces of Br and Cl being incompletely removed or to traces of oxidants which liberate I from KI in acid solution remaining after ashing. P. W. C.

Iodine in blood. A. STURM, K. PLÖTNER, and K. MAASS (Biochem. Z., 1935, 280, 396—412).—A general discussion is given of the various methods for determination of I in blood, the objections raised to the author's modification of the Fellenberg method are refuted, and the interpretation of blood-I vals. particularly in hyperiodæmia is discussed. P. W. C.

Occurrence of bromine in the normal organism. T. LEIPERT (Biochem. Z., 1935, 280, 416—433).—The Br content of normal human blood is 0.160—0.4 mg. per 100 ml. and of plasma 0.18—0.45 mg. per 100 ml. Br, unlike Cl, is retained in the erythrocytes, and the distribution ratio is therefore very variable, and is controlled by the CO_2 tension of the blood. No evidence could be obtained of Br-protein complex formation, and no ultrafilterable org. Br could be detected, Br being present only in the ionised form. Br is excreted together with Cl, but the ratios of Cl to Br in plasma and urine are not identical. Br is constantly found together with Cl in intermediate metabolic processes, and administration of tissue diuretics leads to elimination of Br. Soon after birth, infants' urine has a high Cl : Br ratio (corresponding with the high blood ratio), and this diminishes during nutrition with milk. P. W. C.

Bromine content of the organism in mental patients. T. LEIPERT and O. WATZLAWEK (Biochem. Z., 1935, 280, 434—441).—Tables summarise the Br and Cl contents of the blood, the distribution of Br and Cl between erythrocytes and plasma, the dependence of the Br and Cl index on the CO_2 tension, the Br and Cl contents of the cerebrospinal fluid, and the Br and Cl urinary excretion of mental patients. The Br in these cases is always wholly present as Br^- , and is in no way either chemically or physically different from the normal condition. The preponderance of cases of low Br val. is probably due to deficient diet. No evidence was obtained for the existence of a Br-containing pituitary secretion, the gland exercis-

ing any effect on the Br content of the organism in a secondary way by regulation of the H_2O content.

P. W. C.

Volumetric micro-determination of potassium in blood-serum. P. WENGER, C. CIMERMAN, and C. RZYMOWSKA (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 140—143).—The method of Shohl and Bennett (A., 1928, 1292) has been modified by incorporating a wet incineration ($HClO_4$ and HNO_3) and removal of NH_4 salts with $NaOH$. H. G. R.

Isoelectric point of the erythrocyte membrane and hæmalysis by ammonium chloride. M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1935, 120, 174—176).—Erythrocytes are not hæmolyzed by 4% NH_4Cl solution at p_H 8, the isoelectric point of the cell membrane. Hæmalysis occurs with an unneutralised solution of NH_4Cl at the same concn.

R. N. C.

Hæmalysis by glucosides (saponin and solanin) and production of cholesterol *in vivo*. V. DE LAVERGNE and P. KISSEL (Compt. rend. Soc. Biol., 1935, 120, 149—150).—Hæmalysis in guinea-pigs and rabbits by neutral or alkaline saponin (I) solutions cause an increase in plasma-cholesterol (II). Solanin and acid (I) solutions lower (II) by their pptg. action.

R. N. C.

Follicular hormone and coagulation of blood. M. SAVIANO (Mem. R. Accad. Lincei, 1935, 6, 165—183).—Subcutaneous injection of folliculin (I) in normal male dogs lowers the time of coagulation of the blood, and increases fibrinogen and blood-Ca, the Ca increase occurring almost completely in the diffusible fraction. These effects are not produced by (I) added to normal blood *in vitro*.

R. N. C.

Index of flocculability of sera in flocculation and gelification reactions. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, 120, 430—432).—Serum flocculation by H_2O , melanin, Fe albuminate, urea-stibamine, and sulpharsenol, and CH_2O -leuco- and lacto-gelification, are explained in terms of the index of flocculability.

R. N. C.

Conditions of flocculation and gelification of pathological sera. E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, 120, 428—429).—Flocculation or gelification of pathological sera occurs if euglobulin rises or serin or cholesterol falls below certain limits. An "index of flocculability" is defined.

R. N. C.

Abscess of fixation and serum reaction to resorcinol. P. BORDET (Compt. rend. Soc. Biol., 1935, 120, 91—93).—The reaction of rabbit's serum to $m-C_6H_4(OH)_2$ is increased during formation of an abscess or injection of turpentine; it returns to normal when the abscess has been formed.

R. N. C.

Serum reaction to resorcinol, rate of corpuscular sedimentation, and time of serum lacto-gelification. P. BORDET (Compt. rend. Soc. Biol., 1935, 120, 93—95).—Turpentine or bacterial products that increase the reaction of rabbit's serum to $m-C_6H_4(OH)_2$ also increase the velocity of corpuscular sedimentation and reduce the time of seric lacto-gelification.

R. N. C.

Active group of heparin. S. BERGSTRÖM (Naturwiss., 1935, 23, 706).—By the action of $ClSO_3H$ in C_5H_5N on cellulose, chitin, starch, glycogen, gum arabic, yeast-nucleic acid, and chondroitin-sulphuric acid, acid esters were obtained which possessed anticoagulating action of which the strongest, that derived from cellulose, had an activity $< 1/10$ that of heparin. In contrast to natural heparin, the cellulose ester was markedly toxic to rabbits.

W. O. K.

Anticoagulant properties of the pyrogenic products of citric acid. A. LUMIÈRE and S. SONNERY (Compt. rend. Soc. Biol., 1935, 120, 213—214).—The anticoagulant power of citric acid increases as the successive CO_2H groups are neutralised; that of Na salts of acids produced by heating is $<$ that of citric acid and decreases in the order itaconic and aconitic $>$ citraconic $>$ mesaconic acid. Alkali citrates are more coagulant than heavy-metal citrates.

R. N. C.

Regulation of protein disequilibrium of blood-serum under the influence of injections of serin: animal experiments. G. LEFROU and P. BONNET (Compt. rend. Soc. Biol., 1935, 120, 342—343).—Rabbits injected weekly with serin show necrotic areas at the point of inoculation after 7—9 injections in females, and later in males. The Arthus anaphylactic reactions are probably due to serin in the injected serum.

R. N. C.

Immunology and its connecting links with chemistry. L. E. DEN DOOREN DE JONG (Chem. Weekblad, 1935, 32, 590—601).—A review. S. C.

Production of immune serum by injection of cholesterol adsorbed on kaolin. W. MUTSAARS (Compt. rend. Soc. Biol., 1935, 120, 263—266).—Injection of rabbits with a suspension of pure cholesterol (I) adsorbed on pure kaolin produces an immune serum the complement-fixing power of which with (I) is $>$ that of the serum obtained by injecting (I) in combination with swine serum. Hence foreign proteins are not necessary to give (I) antigenic properties, which are considerably influenced by its physical state.

R. N. C.

Characteristic chemical reaction of formalised toxic filtrates. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 120, 313—316).—Diphtheria and tetanus antitoxins (I) give a red colour, stable for some days, when heated to 100° with small quantities of Na 8-amino- α -naphthol-3:6-disulphonate (II). The toxins (III) give the same reaction if treated with small quantities of CH_2O , but not with excess. The reaction occurs in the cold with (I) from which the active principle has been pptd. with Na β -naphthylamine-3:6:8-trisulphonate and citric acid. (II) gives the same colour with H_2O_2 , peptone containing traces of CH_2O and NH_3 , or formalised broth, suggesting that the reaction with formalised (III) is due to oxidisers formed by the action of CH_2O on the NH_2 of (III). (I) hence contain oxidising substances that are non-sp. components of the formalised (III), which is active only after removal of the active principles by pptn. or destruction.

R. N. C.

Antigenic power of staphylococcal toxin and anatoxin: its resistance to heat. G. RAMON and

R. RICHOU (Compt. rend. Soc. Biol., 1935, 120, 291—293).—The antigenic power of the toxin is destroyed rapidly between 50° and 60°, whereas that of the anatoxin decreases slowly with rise of temp., only disappearing completely at 80°. R. N. C.

Agglutination of *Bacillus pullorum*. A. STAUB (Compt. rend. Soc. Biol., 1935, 120, 341—342).—Agglutination is most intense at p_{H} 7.5—8. Old sera are more sensitive to p_{H} than young sera. R. N. C.

Determination of ash content of the leg bones of chicks with slipped tendon. T. T. MILBY (Poultry Sci., 1935, 14, 247—251).—Bones were freed from flesh and stored in 95% EtOH. Samples were subsequently crushed, wrapped in filter-paper, extracted with hot 95% EtOH, dried at 105°, and ashed at dull red heat. The desirability of making determinations at intervals during the course of experiments on calcification is emphasised. Vals. for chicks having slipped tendon were not significantly different from those for control birds. The ash content of femurs from chicks receiving 3% of MgCO_3 in the ration was < that from chicks given a normal ration, but > that from rachitic chicks. A. G. P.

Chemical topography of the brain. Chemical composition of the brains of normal and fasting cats. H. GORODISSKI (Ber. Ukrain. Biochem. Inst., 1928, 3, 125—142).—In the brains of normal cats, the total P contents of the different parts are in the order: tract. optic. (I) > corp. genic. lat. (II) and corp. quad. post. (III) > nucl. caudat. (IV) > grey substance of the cortical centres (motor, auditory, visual). The distribution of P-containing lipins follows that of total P, and the richer the parts are in P-containing lipins, the greater is the proportion of saturated, and the less of unsaturated, phosphatides. The brains of fasting cats (5—24 days' hunger, 7—44% loss in wt.) show a diminution in total P of (I); the lipin-P (as % of total P) diminishes in all parts. The non-lipin-P increases in (II), (III), and the grey substance of the motor cortical centre. The content of saturated phosphatides diminishes in nearly all parts, but most in (I) and least in (IV). F. A. A.

Chemical composition of parts of the nervous system. I. Grey matter of parts of the central nervous system of dogs. II. Vegetative nervous system of cows. A. V. PALLADIN, E. J. RASCHBA, and R. M. HELMAN (Ukrain. Biochem. J., 1935, 8, No. 1, 5—26, 27—46).—I. As regards the amounts of cholesterol (I) and unsaturated phosphatides (II) the parts form the series: grey matter of the spinal cord > nucleus caudatus > cerebral cortex and cortex cerebelli. The amounts of saturated (II) and cerebrosides in the spinal cord are < in the other parts. For total N, the order is cerebral cortex > cortex cerebelli and nucleus caudatus > spinal cord; as regards creatine, cortex cerebelli > nucleus caudatus > cerebral cortex > spinal cord. The quotients creatine-N:total N are: cortex cerebelli 4.20, nucleus caudatus 3.94, spinal cord 3.42, cerebral cortex 2.66. For amounts of dry residue, the order is: spinal cord > others. These results confirm the data of Abderhalden, Weil, *et al.* (I) is not a constituent of highly differentiated nerve-cells.

II. Ganglion nodosum n. vagi has a higher content of (I) than have ganglion coeliacus and the ganglion of the sympathetic trunk. For unsaturated (II) and acid-sol. P the order is: g. coeliacus > g. of sympathetic trunk, much > g. nodosum n. vagi; and for saturated (II): g. coeliacus (0.439) > g. nodosum n. vagi and g. of sympathetic trunk. The total P contents are: g. coeliacus 1.777, g. of sympathetic trunk 0.939, g. nodosum n. vagi 0.836. The total N is equally distributed. The val. of residual N exhibits considerable individual variations. The proportion of creatine-N is very low especially in g. nodosum n. vagi. The dry residue vals. are: g. coeliacus 24.4, g. of sympathetic trunk 21.1, g. nodosum n. vagi 20.5. The ganglia of the sympathetic and parasympathetic nervous systems differ in biological functions and in chemical composition. E. P.

Creatine content of various parts of the brains of vertebrate animals. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, No. 2, 51—71).—In the cow's brain, the cerebellum contains the largest amount of creatine, and then in decreasing amount the grey matter of the hemispheres, the white matter of the same, and the corpus callosum. The cerebella of rats, rabbits, and guinea-pigs contain most creatine, and the grey matter of the hemispheres of these animals, as well as that of the cow, contains the largest amount of total N and H_2O . J. N. A.

Creatine content of different parts of the brains of vertebrates. II. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 85—116).—In the dog's brain the creatine contents are in the order: cerebellum > cerebral grey matter > white matter of hemispheres > medulla; in the cat: cerebral grey matter, cerebellum > white matter of hemispheres, medulla; in hens: cerebellum > lobi optici, hemispheres. In the pigeon large individual variations occur, vals. for all parts of the brain lying within the same limits. The creatine content of the total brains of lizards, frogs, and toads is > in the brains of mammals and birds. H. D.

Creatinephosphoric acid in the brains of various animals. H. GORODISSKI (Ber. Ukrain. Biochem. Inst., 1928, 3, 109—114).—The acid is present in the brain of various animals, the % being greater in mammals (dog, cat, guinea-pig, rat) than in birds (pigeon, drake, cock, siskin). F. A. A.

Lecithin in brain when the diet contains animal and plant lecithin. S. V. FOMIN (Ukrain. Biochem. J., 1935, 8, No. 1, 47—60).—Food containing lecithin (I) from soya bean or from egg-yolk, or brain (cow, rat) does not increase the (I) content in the brain of rats. E. P.

Studies on osmotic equilibrium and on the kinetics of osmosis in living cells by a diffraction method. B. LUCKÉ, M. G. LARRABEE, and H. K. HARTLINE (J. Gen. Physiol., 1935, 19, 1—17).—A diffraction method, permitting rapid measurement of the average vols. of large nos. of cells, is applied to the unfertilised eggs of *Arbacia punctulata*. Good agreement with previous measurements by other

methods is found for the permeability to H_2O and to $(CH_2OH)_2$, and the relationship $P(V-b)=\text{const.}$ is found to hold. F. A. A.

Increased permeability to water of ageing unfertilised eggs (*Arbacia punctulata*). A. J. GOLDFORB (J. Gen. Physiol., 1935, 19, 149—165).—The rates of swelling of the unfertilised eggs, kept in sea- H_2O for various times after shedding, and transferred to dil. sea- H_2O , are observed. These rates increase with age. This increase in permeability is not correlated with degree of injury. F. A. A.

Effect of temperature on the glutathione content of cold-blooded animals. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1935, 120, 289—290).—Glutathione in frog's muscles is unchanged by temp.; in frog's liver and in *Carassius auratus* it falls with rise of temp. R. N. C.

Distribution of glutathione in the organs of some marine invertebrates. A. MONIER (Compt. rend. Soc. Biol., 1935, 120, 456—458).—The organs in descending order of glutathione (I) content are liver and hepato-pancreas, genital organs, muscles. In all cases reduced (I) is $>$ oxidised (I). R. N. C.

Chemical investigation of the liver oil of *Barbus brachycephalus*. S. EPELBAUM and D. ZUVERKALOV (Ber. Ukrain. Biochem. Inst., 1928, 3, 167—172).—The oil contains triglycerides of palmitic, oleic, and stearic acids. The acids present in the oil mostly have high mol. wt. and low I val. The oil gives a colour test for vitamin-A, approaching in intensity those of the usual liver oils. F. A. A.

Flavinphosphoric acid from liver. H. THEORELL, P. KARRER, K. SCHÖPP, and P. FREI (Helv. Chim. Acta, 1935, 18, 1022—1026).—Partial separation of flavin (I) from flavinphosphoric acid (II) in liver extracts is effected by repeated treatment of the aq. solution with amyl alcohol. Further purification of (II) through the Ca and Hg salts leads to a product giving 42.8% of ash and, as judged by cataphoresis experiments and ability to give the yellow oxidation enzyme with proteins, containing about 25% of (II). The proportion of free (I) in liver is very small. H. W.

Optical activity of lactoflavin. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1935, 18, 1026—1027).—Lactoflavin has $[\alpha]_D^{18} -106^\circ \pm 4^\circ$, $-103^\circ \pm 3^\circ$, $-100^\circ \pm 4^\circ$, $-96.6^\circ \pm 4^\circ$, and $-90.0^\circ \pm 5^\circ$ in 0.05N-NaOH ($c=0.5$, 0.3, 0.25, 0.15, and 0.1, respectively). H. W.

Hepatic chlorine in hyperthyroidised animals. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1935, 120, 52—53).—Liver-Cl in guinea-pigs and rabbits is generally increased by treatment with thyroid powder or extract; occasionally it is diminished. R. N. C.

Comparative chemistry of muscle. I. TAKAHASHI (J. Biochem. Japan, 1935, 22, 1—4).—The H_2O , P_2O_5 , and SO_4 contents of various species of mammals, birds, reptiles, amphibia, fishes, molluscs, and arthropoda are tabulated and discussed. F. O. H.

Influence of extirpation of the motor region of the cerebral cortex on chemical changes in muscle. S. FOMIN and S. EPELBAUM (Ukrain. Biochem. J., 1935, 7, No. 2, 39—50).—Extirpation of the motor region increases the creatinephosphoric acid content of muscle, whilst the inorg. P is decreased, so that the total val. is unaltered. The proteolytic processes in the motor cerebral cortex region undergo no change. J. N. A.

Extractives of giant salamander muscle. F. YAMASAKI (J. Biochem. Japan, 1935, 22, 5—8).—Data are given for the contents of glutathione, creatine (I), creatinine (II), and total S in skeletal muscle and of (I) and (II) in involuntary muscle (heart, stomach, intestine). F. O. H.

Creatinephosphoric acid content of fish muscle. A. V. PALLADIN and R. R. SIGALOVA (Ukrain. Biochem. J., 1935, 7, No. 2, 29—37).—Muscle of *Cyprinus carpio* contained about 0.35% of creatine (I) and about 0.02% of creatinephosphoric acid (II) (expressed as P). With older fish, the (I) content rises to 0.46%. Addition of dried blood to the H_2O causes a very slight increase in (I). There is probably no fundamental difference between fish and mammals as regards the (II) content of their muscles. J. N. A.

Determination of creatinephosphoric acid. I. T. SORENI (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 217—239).—The Fiske-Subbarow (A., 1926, 443) and Lohmann (A., 1928, 665) methods gave similar results with cat, dog, and rabbit muscle, whilst large differences occurred with those from rats and pigeons. H. D.

Influence of various diets on the amino-acids in muscle. S. V. FOMIN and V. DEMIN (Ukrain. Biochem. J., 1935, 7, No. 2, 147—157).—The tyrosine content of rat muscle is fairly const. and is not decreased by continuous protein starvation. The metabolism in the tissues is disturbed by a gelatin and pea diet, and the amount of tyrosine is increased, whilst the proportion of tyrosine-N to total N remains normal. Complete starvation does not affect the tyrosine content of the muscle. J. N. A.

Influence of thyroidectomy on the amino-acid composition of muscle. S. V. FOMIN and I. E. POZNER (Ukrain. Biochem. J., 1935, 7, No. 2, 159—167).—Thyroidectomy increases the tyrosine (I) in muscle, whilst the amount of tryptophan is unchanged; after 40—51 days the (I) returns to normal. The thyroid gland regulates the distribution of (I) in the organism. J. N. A.

Effect of diet on nitrogen and phosphorus compounds of muscles during fatigue. I. Effect on muscle-creatine and -phosphagen of albino rats. M. S. MISCHKIS (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 74—83).—On a protein-free diet the phosphagen, creatine, and H_2O contents of rats' muscles increase. Total N is unaffected. H. D.

Influence of training on the change in the synthetic powers of muscle after work. B. M. KOLDAEV (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 63—73).—Training diminishes to some extent the

reduction in the power of the muscle to synthesise hexosephosphoric acid due to fatigue. H. D.

Influence of work and training on the oxidation-reduction potential of muscle-tissue. R. V. TSCHAGOVETZ (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 31—62).—Fatigue makes the redox potential in rabbit's and frog's muscle more positive; training the muscle makes it more negative. H. D.

Muscle activity and oxidation processes. II. Effect of training and fatigue on muscle-glutathione. A. V. PALLADIN, S. E. BORSHKOVSKI, and L. I. PALLADINA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 5—14).—Training a rabbit's muscle prevents the decrease in reduced glutathione consequent on fatigue. H. D.

Effect of training and fatigue on the power of muscle tissue to reduce methylene-blue by the Thunberg method. A. V. PALLADIN and A. M. KASHPUR (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 15—30).—The reduction of methylene-blue (I) by fatigued rabbit's muscle is slower than normal; a trained muscle reduces (I) more rapidly than normal. H. D.

Physico-chemical constants of muscle-tissue. III. Electrical conductivity and p_H in the autolysis of muscle-tissue of pigeons with avitaminosis-B. S. V. FOMIN and D. N. STRASHESKO. IV. S. V. FOMIN, Z. S. GERSCHENOVITSCH, and D. N. STRASHESKO (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 117—124, 125—133).—III. The *post-mortem* increase in κ of the muscles of pigeons in avitaminosis-B is $<$ normal.

IV. The κ of the muscular tissue of mammals was $7.3\text{--}7.9 \times 10^{-4}$ and that of amphibians and fishes $4.8\text{--}4.9 \times 10^{-4}$ mho. H. D.

Physico-chemical constants of muscle-tissue. I. Influence of various foods on the conductivity and p_H of rat muscle. S. V. FOMIN and Z. S. GERSCHENOVITSCH. II. Influence of training [by electrical stimulation] on the variation of the physical constants of muscle-tissue. S. V. FOMIN, Z. S. GERSCHENOVITSCH, and V. DEMIN (Ukrain. Biochem. J., 1935, 7, No. 2, 133—140, 141—145).—I. Various protein foods produce very little change in the physico-chemical consts. of rat-muscle tissue. A flesh diet causes a fall in $[H^+]$, a bean diet gives a decrease of 12.4% in κ , whilst a gelatin diet produces a rise of 7.13%.

II. Training of the muscle causes a rise of 15.6% in κ and an increase of 8.44% in NH_2 -acid-N. J. N. A.

Phosphorus and nitrogen compounds in fish muscle. E. V. LACHNO (Ukrain. Biochem. J., 1935, 8, No. 1, 61—71).—There are no characteristic differences between the creatinephosphoric acid (I), creatine (II), and total N contents of the muscles of certain vertebrate fishes (e.g., carp, cod, perch, pike). They all contain (I) and their (II) content is slightly $<$ that of mammalian muscles. The total N is 2.79% (average), 5.77% of which is (II)-N. E. P.

Heat-coagulation and colloid structure of albumins.—See this vol., 1460.

Swelling of structured proteins. Influence of the reticular tissue on the swelling of collagen in water and hydrochloric acid. D. J. LLOYD and R. H. MARRIOTT (Proc. Roy. Soc., 1935, B, 118, 439—445).—Swelling of the collagen fibres from rats' tails is accompanied by rupture of the reticular sheath and rolling back to form rings. The reticular tissue of young rats is tougher and the swelling less. In HCl of $p_H < 2$ this tissue is weakened, and no differences were observed with age, but the swelling was $>$ would have been anticipated. H. G. R.

Mol. wt. and isoelectric point of thyroglobulin. M. HEIDELBERGER and K. O. PEDERSEN (J. Gen. Physiol., 1935, 19, 95—108; cf. this vol., 105).—Pig thyroglobulin (I) has a mol. wt. of 650,000 as determined from the sedimentation const. and diffusion data, 700,000 from sedimentation equilibrium measurements. Human (I) has a similar mol. wt. Native (I) has an isoelectric point at p_H 4.58, denatured (I) at p_H 5.0. The sp. vol. of (I) is 0.72. F. A. A.

Albumose and peptone content of the muscle of horned cattle. I. A. SMORODINCEV and N. N. KRILOVA (Bull. Soc. Chim. biol., 1935, 17, 1149—1156).—Failure of erepsin to produce any increase in the NH_2 -N of beef stored at $1\text{--}3^\circ$ for 15 days indicates that no albumoses or peptones are formed. A. L.

Acetylcholine in the tissues of invertebrates. Z. M. BACQ (Compt. rend. Soc. Biol., 1935, 120, 243—245).—Acetylcholine is found in large quantities in the tissues of the octopus, but only in traces or not at all in other invertebrates. Cholinergic nerves probably exist in molluscs, worms, and echinoderms. R. N. C.

Identification of acetylcholine extracted from the ganglionic cells of the octopus. Z. M. BACQ and F. MAZZA (Compt. rend. Soc. Biol., 1935, 120, 246—247).—Acetylcholine (I) is extracted from the ganglia of the central nervous system with $CCl_3 \cdot CO_2H$, and after removal of Cu with H_2S , pptd. with Reinecke's acid. The ppt. is dissolved in aq. $COMe_2$, SO_4 removed with $BaCl_2$, and H_2PtCl_6 and picric acid (II) are added to ppt. other impurities. After removal of excess of (II) with Et_2O and PhMe, (I) is pptd. by $HAuCl_4$ (III) and identified by its m.p. and analysis of the Au salt. A further impure fraction can be pptd. by (III) from the mother-liquor after evaporation. R. N. C.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. X. Reducing action of cholesterol sols. I. REMESOV and O. SEPALOVA (J. Biochem. Japan, 1935, 22, 71—83; cf. A., 1932, 632, 844).—Colloidal cholesterol (I) has a marked reducing action (5 and 10% sols correspond with 0.063 and 0.108% aq. glucose, respectively) which is dependent on concn. of (I), and is exerted in presence of serum or whole blood. Processes, e.g., pptn., filtration, etc., which influence the colloidal condition influence the reducing activity. Direct injection of (I) sols into animals increases the reducing action of the blood; this is probably related to conversion of (I) into sugar by the liver. A correction for presence of (I) is necessary in glucose determinations in blood etc. containing (I). F. O. H.

Electrophoresis of sterols. III. Cholesterol surfaces. L. S. MOYER (J. Gen. Physiol., 1935, 19, 87—94).—Various cryst. forms of cholesterol (I) have the same electrophoretic mobility. The mobility of (I) ground with ice at -10° decreases to one half, reverting to the original val. on drying. The isoelectric point of (I), ground or unground, is near p_H 3.

F. A. A.

Biochemistry of the aphides of the terebinth. J. TIMON-DAVID and B. GOUZON (Compt. rend. Soc. Biol., 1935, 120, 164—166).—Analytical vals. are given for the common constituents. Lipins and glycogen are high, whilst H_2O and total N are low.

R. N. C.

Protective power of lipins.—See this vol., 1202.

Physical chemistry of lipins. III. Relations between the iodine value of monophosphatides and their relations to neutral salts. M. SPIEGEL-ADOLF (Biochem. J., 1935, 29, 2413—2415; cf. A., 1932, 1089).—Sols of egg and brain lecithin and kephalin variously treated show a parallelism between the decrease in I val. and the disappearance of the anomalous effect of Br^+ on viscosity. F. A. A.

Pigments of human fat. L. ZECHMEISTER and P. TUZSON (Bull. Soc. Chim. biol., 1935, 17, 1110—1118).—The distribution of carotene, lycopene, xanthophylls, and capsanthin in the fat from several pathological human tissues is determined by chromatographic analysis. A. L.

Crystal forms produced by the solidification of fatty acids. M. OKRASINSKI (Wiad. farm., 1934, 61, 697—698; Chem. Zentr., 1935, i, 1952).—On cooling molten acids from cattle and horse fats, there are formed from numerous crystallisation centres groups of narrow polyhedra arranged similarly to tissue cells. Each polygon consists of many crystals in forms characteristic of the acids present.

A. G. P.

State of glycogen in the interior of the cell. I. Three-component system from clupein, nucleic acid, and glycogen or dextrin. S. J. VON PRZYŁECKI, W. GIEDROŃC, and H. RAFAŁOWSKA (Biochem. Z., 1935, 280, 286—292).—If mixed in appropriate proportions [small amounts of nucleic acid (I) (from yeast or herring roe) or large excess of glycogen (II)] clupein (III) (as sulphate), (I), and (II) combine in solution (p_H 7.0—7.3) to produce three-component simplexes. Simplexes are also produced with dextrin (IV) instead of (II), (IV) being united to the arginine residue of (I). The affinity of (I) for (III) is much $>$ it is for (II).

W. McC.

Carbohydrates of the albuminous gland of *Rana esculenta*. F. N. SCHULZ and M. BECKER (Biochem. Z., 1935, 280, 217—226; cf. A., 1900, i, 478; 1934, 1251).—Dil. acid hydrolysis liberates from the dried gland 30—35% of reducing sugars (calc. as glucose) consisting of equimol. amounts of galactose (I) and glucosamine. In the gland (I) does not occur in the phosphorylated state. According to the season of the year, 1—1.5% of polysaccharide (almost entirely glycogen, only traces of galactogen) is present.

W. McC.

Determination of tissue-carbohydrates. N. R. BLATHERWICK, P. J. BRADSHAW, M. E. EWING, H. W. LARSON, and S. D. SAWYER (J. Biol. Chem., 1935, 111, 537—547).—Various modifications of other authors' methods of determining glycogen, lactic acid, and fermentable and non-fermentable reducing substances in muscle are described in detail and applied to the determination of carbohydrates in fasting rats. Immediate freezing of the muscle to be examined is necessary.

H. D.

Accumulation of electrolytes. VIII. Accumulation of potassium chloride in models. W. J. V. OSTERHOUT and S. E. KAMERLING (J. Gen. Physiol., 1935, 19, 167—178).—Models are described in which the accumulation of electrolytes, particularly K^+ , in living organisms is imitated.

F. A. A.

Histochemical determination of potassium during the evolution of the oocytes of the hen. V. D. MARZA and L. T. CHIOSA (Compt. rend. Soc. Biol., 1935, 120, 345—347).— K is high in the large globules of the "primordial vitellus," the spherula of the globules of the white vitellus, and the granules within the globules of the yellow vitellus. It is low in all other tissues, but rises slightly in the ovular membranes during the third period of vitellogenesis. The diffused enzymes of the ciatrula in the parablasic region modify the vitellus globules considerably, and cause variations in their K content.

R. N. C.

Fixation of potassium by birds and fish. A. LEULIER and F. PAULANT (Bull. Soc. Chim. biol., 1935, 17, 1124—1136).—The K content of the embryo and the membrane of the eggs of the hen, duck, pigeon, and guinea-fowl is 0.15—0.167%, the corresponding val. for the turkey being somewhat smaller. The K content of hen-egg yolk (0.090%) is $<$ that of the others (0.110—0.156%). The increases in the wt. and K content of the chicken embryo run parallel during incubation, 85% of the available K being absorbed at the time of hatching. Growth and increase in K content of trout fry also follow the same course.

A. L.

Lactation. II. Technique for studying lactation in rats. R. G. DAGGS. **III. Effects of various dietary principles on lactation in rats.** R. G. DAGGS and R. L. TOMBOULIAN (J. Nutrition, 1935, 9, 575—580, 581—592).—A lactation-promoting factor occurs in a variety of natural products. Cystine or glutathione acts as a mammary stimulant.

A. G. P.

Dilatometric study of *in vitro* digestibility of milks. K. BHAGVAT and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1935, 2, B, 316—321).—Digestion of milk preps. and of caseinogen (I) by trypsin is readily followed dilatometrically (A., 1934, 109, 450, 1137), the fall in the dilatometer being strictly \propto liberation of NH_2-N . The hydrolysis of (I) in milk does not differ from that of (I) in artificial media. F. O. H.

Heterogeneity of casein. C. GROH and E. FALTIN (Math. nat. Anz. ung. Akad. Wiss., 1934, 50, 457—466; Chem. Zentr., 1935, i, 1720—1721).—Casein obtained from colostrum milk is sol. in 70% aq. EtOH, particularly if this is slightly acidified.

It resembles the Osborne-Wakeman albumin in solubility, but its composition resembles that of ordinary casein. No essential and regular change in the composition of casein is observed in the first stage of lactation. R. N. C.

Reductase and coreductase of milk. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 166—167).—Dilution of milk inhibits the coreductase which may be added in the form of yeast or meat extract to restore the reducing action. H. G. R.

Standardisation of the methylene-blue reduction test by the use of methylene-blue thiocyanate. H. R. THORNTON and R. B. SANDIN (Amer. J. Publ. Health, 1935, 25, 1114—1117).—It is suggested that the thiocyanate be used, with 1 part of dye to 300,000 parts of milk as the standard concn. H. G. R.

Reductase-time of milk and the bacterial content. J. D. FILIPPO (Chem. Weekblad, 1935, 32, 601—602).—Examination of 426 samples shows that there is no abs. parallelism between the no. of bacteria present in milk and the time taken to decolorise methylene-blue solution. Milk which decolorises the reagent in < 2 hr. is unfit for human consumption, although 3.8% of such samples contained $0.5\text{--}1 \times 10^6$ and 1.3% $< 0.5 \times 10^6$ bacteria per c.c. S. C.

Ammonia content of human and cow's milk. M. POLONOVSKI and P. BOULANGER (Bull. Soc. Chim. biol., 1935, 17, 1178—1183).—The increase in the NH_3 content of human and cow's milk on keeping is mainly of bacterial origin, unlike that taking place in the blood. A. L.

Ammonia content of the liquids of the internal media of some invertebrates. J. SOUTERBICQ (Compt. rend. Soc. Biol., 1935, 120, 453—455).— NH_3 in the blood or secretions of invertebrates is > in vertebrates; max. NH_3 occurs in carnivorous species such as *Maja* and *Sepia*. R. N. C.

Colloid osmotic pressure of the nutrient liquids of the marine invertebrates. P. MEYER (Compt. rend. Soc. Biol., 1935, 120, 305—307).—Vals. are given for a no. of marine invertebrates. The colloid osmotic pressure of the internal medium increases with the species in genealogical order, suggesting a relation with the general organisation of the animal. The tunicates are an exception to this rule, the colloid-osmotic pressure being < that of crustacean internal media. R. N. C.

Application of the micro-quinhydrone electrode to the determination of the p_H of the aqueous humour of rachitic and normal rats. J. A. PIERCE (J. Biol. Chem., 1935, 111, 501—506; cf. this vol., 1218).—The p_H of the aq. humour is scarcely influenced by temp. The average val. for normal rats was 7.46 and for rachitic rats 7.38. H. D.

Secretory phenomena in the oviduct of the fowl including the process of shell formation examined by the microincineration technique. K. C. RICHARDSON (Phil. Trans., 1935, B, 225, 149—195).—The processes leading to the formation of the

chalaza, egg-white, shell-membranes, and shell have been studied by cytological methods. H. G. R.

Bile acids of *Mugil cephalus*, Linn. K. WATANABE (J. Biochem. Japan, 1935, 22, 119—121).—The principal acid is taurochenodeoxycholic acid (A., 1925, i, 405). F. O. H.

Effect of grape as compared with other fruit juices on urinary acidity and the excretion of organic acids. R. C. CLOUSE (J. Nutrition, 1935, 9, 593—610).—Bottled concord grape and orange juices tend, in general, to increase urinary p_H , whereas apple juice has the reverse effect. The CO_2 -combining power of blood is increased by feeding grape and orange juices and decreased by apple. The increased excretion of org. acids caused by grape and orange juices is not due entirely to unoxidised residues of fruit acids, but includes uric and citric acids. Org. acids are concerned in the maintenance of the acid : base ratio of the body. A. G. P.

Water exchange [in the organism]. IX. Variations in diuresis and urinary p_H in animals on acidogenic and alkalogenic diets. M. SAVIANO (Atti R. Accad. Lincei, 1935, [vi], 21, 715—720).—The greater is the diuresis produced in dogs or rabbits, the nearer approaches the urinary to the blood- p_H . With alkalogenic diets, diuresis produces a p_H < that of the blood; this is due to constancy of the CO_2 tension and diminution of HCO_3' in the urine. F. O. H.

Surface-active substances in urine. K. YUSAWA (J. Biochem. Japan, 1935, 22, 49—70).—Normal human urine has σ 78.0—90.0 (average 83.2) dynes per sq. cm.; it is lowest in summer, and higher at p_H 8—9 (NaOH) than at p_H 3—4 (HCl). Separation of the constituents affecting σ by dialysis, extraction with solvents, etc. indicate them to be fatty acid derivatives of indole, C_6H_6 , and pyrrole, conjugated glycuronates, and ethereal sulphates. The effect of substances of these types on σ and the influence of $[\text{H}']$ are tabulated and discussed. F. O. H.

Excretion of the so-called synergistic gonadotropic factor of the anterior pituitary in the urine of castrates. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1934, 13, 1471—1472; Chem. Zentr., 1934, ii, 3268).—The Evans synergistic gonadotropic factor is present in measurable quantities in the urine of castrates and women at the menopause, and in smaller quantities in ox and gelding urine. Methods of testing are described. R. N. C.

Uroerythrin. M. WEISS (Deut. Arch. klin. Med., 1934, 177, 97—106; Chem. Zentr., 1935, i, 2036).—Uroerythrin, an orange-red pigment occurring in urine, is a reducing substance and is decolorised by light. It resembles urobilin in pptn. reactions. It shows weak absorption bands at 525—540 and 490—500 $m\mu$, similar to those of cochineal (I); the bands are sharpened and shifted towards the red by 33% H_3PO_4 . Acids colour it red, alkalis green. It is determined spectroscopically in urine by extracting with $\text{C}_5\text{H}_{11}\text{OH}$, clearing the emulsion with EtOH , adding 33% H_3PO_4 , and comparing with a (I) standard. It is not an elimination product of the bile, its excretion under pathological conditions

depending on the liver. It is possibly identical with xanthorubin from the serum of hepatectomised dogs.

R. N. C.

Factors concerning the solubility of uric acid in urine. M. RANGIER (J. Pharm. Chim., 1935, [viii], 22, 357—364).—Mainly a discussion of the nature of the uric acid-urochrome complex (cf. this vol., 774).

J. L. D.

Origin of the histidine in the urine of pregnant women. R. KAPPELLER-ADLER and F. HAAS (Biochem. Z., 1935, 280, 232—241).—Added histidine (I) is readily destroyed by the healthy and diseased liver of men and women and by the liver of ovariectomised women, but is scarcely or not at all attacked by the liver of pregnant women, in whom the histidase of the liver appears to be inactivated so that (I) passes into the urine and even accumulates in the liver. The liver of gravid animals (cat, guinea-pig) destroys (I). Extracts of placenta contain no preformed (I), and there is no relation between (I) excretion in pregnant women and the function of the placenta. W. McC.

Excretion of cocaine. H. A. OELKERS and E. VINCKE (Arch. exp. Path. Pharm., 1935, 179, 341—348).—Urinary excretion of cocaine (I) (method of determination in urine is given) following subcutaneous injection into mice, rats, guinea-pigs, rabbits, cats, or dogs is slight, max. after 1 hr., and dependent on vol. and reaction of the urine. Thus with marked excretion of acidic urine, 16% of the injected wt. of (I) is excreted. Absorption of (I) occurs through the bladder. Determination of (I) by its mydriatic action in mice is not sufficiently accurate. F. O. H.

Volumetric determination of glucose in urine. E. MEES (Süddeut. Apoth.-Ztg., 1935, 75, 2—3; Chem. Zentr., 1935, i, 1425).—An iodometric method, employing Fehling's solution, is described.

H. N. R.

Micro-determination of urea in blood and urine. M. LEVINSON (Bull. Soc. Chim. biol., 1935, 17, 1157—1162).—The method is based on the oxidation of the urea with excess of NaOBr and determination of the excess iodometrically. A. L.

Determination of minute amounts of lead in urine. J. R. ROSS and C. C. LUCAS (J. Biol. Chem. 1935, 111, 285—297).—The urine is freed from $\text{PO}_4^{'''}$ and metals other than Pb, and then treated with a soln. of diphenylthiocarbazone in CCl_4 in presence of $\text{NH}_3\text{-CN}'$; the red colour produced is compared colorimetrically with Pb standards. Only 100—200 c.c. of urine are required and the error is ± 0.004 mg. of Pb for amounts < 0.1 mg. of Pb. J. N. A.

Approximate determination of stercoporpyrins. I. BOAS (Biochem. Z., 1935, 280, 227—231).—An improvement of the method of Willstätter and Stoll ("Untersuchungen über Chlorophyll," 1913) is described. Account is taken of the amounts of porphyrin which pass into the solvents (COMe_2 , EtOH) used for purifying the faeces. W. McC.

Determination of phosphorus in faeces. C. MARIA (Arch. Farm. sperim., 1935, 60, 386—388).—2 g. of faeces are fused with $\text{Na}_2\text{CO}_3\text{-KNO}_3$ and the residue is extracted with H_2O , neutralised with AcOH, and treated with AcOH-NaOAc. Alternatively 0.2 g.

is ignited with glucose- Na_2O_2 (A., 1904, ii, 516), and the residue is treated with AcOH etc. In each case the liquid is titrated for $\text{PO}_4^{'''}$ by U acetate.

F. O. H.

Importance of ecology in relation to disease. R. P. STRONG (Science, 1935, 82, 307—317).—A lecture.

L. S. T.

Chemical decomposition and characteristics of the substances employed in the therapy of pernicious anæmia. J. SLÁDEK, S. SAWCZYCKA, and M. LIPSCHÜTZ (Časopis českoslov. Lék., 1934, 14, 305—317; Chem. Zentr., 1935, i, 1406).—The tyrosine and tryptophan contents of the albumin fraction of fresh cow's liver are 1.24% and 1.56%, respectively, before and 4.68% and 5.58% after extraction with COMe_2 . The therapeutic activity for pernicious anæmia remains in the residue. The liver extract used for intramuscular injection contains free NH_2 -acids. The method of Duesberg and Koll is recommended for the evaluation of therapeutic liver preps., and gives best results if the preps. are suspended in a buffer solution and filtered after prolonged extraction. The results are more comparable if the absorption in the blue region of the spectrum resembles that of the blank test. There is no clear evidence of a relation between the concn. of the active principle in the prep. and the strength of the absorption bands in the blue region. COMe_2 completely, and aq. COMe_2 partly, extracts the active principle. More active material is extracted by 0.5% HCl in 20% EtOH than by NaOH at the same concn.

R. N. C.

Blindness in cattle associated with a constriction of the optic nerve and probably of nutritional origin. L. A. MOORE, C. F. HUFFMAN, and C. W. DUNCAN (J. Nutrition, 1935, 9, 533—551).—A form of blindness in calves and young growing dairy cattle (distinct from vitamin-A blindness) is associated with the feeding of poor-quality roughage. Deficiency of vitamin-D or of Ca is not the major factor. The latter occurs in maize silage, timothy hay, and cod-liver oil.

A. G. P.

Chemistry of carcinoma. I. A. VON CHRISTIANI (Z. Krebsforsch., 1935, 41, 445—447; Chem. Zentr., 1935, i, 2028).—The Et_2O -sol. substance protecting carcinomatous cells from cytolysis is identified as a cholesteryl ester.

A. G. P.

Effect of X-rays on the metabolism and growth of transplantable tumours. G. BANCROFT, L. V. BECK, and M. A. RUSSELL (Biochem. J., 1935, 29, 2416—2423).—X-Rays are allowed to fall on one of two duplicate tumours implanted in the same rat, and the histological changes and the effect on aerobic glycolysis, R.Q., and O_2 uptake of the excised tissue followed. Using the two tumours Philadelphia 1 sarcoma (I) and Walker 256 carcinoma (II), glycolysis remains unchanged until extensive degeneration has taken place; O_2 uptake is lowered. The R.Q. is always lowered with (I), less definitely with (II). (I) is less sensitive to X-rays than (II); sensitivity does not appear to be directly associated with blood-sugar level.

F. A. A.

Cancer and mineral metabolism. R. BERG (Chem.-Ztg., 1935, 59, 813—815, 834—836).—The

significance of the mineral balance of foodstuffs, notably the Ca/Mg ratio, is discussed. A. G. P.

Synthetic hydrocarbons with carcinogenic action. R. SIBONI (Boll. Chim. farm., 1935, 74, 709—720).—A review.

Action of the serum of mice with tar cancer on the fluorescent power of solutions of uranine. A. BOUTARIC and J. BOUCHARD (Compt. rend. Soc. Biol., 1935, 120, 293).—No inhibition of the fluorescent power is produced by the cancerous sera.

R. N. C.

Existence in the liver of substances inhibitory to benzopyrene cancer of the white mouse. J. MAISIN, H. VASSILIADIS, and A. GODENIR (Compt. rend. Soc. Biol., 1935, 120, 259—261).—The COMe_2 -insol. fraction of Et_2O extract of liver contains a substance that inhibits the growth of experimental (benzopyrene) tumours and cancers in mice. The inhibitory effect is increased by boiling, suggesting that thermolabile activating substances are also contained in the extract.

R. N. C.

Preparation of organic peroxides and peroxidogens. W. KOCH and J. MAISIN (Compt. rend. Soc. Biol., 1935, 120, 104—106).—Acid peroxides are prepared by a modification of the method of D'Ans and Kneip, and ether peroxides by oxidation of the ethers with O_2 in presence of Pt. The name "peroxidogen" is given to the unsaturated compounds prepared from fructose, paraldehyde, MeCHO , and Et_2O by slow dehydration over H_2SO_4 . Peroxides are decomposed by H_2O into H_2O_2 and acids. Their prophylactic effect in benzopyrene cancer in mice is not simply due to O_2 liberation; the most active contain sufficient O for complete combustion to CO_2 and H_2O , and in many cases can, in presence of the corresponding acid, undergo intramol. rearrangement, which liberates a considerable quantity of energy.

R. N. C.

Effect of organic peroxides on the prophylaxis of experimental cancer in mice. W. KOCH and J. MAISIN (Compt. rend. Soc. Biol., 1935, 120, 106—108).—Diformaldehyde diperoxide has a definite prophylactic action on benzopyrene cancer.

R. N. C.

Modification of the Weltmann reaction in cancer: diminution of the coagulation band. G. CARRIERE, P. MARTIN, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 31—32).—The coagulation band is diminished in the sera of most cases of cancer.

R. N. C.

Production of lactic acid in irradiated and non-irradiated tumours. W. HAARMANN (Biochem. Z., 1935, 280, 173—183).—The capability of extirpated human tumours to produce lactic acid (I) from added carbohydrates (II) [glucose (III), fructose, glycogen, Na hexosediphosphate] and AcCO_2Na varies greatly with the kind of tumour, the (II) used and its concn., the nature and amount of other (II) present, and the capability of the tumours anaerobically to destroy (I). Almost always more (I) is produced from (III) than from other (II). Irradiated tumours behave similarly, but in some cases the production of (I) by them is reduced, although destruction of the

cells does not occur. Tumours are more sensitive to irradiation than is normal tissue. W. McC.

Histological modifications at the surface of the graft and the spleen in the course of regression of the Jensen sarcoma under the action of insulin. O. LAMBRET and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 188—190).—Insulin induces disappearance of hepatic and muscular glycogen, and hyperplasia of the spleen, in rats where the graft shows marked regression.

R. N. C.

Variations of the fibrinogen content of the blood in neoplastic affections. R. LOICQ (Compt. rend. Soc. Biol., 1935, 120, 253—255).—Blood-fibrinogen is increased in guinea-pigs with tumours resulting from inoculation with the Murray liposarcoma and in patients with neoplastic tumours.

R. N.

"Polypeptidaemia index" in experimental cancer in the guinea-pig, and in neoplastic tumours in man. R. LOICQ (Compt. rend. Soc. Biol., 1935, 120, 250—253).—The "polypeptidaemia index" represents the difference between the Kjeldahl N vals. of the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and phosphotungstic acid filtrates of the blood. It is increased in guinea-pigs with tumours resulting from inoculation with the Murray liposarcoma, but is scarcely affected in patients with neoplastic tumours in absence of cachexia or infection.

R. N. C.

Action on an experimental tumour of intravenous injections of ascorbic acid unassociated with iron, or associated with copper. F. ARLOING, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1935, 120, 205—206).—Injection of *L*-ascorbic acid in NaHCO_3 solution in rabbits with experimental tumours causes hepatic, renal, and peritoneal lesions. The Cu-dehydroascorbic acid complex causes rapid development of neoplastic lesions and visceral metastases, in sharp contrast with the Fe complexes.

R. N. C.

Action on experimental and human cancer of injections of combinations of iron and vitamin-C (ascorbic acid). F. ARLOING, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1935, 120, 201—204).—In the reaction between Fe salts and ascorbic acid, (I), Fe^{III} is partly reduced by (I) to Fe^{II} , which unites with (I) to form violet, strongly-reducing *ferroscorbon* (II), whilst the unreduced Fe^{III} forms yellow, stable, non-reducing *ferriscorbon* (III) with dehydroascorbic acid. Perifocal reactions appear rapidly on injection of (II) in cases of cancer, but scarcely ever on injection of (III). (III) lends itself more than (II) to use in prolonged stabilisation treatment. Both cause vaso-dilatation.

R. N. C.

Hepatic function. II. In portal cirrhosis and congestive heart failure. A. CANTAROW (Arch. Int. Med., 1935, 56, 521—529).—In cases of liver cirrhosis, the bromosulphonaphthalein (I) test of liver function did not run parallel with the concn. of serum-bilirubin (II), the latter being more closely related to the degree of ascites. Similar observations were made in four cases of Banti's disease. In congestive heart failure the severity was more closely

related to the retention of (I) than to the concn. of (II). W. O. K.

Importance of the "Takata reaction" for the diagnosis of liver disease in its relation to galactose and bilirubin overloading. L. SCHINDEL and E. BARTH (Klin. Woch., 1934, 13, 1329—1332; Chem. Zentr., 1934, ii, 3286).—The reaction is measured by the alterations in the flocculating effect of HgCl_2 on the serum. It is positive in liver disease, particularly cirrhosis. R. N. C.

Pancreatic diabetes in the dog deprived of its sympathetic nervous system. J. T. LEWIS and E. S. TURCATTI (Compt. rend. Soc. Biol., 1935, 120, 274—276).—Pancreatectomy in dogs that have been sympathetomised or deprived of the nervous tissue encircling the large vessels from the coeliac trunk to below the superior mesenteric artery results in diabetic symptoms similar to those appearing in untreated animals. Blood-sugar rises similarly in both cases, but the final rise 24—48 hr. before death, as well as the glycosuria, in the sympathetomised animal is > in animals operated by the other method. R. N. C.

Treatment of severe diabetic acidosis. Comparison of methods, with particular reference to the use of sodium *dl*-lactate. A. F. HARTMANN (Arch. Int. Med., 1935, 56, 413—434).—Parenteral administration of Na *dl*-lactate to combat diabetic acidosis is advocated. W. O. K.

Experimental diphtheric intoxication and ascorbic acid of the adrenals. G. MOURIQUAND, P. SÉDALLIAN, and A. COEUR (Compt. rend. Soc. Biol., 1935, 120, 216—217).—The AgNO_3 reaction of the adrenals of guinea-pigs diminishes 18 hr. after the injection of diphtheria toxin. R. N. C.

Disturbance of corpus luteum formation in avitaminosis-C and diphtheric intoxication. J. VON GAGYI (Virchow's Archiv, 1934, 293, 674—681; Chem. Zentr., 1935, i, 1580).—A physiological relationship is indicated between ovaries and adrenals in respect of vitamin-C economy. A. G. P.

Experimental azotæmia by injection of diphtheria toxin in the guinea-pig. J. CHALIER, M. JEUNE, and R. J. FOURNIER (Compt. rend. Soc. Biol., 1935, 120, 206—207).—Blood-urea begins to rise 6—9 hr. after injection of diphtheria toxin, and continues to rise until death; adrenaline secretion begins to fall at the same time. R. N. C.

Proteinases (cathepsin) in the tissues of the infantile organism with dysentery and toxic dyspepsia. B. GOLDSTEIN and M. GUINZBURG (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 147—159).—The cathepsin per g. of dry matter is < normal in glycerol extracts of liver, kidney, and spleen of children who have died of toxic dyspepsia. H. D.

Composition of the ash of thyroid gland and goitre. J. STRAUB (Endokrinol., 1934, 15, 15—25; Chem. Zentr., 1935, i, 1577).—Glands from Hungarian lowlands have less Ca and more K than those of Switzerland. This is an effect rather than a cause of the goitrous condition. A. G. P.

Chemotherapy of malaria. S. P. JAMES (Nature, 1935, 136, 743—745). L. S. T.

Two cases of myxœdema treated with thyrotropic hormone. M. WACHSTEIN (Klin. Woch., 1934, 13, 1434—1436; Chem. Zentr., 1934, ii, 3269).—Basal exchange is scarcely or not at all affected even by large quantities. R. N. C.

Liver-arginase in myasthenia gravis. Origin of creatine. A. T. MILHORAT (J. Biol. Chem., 1935, 111, 379—384).—The amount of arginase (I) in the liver of a boy with myasthenia gravis was normal, although large amounts of creatine had been excreted in the urine. There is no evidence that the creatinuria occurring in m. gravis is related to a lack of liver-(I), and that an insufficient amount of (I) might permit the preservation of the guanidine group in arginine, and the oxidation and conversion of the latter into creatine. J. N. A.

Indicanæmia in nephritis. I. GAVRILA and MIHAILEANU (Compt. rend. Soc. Biol., 1935, 120, 358—360).—Indicanæmia in patients without renal lesions varies between 0.20 and 0.92 mg. per 1000. Indicanæmia generally \propto blood-N in acute nephritis following scarlatina. In chronic nephritis it is const. if blood-N is < 1 g. per 1000, but increases with N above this level. It bears no relation to blood-Cl, albuminuria, or arterial pressure. R. N. C.

Rôle of cellular lysis (hæmolysis and leucolysis) in the cholesterol content of pleural effusions. V. DE LAVERGNE and P. KISSEL (Compt. rend. Soc. Biol., 1935, 120, 151—152).—Cholesterol (I) in pleural effusions is of local origin and is controlled by cellular lysis, depending on the no. and type of the destroyed cells. (I) is high in hæmorrhagic effusions, suggesting that hæmolysis takes place more readily than leucolysis. In putrid pleurisy, where leucocyte destruction is definite, (I) is > in hæmorrhagic pleurisy. R. N. C.

Inorganic constituents of the central nervous system of rabbits with experimental rabies. N. W. ROMENSKI (Ann. Inst. Pasteur, 1935, Suppl., 181—190).—In experimental rabies, Na is decreased and Ca increased in the brain and marrow. Mg and K are increased in the latter. H. G. R.

Silicosis and anthracotic lungs. F. V. TIDESWELL (Refract. J., 1934, 10, 185—186).—An attempt to separate the "active" SiO_2 producing silicosis from the inactive form by a 2% KOH solution is described. CH. ABS. (e)

Impregnation of the organism by dust. III. Partition of silica dust in the lungs. G. ANTOINE (J. Pharm. Chim., 1935, [viii], 22, 412—430; cf. this vol., 1396).—Determinations on roughly chopped tissue are subject to wide variations (0.0099—0.033%), but results on finely minced material do not vary > 20%. There is a regular increase in the SiO_2 content of a lung with age, and the superior lobe has a larger content than the other parts. The SiO_2 content of silicates from different lungs is fairly const. (86—94%). The two lungs from the same individual give similar results. P. G. M.

Intestinal stasis in low mineral diets. E. C. ROBERTSON and M. E. DOYLE (*J. Nutrition*, 1935, 9, 553—567).—Stasis induced by low-mineral feeding is relieved by supplements of CaCO_3 and K_2CO_3 , but not by vitamin-B. A. G. P.

Effect of traumatism on the distribution of chloride and sodium between the blood and tissues and the acid-base equilibrium. H. CHABANIER, C. LOBO-ONELL, A. DE GASTRO-GALHARDO, and E. LEHR (*Bull. Soc. Chim. biol.*, 1935, 17, 1145—1148).—In the traumatised muscle the increase in Cl' and Na over the normal val. is maintained as long as 48 hr. In the blood, however, whilst the corresponding vals. increase up to 24 hr., there is a subsequent decrease to < normal; at the same time, the alkaline reserve decreases for the first 24 hr. and then increases. A. L.

Chemotherapy of tuberculosis. V. Ethyl silicylricinoleate. E. HESSE, G. MEISSNER, M. SEBELIN, and H. MÜLLER (*Arch. exp. Path. Pharm.*, 1935, 179, 296—309).—The ester (I) is absorbed to the extent of approx. 55% from the intestine (dog). Retention of SiO_3^{2-} does not occur in mice. (I) is excreted through the intestine after oral or subcutaneous, and through the kidneys after intramuscular administration. Favourable results (formation of new tissue and encapsulation) in tubercular rabbits follow continuous administration of (I). F. O. H.

Chemistry of tubercular sputum. S. NAKAYAMA (*J. Biochem. Japan*, 1935, 22, 35—40).—The sputum (H_2O , 96.59%; fat, 0.68%; fat-free residue, 2.72%) yields on fractionation (with EtOH , Et_2O , COMe_2 , etc.) cholesterol, phosphatide (?), a cryst. substance, m.p. 136°, Ca, Mg, P, S, Cl, and protein (the hydrolysate of which yields histidine, arginine, tyrosine, and, in relatively high proportion, lysine). The high P content is characteristic. F. O. H.

Spectrographic investigation of gold distribution following gold therapy in men and animals. W. GERLACH (*Arch. exp. Path. Pharm.*, 1935, 179, 286—295).—Storage of Au occurs mainly in the liver, spleen, and, with greater variations, in the kidney of tubercular men and animals treated with solganal-B; the diseased tissue (e.g., lungs) contains relatively small amounts. Localisation of Au is, however, significantly influenced by calcification of the tissue. The histochemical method of Kurosu (*A.*, 1928, 549) is considered worthless (cf. B., 1932, 266). F. O. H.

Action of magnesium in experimental uræmia. F. AMANTEA (*Arch. Farm. sperim.*, 1935, 60, 353—364).—With rabbits in which uræmia has been produced by nephrectomy, ligature of the ureters, or injection of U salts, administration of Mg salts increases the blood-urea, the level returning to normal within a few hr. This is due to liberation of urea from the tissues. F. O. H.

Metabolism during pregnancy. C. N. COONS [with A. T. SCHIEFELBUSCH, G. B. MARSHALL, and R. R. COONS] (*Oklahoma Agric. Exp. Sta. Bull.*, 1935, No. 223, 113 pp.).—In balance studies retention of Ca was high, that of P and Mg relatively lower, of N

low, of Fe definitely inadequate, and of S usually negative. High storage of Ca, N, and Fe in early pregnancy proceeded independently of, and far in excess of, foetal requirements when conditions were favourable for storage, and in such cases increased retention in late pregnancy was not observed. A. G. P.

Growth and development, with special reference to domestic animals. XXXV. Energetic efficiency of milk production and the influence of body-weight thereon. S. BRODY and R. C. PROCTER. XXXVI. Endogenous nitrogen and basal energy relationships during growth. U. S. ASHWORTH (*Missouri Agric. Exp. Sta. Res. Bull.*, 1935, No. 222, 40 pp., No. 223, 20 pp.).—XXXV. The distribution of the total digestible nutrients in the diet between milk production, maintenance, and live-wt. increase is examined and a mathematical relationship established. Under customary conditions of observation the gross efficiency of milk production decreased with body-wt., but if other related factors were const. milk-production efficiency would probably be independent of body size.

XXXVI. The ratio of endogenous urinary N to the heat of basal metabolism increases with advancing age. Rats receiving a high-N diet excreted more N per unit body-wt. than did those having a low-N diet. Endogenous N approximates more closely to a logarithmic function of body-wt. than to a logarithmic function of basal heat production. More consistent results are obtained by relating min. endogenous N to the initial body-wt. than to body-wt. attained at the time of min. N excretion. A. G. P.

Determination of basal metabolism by interferometric gas analysis. M. BOURDEAU (*J. Pharm. Chim.*, 1935, [viii], 22, 393—411).—The apparatus and method described can be applied to any mixture of three gases which have no action on the metal chamber employed, provided that one of them can be easily eliminated. The results compare favourably with those obtained using Plantefol's precision eudiometer and the time taken for a determination is 15 min. compared with 50 min. P. G. M.

"Water intoxication" and water diuresis in adrenal insufficiency; importance of the adrenals in osmo-regulation. R. RIGLER (*Klin. Woch.*, 1935, 14, 227—228).— H_2O administered orally or 0.2% aq. NaCl injected intraperitoneally in adrenalectomised rabbits, rats, and mice is excreted less rapidly than in normal animals, even if good general health is maintained. The adrenals must therefore function as regulators of the osmotic condition of the body-fluids. R. N. C.

Influence of calcium ions on energy metabolism of the mammalian heart. H. C. PETERS, C. E. REA, and M. B. VISSCHER (*Proc. Soc. Exp. Biol. Med.*, 1934, 32, 268—271).—The mechanical energy of contraction and total liberated energy of the mammalian heart are increased by Ca^{++} . R. N. C.

Depigmentation of the eggs of *Cyprinus carpio*. T. BUSNITA and N. GAVRILESCU (*Compt. rend. Soc. Biol.*, 1935, 120, 224—225).—The deposition of yellow eggs instead of the normal green is associated with the

retention of the green pigment of the bile by the hepatic tissues; the pigmentation of the eggs is hence related to the biliary function. R. N. C.

Individuality in nutritive instincts and causes and effects of variations in the selection of food. W. F. DOVE (Amer. Naturalist, 1935, 69, 469—544).—The genetics and physiology of nutritive instincts are studied. E. A. H. R.

Influence of certain dietary constituents on the response of rats to gossypol ingestion. W. D. GALLUP and R. REDER (J. Agric. Res., 1935, 51, 259—266).—A high protein intake was favourable to the detoxication of gossypol (I). Diets rich in lactose (20%) or acid diets containing much Ca, which were detrimental to growth in normal rats, had relatively small effects on rats receiving (I). Alkaline diets high in Ca (1.2%) were the most satisfactory for nullifying the action of (I). A. G. P.

Effects of common food ingredients on the iodine content of hens' eggs. H. J. ALMQUIST and J. W. GIVENS (Poultry Sci., 1935, 14, 183—190).—Use of marine products (fish meal, oyster shell) in poultry rations provides > the I requirements of hens. The I content of eggs is not closely related to that of the ration. A. G. P.

Effect of mineral supplements on the length of the tail and wing feathers in white Leghorn hens. W. A. HENDRICKS (Poultry Sci., 1935, 14, 221—227).—No effects of practical significance were observed. A. G. P.

Synthetic diets for herbivora, with special reference to the toxicity of cod-liver oil. L. L. MADSEN, C. M. MCCAY, and L. A. MAYNARD [with G. K. DAVIS and J. C. WOODWARD] (Cornell Univ. Agric. Exp. Sta. Mem., 1935, No. 178, 52 pp.).—Prolonged feeding of cod-liver oil caused degeneration of skeletal and heart muscle, and fatty liver. Substitution of a vitamin-A and -D concentrate lessened but did not prevent the injury, which was not entirely prevented by exclusion of cod-liver oil from the diet. Other factors are probably involved. Vitamin-B (yeast) decreased the injury in goats. A. G. P.

Synthetic diet for rabbits. R. PASSMORE (Biochem. J., 1935, 29, 2469—2470).—A diet containing washed Diophane enabled two out of three rabbits to maintain wt. H. D.

Effects of glucose on the respiratory exchange of adrenalectomised dogs. A. MORALES (Compt. rend. Soc. Biol., 1935, 120, 272—274).—The blood-sugar curve falls a little after adrenalectomy and then begins to rise; glucose (I) accelerates the rise, and the curve returns to its initial level after 1 hr. The increase due to (I) is increased 48 hr. after adrenalectomy, and the normal level is not reached again until after 5 hr. Basal metabolism and the R.Q. fall progressively after adrenalectomy. (I) increases basal metabolism and R.Q. R. N. C.

Respiratory quotients of normal and tumour tissue. K. A. C. ELLIOTT and Z. BAKER (Biochem. J., 1935, 29, 2433—2441).—The results differ from those of Dickens and Šimer (A., 1930, 1468), no significant differences being found between the R.Q.

of different tissues or between normal and tumour tissue of well-fed adult animals. F. A. A.

Respiration of the brain. L. CRASNARU and N. GAVRILESCU (Compt. rend. Soc. Biol., 1935, 120, 226—228).—Novarsenobenzene decreases respiration of the brain, although it increases that of other tissues. It serves to distinguish in the brain between O₂ consumption in carbohydrate metabolism and in one or more other undefined oxidative systems co-existent with carbohydrate metabolism. R. N. C.

Oxygen consumption in muscle activity in relation to fibre length. P. W. SMITH (Proc. Soc. Exp. Biol. Med., 1934, 32, 257—260).—O₂ consumption in activity rises on extension to a max., afterwards falling; resting O₂ consumption rises with increasing rapidity, whilst the curve for total O₂ consumption is a straight line. R. N. C.

[Digestion of] bread. W. HEUPTKE (Deut. med. Woch., 1934, 60, 1823—1827; Chem. Zentr., 1935, i, 1464).—Aleurone-protein is digested by pepsin and trypsin in a few hr. without destruction of the cell-wall. The protein of bran is easily digested. High faecal N following the feeding of brown bread is not due to defective resorption, but is derived from the intestinal secretion. Of the dry matter of faeces 4—5% represents intestinal N. The val. of rye bread is discussed. A. G. P.

Protein metabolism of the armadillo, *Chaetophractus villosus*, Desmarest. B. BRAIER (Compt. rend. Soc. Biol., 1935, 120, 361—362).—Total protein catabolism in the fasting state is low compared with those of the dog and rat. After a diet of meat the azoturic coeff. of the urine is raised from 65% to 75%; allantoin, representing 95—96% of the purines, is unchanged. Creatinine is < in the fasting dog or rat. R. N. C.

Biological value of the protein of dry diffusion residues in the beet sugar industry. S. E. BORSHKOVSKI, I. S. ONOPRIENKO, and L. S. TSCHERKASOVA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 177—198).—The biological val. of dry press-cake from the beet industry is equal to that of clover hay and is < that of caseinogen; it is increased by mixing with these materials.

Effect of starvation on aminogenetic and proteolytic processes in the cerebrum. A. V. PALLADIN and M. F. GULI (Ukrain. Biochem. J., 1935, 7, No. 2, 73—89).—The cerebra of dogs, rats, and pigeons showed large variations in the H₂O content and in the coeffs. of aminogenesis and proteolysis, as did also those of the starving animals. There is a definite difference between the summer and winter cerebral metabolism of the pigeon. J. N. A.

Nuclein metabolism. VII. Polynucleotidase. VIII. Bound and free purines in ox organs. IX. Tissue-ammonia and nuclein metabolism. K. MAKINO (J. Biochem. Japan, 1935, 22, 93—96, 97—107, 109—118).—VII. Hydrolysis of yeast- or thymus-nucleic acid by commercial trypsin preps. produces depolymerisation but not fission of the nucleotides (I) or nucleosides (II).

VIII. Data are given for the content and nature

of purines, free and as (I), (II), or nucleoprotein-nucleic acid, in fresh and autolysed spleen, liver, and pancreas.

IX. Autolysis of liver, kidney, and spleen is accompanied by formation of NH_3 , two important sources of which are adenosine-mono- and -tri-phosphoric acids. Added thymus-nucleic or guanylic acid is deaminated to the same extent with each of the three tissues; yeast-nucleic acid differs to an extent dependent on the tissue. F. O. H.

Metabolism of the phospholipins. VIII. Passage of elaidic acid into tissue-phospholipins. Evidence of the intermediary rôle of liver-phospholipin in fat metabolism. R. G. SINCLAIR (J. Biol. Chem., 1935, **111**, 515—526; cf. this vol., 1397).—Rats are fed with elaidic acid (I) and the % of (I) in the tissue-phospholipins is determined by pptn. as its Pb salt. The phospholipins of young rats on a diet rich in (I) contain up to 33% of (I) and of adult rats up to 30%; in the liver the entrance of (I) into the phospholipins is much > in the muscles. It is suggested that there are two classes of phospholipins, one functioning as the constituent of membranes containing a high % of unsaturated fatty acids and another functioning as intermediaries in fat metabolism and containing chiefly saturated fatty acids. H. D.

Creatine formation in the organism. I. TAKAHASHI and T. KUMON (J. Biochem. Japan, 1935, **22**, 9—14).—Arginine, carnitine, or γ -amino- β -hydroxybutyric acid in presence of autolysing liver-tissue (dog) at 37° produces creatine; similar results are obtained by perfusion experiments on the isolated liver. A mechanism is advanced based on methylation or demethylation of these compounds and subsequent addition of guanidine. F. O. H.

Creatine : creatinine ratio in hibernating and spawning frogs. F. YAMASAKI (J. Biochem. Japan, 1935, **22**, 15—34).—Creatine (I) formation in male frogs (whole body) is somewhat > that in females. In both sexes, the (I) content during April is only 50—80% of that during other months, whilst the creatinine (II) level during winter hibernation is < the summer level. In the female, (II) is also min. during April, and is therefore related to the spawning period. F. O. H.

Influence of acid diet on creatine excretion. L. PALLADINA (Ber. Ukrain. Biochem. Inst., 1928, **3**, 23—28).—In opposition to the findings of Underhill (A., 1916, i, 865), feeding rabbits on acid diet does not produce creatinuria unless the food intake is lessened. F. A. A.

Synthesis of aspartic acid from fumaric acid in the liver. K. P. JACOBSON, J. TAPADINHAS, and F. B. PEREIRA (Compt. rend. Soc. Biol., 1935, **120**, 33—36).—Aspartic acid (I) appears in dog's blood that has been mixed with NH_4 fumarate (II) and perfused through the isolated liver. < 10% of the (II) used is transformed into (I). Considerable quantities of (II) are converted by fumarase into malic acid. R. N. C.

Effect of injections of extract of spleen on metabolism of carbohydrates. M. POLONOVSKI,

H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, **120**, 181—182).—Spleen extract does not affect blood-sugar or the residual chromic index in normal subjects, but in cancerous and diabetic subjects the residual chromic index is depressed, indicating that the breakdown of the intermediary products of carbohydrate metabolism is accelerated. R. N. C.

Relation of adrenal cortex to carbohydrate metabolism. T. KONOMI (J. Biochem. Japan, 1935, **22**, 149—161).—Ligature of the pancreatic duct in rabbits produces a slight hyperglycæmia and an increase in the size of the adrenal cortex and in its content of co-enzyme (I) for anaerobic decomp. of hexose phosphate by striated muscle (A., 1934, 1400). Similar effects follow injection of lactic acid. The rate of blood-glycolysis is increased by (I), whilst the ability to decompose hexose diphosphate lost by blood on hæmolysis is restored. F. O. H.

Effect of fatigue on the oxidation of phenol in various diets. A. V. PALLADIN and L. I. PALLADINA (Ukrain. Biochem. J., 1935, **7**, No. 2, 19—27).—On a basic diet (mainly oats) fatigue caused rabbits to excrete nearly all the injected PhOH in the urine. With an acid diet (beet and hay) only 30—40% of the PhOH was oxidised in fatigue, whilst the normal animal oxidised 59—65%. Fatigue also decreases the synthesis of conjugated PhOH compounds, less being formed on a basic than on an acid diet. J. N. A.

Influence of hunger on administered phenol. A. PALLADIN, S. MALLAR, and A. ROZENBERG (Ber. Ukrain. Biochem. Inst., 1928, **3**, 15—21).—During hunger, as on an acid diet, a smaller proportion of PhOH injected into rabbits is excreted in the urine as uncombined PhOH than on a normal diet. F. A. A.

Synthesis of conjugated glycuronic acids during fasting. L. M. MAKAREVITSCH-GALPERIN (Ber. Ukrain. Biochem. Inst., 1930, **4**, 53—63).—During fasting the excretion of conjugated glycuronic acids in the urine of rabbits is decreased, as is also the excretion of mentholglycuronic acid (I) after the subcutaneous injection of menthol in oil. After prolonged fasting the excretion of (I) rises somewhat, but is still < normal. W. O. K.

Synthesis of thymolglycuronic acid on an acid and alkaline diet. M. G. KUSNETZOVA (Ber. Ukrain. Biochem. Inst., 1930, **4**, 17—29).—Rabbits, subcutaneously injected with thymol in EtOH, excreted more thymolglycuronic acid on an alkaline than on an acid diet. W. O. K.

Influence of the character of the diet on the synthesis of mentholglycuronic acid. A. PALLADIN and E. PERSOVA (Ber. Ukrain. Biochem. Inst., 1928, **3**, 7—14).—After the injection of menthol into rabbits, more mentholglycuronic acid is excreted on an acid than on a basic diet. F. A. A.

Influence of the character of the diet on the oxidation of benzaldehyde in the rabbit. D. A. ZUYERKALOV (Ber. Ukrain. Biochem. Inst., 1930, **4**, 174—185).—The excretion of BzOH by rabbits ceases when they are on an acid but increases on an

alkaline diet. The oxidation of PhCHO to BzOH and the excretion of hippuric acid (I) are independent of the acid or basic character of the diet, except that acid diets somewhat decrease the synthesis of (I).

W. O. K.

Ketogenesis-antiketogenesis. II. **Ketogenesis from amino-acids.** N. L. EDSON (Biochem. J., 1935, 29, 2498—2505).—With rat-liver slices the most strongly ketogenic NH_2 -acids are leucine (I), tyrosine (II), and phenylalanine (III), whilst hydroxyproline (IV) has a considerable action. The other NH_2 -acids are either non-ketogenic, or show a slight ketone formation. With the fed rat only (I), (II), (III), and (IV) show ketogenesis, whilst with the starved animal only *dl*-(I) is ketogenic, many of the others being antiketogenic. Muconic acid is not ketogenic and arginine and ornithine are antiketogenic, possibly because they lower the effective concn. of NH_3 by promoting urea synthesis. It is suggested that the catabolism of (III) involves (a) conversion into (II) and breakdown through $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and homogentisic acid, and (b) deamination and formation of $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$.

J. N. A.

Influence of various carbohydrates on formation of lactic acid and lactacidogen in aqueous brain extract. H. GORODISSKI and S. EPELBAUM (Ber. Ukrain. Biochem. Inst., 1930, 4, 115—121).—Lactic acid and lactacidogen are formed from mannose, glucose, galactose, maltose, dextrin, and starch in aq. extracts of cat's brain.

W. O. K.

Lactic acid and lactacidogen during short autolysis of aqueous extracts of cat's brain. H. GORODISSKI and S. EPELBAUM (Ber. Ukrain. Biochem. Inst., 1930, 4, 123—133).—During autolysis of aq. brain extracts, lactic acid (I) disappears and lactacidogen (II) is synthesised, (I) being utilised for the synthesis of (II). During the autolysis of the whole brain, (I) may either increase or decrease, but (II) always decreases.

W. O. K.

Formation of acetaldehyde from lactic acid. A. UTEVSKI (Ber. Ukrain. Biochem. Inst., 1930, 4, 89—97).—Addition of 0.05*N*-Na lactate to the minced pectoralis of the pigeon did not result in an increased formation of MeCHO, except in the presence of $\text{C}_2\text{O}_4^{''}$ or F^- .

W. O. K.

Velocity of resorption of alcohol in the "small stomach" (Pavlov). R. O. FAITELBERG and B. M. MEDVEDEV (Ukrain. Biochem. J., 1935, 8, No. 1, 169—190).—1 c.c. of 40% EtOH (I) per kg. body-wt. is introduced into the small stomach of a dog. After 20—30 min. (I) appears in the blood and in the breath, whilst the resorption of O_2 and the elimination of CO_2 increase, and the R.Q. decreases. (I) is completely eliminated after 5 hr. Catarrh of the mucous membrane retards resorption of (I).

E. P.

Coefficient of ethyl alcohol oxidation and basal metabolism in some homœothermic species. E. LE BRETON, M. NICLOUX, and G. SCHAEFFER (Compt. rend., 1935, 200, 1133—1135).—The velocity of EtOH oxidation in the mouse, rat, guinea-pig, rabbit, and pigeon \propto the intensity of basal exchange. The fowl gives anomalous results.

R. N. C.

Adjustment of the mineral nutrition of test animals during investigation of the biological value of proteins. S. E. BORSHKOVSKI and L. S. TSCHERKASOVA (Ukrain. Biochem. J., 1935, 7, Nos. 3—4, 199—216).—Feeding of $\text{Ca}_3(\text{PO}_4)_2$ to rabbits on a diet of sedge hay increased assimilation of Ca, P, and N. The necessity for control of the mineral balance of the test animals during a determination of the biological val. of proteins is emphasised.

H. D.

Bile acids and calcium metabolism. XI. **Calcium excretion in thyroparathyroidectomised dogs.** S. TUZIOKA (J. Biochem. Japan, 1935, 22, 123—137).—Excretion of Ca in dog's bile is > that in the urine; thyroparathyroidectomy primarily (after 1 day) decreases the former and does not affect the latter, but 6—7 days later markedly diminishes both excretions. The diminished level of bile-Ca, but not that of urine-Ca, is increased (but not to normal levels) by administration of thyroparathyroid extracts and, to a greater extent, by that of cholic acid.

F. O. H.

Radioactive indicators in the study of phosphorus metabolism in rats. O. CHIEWITZ and G. HEVESY (Nature, 1935, 136, 754—755).—The distribution of P in the excreta and organs of rats fed daily with small amounts of Na phosphate containing ^{32}P as a radioactive indicator is recorded. The average time which a P atom spends in the organism of a normally fed rat is approx. 2 months. Bone formation appears to be a dynamic process involving continuous loss and replacement of P atoms.

L. S. T.

Resorption and excretion of calcium, magnesium, and phosphorus. Distribution of inorganic phosphate in the different sections of the digestive tract. J. MAREK, O. WELLMANN, and L. URBÁNYI (Math. nat. Anz. ung. Akad. Wiss., 1934, 51, 329—331; Chem. Zentr., 1935, i, 2039).—Analytical vals. are given for the contents of the various sections of the digestive tracts in young pigs after a long period of feeding with a basal diet supplemented by vitamin-D or different mineral substances. The solubility of the latter in dil. HCl and their elimination as $\text{PO}_4^{'''}$ are established.

R. N. C.

Comparative pharmacodynamic properties of some cardiotonic glucosides. A. BEAUNE (Bull. Sci. pharmacol., 1934, 41, 590—594; Chem. Zentr., 1935, i, 1413—1414).—The pharmacological actions on the heart of a no. of drugs of the digitalis, strophanthus, and intermediary groups are compared.

R. N. C.

Determination of cardio-active glucosides by the step-photometer. F. HAUSCHILD (Arch. exp. Path. Pharm., 1935, 179, 255—259).—The aq. glucoside (0.004—0.0025% of digitoxin, *g*- or *k*-strophanthin) is treated with alkali and picric acid (A., 1922, ii, 882) and the resulting colour is compared with suitable standards by means of the step-photometer. The average error is 1.3%.

F. O. H.

Ergot alkaloids.—See this vol., 1512.

Pharmacology of ergometrine. G. L. BROWN and H. H. DALE (Proc. Roy. Soc., 1935, B, 118,

446—477).—Ergometrine produced central excitation with general sympathetic stimulation, but with only a trace of the sp. paralysing action on motor sympathetic effects. It causes cyanosis of the cock's comb, but, unlike ergotoxine (I), does not lead to gangrene. It is less toxic than (I) and causes a rise in body-temp. in toxic doses. A pressor action is exhibited in the spinal cat, which is < that of the alkaloids of the (I) group.

H. G. R.

Comparative toxicity of aqueous extracts of *Ustilago maidis* and ergot preparations. B. DRAGIŠIĆ and B. VARIČAK (Arch. exp. Path. Pharm., 1935, 179, 319—326).—Aq. extracts of *U. maidis* (corn-ergot) produce similar but more marked symptoms of toxicity in mice than does ergotamine (I) or ergotine, indicating a high content of (I)-like substances.

F. O. H.

Toxicity of ripe poppy capsules. R. BUNGE (Arch. exp. Path. Pharm., 1935, 179, 465—474).—The pharmacological properties (mice, frogs) of the crude contents and alkaloid fractions of ripe and unripe poppy capsules indicate that, in addition to morphine (I), other alkaloids present include codeine (II) and thebaine (III), but not narcotine or papaverine. The toxicity of the crude alkaloid prep. is the same for ripe and unripe capsules, and is > that corresponding with the (I) content owing to the presence of (II) and (III).

F. O. H.

Increase in local anaesthesia by morphine. W. KEIL and G. HEPP (Arch. exp. Path. Pharm., 1935, 179, 420—424).—Min. effective concns. for complete anaesthesia of rabbits' cornea for 15—20 min. are novocaine (I) 2%, tutocaine (II) and cocaine (III) 0.5%, pantocaine (IV) 0.02%, percaine (V) 0.002%. At the conclusion of anaesthesia, intravenous injection of 5 mg. of morphine produces a second anaesthesia of duration 20—25 min. for (I), (II), and (IV), 40 min. for (III), and 70 min. for (V). The application of this phenomenon to the determination of analgesic activity is discussed.

F. O. H.

Increase and diminution of the convulsive action of local anaesthetics. W. KEIL and I. RÜHLING (Arch. exp. Path. Pharm., 1935, 179, 415—419).—The toxicity of intravenously injected novocaine or percaine in rats is increased nearly 4 times by administration of adrenaline or "corbasil" (o-dihydroxyphenylpropanolamine hydrochloride). Similarly ephedrine (*d*, *l*, or *dl*) increases the convulsive action of cocaine by 200—250%. Slight novocaine convulsions are reduced by NaNO₂ (2 mg. per kg.) or glyceryl nitrate (5 mg. per kg.); adonine has a similar action.

F. O. H.

Anæsthetic properties of trichloroethylene. J. C. KRANTZ, jun., C. J. CARR, and R. MUSSER (J. Amer. Pharm. Assoc., 1935, 24, 754—756).—Anaesthesia by inhalation in the rat and rabbit is accompanied by stimulation of the skeletal muscles and a mild hyperglycæmia. No anaesthesia is obtained on rectal administration.

H. G. R.

Pharmacological differentiation of veramon and a mixture of its components. R. FISCHER and H. SALZER (Arch. exp. Path. Pharm., 1935, 179, 327—333).—Solutions of veramon cannot be

differentiated from those of the 1:1 mol. mixture of veronal and pyramidone by physico-chemical tests or by their pharmacological action in rabbits (cf. A., 1933, 74).

F. O. H.

Toxicity of pyramidone-veronal mixture. H. SALZER and R. FISCHER (Arch. exp. Path. Pharm., 1935, 179, 334—340).—The central action of pyramidone (I) following administration of (I)-veronal (II) mixtures to rabbits rapidly and proportionately disappears, so that finally a pure (II) action is shown. (I) also retards the excretion of (II) and hence prolongs the narcosis.

F. O. H.

Asymmetrical arylalkylcarbamides.—See this vol., 1488.

Toad poisons. VII.—See this vol., 1502.

Mode of action of commercial preparations of histidine. A. SCHWARTZ, L. ISRAËL, and A. JACOBI (Compt. rend. Soc. Biol., 1935, 120, 124—126).—The production of urticaria on the skin by commercial preps. of histidine is due to traces of histamine.

R. N. C.

Hyperpolypeptidæmia induced by intraperitoneal injections of peptone in the rabbit. C. LAMBRET and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 184—186).—Injection of peptone induces const. hyperpolypeptidæmia, the intensity of which varies with the rabbit. Non-protein-N rises, whilst NH₂-acids vary. The increased polypeptide content disappears in 24 hr. At the same time corpuscular and plasma-Cl fall and blood-sugar rises.

R. N. C.

Liberation of histamine-like substances in the infarction of the intestine. G. UNGAR, X. J. CONTIADES, and R. G. PALMER (Compt. rend. Soc. Biol., 1935, 120, 326—328).—Embolisms provoked by lycopodium in the intestinal arteries of the dog cause an increase of gastric secretion both in the embolised animal and in another animal with which it is cross-circulated, suggesting that histamine-like substances are liberated; infarction appears in the intestine in 3—4 hr. The same effects occur with non-embolising irritants.

R. N. C.

Effect of glycerophosphate and lecithin-fatty acids on sensitivity of cats to adrenaline. A. VON JENY and J. VON MÉHES (Arch. exp. Path. Pharm., 1935, 179, 403—414).—Aq. glycerophosphate (I) (0.001—1.0%) has a slight choline-like peripheral action, inhibited by atropine (II). Suspensions of fatty acids (III) from egg-lecithin have a slight depressor action, decreasing on continuous administration and inhibited by (II). The ester (IV) from (I) and (III) has a choline-like depressor action and is inhibited by (II). (IV) enhances the pressor action of adrenaline, especially in decapitated, (II) treated cats even after adrenalectomy. (IV) probably combines with adrenaline-antagonistic choline in the blood.

F. O. H.

Effect of tetrahydro-β-naphthylamine on the creatinephosphoric acid, creatine, and lactacidogen of white and red muscle. A. PALLADI and E. SAVRON (Ber. Ukrain. Biochem. Inst., 1928, 3, 65—70).—Tetrahydro-β-naphthylamine (I) leads

to a diminution in the lactacidogen content of the biceps muscle of rabbits, and to a smaller diminution in the semitendinosus. (I) increases the creatine (II) content of red and white muscle, and the increase in the red is > in the white. Rabbits poisoned with (I) show a greater % of (II) as creatinephosphoric acid than normal rabbits.

F. A. A.

Experimental intoxication by apiole : toxicity ; lesions of the liver and kidney. A. PATOIR, G. PATOIR, BEDRINES, and PAYEN (Compt. rend. Soc. Biol., 1935, 120, 192—194).—The lesions are described. The same alterations are produced by cryst. apiole, free from $(o\text{-C}_6\text{H}_4\text{Me})_3\text{PO}_4$, as by green apiole.

R. N. C.

Physiological inversion of the hypertensive effects of 3:4-dihydroxyphenylaminomethylcarbinol. RAYMOND-HAMET (Compt. rend. Soc. Biol., 1935, 120, 421—424).—The pressor effect in the dog is inverted by raising the arterial pressure by pinching the second carotid artery.

R. N. C.

Effects of dinitrocresol on oxidation and fermentation. M. E. KRAHL and G. H. A. CLOWES (J. Biol. Chem., 1935, 111, 355—369; cf. this vol., 1027).—The principal effect of 4:6-dinitro-*o*-cresol (I) on oxidation precedes and is not directly concerned with O activation and transfer. (I) does not increase the rate of O_2 consumption in dehydrogenase systems or in a tissue which has been frozen and thawed, and its effect on oxidations depends largely on the active functioning of a naturally occurring O transfer system. (I) markedly stimulates the anaerobic fermentation of yeast, the effect varying with the type of yeast.

J. N. A.

Action of *p*-phenylenediamine on the chemical processes in striped muscle. A. PARSCHEIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 113—116).—Injection of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ hydrochloride or sulphate into the dorsal sac of the frog produces rigidity of the muscles and an increased formation of lactic acid. The amount of creatinephosphoric acid is unchanged.

J. N. A.

Sodium salicylate poisoning ; favourable influence of glucose. H. MADISSON (Deut. Arch. klin. Med., 1934, 176, 612—625; Chem. Zentr., 1934, ii, 3277).—Fatty degeneration is attended by disappearance of glycogen, and is lessened by treatment with glucose.

R. N. C.

Effect of bromobenzene on the utilisation of cystine and methionine by the growing rat. A. WHITE and R. W. JACKSON (J. Biol. Chem., 1935, 111, 507—513).—The normal growth of rats fed on a diet containing caseinogen (I), starch, sugar, and lard is inhibited by feeding PhBr; the effect is counteracted by feeding cystine or methionine although taurine, Na_2SO_4 , or a digest of (I) is ineffective. Bromophenylmercapturic acid is isolated from the urine of rats fed with PhBr.

H. D.

Acute toxicity of ethyl chaulmoograte. G. A. EMERSON and H. H. ANDERSON (Proc. Soc. Exp. Biol. Med., 1934, 32, 289—291).

R. N. C.

Toxicity of carbon tetrachloride. E. CIARAVINO (Boll. Chim. farm., 1935, 74, 741—748).— CCl_4

or CHCl_3 (≤ 0.55 mg.) is detected (e.g., in cadavers) by vaporisation in a current of H_2 , which on ignition in contact with Cu produces a green flame (due to formation of HCl). Aspiration of the products of combustion and absorption in aq. NH_3 , the Cl content of which is subsequently determined, affords a quant. method. CCl_4 and CHCl_3 are differentiated by suitable colour reactions.

F. O. H.

Relative toxicological effects of synthetic ethanol and grain fermentation ethanol in blended whiskies. C. W. MUEHLBERGER (Amer. J. Publ. Health, 1935, 25, 1132—1134).—The effects on man are identical.

H. G. R.

Aluminium as a factor contributing to the rise and progress of different pathological processes in the organism. A. L. TCHIJEVSKI and T. S. TCHIJEVSKAJA (Acta Med. Scand., 1934, 83, 501—504).—Food cooked in Al vessels increases the no. of cases of inflammation of the gastro-intestinal tract, colitis, and nephritic and hepatic diseases. Al salts and colloids react with biological membranes and may alter the charges they carry from negative to positive. Feeding white mice from Al vessels increases the no. of cases of spontaneous cancer.

G. H. F.

Therapeutic action of organic arsenic compounds. H. SCHLOSSBERGER (Ber., 1935, 68, [A], 149—163).—A review.

Synthesis of menthologlycuronic acid in arsenic poisoning. E. M. PERSOVA (Ber. Ukrain. Biochem. Inst., 1930, 4, 43—51).—After injection of a solution of menthol in oil into normal rabbits, up to 22% was excreted in the urine combined with glycuronic acid, whilst in the case of rabbits poisoned with As only 1—10% was so excreted.

W. O. K.

Antagonistic effect of potassium iodide in baldness due to thallium acetate. O. V. HYKES and F. A. DIAKOV (Nature, 1935, 136, 685).—KI reduces the toxicity of TlOAc to rats and prevents the loss of hair produced by Tl poisoning.

L. S. T.

Histo-spectrographic study of the fixation of manganese in experimental chronic intoxication by manganese dioxide. A. POLICARD (Compt. rend. Soc. Biol., 1935, 120, 364—366).—Rats on a diet containing MnO_2 excrete most of it in their faeces, but exhibit renal sensitivity after some weeks. Mn can be detected histo-spectrographically in the renal cortex and the liver, but in later stages tends to pass the cerebral cortex and base; if the MnO_2 is then discontinued Mn may also be carried to the lung and testicle.

R. N. C.

Influence of phosphorus poisoning on the synthesis of menthologlycuronic acid. B. NAZARJANZ (Ber. Ukrain. Biochem. Inst., 1928, 3, 159—165).—A diminution in the spontaneous excretion of glycuronic acid during P poisoning depends on the diminution in the food intake. P poisoning, if accompanied by pathological changes in the liver, is accompanied by a diminution in the synthesis of menthologlycuronic acid.

F. A. A.

Influence of phosphorus poisoning on the creatinephosphoric acid, lactacidogen, and creatine content of red and white muscle. A.

PALLADIN and A. KUDRJAVZEVA (Ber. Ukrain. Biochem. Inst., 1928, 3, 57—63; cf. A., 1924, i, 915).—Poisoning with large doses of P leads to an increase of creatinephosphoric acid (I) and creatine (II), and a decrease in lactaciden in red and white muscle. The increase in (I) is much greater in red than in white muscle. The % of (II) combined with H_3PO_4 is increased, and the increase is greater in red than in white muscle. Poisoning with small doses of P leads to increase of (I) and of bound (II) in red muscle, but the (I) content of white muscle remains normal.

F. A. A.

Treatment of poisoning due to inhalation of hydrocyanic acid. W. WIRTH (Arch. exp. Path. Pharm., 1935, 179, 558—602).—S compounds (e.g., $Na_2S_2O_3$, $Na_2S_4O_6$), some heavy metals (Ni and Co and a few Fe salts), methæmoglobin-producing substances (e.g., $NaNO_2$), aldo- and keto-derivatives (e.g., glucose and dihydroxyacetone), and alkali carbonates are efficacious, the prophylactic activity being > the curative power. Characteristic changes in blood-[H⁺] occur in rabbits after inhalation of HCN.

F. O. H.

Effects of inhalation of hydrogen fluoride. II. Response following exposure to low concentration. W. MACHLE and K. KITZMILLER. III. Fluorine storage following exposure to sublethal concentrations. W. MACHLE and E. W. SCOTT (J. Ind. Hyg., 1935, 17, 223—229, 230—240).—II. A concn. of 0.0152 mg. per litre, although slightly irritating, was tolerated by guinea-pigs, but growth-rate was somewhat slower than usual. The erythrocyte count was decreased and lesions, similar to but less severe than those observed with higher concns., developed.

III. Normal rabbits contain 10 mg. of F per kg., but this may be increased as much as 10-fold by exposure to sublethal concns. of HF. The bulk of the F is stored in the bones, but it is found in all other tissues except the blood, fat, and liver.

H. G. R.

Action of nitrites on the intestine. F. BERNHEIM (Arch. int. Pharmacodyn. Thérap., 1934, 48, 91—96; Chem. Zentr., 1934, ii, 3275).— $MeNO_2$ and $EtNO_2$ relax guinea-pigs' intestines, $MeNO_2$ being 5—10 times more active.

R. N. C.

Nitric oxide and toxicity of nitrous gases. G. PFLESSER (Arch. exp. Path. Pharm., 1935, 179, 545—557).—Exposure of mice to NO+air in an apparatus such that oxidation is retarded indicates that NO is more toxic than equiv. concns. of other N oxides. Thus max. concns. tolerated are 0.03% for NO and 0.12% for NO_2 , whilst the respective toxic symptoms are markedly different. The results are correlated with the toxicity of mixed nitrous gases.

F. O. H.

Toxicity of concentrated salt solutions. F. LASCH and D. ROLLER (Arch. exp. Path. Pharm., 1935, 179, 459—464).—Intravenous injection of hypertonic (20—30%) aq. Na or Li sulphate, tartrate, H phosphate, citrate, or chloride has a lethal action, producing tetanic convulsions, respiratory and circulatory failure, and finally pulmonary oedema, due to disturbances of ionic equilibrium of the blood. Follow-

ing such treatment, intravenous injection of org. Ca before the onset of oedema alleviates or inhibits the toxicity.

F. O. H.

Effect of sodium hydrogen carbonate on glycæmia from pilocarpine and from ligature of the portal vein. V. PAPILIAN and V. PREDA (Compt. rend. Soc. Biol., 1935, 120, 58—60).— $NaHCO_3$ inhibits the hyperglycæmia produced by ligature of the portal vein, by mobilising glycogen in the liver. It has no effect on hyperglycæmia produced by pilocarpine.

R. N. C.

Effect of radium rays on living cells. C. S. GAGER (Science, 1935, 82, 327).—A discussion.

L. S. T.

Action of radium on glycolytic activity of neoplastic tissues. C. GRANDCLAUDE, M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1935, 120, 183—184).—Ra irradiation disturbs carbohydrate metabolism in tumours; glycolytic activity in the neoplastic tissues is depressed.

R. N. C.

Effects of rare earths on the polarisation capacity of frog's skin and their significance in relation to colloidal chemistry and permeability. K. YOMOGITA (Z. Biol., 1935, 96, 487—501).—The salts of certain tervalent rare earths in low concns. (0.001—0.0005M) irreversibly decrease the polarisation capacity of surviving frog-skin, but in higher concns. (0.0025—0.0015M) they produce only a reversible reduction, whilst in still higher concns. the effect is again irreversible. The results are considered in relation to the action of positively charged multivalent cations on the negatively charged cell colloids.

W. O. K.

Influence of functional changes in the auditory centres on proteolysis. S. FOMIN (Ber. Ukrain. Biochem. Inst., 1928, 3, 143—146).—A lessening of auditory stimulation is accompanied by a retardation of proteolysis in the auditory centres, and the ratio of residual N to total N is less in the experimental animals (young dogs) than in controls.

F. A. A.

Liberation of histamine-like substances by excitation of the peripheral end of the splanchnic nerve: hæmorrhagic lesions of the intestine by intra-arterial injections of histamine. G. UNGAR, X. J. CONTIADES, and A. GROSSIORD (Compt. rend. Soc. Biol., 1935, 120, 328—330).—Splanchnic excitation in one dog causes increase of gastric secretion in another animal cross-circulated with it, hæmorrhagic lesions occurring in the intestine of the former animal. Injection of histamine in the afferent artery of an intestinal loop produces similar lesions.

R. N. C.

Delayed effects of denervation of the adrenal gland on adrenaline secretion. J. A. SGROSSO (Compt. rend. Soc. Biol., 1935, 120, 270—272).—Electric excitation of the recently denervated adrenal of the dog provokes a discharge of adrenaline (I), which does not occur 2—3 months after denervation. (I) discharge is also provoked from the recently denervated gland by nicotine, coniine, or candicine iodide (II), but the response decreases with the passage of time. The response to (II) is increased

by previous electric excitation, but is unaffected by yohimbine. R. N. C.

Displacement of ions in electrolytes during the very short discharges employed in electrophysiology. P. FABRE (Compt. rend. Soc. Biol., 1935, 120, 23—26).—The inertia factor involved in the displacement of ions by ordinary shocks of 10^{-4} sec. duration does not appear in shocks of 10^{-6} sec. duration. R. N. C.

Determination of [the concentration of] enzymes. B. RUBIN and L. NAUMOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 83—86).—An investigation of difficulties that arise in extracting completely and in determining the concns. of enzymes. J. L. D.

Spectroscopy of an enzyme reaction.—See this vol., 1189.

Embryo-chemistry of amphibia. VII. Enzymes in eggs of giant salamander. I. TAKAHASHI (J. Biochem. Japan, 1935, 22, 45—47).—After 2—3 weeks' development, the embryos contain amylase, nuclease, and glycerophosphatase, but not esterase, trypsin, arginase, or urease. F. O. H.

Action of hydrogen cyanide on the oxidase of *Althaea rosea*. V. ZANOTTI (Boll. Chim. farm., 1935, 74, 669—670).—Exposure to gaseous HCN temporarily inhibits the oxidase activity of *A. rosea* leaves. F. O. H.

Influence of reduced glutathione and ascorbic acid on the destruction of adrenaline by the oxidising enzymes of the potato. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 45—48).—Asparagine, alanine, glycine, and leucine inhibit the spontaneous oxidation of adrenaline (I) in decreasing order of activity, but have no effect on the oxidation of (I) by potato juice. This oxidation is inhibited by ascorbic acid and by reduced, but not by oxidised, glutathione. R. N. C.

Spectroscopy of purified enzymes. I. Xanthine oxidase and catalase. R. ITOH (J. Biochem. Japan, 1935, 22, 139—148).—Purified xanthine oxidase (from milk) has an absorption max. at 279 $m\mu$ at p_H 7; with increased alkalinity the val. shifts to a longer λ . Liver- and blood-catalase have max. at 406 and 266 $m\mu$ and haemin one at 406 $m\mu$. The activity of these catalases is not related to flavins, traces of which occur even in highly purified preps. F. O. H.

Catalase in embryonic development. III. Catalase activity during growth period of *Salmo irideus* and *Esox lucius* embryos. U. SAMMARTINO (Arch. Farm. sperim., 1935, 60, 372—385).—Fertilised eggs of *S. irideus* exhibit a continuous increase in catalase activity after approx. 12 days' incubation; this increase is associated with the initiation of blood circulation and general growth of the embryo. Similar phenomena occur in *E. lucius*, in which catalase activity begins to increase on the 5th day. F. O. H.

Influence of training [by electrical stimulation] and fatigue on the catalase of muscle. A. V. PALLADIN and E. J. RASCHBA (Ukrain. Biochem. J., 1935, 7, No. 2, 5—18).—Training increased the cata-

lase content of rabbit muscle, whilst fatigue caused no essential change, but on the earlier trained muscle it increased the catalase activity. Experiments with glutathione showed that after training the conditions for oxidation-reduction processes in muscle were improved. J. N. A.

Ascorbic acid and blood-catalase. II. Demonstration of vitamin-C deficiency. G. TÖRÖK and L. NEUFELD (Klin. Woch., 1934, 13, 1816—1818).—Injection of ascorbic acid increases the catalase action of blood in cases of known vitamin-C deficiency; it has no similar effect on normal cases. By this method, latent -C deficiency, with no clinical symptoms, can be recognised. G. H. F.

Dilatometric studies in the enzymic hydrolysis of polysaccharides. III. Hydrolysis of starch, amylose, and amylopectin by taka-diastase. H. B. SREERANGACHAR (Proc. Indian Acad. Sci., 1935, 2, B, 333—341; cf. this vol., 250).—When sol. starch is hydrolysed by takadiastase, the dilatometric depression per millimol. of maltose liberated is 4.0, whilst the depression per 1° fall in α is 10.7. For potato starch and two amylopectin (I) preps., the respective vals. are 4.0, 3.6, and 3.7 per millimol. of maltose and 10.7 [for one of the (I) preps.] per 1° fall in α . F. O. H.

Taka-amylase. IV. Effect of alcohol and salts on amylase and maltase action. V. Changes in amylase and maltase activities of a taka-diastase solution on keeping. VI. Proportion of amylase and maltase in taka-diastase on purification. T. KITANO (J. Soc. Chem. Ind. Japan, 1935, 38, 447B, 447—449B, 449—450B).—IV. Maltase (I) activity of a taka-diastase (II) solution is largely inhibited by 40% EtOH, but amylase (III) inhibition is slight. No such preferential inhibition is obtained with 25% NaCl.

V. The (I) of a (II) solution is more thermolabile than the (III). Acid destroys both enzymes to about the same extent, but alkali destroys (III) more rapidly than (I).

VI. In the fractional pptn. of (II) with EtOH, the first fractions are richer in (III), and the later richer in (I). Dialysis, especially after keeping, causes a greater decrease in (I) than in (III).

E. A. H. R.

Salt activation. II. Influence of salts on the stability of amylase. K. V. GIRI (J. Indian Chem. Soc., 1935, 12, 567—574; cf. this vol., 1162).—The alteration of the rate of hydrolysis of starch by the amylase of sweet potato is due to stabilisation or sensitisation of the enzyme by the added salt. At $p_H < 6$ (the optimum) 0.05N-NaCl increases the stability; at p_H 6 it is without effect. Higher salt concns. decrease the stability. The following orders of efficiency are found: $\text{NaF} > \text{NaCl} > \text{Na}_2\text{SO}_4 > \text{NaNO}_3$; $\text{CaCl}_2 > \text{NaCl} > \text{KCl} > \text{LiCl}$. R. S. C.

Action of different amylases on starch. E. OHLSSON and O. ROSEN (Svensk farm. Tidskr., 1934, 38, 497—552; Chem. Zentr., 1935, i, 1402).—The activities of taka-diastase, amylase from ungerminated barley, and amylase from green malt are compared. Differences in the activity curves

for the two malt amylases were apparent under all experimental conditions (A., 1932, 303). Ungerminated barley and saccharogen-amylase, as prepared by the authors, contain small proportions of dextrinogen-amylase.

A. G. P.

Direct and quantitative study of amylolytic activity of amylases. M. L. CALDWELL and F. C. HILDEBRAND (J. Biol. Chem., 1935, 111, 411—420).—An accurate method for the measurement of amylase activity depends on the determination of residual starch or amylose (I) at any stage of its hydrolysis by various amylases through its quant. pptn. by EtOH. Under specified conditions the ppts. are not appreciably contaminated by dextrans or maltose, and the difference between the wts. of original (I) and pptd. (I) gives a measure of the amylolytic activity of the amylase.

J. N. A.

Blood-amylase response to acetylcholine and its modification by eserine and atropine. W. ANTROPOL, A. SCHIFFRIN, and L. TUCHMAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 383—385).—Blood-amylase is increased by intramuscular administration of acetylcholine. The response is increased by previous administration of eserine and inhibited by atropine.

R. N. C.

Emulsin. XXIII. Influence of substitution in the benzene nucleus on the enzymic fission of phenol- β -D-glucosides. II. B. HELFERICH and C. P. BURT (Annalen, 1935, 520, 156—163; cf. this vol. 964).—Guaiacol with tetra-acetylglucosidyl bromide and NaOH-aq. COMe₂ affords the Ac₄ derivative, m.p. 155—157°, $[\alpha]_D^{20}$ —30.2° in CHCl₃, of *guaiacol*- β -D-glucoside (I), m.p. 155.5—157.5°, $[\alpha]_D^{25}$ —66.8° in H₂O, obtained by deacetylation with NaOMe-MeOH. By similar methods are obtained *isoeugenol*- β -D-glucoside (II), m.p. 187.5—189.5°, $[\alpha]_D^{20}$ —60.0° in EtOH (Ac₄ derivative, m.p. 140—143°, $[\alpha]_D^{21}$ —24.8° in CHCl₃), and the 3-CH₂Ph ether, m.p. 165—168°, $[\alpha]_D^{22}$ —60.20° in EtOH, of *protocatechualdehyde*-4- β -D-glucoside (III). The Ac₄ derivative of (III) with tetra-acetylgalactosidyl bromide-NaOH-aq. COMe₂, and deacetylation of the Ac₃ derivative gives *protocatechualdehyde*-4- β -D-glucoside-3- β -D-galactoside + H₂O, $[\alpha]_D^{20}$ —100.5° in H₂O, hydrolysed by emulsin, at p_H 5.0, more slowly than the corresponding β -D-diglucoide (*loc. cit.*). (I) (*p*-position free) and (II) (C:C in *p*-position) are both attacked more slowly by emulsin than is vanillin- β -D-glucoside (*p*-CHO).

J. W. B.

Inactivation and regeneration of the glycolytic enzyme system of muscle extract. L. MICHAELIS and J. RUNNSTRÖM (Proc. Soc. Exp. Biol. Med., 1934, 32, 343—349).—The glycolytic enzyme (I) of muscle extract, after inactivation by exposure to O₂, can be reactivated to a degree > the original activity by thioglycollic acid, thus corroborating the oxidation-reduction reversible inactivation hypothesis. There is evidence that (I) contains ·SH.

R. N. C.

Mechanism of glyoxalase activation by glutathione. J. GIRŠAVIČIUS and P. A. HEYFETZ (Nature, 1935, 136, 645—646; cf. this vol., 476).—The compound formed between glutathione (I) and

AcCHO (II) is regarded as the true substrate of glyoxalase action. From the rate at which lactic acid is produced and the changes in free ·SH which occur in the reaction between (I) and (II), it is concluded that (I) first combines by means of its ·SH with the substrate, (II), and then, as the enzyme-catalysed reaction develops, enters into further transformations in which its ·SH is again involved.

L. S. T.

Inactivation of fumarase. K. P. JACOBSON and J. TAPADINHAS (Compt. rend. Soc. Biol., 1935, 120, 36—38).—The inactivation of fumarase (I) by Ag⁺ depends on the time of incubation; (I) is completely inactivated in 6 hr. but a reactivation occurs in 24 hr. (I) in fresh liver extract is more resistant to Ag⁺ than in old extracts.

R. N. C.

Influence of different diets on the enzymes of the organism. IV. Fasting and the enzymes of the tissues. B. GOLDSTEIN and K. I. KATKOVA. **V. Protein-free food and the enzymes of blood and tissues.** B. GOLDSTEIN, R. R. SIGALOVA, and V. D. MELNISHENKO (Ukrain. Biochem. J., 1935, 7, No. 2, 91—101, 103—129).—IV. In starving rabbits there is no alteration in the lipase (I) of liver, kidney, and lung. The wt. of the liver decreases rapidly, due to a decrease in the total quantity of tissue, and this simultaneously produces a decrease in the blood-(I). The amylase of the liver is not affected.

V. Rabbits fed on a protein-free diet live 1.5—2 months. There is no alteration in the amylase of the blood and liver, or in the (I) of the lung. There is a very small increase of (I) in the liver, and a marked increase in the kidney. Sometimes there is an increase of (I) in the blood.

J. N. A.

Thyroid gland, lipase, and catalase. E. KEESER (Arch. exp. Path. Pharm., 1935, 179, 310—318).—Liver-lipase is inhibited *in vitro* by thyroxine (I), thyroid extracts, thyronine (II), di-iodotyrosine (III), and extracts of blood, brain, liver, spleen, and anterior and posterior pituitary lobes. The inhibition by (I) is suppressed by the anti-thyroid factor from thyroidectomised animal's serum. Blood- and organ-catalase *in vitro* are activated by thyroid and anterior pituitary preps. and inhibited by (III), KI, and anti-thyroid factor, whilst (I), (II), iodo-dihydroxypropane (IV), and glutathione (V) are without action. The catalytic activity of thyroid gland sections is enhanced by (IV) and (V) and inhibited by (III), NH₄SCN, and quinol. The mechanism of these and allied phenomena is discussed.

F. O. H.

Choline-esterase in invertebrates. Z. M. BACQ (Compt. rend. Soc. Biol., 1935, 120, 247—248).—Choline-esterase is present in the blood and tissues of molluscs, the blood of *Sipunculus*, and the muscles of *Spirographis*, *Holothuria*, and *Ascidia*. It is absent from crustacean blood and tissues, ascidian and insect blood, and beetle and sponge tissues. Crustacean muscles are insensible to acetylcholine, which disappears rapidly on injection without being fixed by the tissues.

R. N. C.

Cholesterol esterase in blood. W. M. SPERRY (J. Biol. Chem., 1935, 111, 467—478).—When serum or heparinised human plasma is incubated at 37—40°,

the ratio of combined to total cholesterol (I) increases several fold. Heating to 55–60° destroys this effect, attributed to an enzyme having an optimum at p_H 8. The free (I) of red blood-cells is not esterified under these conditions, and the esterification is less in hæmolyzed whole blood. F. A. A.

Tyrosine-tyrosinase reaction in presence of l-ascorbic acid. F. SCHAAT (Helv. Chim. Acta, 1935, 18, 1017–1021).—In spite of the presence of l-ascorbic acid (I) the typical tyrosinase (II) reaction (introduction of a second OH in the mol.) can proceed unchecked under the influence of (II); the solution remains colourless, although frequently saturated with O_2 , but the presence of appreciable amounts of 3:4-dihydroxyphenylalanine (III) is soon detected by $FeCl_3$. Restriction of oxidation by (I) takes place only when the change does not require further aid from (II) and there is no evidence of direct influence of (I) on the actual (II) action. (III) is also produced from tyrosine in presence of (I), but in much smaller amount than when (II) is present. H. W.

Antityrosinase function of glutathione in vitro. F. CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 73–74).—0.5% of glutathione completely inhibits tyrosinase reactions in vitro. H. G. R.

Occurrence of arginase in the giant salamander. T. KUMON (J. Biochem. Japan, 1935, 22, 41–43).—*In-vitro* experiments in PO_4''' buffer at p_H 6.6 indicate a high arginase content in the liver, smaller amounts in the kidney, blood, and spleen, and its absence from the pancreas, heart, and skeletal muscle. F. O. H.

Affinity relations of animal and vegetable dipeptidases. W. GRASSMANN, L. KLENK, and T. PETERS-MAYR (Biochem. Z., 1935, 280, 307–324).—Animal (kidney) and vegetable (yeast) dipeptidases do not differ as regards their affinities for dipeptides. The affinity for leucylglycine is < 10 times that for alanylglycine (I) and the affinity for (I) is 4–9 times that for glycylglycine (II), whilst the affinity for glycyl-leucine is $>$ that for glycyl-alanine (III) and that for (III) is $>$ that for (II), although, in the second series, the differences are less pronounced. Regularities are also observed in the variation of the degree of restriction of the dipeptidases by NH_2 -acids, which then form the series leucine $>$ valine (IV) $>$ alanine (V) $>$ glycine. Glutamic acid has no restrictive power, but phenyl-alanine and tryptophan are powerful inhibitors, and proline, asparagine, and arginine have effects intermediate between those of (IV) and (V). Glycyl-aminobenzoic acids (VI) are slightly attacked by dipeptidases practically free from aminopolypeptidase (from yeast) and much more attacked by non-purified liver extracts of about the same dipeptidase content. The enzymic hydrolysis of (VI) is affected by H_2S much $<$ is that of ordinary dipeptides. As regards enzymic hydrolysis (VI) do not differ qualitatively (cf. Balls *et al.*, A., 1931, 392).

W. McC.

Behaviour of pepsin in the ultracentrifuge after alkaline inactivation. J. ST. L. PHILPOT (Biochem. J., 1935, 29, 2458–2464).—The sediment-

ation const. (s) of pepsin (I) brought to $p_H < 7$ falls by about 1/3, although the (I) remains homogeneous. Reduction of the p_H of such a prep. to < 4.8 is accompanied by a large rise in s, and loss of homogeneity, three distinct components being present having s 10, 20, and 25 times that of normal (I). Thus alkali-inactivated (I) is unlike denatured proteins in being homogeneous, but has undergone some change which makes it more readily denatured by acid. F. A. A.

Cathepsin of tissues. B. GOLDSTEIN (Ukrain. Biochem. J., 1935, 8, No. 1, 87–104).— H_2S , used as activator for cathepsin (I), sometimes restricts its activity. A weak activation or inhibition but not a strong inhibition is converted into a strong activation by dilution. E. P.

Cathepsin in the embryo and in maternal tissues. I. B. GOLDSTEIN and E. J. MILGRAM (Ukrain. Biochem. J., 1935, 8, No. 1, 139–168).—The difference between the amounts of activated (I) and non-activated (II) cathepsin increases in the maternal organs during (and possibly parallel with) the growth of the embryo. In the placenta the val. of (II) is very low; the difference between the amount of (I) and (II) is very great in rat's, less in rabbit's and guinea-pig's, and very low in human placenta. The concn. of (I) and (II) in the embryo is low and increases with the growth. After birth the concn. increases, being $>$ in the corresponding maternal organs. After reaching a max. it falls to the normal val. The difference between the amounts of (I) and (II) increases rapidly. Thus the protein metabolism of the embryo is controlled by the maternal organs and by the placenta. The difference between the amounts of (I) and (II) increases parallel with the synthetic action. E. P.

Proteinases and proteolytic processes of muscle tissues. I. Activity of muscle proteinases on qualitatively different protein diets. S. FOMIN and M. MISCHKIS (Ukrain. Biochem. J., 1935, 7, Nos. 3–4, 135–145).—The activity of the muscle proteinases of rats is increased by incomplete diets of beans or gelatin. H. D.

Proteinases and proteolytic processes in muscle. II. Activity of muscle proteinases of the dog's leg after training. S. V. FOMIN and V. I. DEMIN (Ukrain. Biochem. J., 1935, 8, No. 1, 73–85).—The activity of the muscle proteinases in the weighted hind leg of a dog was increased $>$ in the other leg, due to increased oxidation. E. P.

Tissue proteinases in organs of animals in different stages of phylogenetic evolution. B. GOLDSTEIN and E. J. MILGRAM (Ukrain. Biochem. J., 1935, 8, No. 1, 105–138).—As regards concn. of cathepsin (I), the organs form the series: kidney $>$ liver $>$ spleen $>$ muscle; and the animals the series: rat, frog, pigeon $>$ dog, cat, hen, rabbit, guinea-pig $>$ cow. The concn. of (I) is possibly related to the intensity of the metabolism, which decreases as body-wt. increases. With mammals kidney-(I) is strongly activated, but liver-(I) is slightly inhibited or slightly activated by H_2S . With amphibia, H_2S has no action or restricts slightly the activity of liver-(I), but activates kidney-(I) slightly. With

birds H_2S strongly restricts the activity of kidney-(I) and slightly that of liver-(I). The different actions of H_2S on kidney extracts are possibly due to the different end-products of protein metabolism with mammals and birds. With mammals H_2S activates spleen-(I); with frogs it greatly restricts its activity.

E. P.

Intracellular proteinases. XVI. Activation and inhibition of papain. E. MASCHMANN and E. HELMERT. **XVII. Effect of arsenic compounds on the activity of liver-cathepsin.** E. MASCHMANN (Biochem. Z., 1935, 280, 184—203, 204—212; cf. this vol., 1279).—XVI. Papain, if activated as much as possible by a $\cdot\text{SH}$ compound [cysteine (I), reduced glutathione (II)], is further activated by certain substances [e.g., citric acid, malic acid (III), AcCO_2H , $\text{K}_4\text{Fe}(\text{CN})_6$] which sometimes have sp. effects. O_2 and a heavy metal are also involved. Very small amounts of (I) [but not of reduced (II)] inhibit and even irreversibly inactivate papain with disappearance of (I). For activation (I), (II), or O_2 and heavy metal can be replaced or (when these are present in insufficient quantity) strengthened by Fe^{II} in complex combination [but not by $\text{K}_4\text{Fe}(\text{CN})_6$ if certain substances [e.g., ascorbic acid (IV), (III), tartaric acid, but not lactic or glycollic acid or AcCO_2H] which bind Fe are present. Fe^{II} in complex combination can be partly replaced by (IV). No part is played by any (I)—Fe compound. Results differ according to the type of buffer (acetate, citrate) used.

XVII. The degradation of gelatin (V) (at p_{H} 4) and clupein (VI) (p_{H} 5) by liver-cathepsin (pig) is usually inhibited by As compounds (15 tested), although occasionally slight activation or no action results. The degradation of (VI) is sometimes unaffected by compounds which check that of (V).

W. McC.

Activation of the proteolytic enzymogen system of the ventricle. R. EGE and J. OBEL (Biochem. Z., 1935, 280, 265—275; cf. A., 1934, 450).—Neutral or slightly acid extracts of the mucous membrane of the stomach (man, dog, pig, ox, cod) contain small amounts of preformed enzymes capable of coagulating milk. Activation of the enzymes sets in at $p_{\text{H}} < 5$ and the rate increases as $[\text{H}^+]$ increases, the degree of acceleration varying from species to species of animal. There is no relation between dependence of the rate on $[\text{H}^+]$ and the ratio pepsin:rennin. At alkaline reaction the stability of the enzymogen is in all cases $>$ that of the activated enzymes.

W. McC.

Initial phosphorylations of glycogen. J. K. PARNAS and T. BARANOWSKI (Compt. rend. Soc. Biol., 1935, 120, 307—310).—In the hydrolysis of adenosinetriphosphoric acid (I) by muscle pulp in presence of glycogen (II), the liberated PO_4^{III} preferably esterifies (II), but a certain quantity forms free H_3PO_4 . The amounts of hydrolysis and esterification increase with dilution and (II) concn. The enzymes of muscle extract transform (I) into inosinic acid, and rapidly hydrolyse (II) in presence of PO_4^{III} , forming the Robison-Embsden hexose monophosphoric ester. (I) and (II) in absence of free PO_4^{III} are

transformed into the Harden-Young fructose diphosphoric ester. $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ does not affect this reaction. Both reactions proceed independently if (I), (II), and PO_4^{III} are all added to the extract.

R. N. C.

Action of ultra-violet light on yeast-invertase. VI. The activating zone. G. GORBACH and H. RUESS (Biochem. Z., 1935, 280, 213—216; cf. A., 1934, 1033).—It is light of λ 365—366 $\text{m}\mu$ which directly activates the invertase (I) of yeast autolysates and dialysates on short irradiation. There is no connexion between the activation and the light blue fluorescence of the (I) solutions.

W. McC.

Preservation and the rate of respiration of yeasts. F. CHODAT and A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 74—76).—The ageing of yeast is much slower at 6° than at 25° . In 48 hr. at 25° the respiratory activity is reduced by 50%.

H. G. R.

Assimilation by yeast of high and low mol. wt. nitrogen compounds. N. NIELSEN (Compt. rend. Lab. Carlsberg, 1935, 21, No. 6, 139—150; cf. A., 1934, 1034).—The N compounds of wort can be separated by dialysis into fractions of low and high mol. wt., the former of which is much the more readily assimilated by yeast.

E. A. H. R.

Action of glutathione on cytochrome-C *in vitro*. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, 120, 69—72).—Glutathione (I) rapidly reduces cytochrome-C (II) *in vitro* in neutral solution. Reduced (I) is responsible for keeping (II) in its reduced form in boiled yeast, in plasmolysis of which it is released in large quantities.

R. N. C.

Reaction chain of alcoholic fermentation. O. MEYERHOF (Helv. Chim. Acta, 1935, 18, 1030—1052).—A lecture.

H. W.

Chemical actions taking place in the fermentation (organic) cell. M. C. POTTER (Zentr. Bakt. Par., 1935, II, 93, Reprint. 11 pp.).—During yeast fermentation of 1 mol. of sucrose, approx. 8 coulombs of energy are liberated. The e.m.f. of a fermenting cell depends on the chemical reactions involved, and is developed in open or closed circuit. The electricity liberated is independent of the p_{H} of the medium if this does not restrict the activity of the organism.

A. G. P.

Kinetics of alcoholic fermentation of sugars by brewer's yeast. III. Temperature coefficients of the rates of fermentation of glucose and fructose. R. H. HOPKINS and R. H. ROBERTS (Biochem. J., 1935, 29, 2486—2490).—The method of Hopkins (this vol., 661) was used. The temp. coeff. of fermentation of glucose by yeast is independent of concn. between 0.25 and 5.0%, varying between 2.0 and 1.24 between 15° and 35° . With fructose (I) the temp. coeff. decreases at concns. $< 1\%$. Below 0.25% concn. the temp. coeff. agrees with that for the mutarotation of β -(2:6)-fructose, and it is concluded that the enzyme attacks only one form of (I), and the rate of conversion into this form determines the rate of fermentation at low concns.

H. D.

Mechanism of oxidation processes. XLII. Decomposition of citric acid by yeast. H. WIE-

LAND and R. SONDERHOFF (Annalen, 1935, 520, 150—156).—Contrary to the earlier statement (A., 1933, 865) gaseous H_2 (3 mols.) is evolved in the anaerobic fermentation of citric acid (I) by "impoverished" yeast (II). Since no H_2 is obtained with (II) alone, whereas HCO_2Na and (II) give H_2 , it is assumed that the H_2 is produced from the HCO_2H first split off from (I). A little $MeCHO$ (but no $COMe_2$) was detected as its 2:4-dinitrophenylhydrazone; 70% decomp. in accordance with the equation given (*loc. cit.*) is thus observed. Since (II) is unable to decompose $CO(CH_2 \cdot CO_2H)_2$ (III) into CO_2 and $2AcOH$, it is suggested that, in the anaerobic decomp. of (I), fission of HCO_2H affords the keto-form of (III) which decomposes $\rightarrow AcOH + CH_2(CO_2H)_2$, followed by $CH_2(CO_2H)_2 \rightarrow AcOH + CO_2$. In agreement, it is shown that $CH_2(CO_2H)_2$ is decarboxylated by (II) at p_H 7.0. The aerobic decomp. of (I) with (II) begins more rapidly than the anaerobic reaction, and the initial stage is probably the dehydrogenation $(CO_2H \cdot CH_2)_2C(OH) \cdot CO_2H - 2H + O \rightarrow CO(CH_2 \cdot CO_2H)_2 + CO_2 + H_2O$. The velocity of dehydrogenation of (I) by methylene-blue in presence of (II) is reduced as (I) is replaced by HCO_2H .

J. W. B.

Action of organic substances on alcoholic fermentation. V. Folliculin. A. MOSSINI (L'Ind. Chimica, 1935, 17, 524—526; cf. A., 1934, 1261).—The evolution of CO_2 during alcoholic fermentation is increasingly accelerated in presence of amounts of folliculin rising from 0.00005 to 0.05 mg. %. When the fermentation slackens owing to decrease in the amount of sugar present, addition of fresh sugar is followed by increased gas evolution. Degenerated yeast also responds to the stimulating effect of folliculin.

T. H. P.

Pseudo growth-factors of grape must. A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 172—178).—A feebly acidic substance which inhibits yeast growth is formed by sterilisation of must at 110° .

H. G. R.

Effects of 2:4-dinitrophenol on respiration of commercial cake yeast. J. FIELD, jun., A. W. MARTIN, and S. M. FIELD (Proc. Soc. Exp. Biol. Med., 1935, 32, 1043—1046; cf. A., 1934, 1262).—The total concn. of 2:4- $C_6H_3(NO_2)_2 \cdot OH$ (I) causing optimal stimulation of yeast respiration $\propto p_H$, but the concn. of undissociated (I) is const. for a wide p_H range. Any fixed (I) concn. may stimulate respiration at one p_H and inhibit it at another. Reduction of p_H to a sufficient extent in a suspension of yeast cells in liquid containing (I) suspends respiration immediately. The results suggest that the active agent in stimulating respiration is undissociated (I).

R. N. C.

Inhibitory action of the lower aliphatic acids and aldehydes on cytochrome reduction in yeast. L. V. BECK (Biochem. J., 1935, 29, 2424—2432).—Marked inhibition is shown by fatty acids (concn. 0.01M), less by the corresponding aldehydes, and none by the alcohols or urethanes. HCO_2H and CH_2O act differently from the other members of the series. Strong acids have a small action. The Na salts

diminish the inhibiting action of their acids. All inhibitions are reversible on addition of glucose.

F. A. A.

Effects of certain organic acids and protein derivatives on the growth of *Colpidium*. A. M. ELLIOTT (Arch. Protistenk., 1935, 84, 472—494).—Single NH_2 -acids were unsatisfactory N sources for *C. striatum* and *C. campylum*, but proteins and their products of partial hydrolysis were suitable. Among peptones examined those containing high proportions of NH_2 -acids and NH_2-N (Van Slyke) were the more effective. Relationships exist between p_H , growth, and the nature of the N source utilised. The Na salts of the 5 lower fatty acids and Na citrate were toxic at p_H 5.8, whereas glycollate, pyruvate, and tartrate were only moderately toxic. Growth of *C. striatum* was accelerated by $NaOAc$ at p_H 6.5—7.5 and that of *C. campylum* at p_H 7.0. $PrCO_2Na$ accelerated growth of both species at $p_H > 7.0$.

A. G. P.

Effect of certain carbohydrates and organic acids on growth of *Chlorogonium* and *Chilomonas*. J. B. LOEFER (Arch. Protistenk., 1935, 84, 456—471).—Greatest acceleration of growth of *Chlorogonium euchlorum* was produced by fructose (I), galactose (II), maltose (III), and lactose (IV), less by glucose (V), arabinose (VI), xylose (VII), and rhamnose (VIII); negative effects were obtained with sucrose (IX), starch (X), and dextrin (XI). *C. elongatum* was similarly affected except that (IV) proved a poor source of C. The order of efficiency with *Chilomonas* was (XI) > (I), (IV), (II), (III) > (VI), (V), (IX), (VII), whereas (VIII) and (X) were inactive. The growth of *Chilomonas* was accelerated by fatty acid salts in the descending order $AcOH$, Pr^oCO_2H , $BuCO_2H$, $EtCO_2H$, Pr^sCO_2H . Negative results were obtained with hexoate. The two species of *Chlorogonium* were affected similarly, except that $EtCO_2H$ produced no effect.

A. G. P.

Colloidal changes indicated by experiments on *Paramecia* as the basis of sympathetic nervous processes. T. WENSE (Arch. exp. Path. Pharm., 1935, 179, 475—482).—In their influence on vacuole pulsations, chemotaxis, protoplasmic viscosity, and rate of movement of *Paramecia*, choline (I) and pilocarpine show a marked antagonism to adrenaline (II). The action of (I) is inhibited by atropine and curare. K and Ca resemble (I) and (II), respectively. These phenomena indicate a colloid-chemical basis for the transmission of sympathetic nerve stimuli.

F. O. H.

Biological action of rays from radioactive substances. I. Effect of small dose radiation on the reproductive activity of a unicellular organism. Y. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 27—47).—Irradiation of *Paramecium caudatum* with β - and γ -radiation from pitchblende, monazite, and a U-X prep. caused an increased rate of reproduction, the γ -rays being mainly responsible. No concomitant pathological effects on the organism were produced.

A. L.

Mode of action of chemotherapeutically-used dyes. V. FISCHL and E. SINGER (Z. Hyg. Infektionskrankh., 1934, 116, 348—355; Chem. Zentr., 1934,

ii, 3276).—*T. nagana* absorbs both trypanflavin (I) and atebrian (II), but only (I) is trypanocidal. The fluorescence intensity produced by (II) is exceedingly small. Immobilisation by light is not obtained with fluorescent dyes other than (I). The therapeutic effect of (I) is not related to its photodynamic property. (II) has an affinity for malaria plasmodia, whilst (I) is absorbed by certain development forms of the parasite.

R. N. C.

Superiority of silver nitrate over mercuric chloride for surface sterilisation in the isolation of *Ophiobolus graminis*, Sacc. F. R. DAVIES (Canad. J. Res., 1935, 13, C, 168—173).—The organism was isolated more readily from plant tissue treated with AgNO_3 than from that sterilised with HgCl_2 .

A. G. P.

Reversible heat-activation inducing germination and increased respiration in the ascospores of *Neurospora tetrasperma*. D. R. GODDARD (J. Gen. Physiol., 1935, 19, 45—60).—Heat-activated *N. tetrasperma* ascospores may be rendered dormant again by preventing respiration; these dormant spores may be caused to germinate by reheating. Respiration increases after activation and again at the time of germination; these changes also occur in the reversible activation. The heat-activation takes place within the temp. limits 49—52°; heat-killing begins at about 62°. $\text{CH}_3\text{I}\cdot\text{CO}\cdot\text{NH}_2$ inhibits germination without greatly affecting respiration; respiration is diminished by CN' .

F. A. A.

Role of vitamin- B_1 in nitrogenous metabolism of *Phycomyces*. W. H. SCHOFFER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 113—115).—The beneficial effect of vitamin- B_1 is limited by the amount of asparagine present in the medium.

H. G. R.

Mould sterols. I. Formation of sterols by *Aspergillus niger*. K. BERNHAUER and G. PATZELT (Biochem. Z., 1935, 280, 388—393).—The formation of sterols on solutions of varying sugar content proceeds in general parallel with the formation of mycelium, and on the Ca salts of gluconic and quinic acids is only half that on glucose. The mechanism of sterol formation is discussed.

P. W. C.

Optimal conditions for accumulation of citric acid and the mechanism of citric acid formation [by moulds]. T. CHRZASZCZ and E. PEYROS (Biochem. Z., 1935, 280, 325—336).—For optimal yields of citric acid (I), the choice of strain of organism is very important, the initial concn. of sugar should be 20%, the salts should include 0.3% NH_4NO_3 , 0.1% KH_2PO_4 , and 0.1% MgSO_4 and a trace of FeCl_3 , the temp. should be 28—30°, and the duration of fermentation 7—11 days. Zn salts inhibit formation of (I). It is advantageous partly to neutralise the (I) formed with CaCO_3 , but the reaction fluid must be always acidic. The view of Emde (this vol., 407) that (I) is formed from sugar by way of quinic acid cannot be correct since yields of (I) much > theoretically possible by this mechanism have frequently been obtained.

P. W. C.

Utilisation of organic acids by *Aspergillus niger*. T. A. BENNET-CLARK and C. J. LA TOUCHE

(New Phytol., 1935, 34, 211—231).—Removal of external sugar supplies from *A. niger* causes a decline in the respiration rate to a low level (starvation rate). Prolonged starvation does not permanently injure the fungus, which recovers when sugar is again supplied. Addition of citric, malic, glycollic, or oxalic acid to starving cultures does not increase the CO_2 output, although the acid disappears rapidly, probably through reduction to OH-aldehyde.

A. G. P.

Flavour of shōyu. I. K. SHŌJI (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 872—877).—The aromatic substances in shōyu, a seasoning material prepared by fermenting koji with *Aspergillus oryzae*, consist of AcOH , BuCO_2H , and hexoic acid, amyl, hexyl, and higher alcohols, aldehydes, ketones, and phenolic compounds, the last-named being the most important.

A. L.

Reaction of the medium and the activity of ordinary and preformed felts of an *Aspergillus*. V. BOLCATO (Annali Chim. Appl., 1935, 25, 423—432).—When an *Aspergillus* capable of forming citric (I) and gluconic (II) acids is grown in sucrose solution containing mineral nutrients, (I) is formed when the p_{H} is <, and (II) when it is >, 3.4. Preformed felts, especially if they have had prolonged contact with the culture liquid, form (I) at p_{H} vals. much > 3.4. Formation of (II), however, requires limited conditions, outside of which (I) is formed. T. H. P.

Interconversion of aromatic and hydroaromatic compounds by micro-organisms. II. Quinic acid and inositol. K. BERNHAUER and B. GÖRLICH (Biochem. Z., 1935, 280, 394—395).—*B. gluconicum*, *B. xylinoides*, and *P. griseofulvum* convert quinic into protocatechuic acid. With these organisms and inositol the formation of aromatic substances could not be detected, the mol. being degraded to AcOH and lactic acid.

P. W. C.

Effect of glucose and mineral elements on the growth of *B. pyocyaneus*. J. RÉGNIER, R. DAVID, and J. MORCHOISNE (Compt. rend. Soc. Biol., 1935, 120, 418—420).—Growth in peptone- H_2O is accelerated by glucose (I) or a mixture of NaCl , KCl , MgSO_4 , and Na nucleate, or by both together. (I) increases NH_3 production.

R. N. C.

Effect of the constitution of peptones on the growth of *B. pyocyaneus*. J. RÉGNIER, R. DAVID, and J. MORCHOISNE (Compt. rend. Soc. Biol., 1935, 120, 415—418).—The nutrient vals. of different peptones are of the same order, and are unaffected by dialysis except for mucus peptone, where rate of growth is reduced considerably. Growth is also slow with gelatin peptone. The type of enzyme used for preparing the peptones appears to have no influence on the nutrient val.

R. N. C.

Effect of bongkreik acid on carbohydrate metabolism. A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1935, 54, 373—380, and Geneesk. Tijds. Ned.-Indië, 1935, 75, 1059—1071, 1116—1127).—Bongkreik acid, $\text{C}_{11-13}\text{H}_{16-20}\text{O}_3$, containing OH and three double linkings, is obtained together with toxoflavin (I) (cf. A., 1934, 454, 537) by the action of bongkreik bacteria on coconut. It is optically

active and stable in a fatty medium, but in a pure state is prone to oxidation and polymerisation. Alkaline solutions are more stable. It is extremely toxic to men and apes (lethal dose < 0.5 mg.), being much more virulent than (I), whilst the polymeride is non-toxic and optically inactive. It causes the glycogen content of the liver to disappear rapidly; the blood-sugar at first increases rapidly, but finally falls to the lethal limit. Administration of glucose alone or in conjunction with insulin, or of ergotamine, has no beneficial effect. The lactic acid, NH_2 -acid, inorg. P, and "guanidine" contents of the blood are increased, but the NaCl content is unchanged. Bongkreik poisoning is very similar to that caused by "synthalin" (decamethylenediguanidine), but is much more severe. S. C.

Dehydrogenase of *B. aertrycke* S. and R. E. SORU (Compt. rend. Soc. Biol., 1935, 120, 232—235).—The velocity of decolorisation of methylene-blue by *B. aertrycke* S and R varies with the H donator, and decreases in the order glucose, Na lactate, asparagine, Na succinate, glycerol; glycine does not cause decolorisation. In all cases decolorisation by the S bacillus is more rapid than by the R bacillus. R. N. C.

Respiration of acetone bacteria and bacterial autolysates. O. EHRLMANN (Z. Hyg., 1934, 116, 490—494; Chem. Zentr., 1935, i, 1887).—The effect of redox indicators on respiratory activity in lactate-oxidising cultures of COMe_2 bacteria is a function of its redox potential. The solubility of the dye, its composition (no. of SO_3H groups), and the electrolyte content of the medium are important factors. The enzyme system indicated by Barron and Hastings (A., 1933, 533) for *Gonococcus* can be demonstrated in other species. A. G. P.

Respiratory system of bacteria. W. FREI (Zentr. Bakt. Par., 1935, I, 134, 26—35).—Bacteria are classified according to the presence of cytochrome, indophenol oxidase, peroxidases, catalases, and sp. respiratory pigments. The chemical mechanism of respiration in the various classes of organisms is discussed. A. G. P.

Formation and structure of cellulose membranes. W. K. FARR (Paper Trade J., 1935, 101; T.A.P.P.I. Sect., 183—186).—The cellulose (I) membrane present in cultures of *Acetobacter xylinus* is a part of the organism itself, and has not been synthesised from the culture medium by enzymes of bacterial origin. Each bacterium also possesses a coating of non-(I) material which serves as its contact surface with the nutrient solution. The presence of this material, largely pectic in nature, may be detected by solubility tests, and located by staining with Ru-red. It constitutes only about 2% of the membrane. In the filamentous alga *Spirogyra*, the (I) units are definitely oriented with respect to the surface of the protoplasm. H. A. H.

Fate of vitamin-C in the digestive tract. I. Action of intestinal bacteria on vitamin-C. W. STEFF and H. SCHRÖDER (Klin. Woch., 1935, 14, 147—148).—The effect of common *B. coli* and intestinal bacteria on ascorbic acid varies. It is destroyed

in 24 hr. by some strains of *B. coli* and by *B. paratyphosus* B, p_{11} possibly having some influence. R. N. C.

Oxidations by means of acetic acid bacteria. III. Formation of a reducing saccharic acid (aldehydogluconic acid) and 5-ketogluconic acid. K. BERNHAUER and K. IRRGANG. IV. Formation of 2-ketogluconic acid by *Bact. gluconicum*. V. Comparative experiments on the preparation of *l*-sorbitol by different bacteria. K. BERNHAUER and B. GÖRLICH (Biochem. Z., 1935, 280, 360—366, 367—374, 375—378).—III. In the action of *B. gluconicum* on Ca gluconate (I) small amounts of Ca 5-ketogluconate are formed together with a large amount (50% of the gluconate) of a reducing very sol. Ca salt which gives an intense naphthoresorcinol-HCl test and the same osazone as 5-ketogluconic acid (II) and is probably an aldehydogluconic acid (III) (*l*-guluronic acid). The same substance is obtained in small amounts when *B. xylinum* ferments a solution of glucose in presence of CaCO_3 or containing (I).

IV. *B. gluconicum* produces, in addition to (II) and (III), also 2-ketogluconic acid, isolated as the K salt and identified by comparison of its Me ester and quinoxaline derivative with authentic specimens.

V. The yields of *l*-sorbitol isolated from glucose with *B. xylinum*, *B. xylinoides*, and *B. gluconicum* were 48, 53, and 64%, respectively, the material with the latter organism being almost pure. P. W. C.

Butyl- and acetone-fermentations. I. Intermediate products of the butyl alcohol-acetone fermentation. K. BERNHAUER and K. KÜRSCHNER (Biochem. Z., 1935, 280, 379—387).—Using fresh active cultures of *Clostridium butyricum*, AcOH is converted almost exclusively into COMe_2 (yield 97%). The organism during fermentation loses its physiological character and then converts AcOH chiefly into EtOH (yields COMe_2 30%, EtOH 70%). The organism after transfers in a cereal mash with and without CaCO_3 recovered its power to give large yields of COMe_2 . In fermentation of starch, PrCO_2H is the precursor of BuOH. Added acetaldehyde and β -hydroxybutyric acid are not converted into PrCO_2H , but added crotonic acid is converted partly into BuOH and partly into AcOH and COMe_2 . P. W. C.

Formation of hydrogen from glucose and formic acid by so-called "resting" *B. coli*. II. A. TASMAN (Biochem. J., 1935, 29, 2446—2457; cf. this vol., 1028).—The fermentation of glucose by both growing and resting *B. coli* takes place mainly by way of HCO_2H , but partly by way of AcCO_2H : in only a few cases (different bacterial strains) is the latter the chief reaction. F. A. A.

Determination of volatile acids in bacterial cultures. L. A. ALLEN and J. HARRISON (Biochem. J., 1935, 29, 2471—2476).—Volatile acids are determined in bacterial cultures in the presence of lactic acid and CO_2 by acidification and steam-distillation at const. vol. and each 100-ml. fraction is titrated with aq. Ba(OH)_2 until a const. titre is obtained. The neutralised acids are acidified and the process is repeated, the total titre in the latter case representing volatile acids. H. D.

Soluble dry filter for bacterial count in air. P. OESTERLE (Arch. Hyg. Bakt., 1934, 113, 137—142; Chem. Zentr., 1935, i, 2052).—A 2 : 1 : 1 mixture of NaCl, cryst. MgSO_4 , and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is dried at 100—150° and sterilised at 180°. J. S. A.

Antigenic fixatives of tubercle bacilli. II. Purification of the lipin fraction with hapten activity extracted from heat-killed bacilli. M. A. MACHEBŒUF and A. BONNEFOI. **III. Separation of the hapten-active phosphatides from the nitrogenous impurities.** M. A. MACHEBŒUF, G. LÉVY, and M. FAURE (Bull. Soc. Chim. biol., 1935, 17, 1201—1209, 1210—1234; cf. this vol., 256).—II. Fractional pptn. with COMe_2 of a CHCl_3 solution of the COMe_2 -insol. fraction of the lipins of the tubercle bacillus does not lead to any concn. of the hapten activity. Fractional pptn. with MeOH, although somewhat more effective, shows that the difference in solubility between active and inactive substances is very small and yields in the least sol. fraction a product of increased activity.

III. Repeated fractional pptn. of the COMe_2 -insol. lipins with MeOH yields a product (I) of high hapten activity sparingly sol. in MeOH and containing P 3.36%, N 0.13%, 3.3% of reducing sugars after hydrolysis, and no unsaponifiable matter. (I), although very active in the fixation of complement, has no pptn. activity. It is very sol. in H_2O , to which it passes from Et_2O solutions, the rate being dependent on the p_{H} of the aq. layer. A. L.

Relationship between electrophoretic migration velocities, virulence, and types of diphtheria and diphtheria-like bacilli. K. P. DOZOIS and K. F. RAUSS (Amer. J. Publ. Health, 1935, 25, 1099—1102).—The diphtheroid strains show the max., avirulent strains the min., and virulent strains an intermediate velocity. The demarcation between the zones is not sharp and determinations show an error of 14% compared with virulence tests on guinea-pigs. H. G. R.

Variation in the buffering power of the culture fluid during bacteriolysis. F. CHODAT and M. RAAD (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 109—112).—During the true period of lysis there is a diminution in buffering power. H. G. R.

Action of respiratory and cellular fermentation inhibitors on transmissible bacterial lysis. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 156—160).—Lysis is inhibited by concns. of $\text{CH}_3\text{I}-\text{CO}_2\text{H}$ which do not affect bacterial growth. KCN, CO, or phenylurethane has no effect on lysis. H. G.

Peroxidase and transmissible bacterial lysis. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, 164—166).—Thermolabile peroxidase of the culture is not removed by ultra-filtration (cf. following abstract), but is rendered thermostable. H. G. R.

Size of phage particles. Preparation of a purified lytic principle. F. WYSS-CHODAT (Arch. Sci. phys. nat., 1935, [v], 17, 161—164).—Using a Seitz filter No. 6, the lytic activity can be filtered out and eluted with physiological saline. It is not affected by washing with C_6H_6 or Et_2O on the filter. H. G. R.

Accelerating effect of manganous ions on phage action. A. P. KRUEGER and N. S. WEST (J. Gen. Physiol., 1935, 19, 75—86).—Phage action on *Staphylococcus aureus* is accelerated by the presence of Mn^{++} . Phage formation is not increased or bacterial growth affected, but the Mn^{++} lowers the lytic threshold; lysis occurs when the phage/bacterium ratio is about 12 instead of 54. The phage distribution is altered in growing phage-bacterium mixtures, the extra-cellular phage concn. being 4 times that in the absence of Mn^{++} . F. A. A.

Action of mercury-lamp radiations on various bacteriophages. C. LEVADITI and J. VOET (Compt. rend. Soc. Biol., 1935, 120, 385—387).—The bacteriophages for *B. coli*, *Staph. K*, and the C_{16} bacteriophage are equally sensitive to Hg-lamp radiations, all being destroyed by exposure for 1 hr. R. N. C.

Cultivation of human influenza virus in an artificial medium. T. FRANCOIS, jun., and T. P. MAGILL (Science, 1935, 82, 353—354).—The culture virus has been readily transmitted to mice and ferrets. Its capacity to infect experimental animals is inhibited by sp. anti-influenza immune serum. After repeated cultivation *in vitro*, certain alterations in the immunological characteristics of the virus occur. L. S. T.

Sensitivity of the influenza bacillus against vitamin-C and quinol. O. GROOTEN and N. BEZSSONOFF (Compt. rend. Soc. Biol., 1935, 120, 121—123).—The development of the Bordet-Gengou bacillus (*B. pertussis*) is arrested and the bacillus itself killed by reductone, ascorbic acid (I), and hydroxybenzenes. Generally, the bactericidal power \propto the reducing power, except in the case of quinol (II), which is a more effective bactericide than pyrogallol. E_h of the cultures falls approx. 170 mv. on addition of (I), but only 5 mv. on addition of (II). R. N. C.

Action of medicaments *in vitro*. E. SINGER and V. FISCHL (Z. Hyg. Infektionskrankh., 1934, 116, 356—360; Chem. Zentr., 1934, ii, 3276).—Atoxyl (I) associated with liver-pulp is adsorbed more readily by *Spirochaetus recurrentis*, *B. proteus*, red corpuscles, collodion, and animal C than when untreated with liver. Addition of glutathione (II) and lentils increase As absorption *in vitro* by trypanosomes and spirochaetes. Liver or lentil pulp also increases Au absorption by spirochaetes. Glycogen, cystine, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and Na thioglucose are inactive. Ascorbic acid destroys trypanosomes *in vitro*, the effect being increased by (I), but it attacks spirochaetes only in combination with the Au-CS(NH_2)₂ compound. (I) solution becomes trypanocidal on addition of (II). R. N. C.

Chemotherapy of bacterial infections. G. DOMAGK (Angew. Chem., 1935, 48, 657—667).—The application of chemotherapeutic substances in infections due to various types of pathogenic bacteria is discussed. F. O. H.

Effect of adrenaline on the utilisation of fructose introduced at constant velocity into the circulation at the three levels of assimilation. M. WIERZUCHOWSKI and H. FISZEL (Compt. rend. Soc. Biol., 1935, 120, 377—380; cf. this vol., 1017).—The blood-fructose (I) level reached on continuous

injection of (I) into normal dogs on a protein diet is $>$ the carbohydrate diet level, but $<$ the fasting level; adrenaline (II) raises the three levels. Urinary (I) at the three levels increases in the same order as above, and is also further increased by (II); 1 mg. of (II) lowers (I) assimilation by 6.03 mg. at the carbohydrate, 10.5 mg. at the protein, and 23.18 mg. at the fasting level. Hence (II) determines the glycogenolysis of glycogen (III) formed from injected sugars such as (I), as well as that of the body-(III).

R. N. C.

Inactivation of adrenaline by extracts of organs. J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 42—45).—Adrenaline is inactivated *in vivo* by extracts of animal organs to varying extents according to the organ concerned and the species. The max. effects are obtained with extracts of guinea-pig liver and kidney and dog spleen, whilst extracts of muscular tissue are always inactive.

R. N. C.

Effect of cortin on adrenaline secretion. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1935, 120, 248—250).—Injection of cortin in the dog induces hyperglycemia by augmenting adrenaline secretion, the increased secretion appearing 20—40 min. after injection and persisting for 60—90 min.

R. N. C.

Chemical basis of the panoptic reaction applied to the detection of adrenaline in the tissues. T. PAWLIKOWSKI and T. SLEBODZINSKI (Compt. rend. Soc. Biol., 1935, 120, 465—466).—Adrenaline (I) reduces $K_2Cr_2O_7$ *in vitro*, forming CrO_2 , which oxidises methylene-blue to a green compound. These reactions are responsible for the metachromatic green coloration of the cells of the medulla in the panoptic reaction.

R. N. C.

Absorption and fate of insulin following percutaneous application. I. S. HERMANN and H. KASSOWITZ. II. S. HERMANN (Arch. exp. Path. Pharm., 1935, 179, 524—528, 529—536).—I. Application of paste containing insulin (I) (5 units) to the washed (light petroleum) skin of rabbits reduces the blood-sugar from approx. 90 to 14—30 mg. per 100 c.c., producing convulsions in 30% of the animals. The effect is partly or wholly inhibited by addition of cholesterol to the paste and is dependent on the site of application, being greatest above compact red muscle. The hypoglycemic activity of extracts from dog's skin treated with (I) paste indicates that (I) permeates both horizontally and vertically.

II. Presence of lipin-sol. acids (e.g., AcOH) inhibits the action of (I) paste. For max. absorption of (I), the skin must be freed as far as possible from lipins and an alkalinisation of the skin induced (e.g., by meat diets). The results are discussed with reference to lymph transport and cell permeability.

F. O. H.

Action of insulin in fasting pigeons. D. GIGANTE (Atti R. Accad. Lincei, 1935, [vi], 21, 763—768).—The resistance of the pigeon to insulin (a single dose) shows not so much gradual diminution as fasting is prolonged, as a sudden fall when the critical stage of inanition is reached.

T. H. P.

Influence of insulin on the phosphorus exchange in muscle. S. F. EPSTEIN (Ber. Ukrain.

Biochem. Inst., 1930, 4, 107—114).—Administration of 5—20 clinical units of insulin (I) to rabbits results after 15 min. in a rise in the hexosemonophosphoric acid (II) and a fall in the creatinephosphoric acid (III) and $H_4P_2O_7$ (IV) in muscle. In pigeons, muscle-(II) is unaltered but -(III) and -(IV) are decreased after administration of (I).

W. O. K.

Influence of insulin on the production of optically active substances in muscle-glucose-salt mixtures. P. NORMARK and E. SAVRON (Ber. Ukrain. Biochem. Inst., 1930, 4, 31—42).—Mixtures of minced muscle, glucose, and NaCl in phosphate buffer (p_H 7.3) with and without insulin (I) were incubated and then dialysed through a collodion membrane against isotonic aq. NaCl. The α and reducing power of the dialysate were the same whether (I) was present or absent.

W. O. K.

Inactivation of insulin. Effects of certain metal derivatives and of thiol compounds. E. D. SCHOCK, H. JENSEN, and L. HELLERMAN (J. Biol. Chem., 1935, 111, 553—559).—Insulin (I) is inactivated by benzoquinone (II) in 0.067*M*- Na_2HPO_4 (but not in 0.01*N*-HCl) and by thiolsalicylate, Cu_2O , phenylmercuric oxide, thioglyoxalene, thiohistidine, ergothionine, and ascorbic acid do not inactivate (I). (I), inactivated by (II), suffers a decrease in NH_2 -groups.

H. D.

Parathyroid hormone and vitamin-A. F. HOFF and B. ZU JEDDELOH (Z. ges. exp. Med., 1934, 95, 67—75; Chem. Zentr., 1935, i, 2036).—Parathyroid hormone injected into rats in large doses produces Ca deposition in the heart muscles and subcutaneous connective tissue as occurs in human osteitis fibrosa generalisata. Excess of vitamin-A (I) ("Vogan") in growing rats induces skeletal decalcification and spontaneous fracture, but no Ca metastasis or hypercalcaemia. Symptoms follow resembling those in (I) deficiency. The observed fat deposition in the organs is considered to be due to the fat present in the "Vogan" preps. rather than to (I).

R. N. C.

Relation of the thyrotropic hormone to the sugar and ketone content of the blood. F. SILBERSTEIN and F. GOTTDENKER (Klin. Woch., 1934, 13, 1434; Chem. Zentr., 1934, ii, 3269).—Injection of large quantities of thyrotropic hormone (I) in normal cats causes a considerable increase in blood-ketones and -sugar (II). In thyroidectomised animals (II) only is raised. Repeated injections of (I) in both normal and thyroidectomised animals cause a weaker (II) reaction.

R. N. C.

Basic amino-acids yielded by thyroglobulin. A. WHITE and W. G. GORDON (Proc. Soc. Exp. Biol. Med., 1934, 32, 354—357).—Thyroglobulin contains 0.62% of histidine, 8.22% of arginine, and 1.93% of lysine.

R. N. C.

Significance of thyroid gland in antithyrotropic-protective action of the blood. H. EITEL and A. LOESER (Arch. exp. Path. Pharm., 1935, 179, 440—447).—Stimulation of the thyroid gland by thyrotropic hormone from anterior pituitary gland increases the protective action of the blood for antithyrotropic activity (this vol., 1171). Hence the thyroid is related to the formation of the protective

principle, a relation confirmed by diminution in protective action on thyroidectomy and return to normal levels on subsequent administration of thyroid hormone. Thus the increase in protective action is not a sp. result of anterior pituitary secretion, but follows increased thyroid activity. F. O. H.

Thyroid and ovary. Experimental basis for the di-iodotyrosine treatment of climacteric disturbance. A. LOESER (Klin. Woch., 1935, 14, 4—6).—Removal of the ovaries in female guinea-pigs causes a hyperactivity of the thyroid, due to increased secretion of the thyrotropic hormone of the anterior pituitary. The enhanced secretion is suppressed by oral administration of di-iodotyrosine. R. N. C.

Strengthening of the anti-thyroid protective power of blood by the thyrotropic hormone of the pituitary. H. EITEL and A. LOESER (Klin. Woch., 1934, 13, 1677—1678).—If guinea-pigs are injected with sheep serum and thyrotropic substance (I) simultaneously, the two counterbalance each other; this is a method of assay of the anti-thyrotropic substance (II) of serum. If serum donors are previously treated with (I), the anti-thyroid potency of their blood is increased; it is not increased by previous treatment with thyroxine, and it is not high in serum from cases of Graves' disease. (II) is present in serum, and to a smaller extent in corpuscles.

G. H. F.

Action of anterior pituitary fractions on the blood-sugar. K. J. ANSELMINO and F. HOFFMANN (Arch. exp. Path. Pharm., 1935, 179, 273—285).—Single injections of total extracts of anterior pituitary lobe induce an increase in blood-sugar in dogs. Repeated administration, however, produces a refractory period during which the level may even diminish. Anti-insulin preps. of Lucke (A., 1933, 643) have an indefinite hyperglycaemic action which is probably due to traces of posterior lobe hormone. Extracts of the anterior lobe contain a hypoglycaemic (pancreatropic) factor which markedly stimulates the islets of Langerhans. Ultrafiltrates of the total extract at pH 5.4 have a hypoglycaemic action; heating at 100° for 15 min. to destroy the pancreatic hormone reveals, however, the presence of the hyperglycaemic factor. F. O. H.

Antuitrin-S and blood-elements. S. H. GEIST and F. SPIELMAN (Proc. Soc. Exp. Biol. Med., 1934, 32, 353—354).—Injections of antuitrin-S do not affect the formed blood-elements. R. N. C.

Experimental dissociation of the effects of anterior pituitary glands of various species on thyroid and ovary. L. LOEB, W. C. ANDERSON, J. SAXTON, S. J. HAYWARD, and A. A. KIPPEN (Science, 1935, 82, 331—333).—The changes induced in the ovary and the thyroid gland of the immature guinea-pig by substances present in the anterior pituitary glands of various species are described. Experimental changes in the preponderance of these various effects have been produced and the action of the gland of one species has been made like that of another in its effect on the guinea-pig. This has been accomplished by the use of H_2O , aq. NaCl, EtOH, Et₂O, glycerol, and dil. aq. CH₂O. The data

obtained suggest that the effect of the various hormones may depend on the presence of certain NH₂-acids, which form part of one or more polypeptide or protein mols. L. S. T.

Thyrotropic activity of pituitary gland in man. R. MÜLLER, H. EITEL, and A. LOESER (Arch. exp. Path. Pharm., 1935, 179, 427—439).—The thyrotropic hormone content (A., 1934, 1410) of pituitary gland in men (74 *post-mortem* cases) approximates to that of animals. The level, which is independent of age and sex, varies considerably, but the high content in sufferers from tuberculosis and other infectious diseases is noteworthy. F. O. H.

Testis-stimulating potency of frozen turkey pituitaries injected subcutaneously into young male chicks. T. C. BYERLY, W. H. BURROWS, and H. W. TITUS (Poultry Sci., 1935, 14, 189—190).—Cockerel pituitaries had higher gonad-stimulating potency than did those of turkeys. A. G. P.

Gonad-stimulating potency of individual pituitaries. R. H. JAAP (Poultry Sci., 1935, 14, 237—246).—The stimulatory effect of pituitary was increased by injection of blood-sera in ducks but not in chickens. A. G. P.

Hormone content of the pituitary of the blue whale (*Balaenoptera sibbaldi*). J. VALSÖ (Klin. Woch., 1934, 13, 1819—1820).—Neither prolactin nor intermedin is found in the posterior lobe. R. N. C.

Corpus luteum hormone.—See this vol., 1195.

Dependence of the function of the corpus luteum on the ovarian follicles and the place of origin of the hormone in the ovary. A. WESTMANN (Arch. Gynäkol., 1934, 158, 476—504; Chem. Zentr., 1935, i, 1726).—The lutein cell formed in the rabbit's ovary from the granulosa of a ripe follicle by cauterisation of the ovum and of the follicle is abnormal in that it secretes no corpus luteum hormone (I). Destruction of the follicle also hinders the growth of an already existing corpus luteum, but growth is normal if some follicles are left or follicular hormone (II) is administered. Hence (II) is necessary for the function of the corpus luteum to be fulfilled, and is possibly used by the granulosa cell for the formation of (I). R. N. C.

Extraction of folliculin and an associated pharmacological problem. K. GAD-ANDERSEN and E. JARLØV (Acta med. Scand., 1934, 84, 233—240; Chem. Zentr., 1935, i, 1889).—The activities of commercial folliculin preps. when given subcutaneously and orally are compared. Preps. obtained without the use of Et₂O show good activity orally. R. N. C.

Doses of folliculin necessary to produce intersexuals and the limiting stage of intervention. E. WOLFF and A. GINGLINGER (Compt. rend. Soc. Biol., 1935, 120, 114—116).—The limiting stage of incubation of the hen's egg, beyond which it is no longer possible to transform male embryos into intersexuals by injections of folliculin, is approx. the 8th day. The threshold dose for feminisation is approx. 25 units. R. N. C.

Gonadotropic substances in mare's serum. H. H. COLE and G. H. HART (Proc. Soc. Exp. Biol.

Med., 1934, 32, 370—373).—Pregnant and non-pregnant mare's serum contains a prol-an-like substance that stimulates the gonads when combined with the pituitary synergist. Pregnancy serum contains a second substance that is active *per se*. R. N. C.

Disappearance of prol-an from the blood of the nephrectomised female rabbit. A. LIP-SCHÜTZ, A. FUENTE-ALBA, and T. VIVALDI (Compt. rend. Soc. Biol., 1935, 120, 323—326).—Prol-an injected intravenously is removed from the blood less rapidly in the nephrectomised than in the normal rabbit, suggesting that under normal conditions it is not all excreted in the urine, but partly destroyed in the organs. R. N. C.

Assay of the gonadotropic hormone of pregnancy urine on male rats. V. KORENCHESKY, M. DENNISON, and S. L. SIMPSON (Biochem. J., 1935, 29, 2522—2533).—The method is described. There is a regular relation between the dose of gonadotropic hormone (I) and the effect on the prostate (II), seminal vesicles (III), and penis. It is suggested that one male rat unit (Ml. R.U.) be the min. total dose, injected in 6 equal portions on 3 days, which on the 5th day produces an increase of 40% in the actual wt. of (II) and about 70% in the wt. of (III). 1 Ml. R.U. was equal to about 5 F.R.U. The qual. effect of (I) on the sexual organs is very similar to that of androsteronediol, but different from that of androsterone. J. N. A.

Testicular hormone.—See this vol., 1500.

Synthetic preparation of testosterone.—See this vol., 1371.

Influencing of the secondary sex characteristics of the carp (*Rhodeus amarus*) by hormones and other means. W. WUNDER (Med. Klin., 1934, 30, 874—876; Chem. Zentr., 1934, ii, 3267).—Subcutaneous injection of testicle extract in normal male carp produces mating colours, which persist for a period dependent on the amount of hormone and the time of the year. Adrenaline and yohimbine (I) also exhibit this activity, and prol-an at spawning time, whilst folliculin (II), 0.9% NaCl, trichlorobutyl alcohol, and acetylcholine are inactive. The action of (II) on the oviduct of the female carp is sp., 0.9% NaCl, thyroid, and anterior pituitary hormones being inactive. R. N. C.

Prolonged treatment of male and female rats with androsterone and its derivatives, alone or together with oestrone. V. KORENCHESKY, M. DENNISON, and S. L. SIMPSON (Biochem. J., 1935, 29, 2534—2552).—Prolonged treatment of castrated rats with androsterone (I), androsteronediol (II), and their H₂O-sol. esters not only restored the sexual organs to or towards the normal condition, but also increased the wts. of adrenals, thymus, liver, kidneys, and heart. (II) had all the properties of a true male hormone, but very large doses of (I) and H₂O-sol. (II) had a depressing effect on the gain in body-wt., deposition of fat, and stimulation of the liver. (I) and oestrone (III) had a co-operative effect on the prostate and seminal vesicles, but an antagonistic action on the adrenals. (I) and (II) have no rejuvenating effect. With ovariectomised rats large doses of

(II) caused a partial recovery of the atrophied uterus and vagina, the effect being less with (I). (III) caused a return towards the normal wt. of these organs and (III) together with (I) or (II) showed a co-operative recovery effect. It is suggested that the male hormones, being natural stimulants, may be used for treating suitable human diseases. J. N. A.

Vitamin-A content of eggs as related to rate of production. M. C. KOENIG, M. M. KRAMER, and L. F. PAYNE (Poultry Sci., 1935, 14, 178—182).—Eggs from low-producing pullets had higher vitamin-A contents than those from high-producing pullets when nearing the end of the first year of production. After only 4 months' production no difference was apparent, the -A val. being intermediate between those of the two groups after 1 year. A. G. P.

Growth-promoting effect of flavin on the chick. S. LEFKOVSKY and T. H. JUKES (Science, 1935, 82, 326).—Liver extract contains two H₂O-sol. factors which promote growth in chicks. The first promotes growth when added to a heated diet of yellow maize meal, wheat middlings, and commercial casein, supplemented with salts and cod-liver oil, and is the factor of Elvehjem and Koehn (this vol., 669). The second factor is flavin, which has no effect when added to this diet, but promotes growth when added to the unheated diet. Both factors are distinct from vitamin-B₁. L. S. T.

Effect of heavy administration of viosterol on the metabolism of the rat. C. I. REED (Proc. Soc. Exp. Biol. Med., 1934, 32, 274—277).—Small quantities of viosterol increase the metabolic rate; larger (toxic) doses produce a transient elevation of the metabolic rate followed by a decline below the original level. R. N. C.

Carotene and vitamin-A metabolism. H. WENDT (Klin. Woch., 1935, 14, 9—14; Chem. Zentr., 1935, i, 1730).—Prolonged feeding of carotene and vitamin-A increased the proportion of these in the serum to a max. of 58 Lovibond yellow units and 4.5 blue units, respectively. Large dosages of -A caused hyperlipæmia and hyperlipinæmia in rabbits but not in dogs. Diseases affecting fat resorption caused low vals. for carotene and -A. Neither was present in cases of goitre, but administration of I effected a return toward normal levels. Highest vals. occurred in diabetes. A. G. P.

Carotenoids and vitamin-A in cow's blood-serum. A. E. GILLAM and M. S. E. RIDI (Biochem. J., 1935, 29, 2465—2468).—The average contents of carotene, determined spectrophotometrically, in cow's and bull's blood sera were, respectively, 0.40 and 0.08 mg. per 100 ml. in summer and 1.11 and 0.42 in winter. The presence of vitamin-A, lutein, and occasionally cryptoxanthine in the serum was established. H. D.

Physiologically active crystalline esters of vitamin-A. S. HAMANO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 69—73).—Vitamin-A concentrate (Biosterin) with β -C₁₀H₇·COCl in C₅H₅N gave the physiologically active cryst. β -naphthoate, C₃₁H₃₆O₂, m.p. 76°, which readily promoted the growth of albino rats and cured xerophthalmia. On hydro-

lysis, vitamin-A, $C_{20}H_{30}O$, was obtained. Similarly an active ester, $C_{35}H_{36}O_2$, m.p. 124° , was obtained from anthraquinone-2-carboxylic acid. J. N. A.

Preparation of a potent vitamin-A concentrate. H. N. HOLMES, H. CASSIDY, R. S. MANLY, and E. R. HARTZLER (J. Amer. Chem. Soc., 1935, 57, 1990—1993).—Saponified halibut-liver oil (freed from unsaponifiable matter and most of the cholesterol) in C_5H_{12} , when cooled in EtOH-solid CO_2 and filtered through solid CO_2 on sintered glass, gives a concentrate with a blue val. 45,000—60,000. Filtration through C and MgO gives a concentrate with a blue val. 90,000—140,000. The blue val. is decreased by about 10% if the humidity of the air around the tintometer rises from 35 to 60%. R. S. C.

Crystalline vitamin- B_1 .—See this vol., 1510.

Relative vitamin- B_2 contents of dried whey and dried skim-milk. V. HEIMAN (Poultry Sci., 1935, 14, 137—146).—A relationship between the vitamin- B_2 content of the diet and the growth rate of chicken is established. The $-B_2$ ratio of dried skim-milk : dried whey is 1 : 1.5. Egg production is not appreciably affected by the amount of $-B_2$ supplied. The hatchability of eggs from pullets receiving suboptimal amounts of dried whey or skim-milk is slightly higher in the case of the former feed. The $-B_2$ content of eggs and the greenish-yellow pigment of the whites are directly related to the $-B_{2c}$ content of the diet. Dried egg whites are richer in $-B_2$ than are dried yolks. The lactochrome content of dried whey is $>$ that of dried skim-milk and the quantity present is correlated with growth response and hatchability. A. G. P.

Suggested relation between cystine and vitamin- B_2 . F. T. G. PRUNTY and M. H. ROSCOE (Biochem. J., 1935, 29, 2491—2497).—There is no relation between cystine (I) and the vitamin- B_2 complex in the nutrition of the rat, and a deficiency of vitamin- B_2 together with a deficiency of (I) such that growth was affected had no effect on the incidence of dermatitis. The (I) intake of rats had no effect on the glutathione content of the tissues. Some of the purified caseinogen used in basal diets for vitamin work is deficient in (I). J. N. A.

Vitamin-B and -C in preserved spinach and acid preserved foods. S. V. FOMIN and P. T. MAKAROVA (Ukrain. Biochem. J., 1935, 8, No. 1, 191—202).—Vitamin-B is destroyed; -C is almost intact. E. P.

Determination of ascorbic acid.—See this vol., 1483.

Electrometric determination of vitamin-C (ascorbic acid). J. DIGLERIA (Mezőg.-Kutat., 1934, 7, 226—235; Chem. Zentr., 1935, i, 1409).—Pure ascorbic acid (I) gives identical results when determined by I or 2 : 6-dichlorophenol-indophenol (II). (I) is decomposed in feebly acid or neutral solution, even during the short time lag, but the decomp. is negligible at $p_H \geq 4$. E_h of (I) is strictly dependent on p_H , the change for 1 p_H unit being 58 mv.; E_{REG} at p_H 0 is $+0.3295$ volt. The I titration vals. in fruits and vegetables are $>$ the (II) titration vals., the deviations occasionally being $>$ 100%. R. N. C.

Vitamin-C in the medlar and alkekengi. E. CASERIO (Ind. ital. conserve aliment., 1934, 9, 190—192; Chem. Zentr., 1934, ii, 3272).—The juice of the ripe alkekengi contains twice as much vitamin-C as lemon-juice. The ripe medlar contains relatively no vitamin. R. N. C.

Relation between the vitamin-C contents of various vegetable tissues and the presence or absence of chlorophyll. L. RANDOIN, A. GIROUD, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 297—300).—The chemical and biological vitamin-C vals. of the green and white parts of the leaf tissue show a clear relation to their chlorophyll contents. R. N. C.

Normal content of ascorbic acid in the organism. A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935, 120, 414—415).—The mean normal ascorbic acid contents of the adrenals, liver, and muscles of animals are given. In animals in which scurvy cannot be produced, the vals. on a vitamin-C-deficient diet are slightly less. R. N. C.

Fixation and elimination of ascorbic acid. A. GIROUD, R. CHUC, R. RATSIMAMANGA, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 330—333).—Ascorbic acid (I) injected intravenously in guinea-pigs is rapidly oxidised to dehydroascorbic acid and is stored in the adrenals, liver, and kidney (greatest accumulation). In all organs (I) reaches a max. and then falls. Kidney-(I) is excreted in the urine, excretion beginning immediately (I) rises. Some (I) is fixed by the liver. R. N. C.

Ascorbic acid (vitamin-C) and the blood-aqueous humour barrier. H. GOLDMANN and W. BUSCHKE (Klin. Woch., 1935, 14, 239).—Increase of the permeability of the blood-aq. humour barrier by subconjunctival injection of NaCl lowers the ascorbic acid (I) content of the aq. humour; it becomes normal again with the permeability. Adrenaline, which prevents the increase of permeability, also brings the (I) of the aq. humour to normal if injected after NaCl; it has no effect when injected alone. Injection of (I) into the blood-stream to one eye increases (I) in the anterior chamber of that eye only. (I) probably diffuses from the blood into the aq. humour in the reversibly-oxidised form, and is then reduced by the cryst. lens. R. C. N.

Comparison of the antirachitic potency of cod-liver oil and irradiated ergosterol on a curative and preventive basis. W. C. RUSSELL, M. W. TAYLOR, and D. E. WILCOX (J. Nutrition, 1935, 9, 569—574).—The two sources of vitamin-D produced similar curative responses when fed to white rats on an equiv. preventive basis. With chickens, cod-liver oil was superior. A. G. P.

Antirachitic effect of ultra-violet radiation transmitted by a smoky atmosphere. H. M. BARRETT (J. Ind. Hyg., 1935, 17, 199—216).—Development of rickets in rats on a rachitic diet is not prevented by irradiation through smoke similar to that of an average urban atm. H. G. R.

Crystalline derivatives of vitamin-E. R. KIMM (Sci. Papers Inst. Phys. Chem. Res. Tokyo,

1935, 28, 74—76).—Vitamin-*E* concentrate from rice embryo oil when treated with β -C₁₀H₇·COCl in C₅H₅N gave a cryst. β -naphthoate, C₄₀H₅₄O₂, m.p. 156°, from which the free vitamin-*E* is calc. to be C₂₉H₄₈O. On regeneration it had a high activity. Three other cryst. substances, C₄₃H₆₀O₂, m.p. 158°, C₄₀H₅₄O₂, m.p. 134°, and an uninvestigated fraction, m.p. 168°, were obtained. An amorphous ester of anthraquinone-2-carboxylic acid was prepared.

J. N. A.

Vitamin-*E* content of eggs as related to the diet of the hen and to hatchability. G. L. BARNUM (J. Nutrition, 1935, 9, 621—635).—Vitamin-*E* may be a limiting factor in the hatchability of eggs from hens on certain diets. Deficiency of -*E* is associated with first-week embryonic mortality, and may be reduced by supplying -*E* in poultry diet.

A. G. P.

Pituitary. IV. Effect of vitamin-*E* deficiency on the female albino rat. S. I. STEIN (J. Nutrition, 1935, 9, 611—619).—No difference in the wt. of the pituitary, differential counts of cells in the anterior lobe, or histology was observed between sterile (vitamin-*E*-deficient) and pregnant rats cured of the deficiency.

A. G. P.

Salt-tolerance of *Ruppia maritima* in lakes of high magnesium sulphate content. E. MCKAY (Plant Physiol., 1935, 10, 425—446).—Periodic examinations are recorded of the p_H , d , and osmotic pressure of the lake-H₂O, and the sap composition of the plants growing thereon. *Ruppia* tolerates high [Mg⁺⁺] and [SO₄⁼⁼], its distribution being limited by the Na₂SO₄ concn. of the H₂O. The time of flowering and seed development is influenced by the salt concn. of the lake. The p_H of the lake-H₂O is not a factor governing plant distribution. A. G. P.

Physiological rôle of asparagine and related substances in nitrogen metabolism of plants. A. E. MURNEEK (Plant Physiol., 1935, 10, 447—464).—A discussion of current views. A. G. P.

Stock-scion chemistry and the fruiting relationships in apple trees. H. L. COLBY (Plant Physiol., 1935, 10, 483—498).—The translocation of nutrients and the distribution of reserves between stock and scion are examined in relation to root and shoot development. A. G. P.

Factors rendering the plasmolytic method inapplicable in determining the osmotic values of plant cells. E. C. M. ERNEST (Plant Physiol., 1935, 10, 553—558).—When the osmotic pressure of the external liquid surrounding the cell is only slightly different from that of the cell fluid, plasmolysis becomes so slow that secondary changes may occur within the cell, which invalidate the customary interpretation of the data. A. G. P.

Growth and composition of Deglet Noor dates in relation to water injury. A. R. C. HAAS and D. E. BLISS (Hilgardia, 1935, 9, No. 6, 295—344).—Changes in the mineral and org. constituents and in the H₂O content of dates with advancing growth are recorded. The nature of "H₂O injury" and factors affecting it are examined. A. G. P.

Physiological gradients in citrus fruits. A. R. C. HAAS and L. J. KLOTZ (Hilgardia, 1935, 9, No. 3, 181—217).—Variations in the end-to-end distribution of N, sugar, oil, mineral matter, and carotenoid substances of lemon, orange, and grapefruit are recorded. K manuring increased the K content of Valencia oranges. Deficiency of K is associated with breakdown of the peel. Fumigation with HCN increased the permeability of the peel, notably at the calyx end. A. G. P.

Inhibition of photosynthesis in *Chlorella pyrenoidosa* by the iodoacetyl radical. H. L. KOHN (J. Gen. Physiol., 1935, 19, 23—34).—CH₂I·CO·NH₂ (I) inhibits photosynthesis in *C. pyrenoidosa*, interfering with the dark (Blackman) reaction. This action, which is slow owing to the slow penetration of the radical, is also shown by CH₂I·CO₂H, but not by NH₂Ac. Concns. of (I) which inhibit photosynthesis (about 10⁻⁴M) increase respiration; smaller concns. (> 10⁻⁵M) may increase the rate of photosynthesis by reacting with the photochemical complex, and higher concns. (< 10⁻³M) inhibit respiration. F. A. A.

Effect of blue-violet rays on photosynthesis [in plants]. R. H. DASTUR and R. J. MEHTA (Ann. Bot., 1935, 49, 809—821).—Rates of photosynthesis increase with the intensity of blue-violet rays from various sources. Photosynthetic activity is greatest in white light, intermediate in red, and feeble in the blue-violet region. In white light, assimilation is related not only to the total intensity, but also to the distribution of radiations of different λ . A. G. P.

Wound healing in *Tradescantia fluminensis*, Vell. R. BLOCH (Ann. Bot., 1935, 49, 651—670).—Healing processes in wounded stems involve cell division and elongation, thickening of walls, formation of suberin lamellae, and the impregnation of walls with lignin and fatty matter. Disturbed metabolism leads to increased protein and decreased carbohydrate contents of adjacent areas of stems, and the deposition of tetragonal CaC₂O₄·3H₂O (distinct from the normal raphides) in pith parenchyma. A. G. P.

Non-dependence of carbon dioxide assimilation of green plants on the presence of small amounts of oxygen. Reversible inhibition of assimilation by carbon monoxide. H. GAFFRON (Biochem. Z., 1935, 280, 337—359).—Mol. O₂ is not necessary either in the free or bound condition for CO₂ assimilation in green plants (*Chlorella* etc.) and the hypothesis that the mechanism involves a reaction between irradiated chlorophyll and O₂ is discounted (A., 1935, 1288). A reversible inhibition of assimilation occurs when the plants are exposed to the action of CO in the dark, and suggests that the enzyme responsible for the Blackman reaction is closely related to catalase. P. W. C.

Seasonal changes in the acidity of the rhubarb (*Rheum hybridum*). T. A. BENNET-CLARK and W. M. WOODRUFF (New Phytol., 1935, 34, 77—91).—Sprouting of rhizomes is associated with an increase in NH₄ compounds or in "malate" (I) [acids of the malic group and including citric acid]. Translocation of (I) from rhizome to young leaves takes place,

but deamination of NH_2 -acids to form NH_4 malate is probably not an intermediate stage. Formation of *l*-malic acid occurs principally at the height of summer and not during sprouting. The acid is associated with carbohydrate rather than protein metabolism. The mol. ratio of NH_4^+ : malic acid in the plant is at all times small (0.1). A. G. P.

Testing plant tissue for emanations causing leaf epinasty. F. E. DENNY (Contr. Boyce Thompson Inst., 1935, 7, 341—347).—Apparatus and technique are described. Epinasty was produced by volatile products from a no. of plants. Positive responses were given by petals, anthers, pistils, immature fruits, leaves, and tubers. Potato tubers, germinating maize, wheat, and oats, mycelium of *Rhizopus nigricans*, and mature sporophores of two species of mushrooms failed to produce epinasty. A. G. P.

Effects of zinc and iron salts on the cell structure of mottled orange leaves. H. S. REED and J. DUFRENOY (Hilgardia, 1935, 9, No. 2, 113—141).—Mottle-leaf of citrus is associated with a change in the oxidation-reduction equilibrium of the leaf cells. Nitrites occur in the sap of mottled but not of normal leaves. Cytological changes in mottled trees during recovery following application of Zn are described. In the new shoots thus formed neither Ca deficiency nor phloem necrosis is apparent, whilst chloroplastids develop and form starch. Beneficial effects of Fe on hypoplastic cells of mottled leaves are negligible. Zn is intimately concerned with the oxidation-reduction potential of the cell. A. G. P.

Several chemical growth-substances which cause initiation of roots and other responses in plants. P. W. ZIMMERMANN and F. WILCOXON (Contr. Boyce Thompson Inst., 1935, 7, 209—229; cf. A., 1933, 437; B., 1933, 1027).—Plant responses to a no. of growth-stimulating substances are examined. α -Naphthylacetic and indolylbutyric acids were the most active root-forming substances. Both caused less epinastic response than indolylacetic acid. Local application of C_2H_4 or C_3H_6 in lanoline paste stimulated root initiation. Evidence is obtained of the utilisation of $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ by plants for the production of growth substance. Emanations from plants (probably C_2H_4) causing epinasty were increased by treatment with growth-substance. Positive growth-responses were also obtained with β -naphthylacetic, acenaphthyl-5-acetic, phenylacetic, fluoreneacetic, and anthraceneacetic acids (see also Hitchcock, this vol., 795). A. G. P.

Tobacco as a test plant for comparing the effectiveness of preparations containing growth-substances. A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1935, 7, 349—364).—The relative efficiency of growth-substances in causing epinasty in tobacco leaves was, naphthylacetic (I) and indolylacetic (II) > indolylbutyric (III) and indolylpropionic (IV) > phenylacetic (V) > phenylpropionic (VI) > phenylacrylic (VII) acids. The rooting response of tobacco was in the order (III) > (II) > (VII) > (V) > (I) > (VI) > (IV). Application of lanoline preps. of the substances to decapitated tobacco stems retarded the growth of upper buds but stimulated

that of middle and lower buds. Lanoline preps. of C_2H_4 and C_3H_6 caused similar effects. The epinastic was more suitable than the rooting response of tobacco for comparative tests. A. G. P.

Presence of ozone in air and its effect on the growth of plants. E. BRINER, F. CHODAT, and H. PAILLARD (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 128—132).—Samples of the plants *Zea mays* and *Avena sativa* exposed for 8—25 days to air containing 0.01—10 p.p.m. of O_3 showed a higher rate of growth than samples exposed to de-ozonised air. O_3 favoured production of pigments of the xanthophyll group. S. J. G.

Similarities in the effects of ethylene and the plant auxins. W. CROCKER, A. E. HITCHCOCK, and P. W. ZIMMERMANN (Contr. Boyce Thompson Inst., 1935, 7, 231—248).—The action of C_2H_4 , C_3H_6 , C_2H_2 , and CO on plants is principally that of anaesthetics and stimulants, and resembles in many respects that of a no. of growth-promoting substances. A. G. P.

Effect of auxins on *Phytophthora cactorum*. L. H. LEONIAN (J. Agric. Res., 1935, 51, 277—286).—The presence of substances promoting growth and reproduction of *P. cactorum*, in canned peas and in sprouting maize roots, is demonstrated. The last named are active after crushing or autoclaving. Norit adsorbs growth-promoting but not sexuality-promoting substances. A. G. P.

Pantothenic acid as a nutrilit for green plants. R. J. WILLIAMS and E. ROHRMAN (Plant Physiol., 1935, 10, 559—563).—The growth of *Ricciocarpus natans* is stimulated by pantothenic acid (A., 1933, 982). A. G. P.

Do sexual hormones influence the germination and growth of plants? K. GAD-ANDERSEN and E. JARLØV (Acta med. scand., 1934, 84, 241—252; Chem. Zentr., 1935, i, 1889).—The favourable action of follicular hormone (I) preps. on the growth of hyacinths is not due to (I), but to an associated plant-growth hormone. R. N. C.

Effects of animal hormones on plants. L. HAVAS and J. CALDWELL (Ann. Bot., 1935, 49, 729—747).—A prep. of the oestrogenic hormone was toxic to tomato plants when administered by the root or through cut petioles. Extracts of testis, ovary, pituitary, adrenal, thyroid, and thymus produced no marked stimulatory or toxic effects. A. G. P.

Changes in the chemical composition of developing apples. H. O. ASKEW (J. Pomology, 1935, 13, 232—246).—Starch formation begins in apple tissue near the periphery and extends towards the core area. During maturation hydrolysis of starch proceeds from the core outwards. The decline in % of N and ash with advancing growth follows the relationship $\log_{10} C = a + bt$ (C = concn. of constituent concerned, t = time from first sample, and a and b are consts.). The rate of increase of dry matter declined slightly and that of N and ash intake considerably, approx. 95 days from full bloom. After a further 25 days the intake of N and ash ceased. A. G. P.

Accumulation of boron by reciprocally grafted plants. F. M. EATON and G. Y. BLAIR (Plant Physiol., 1935, 10, 411—424).—The distribution of

B in plant organs is effected by the transpiration stream and is irregular. B combines with org. matter in the tissues, the compounds having low mobility. Accumulation of B in leaves of grafted scions is partly controlled by that of the stock. The intake of B is controlled by the characteristics of the root cells, by the nature of the B compounds in the plant, and by the form of the equilibrium between mobile and immobile B compounds. A. G. P.

Solubility of potassium in maize tissues. V. H. MORRIS and J. D. SAYRE (Plant Physiol., 1935, 10, 565—568).—In maize tissue K exists entirely in solution in the cell sap. There is no evidence of fixed or non-ionisable K in any tissue except, possibly, in cob tissue. A. G. P.

Changes in nitrogen compounds in the wheat grain at different stages of development. G. L. TELLER (Plant Physiol., 1935, 10, 499—509).—Changes in the N distribution of developing grain are examined. The early stages, marked by high proportions of non-protein N, are associated with increasing gliadin and decreasing glutenin contents, and a slight decline in albumins and globulins. These changes are partly due to the filling of the grain with endosperm, which contains more gliadin and less glutenin than the bran. The total N of the grain is influenced by seasonal conditions. A. G. P.

Distribution of nitrogen in the seed of *Zea mays* at different stages of maturity. L. ZELENY (Cereal Chem., 1935, 12, 536—542).—Globulin and glutelin are synthesised at a relatively uniform rate throughout the growth period of the maize grain, whilst zein is present only in very small quantities in the early stages and is rapidly synthesised as the grain approaches maturity. This rapid increase in the ratio of zein-N to total N is closely paralleled by the decrease in H₂O-sol. non-protein-N, indicating that the H₂O-sol. N compounds are largely utilised in the synthesis of the zein. The asparagine, glutamine, or other content of the non-protein-N fraction remains relatively const. throughout the growth period of the kernel. The simpler NH₂-compounds undergo rapid condensation (probably chiefly the condensation of NH₂-acids into polypeptides) as the grain approaches maturity. The basic N of the H₂O-sol. non-protein-N increases as the grain approaches maturity, simultaneously with a considerable decrease in the basic NH₂-N, which indicates that the H₂O-sol. basic N compounds in mature maize mainly consist of org. N bases which do not yield primary alkylamines on hydrolysis. Proteose or peptone is present in maize. E. A. F.

Biochemical phases of oleoresin production. E. GERRY and J. A. HALL (Plant Physiol., 1935, 10, 537—543).—The nature and formation of oleoresins and their precursors are discussed. A. G. P.

Insulin-like materials from plant tissues. C. E. BRAUN and F. M. REES (J. Chem. Educ., 1935, 12, 453—458).—A review and discussion. The presence of an insulin-like substance in plant tissues is still a matter of doubt. L. S. T.

Proteins of tobacco seed. II. G. S. ILJIN (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 163—

168).—The solubility of the proteins of tobacco seed is increased by phosphates but not by acids.

E. P.

Alkaloids of hanfangchi.—See this vol., 1257.

Tubocurarine.—See this vol., 1514.

Composition of purple-flowered i-mao-tsao [*Leonurus sibiricus*, L.]. T. H. TANG and C. W. HSÜ (Nat. Shangtung Univ. Chem. Lab. Repts., 1934, Nos. 3—4, 93—104).—No evidence of the presence of alkaloids was found. CH. ABS. (p)

Alkaloids of *Cytisus caucasicus*. A. OREKHOV and S. NORKINA (Arch. Pharm., 1935, 273, 369—372).—The leaves of this plant contain *d*- α -lupanine, pachycarpine, and a little of a base, m.p. 120—122°, insol. in Et₂O, but sol. in CHCl₃. R. S. C.

Characteristics of *Nicotiana* species. M. I. CHMURA (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 107—116).—*Nicotiana* species contain alkaloids volatile and non-volatile with steam. The m.p. of their picrates are different from those of *N. tabacum*. Some species contain much citric and maleic acids and ash. In *N. glauca* after topping, the amount of alkaloids, N, proteins, and citric acid is increased, that of carbohydrates is decreased. E. P.

Electrolysis in the isolation of plant products. A. A. SCHMUK (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 47—54).—Acids and bases (e.g., citric acid and nicotine) may be separated by electro-dialysis, which reduces the nicotine content of tobacco, but has no influence on its quality. E. P.

Crystalline bitter principle from *Andrographis paniculata*. S. S. G. SIRCAR and A. MOKTADAR (Sci. and Cult., 1935, 1, 300).—A bitter principle of this plant (cf. A., 1914, i, 1118, 1204) is isolated as a substance (I), C₂₀H₃₀O₅, m.p. 220° (decomp.), [α]_D —123.5° in AcOH, which contains OH (not acetylated under ordinary conditions) and CH₂O₂ groups, and one double linking (which is hydrogenated, and combines quantitatively with HCl and ICl). The presence of a lactone group is shown by hydrolysis to two isomeric *OH-acids*, m.p. 156° and 180°, respectively, both reconverted into (I). (I) is readily dehydrated above its m.p., and combines with POCl₃ and with PhNCO. E. W. W.

Concentration of heavy isotopes in cellulose.—See this vol., 1469.

Cress-seed mucilage. K. BAILEY (Biochem. J., 1935, 29, 2477—2485).—The dispersible cellulose component of cress-seed mucilage gave *l*-arabinose, *d*-galactose, *l*-rhamnose, *d*-glucose, and *d*-galacturonic acid on acid hydrolysis. The mucilages of cress seed, mustard seed, and linseed are systems of polyuronides and may be fractionated by their solubilities in dil. aq. Ba(OH)₂, 1% NaOH, and in aq. EtOH. H. D.

Phosphorus of starches. T. POSTERNAK (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 182—183).—Starches can be divided into two groups: (1) those of rhizomes, where P is combined as an ester-salt with a glucose residue; (2) those of cereals where P is in the form of lecithins and not directly linked to the polysaccharide. H. G. R.

Isolation and determination of starch in plant tissue. C. NIEMANN, R. H. ROBERTS, and K. P. LINK (Plant Physiol., 1935, 10, 579—580).—Plant material is extracted with C_6H_6 -EtOH (2:1) and the residue boiled with 1% HNO_3 in 85% EtOH (reflux). The filtered residue is washed free from acid with 95% EtOH, and after partial drying is extracted with 20% EtOH. The extract is evaporated to small vol. and the starch polysaccharides are pptd. by pouring into $COMe_2$ -EtOH (1:1), separated by centrifuge, dried, and weighed. For determining starch in the 20% EtOH extract, the latter is evaporated to small bulk, boiled with HCl, and examined by customary methods for glucose. A. G. P.

Constituents of lesser centaury (*Erythraea centaurium*). T. KARIYONE and K. KASHIWAGI (J. Pharm. Soc. Japan, 1934, 54, 1077—1090).—"Erytaurin" (I) (A., 1908, i, 903) on hydrolysis by emulsin yielded erythrocentaurin, which is assumed to be an aglucone of (I). CH. ABS. (p)

Tobacco glucoside. M. E. KURLO (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 117—131).—A glucoside, $C_{21}H_{20}O_{12}$, or $4H_2O$, m.p. 220—232°, isolated from tobacco, is possibly composed of *d*-glucose and quercetin. The sugar residue is in the 3, 3', or 4' position. E. P.

Isolation of stachyose from the pea (*Pisum sativum*). G. TANRET (Bull. Soc. Chim. biol., 1935, 17, 1235—1236).—The method is described. A. L.

Carbohydrates of tobacco. J. M. SCHABANOV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 133—135).—The medulla of the "Camel" tobacco plant stem contains 2.5% of carbohydrates, chiefly fructose. E. P.

Electrometric determination of carbohydrates and reducing substances in makhorka tobacco. N. P. GOVOROV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 181—197).— Fe^{III} salts are added to an aq. extract of makhorka and the solution is electrometrically titrated with $K_2Cr_2O_7$. E. P.

Extraction of inositol from tobacco. A. P. SMIRNOV (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 75—86).—Aq. extract of tobacco is pptd. with $Pb(OAc)_2$, Pb is removed with H_2S , the filtrate heated with NaOH, cooled, exposed to the atm., treated with conc. aq. Na plumbite, and the pptd. Pb-inositol compound is decomposed with H_2S . E. P.

Supposed occurrence of acids with uneven number of carbon atoms in vegetable oils and fats. II. Acid fraction of mean mol. wt. 354 from the seeds of *Butea frondosa*, Roxb. U. S. K. RAO and B. L. MANJUNATH (J. Indian Chem. Soc., 1935, 12, 611—615; cf. this vol., 1435).—The acid A, m.p. 74.5—75.5°, of Katti *et al.* (B., 1930, 292) is an inseparable, eutectic mixture of behenic (I) and lignoceric (II) acid. Fractionation/1 mm. of the Me ester gives a little pure (II). (II) gives eutectics, m.p. 62° and 56.5°, with stearic and palmitic acid, respectively. The following are described: *p*- $C_6H_4Ph\cdot CO\cdot CH_2$ behenate, m.p. 101—102°, and erucate, m.p. 72.5—73.5°; *p*- $C_6H_4Br\cdot CO\cdot CH_2$ palmitate, m.p. 83—84° (lit. 81.5°), stearate, m.p. 87.5—88.5° (lit.

78.5°), behenate, m.p. 93—94°, and erucate, m.p. 60—60.5°. These and similar esters give only slight depressions of the m.p. when mixed and cannot be separated by crystallisation. R. S. C.

Resin of *Nicotiana rustica*. V. N. SCHIROKALA (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 151—162).—The acids obtained from the resin were esterified with MeOH. Palmitic and linolenic acids were identified. E. P.

Point fern (*Engelsiuss*) and some of its relatives as medicinal plants. F. W. FREISE (Sci. pharmaceutica, 1934, 5, 129—131; Chem. Zentr., 1935, i, 1585—1586).—The rhizomes, roots, and fronds of *Polypodium vulgare*, L., *P. lepidopteris*, Kunze, *P. incanum*, Schw., *P. squalidum*, Vel., and *P. percursum*, Cav., yield a volatile oil (rhizomes and roots), d_4^{20} 0.8385—0.8412, n_D^{20} 1.4855, $[\alpha]_D^{20}$ —8° 45' to —2° 50', containing butyric, hexoic, lauric, and succinic acids, Me salicylate, butyric, isovaleric and α -methylbutyric esters; a fatty oil d_4^{20} 0.9355—0.9385, f.p. —7°, b.p. 245—248° (decomp.), containing 1.10—1.37% of unsaponifiable matter and no filicic acid and acting as an energetic purgative, but not as an anthelmintic; a resin, m.p. 74—86°, acid val. 22—26, sap. val. 55—65; another resin, acid val. 110—145, sap. val. 155—210, containing BzOH and its esters, which is strongly anthelmintic. A glucoside, samambain, and saponins (stem, rind, and rhizome scales) are also present. H. N. R.

Citric acid content of *Nicotiana rustica*. M. L. KOLESNIK (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 41—46).—*N. rustica* from different districts of U.S.S.R. contains 3.6—11.8% of citric acid (I). Plants grown in some districts have high (I) and nicotine contents. E. P.

(A) Citrates occurring in some species of *Kleinia*. A new succulent type. (B) Citrates in succulent plants. G. A. BORGSTRÖM (Kung. fysiogr. Sällsk. Lund. Forhandl., 1934, 4, No. 16, 8 pp., No. 25, 8 pp.; Chem. Zentr., 1935, i, 2034).—(A) Citric acid (I) was detected in leaves of a no. of species of *Kleinia*, but not in stems of others. The amount of acid present declined during the day.

(B) No (I) was found in *Crassulaceae*. A. G. P.

Constituents of *Ramalina scopularum*.—See this vol., 1501.

Constituents of pyrethrum flowers. II. Isolation of pyrethrin-II. F. B. LAForge and H. L. HALLER (J. Amer. Chem. Soc., 1935, 57, 1893—1896; cf. B., 1935, 1068).—Pure pyrethrin-II is isolated for the first time. Purification is effected without heat or chemical reaction until the essential final stage, distillation at 10^{-6} mm. The substance obtained from semicarbazones is impure. Purity is checked by OMe content. Seil's method shows an apparent pyrethrin-I content in the pure material and slightly too low a purity for the nearly pure. R. S. C.

***Cuscuta reflexa*, Roxb. II. Constitution of cuscutalin.** R. R. AGARWAL and S. DUTT (J. Indian Chem. Soc., 1935, 12, 586—590; cf. this vol., 1432).—Cuscutalin (I), m.p. 68° (Ac, m.p. 74°, and CO_2Et -derivative, m.p. 105°), a OH-lactone, contains two ethylenic linkings, of which one is α to the lactone

grouping. With $\text{Me}_2\text{SO}_4\text{-KOH}$ it gives *dimethoxycuscutalin Me ester*, m.p. 78° , by opening of the lactone ring, and with hot conc. HCl *anhydrocuscutalin* (II), $\text{C}_{18}\text{H}_{26}\text{O}_3$, m.p. $71\text{--}72^\circ$. With Br-CHCl_3 , (I) gives "*dibromocuscutalin bromide*" (*bromocuscutalin dibromide*), $\text{C}_{18}\text{H}_{20}\text{O}_4\text{Br}_2$, m.p. 63° , reduced (Zn dust-AcOH) to *dihydrocuscutalin*, m.p. 91° . (I) is monobasic, with slow neutralisation, when titrated with alcoholic alkali. With hot $0.1N\text{-KOH-EtOH}$ it gives a yellow solution, whence AcOH ppts. an *isomeride*, m.p. 102° . With KOH at $140\text{--}180^\circ$ (I) gives $\text{CHPh:CH-CO}_2\text{H}$, HCO_2H , and an unsaturated, aromatic *hydrocarbon*, m.p. $80\text{--}82^\circ$. With 3% KMnO_4 it gives $\text{H}_2\text{C}_2\text{O}_4$ and PhCHO . When (I) is dry distilled, some sublimes and some carbonises, whilst a little (II) is also formed. R. S. C.

Absorption spectra of α - and β -carotenes and lycopene.—See this vol., 1189.

Reaction of trichloroacetic acid and of chloral hydrate with carotene. V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1934, 32, 335—337).— $\text{CCl}_3\text{-CO}_2\text{H}$ and $\text{CCl}_3\text{-CHO}$, H_2O give an intense blue colour with carotene in CHCl_3 solution, the absorption spectrum showing a band between $640\text{ m}\mu$ and the end of the visible spectrum. The colour is thermostable, but is discharged by H_2O or EtOH . Ergosterol with both reagents gives an initial red which changes through green to blue. R. N. C.

Constituents of the unsaponifiable fraction of wheat-germ oil with particular reference to vitamin-E. J. C. DRUMMOND, E. SINGER, and R. J. MACWALTER (Biochem. J., 1935, 29, 2510—2521).—The unsaponifiable fraction contains approx. 3% of a *hydrocarbon*, $\text{C}_{18}\text{H}_{38}$, $n_D^{40} 1.4722$, and 7% of a *hydrocarbon*, $\text{C}_{45}\text{H}_{76}$ [*hydrochloride* (HCl), m.p. $116\text{--}120^\circ$; *bromide* (16Br), decomp. $160\text{--}180^\circ$]. The vitamin-E (I) fraction contains a sterol-like substance, $\text{C}_{29}\text{H}_{48}\text{O}_2$ (?), m.p. $105\text{--}106^\circ$, $[\alpha]_D^{20} +58.5^\circ$ in C_6H_6 (*acetate*, m.p. $98\text{--}100^\circ$, $[\alpha]_D^{20} +65.7^\circ$ in C_6H_6 ; *dinitrobenzoate*, m.p. $156\text{--}158^\circ$, $[\alpha]_D^{20} +56.9^\circ$ in C_6H_6). It is of no val. in counteracting (I) deficiency in female rats. Hot alkalis seem to inactivate (I), and there is considerable loss of activity on distillation in high vac. The most active fractions of (I) show the characteristic absorption band at $294\text{ m}\mu$, but this probably is due to another substance, and not to (I). The unsaponifiable fraction from cotton-seed oil contains (I), but it is absent in the fractions from linseed and sunflower-seed oils. J. N. A.

Phytosterol of wheat-germ oil. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 112—123; cf. Anderson *et al.*, B., 1927, 49).—The mixture obtained from the oil by saponification and extraction of the residue with Et_2O yielded dihydro-sitosterol, m.p. $142\text{--}143$, $[\alpha]_D +24.04^\circ$, α -sitosterol (I), m.p. $134\text{--}135^\circ$, $[\alpha]_D -22.71^\circ$ (*acetate*, m.p. $116\text{--}117^\circ$, $[\alpha]_D -23.55^\circ$), β -sitosterol (II), m.p. $136\text{--}137$, $[\alpha]_D -31.53^\circ$ (*acetate*, m.p. $122\text{--}123^\circ$, $[\alpha]_D -36.7^\circ$; *benzoate*, m.p. $146\text{--}147^\circ$, $[\alpha]_D -12.3^\circ$), γ -sitosterol, m.p. 147° , $[\alpha]_D -43.13^\circ$ (*acetate*, m.p. $143\text{--}143.5^\circ$, $[\alpha]_D -47.7^\circ$; *acetobromide*, m.p. $140\text{--}141^\circ$, $[\alpha]_D -46.23^\circ$; *benzoate*, m.p. 152° , $[\alpha]_D -19.63^\circ$), a δ -sterol (III) m.p., $146\text{--}147^\circ$, $[\alpha]_D -23.9^\circ$ [*acetate*,

m.p. $113.5\text{--}114.5^\circ$, $[\alpha]_D -24.35^\circ$; *benzoate*, m.p. $157\text{--}158^\circ$, $[\alpha]_D -15.98^\circ$; *acetobromide* (IV), m.p. $118\text{--}120^\circ$], and a *hydrocarbon*, m.p. 66° . (I) and (II) were not completely purified and (III) may have been contaminated with ergosterol. Debromination of (IV) with Zn and AcOH yields a *cryst. substance*, m.p. 115° , and a resin containing Br . W. McC.

Phytosterolin of wheat-germ. II. A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 124—127).—The substance is a mixture chiefly composed of the glucosides of β - and γ -sitosterol. A substance not pptd. by digitonin and exhibiting absorption bands at 328 and $280\text{ m}\mu$ is also present. W. McC.

Chemical nature of the amino-acids excreted by leguminous root nodules. A. I. VIRTANEN and T. LAINE (Nature, 1935, 136, 756—757).—About one half of the mixture of NH_2 -acids excreted by the nodules of leguminous plants consists of aspartic acid (I) (cf. A., 1933, 437). Cystine, arginine, histidine, and aromatic NH_2 -acids are absent, and the remaining N, precipitable by phosphotungstic acid, probably comes from lysine (II). (I) and (II) probably represent the primary NH_2 -acids formed in the fixation of N by leguminous plants. L. S. T.

Simplified determination of the Schmul and polyphenol coefficients [of tobacco]. E. I. KOVALENKO (Sborn. Rabot Chim. Tabak, 1935, Bull. 125, 147—150). E. P.

Determination of small amounts of chloride in plant tissue. M. CATTLE (New Phytol., 1935, 34, 151—154).—The material is ground to a paste with H_2O and the mixture heated with a few drops of octyl alcohol (to prevent frothing). AgNO_3 , HNO_3 , and H_2O_2 are added in the order named and the mixture is boiled. After a second treatment with H_2O_2 the solution is conc. and excess of Ag determined by Volhard's method. "Wet ashing" with acid is preferable to that with alkali. A. G. P.

Analysis of chloride in *Cladophora*. E. W. JONES (New Phytol., 1935, 34, 155).—The alkaline "wet ashing" method (cf. preceding abstract) is modified for very small amounts of Cl. The determinations are made nephelometrically. A. G. P.

Sulphur content of plants. J. FRAZER (Plant Physiol., 1935, 10, 529—535).—The S content of coniferous and other plants in localities in which the atm. is contaminated by factory chimneys etc. is notably $>$ that in unpolluted areas. A. G. P.

Action of sulphurous acid on leaf cells. A. ANDRÉ (Angew. Bot., 1935, 17, 207—221).—A discussion of smoke injury problems. A. G. P.

Problem of a plant virus infection. K. M. SMITH (Nature, 1935, 136, 395—396).—The occurrence of a virus in the roots of a high proportion of normal tobacco plants under conditions usually regarded as virus-proof is described and possible explanations are advanced. L. S. T.

Heavy hydrogen in biology. G. VON HEVESY (Naturwiss., 1935, 23, 775—780).—A review.

Apparatus for heavy water studies in small animals. H. G. BARBOUR and F. J. COCHRAN

(Science, 1935, 82, 179—180).—A modified Haldane metabolism train is described. L. S. T.

Analysis of small volumes of gas.—See this vol., 1476.

Micro-method of gas analysis. J. A. CAMPBELL and H. J. TAYLOR (J. Physiol., 1935, 84, 219—222).—Modifications introduced into Krogh's method render it easier, more rapid, and of wider application.

R. N. C.

Determination of intracellular p_{H} by the method of vital stains. L. LISON (Compt. rend. Soc. Biol., 1935, 120, 102—104).—The presence of chromotropes in cells introduces errors into the determination of intracellular p_{H} by vital stains, since all the basic p_{H} indicators are metachromatic. The metachromatic error may reach 6 p_{H} units. R. N. C.

Electrodes for parallel determination of the oxido-reduction potential and p_{H} in biological media. R. TSCHAGOVETZ and Z. S. GERSCHENOVITSCH (Ukrain. Biochem. J., 1935, 8, No. 1, 203—209).—The apparatus is described. E. P.

Unpolarisable electrodes to carry action currents. E. SCHÜTZ (Z. Biol., 1935, 96, 510—512).—The connexion is made through Ringer's solution to a Pt electrode covered with Pt-black to prevent polarisation. W. O. K.

Apparatus for physiological experiments. F. F. ANDERSON (Chinese J. Physiol., 1935, 9, 209—212).—The following are described: Et₂O bottle for mammalian experiments, pressure bottle for anticoagulant, contact breaker for use with a sensitive thermo-regulator, and apparatus for isolated smooth muscle prep. E. P.

Colour reaction of fructose.—See this vol., 1484.

Colour standard for cholesterol determinations. A. SHAPIRO, H. LERNER, and E. POSEN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1300—1301).—A colour standard for use in Schoenheimer and Sperry's micro-method for determination of serum-cholesterol is prepared by diluting 1 c.c. of Carter's Midnight Black Ink to 1 litre with 10% AcOH. The method is simplified by using a mixture of H₂SO₄ and Ac₂O. R. N. C.

Determination of urea. N. N. DASTUR, R. KARNAD, B. N. SASTRI, and A. VENKATASUBBAN (Proc. Indian Acad. Sci., 1935, 1, B, 817—822).—(NH₄)₂CO₃ produced by enzymic decomp. of urea may be titrated directly with HCl in EtOH after adding COMe₂ to the solution, using naphthyl-red. The method is applicable to urine analysis. A. G. P.

Removal and determination of small amounts of benzene in biological material. W. P. YANT, H. H. SCHRENK, and P. H. MAUTZ (U.S. Bur. Mines, Rept. Invest., 1935, No. 3282, 7 pp.).—The material in a macerated, finely-ground, or fluid condition is mixed with H₂O and acidified. The C₆H₆ is removed from the refluxing mixture by bubbling through a current of N₂, and absorbed in nitrating acid. The

C₆H₄(NO₂)₂ formed is determined by the Smyth modification of the Elliott and Dalton method.

W. O. K.

Spectrophotometric methods for determining porphyrins. E. VIGILIANI (Diagnostica tec. lab. [Napoli], Riv. mensile, 1934, 5, 625—654).—Copro-porphyrin and protoporphyrin are very unstable in HCl. A spectrophotometric method for urinary porphyrins is described and is compared with the fluorometric method. CH. ABS. (p)

Isolation and determination of volatile substances from biological fluids and other mixtures. F. LAUERSEN (Biochem. Z., 1935, 280, 38—40).—An apparatus is described and its use illustrated by determinations of COMe₂ and β -hydroxybutyric acid in deproteinised blood filtrates. P. W. C.

Titration of fluorine in biological materials. E. W. SCOTT and A. L. HENNE (Ind. Eng. Chem. [Anal.], 1935, 7, 299—300).—A suitable technique for ashing, volatilisation of F as SiF₄ by distillation with HClO₄, and titration with Ce(NO₃)₃ or Th(NO₃)₄ is described (cf. A., 1933, 242). F. O. H.

Micro-determination of total sulphur in biological substances. H. TOYODA and S. KISHI (Gann, 1934, 28, 458—461).—Org. matter is destroyed by fusion with KClO₃-Na₂O₂. The residue is dissolved in hot H₂O, treated with 50% HCl and Br, and S is pptd. as BaSO₄. CH. ABS. (p)

Micro-determination of calcium in small quantities of biological liquids. M. SAVIANO (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 460—463).—Norbo's method (A., 1932, 531) is modified by substitution of an iodometric for the acidimetric titration. CH. ABS. (p)

Spectrographic determination of lead in biological material. J. CHOLAK (Ind. Eng. Chem. [Anal.], 1935, 7, 287—290).—The material (blood, liver, spleen, muscle, foods) is digested with H₂SO₄-HNO₃, ashed at 500°, and the solution of the ash in dil. HCl is examined spectrographically, using a microphotometer and comparing with known standards of Pb and Bi in suitable media (cf. this vol., 399). The accuracy is ± 0.01 mg. for 0.01—0.20 mg. Pb per 100 c.c. F. O. H.

Determination and recognition of lead in biological tissues and fluids. C. N. MYERS, F. GUSTAFSON, and B. THORNE (J. Lab. Clin. Med., 1935, 20, 648—657).—Fairhall's method gives satisfactory results in the micro-determination of Pb (0.02—> 0.50 mg.) in biological specimens if a micro-burette is used in the final titration. Certain elements (e.g., Cu, Bi) interfere. NUTR. ABS. (m)

Histochemical demonstration of gold. F. GUERCIO and U. CIULLA (Diagnostica tec. lab. [Napoli], Riv. mens., 1934, 5, 456—459).—Tissue is treated with 2% H₂C₂O₄ for 24—48 hr., washed, fixed in CH₂O, and paraffined in the usual way. The prep. is dipped in H₂O₂ for 24 hr. A red coloration due to an oxide of Au develops. CH. ABS. (p)

